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Spacers for Geometrically Well-Defined Water-Soluble Molecular Rulers and Their Application

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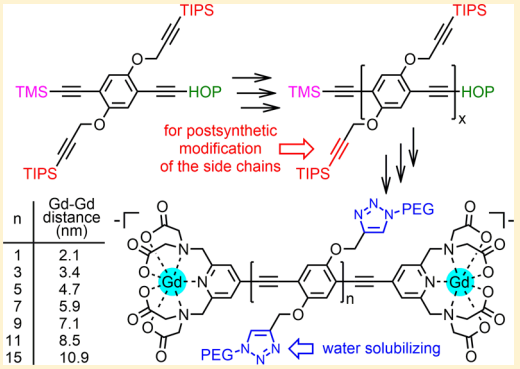
Supporting Information

ABSTRACT: The synthesis and application of monodisperse oligo(*para*-phenyleneethynylene)s (oligoPPEs) with side chains that are adjustable to specific needs, such as water solubility, on a very late stage of the multistep synthesis are described. The adjustable side chains allow for circumventing problems associated with the isolation of highly hydrophilic compounds during early stages of a synthesis. Furthermore, these oligoPPEs can be stocked as adaptable advanced building blocks for rapid assembly of tailor-made spacers and rulers. A rapid growth synthesis provides oligoPPEs with alkyne termini protected with the orthogonal groups trimethylsilyl and 1-hydroxy-1-methylethyl (HOP) and with propargyloxy side chains protected with the triisopropylsilyl group. The three protecting groups allow independent modification of the two termini and the side chains. The HOP group not only acts as a protecting group but also as a polar tag for simple product isolation. We demonstrate one application of these oligoPPEs as spacers for the water-soluble Gd rulers of the type Gd-PyMTA−spacer−Gd-PyMTA with Gd−Gd distances of 2.1−10.9 nm. For this purpose, the terminal alkyne units were used for backbone assembly and attachment of the ligand PyMTA, and the porpargyloxy side chains were used to attach water solubilizing poly(ethylene glycol) chains through a click reaction after spacer assembly.



INTRODUCTION

Rodlike structural units consisting of several *para*-phenylene and ethynylene moieties are frequently found as parts of nanoscopic molecules. Additionally, their geometrically unambiguous structure and the good accessibility of a set of such units as monodisperse materials covering a broad range of finely tuned lengths is highly valued in the evaluation and advancement of electron paramagnetic resonance (EPR) techniques for distance determination, such as the double electron−electron resonance (DEER) technique also called the pulsed electron double resonance (PELDOR) technique,[1−25] RIDME,[26,27] and *cw* EPR.[11] These spectroscopic rulers use the distance dependency of the through space dipolar coupling of two unpaired electrons to determine the distance between two specific sites of a molecule or a molecule aggregate. In this way, information on the structure and dynamics of (bio)-macromolecules in the noncrystalline state is obtained. Because most of the molecules are diamagnetic, paramagnetic moieties, so-called spin labels, are attached highly site-selectively.[28−30] It is noteworthy that because most of the matter is diamagnetic it is EPR-transparent and therefore spin-labeled molecules can be studied in complex surroundings, including inside a living cell.[31−37] Today, the DEER technique is an analytical tool widely used in structural biology to determine distances and distance distributions in the range of 2−6 nm with nitroxyl radicals as spin labels.[3,4,38−53] From early on the development of spectroscopic rulers is tightly interlinked with the availability of sets of compounds, so-called molecular rulers, displaying two spin labels kept at a well-defined distance by a PPE-spacer, i.e., a rodlike moiety consisting of *p*-phenylene (PP) or PP and ethynylene (E) units.[5−25,27,37] These molecular rulers were and are needed to evaluate the EPR techniques and to explore and demonstrate their potentials and limits. They have also spurred the advancement of the EPR techniques.

Although the spectrosopic rulers are nearly exclusively applied to biomolecules and therefore to molecules in a protic environment, typically a water/glycerol mixture, all of the molecular rulers were studied in organic aprotic solvents, such as *o*-terphenyl, toluene, and 2-methyltetrahydrofuran, because they are insoluble in water/glycerol media as a consequence of the hydrophobic spacers. Water/glycerol compatible spacers and therefore water/glycerol soluble molecular rulers would enlarge the applicability of the rulers, e.g., for gaining experimental data on the (de)localization of spin labels bound via a conformational flexible tether, as is the most frequent case, and for exploring in-cell EPR.[37] Furthermore, water/glycerol compatible spacers appeared to us as a requirement for rulers with Gd(III) complexes as spin labels. Gd(III) complexes had been introduced as a very promising

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spin label some years ago.[21,54−64] However, disagreement between expected and experimental results stayed throughout the years and pointed to the need for an in-depth study on a set of well-defined Gd rulers. Because the Gd(III) complexes are highly polar and most are charged, we expected insolubility or aggregation when combining them with the established hydrophobic spacers.

For all of the reasons mentioned, we developed the herein disclosed access to highly hydrophilic PPE spacers and the Gd rulers derived thereof, which are soluble in water, water/glycerol, and aqueous buffers. With the obtained Gd rulers, it was possible to determine some of the specific features of Gd(III) spin labels and their impact on the application of the Gd-based DEER technique.[5] They further served in the improvement of the Gd-based DEER technique,[6,7] the development of the Gd-based RIDME technique,[26] and a study on the application of a Gd(III) complex as a spin label for in-cell EPR.[37]

Rodlike spacers are not only of interest for rulers for the EPR techniques but also for the rulers needed in investigations on the Förster resonance energy transfer (FRET) technique. The FRET technique relies on two, most often different, chromophores that are site selectively attached to the molecule. The distance-dependent energy transfer between the two chromophores is determined and thus structural information is gained. Interestingly, in contrast to the molecular EPR rulers, the spacers of molecular FRET rulers are typically biomolecules, most often oligoproline and occasionally ds-DNA. Although oligoprolines are rather imperfect spacers because of the possibility for E/Z-isomerization of the peptide bond in response to, e.g., the type of solvent and the type of terminal substituents,[64−68] they are widely used.[65,66,69−74] One reason for their widespread use is probably their history of development. The applicability of FRET for distance determination was first demonstrated on oligoprolines of different lengths with two chromophores, one attached at each end,[74] at a time in which the techniques needed for the syntheses of rodlike spacers consisting of phenylene and ethynylene units had not yet been developed. Another and important reason is the requirement for studies in an aqueous solution if FRET is going to be applied in such an environment because the environment has a major impact on the optical properties of the chromophores and therefore on FRET. With the herein described highly hydrophilic PPE spacers, an alternative to the problematic oligoprolines is presented. The PPE spacers are conformationally unambiguous and are substantially stiffer than oligoprolines. The persistence lengths of oligoproline and oligo(*para*-phenyleneethynylene) (oligoPPE) at 298 K are approximately 3.5[64] and 14 nm,[15] respectively.

Only a very few approaches toward monodisperse water-soluble rodlike spacers besides oligoprolines are known to us from the literature: oligopiperidines,[75] spirocyclic bis-peptides,[76−78] and oligoamides of 4′-amino-1,1′-biphenyl-4-carboxylic acid.[79] The oligoamides have been published as molecular rods, although the overall molecular shape is variable due to rotation around the C_{Ar}−CO bond. Except for the oligoamides with lengths up to 10 nm, the lengths of the other spacers stayed below 4 nm. Experimental data on the stiffness are only available for spirocyclic bis-peptides.[80−82] The presented broad end-to-end distance distributions indicate a rather low stiffness. Our approach makes use of a PPE backbone whose stiffness is well-known and high,[15] and whose lengths can easily go up to 10 nm and even beyond. Water solubility is attained through short, branched poly(ethylene glycol) (PEG) chains as side chains, which may even make these rulers biocompatible.

This paper presents the synthesis of PEG-substituted PPE spacers and their application for making a set of water-soluble Gd rulers with Gd−Gd distances of 2.1−10.9 nm. The disclosed strategy avoids problems with isolation of spacers and spacer precursors that are highly polar and water-soluble through a very well working switchover from side chains of little polarity to the highly hydrophilic PEG side chains in a late stage in the multistep synthesis. We expect this strategy to be of general usability when the side chains need to be adjusted for diverse purposes, i.e., solubility adjustment as well as the introduction of additional functional groups. This presents options to have building blocks of advanced stage on the shelf, ready-made for multiple purposes, and thus ready for rapid assembly of tailor-made spacers and rulers.

The paper is organized as follows. First, the overall strategy is displayed with the synthesis of Gd rulers. Details on the individual steps are presented in the following chapters.

RESULTS AND DISCUSSION

Synthetic Strategy. The synthesis design was led by the goal of preserving the adjustability of the two terminal functional units and the adjustability of the side chains until a late stage in the multistep synthesis and to minimize time and effort when it comes to isolation of the products of the many discrete synthetic steps. Accordingly, as outlined in Scheme 1, first the monodisperse oligoPPEs **A** with an arbitrarily tunable number *n* of repeating units and selectively modifiable termini and side chains are assembled. Then, the terminal functional unit, here in the case of the PyMTA ester, i.e., the precursor of the Gd-complexing moiety, is attached, giving functionalized oligoPPEs **B**. Two oligoPPEs **B** are connected through a benzene ring, which carries PEG side chains for the sake of easy product isolation. With this step, the backbone assembly is completed. Then, the side chains are adjusted to the demand of water solubility through an alkyne-azide cycloaddition (click reaction) with a PEG-azide (PEG-N_3). Finally, the ester groups are hydrolyzed and the Gd-PyMTA complexes are formed. Before side chain modification, the products of all synthetic steps are of sufficiently low polarity to enable standard column chromatography on silica gel. Beyond backbone assembly, chromatography was unnecessary because the reactions proceeded cleanly and quantitatively. An extractive procedure was sufficient to remove byproducts and excess reagents.

Spacer backbone build-up and attachment of the terminal functional units are achieved with the alkynyl-aryl coupling (Sonogashira−Hagihara coupling). This coupling as well as the alkyne-azide cycloaddition used for side chain modification are reactions of monosubstituted ethyne groups. These ethyne units are already present in the basic building block for the spacer, i.e., in oligoPPE **A** with $n = 1$, also named monomer. Three different protecting groups make the alkyne units highly selectively addressable: the trimethylsilyl (TMS) group and the 1-hydroxy-1-methylethyl (2-hydroxyprop-2-yl, HOP) group protect the ethyne units that are utilized for backbone assembly, and the triisopropylsilyl (TIPS) group protects the ethyne units that are needed for side chain adjustment. The HOP group is reported to be orthogonal to the TMS group and the TIPS group.[83] The protecting groups TMS and TIPS are not orthogonal to each other, but the difference in the steric demand of the alkyl groups at the silicon atom causes a steep

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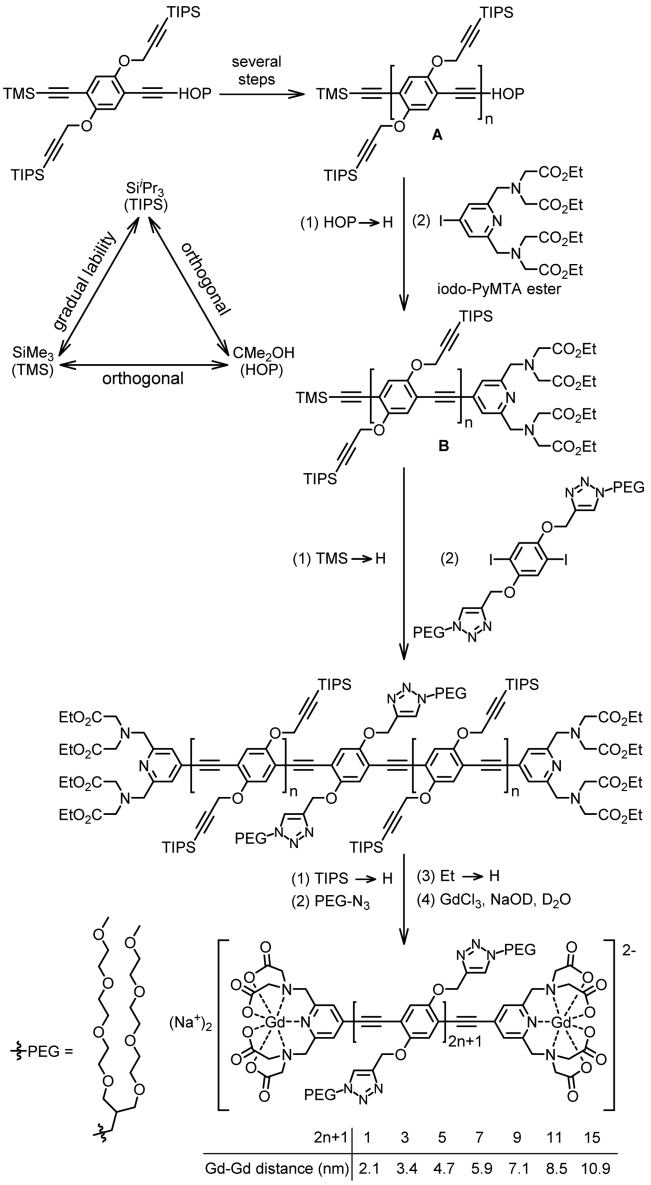
Scheme 1. Synthesis of Monodisperse OligoPPEs with Gd-PyMTA Units at Both Termini and with Side Chains Tailor-Made for the Needs of Water Solubility[a]

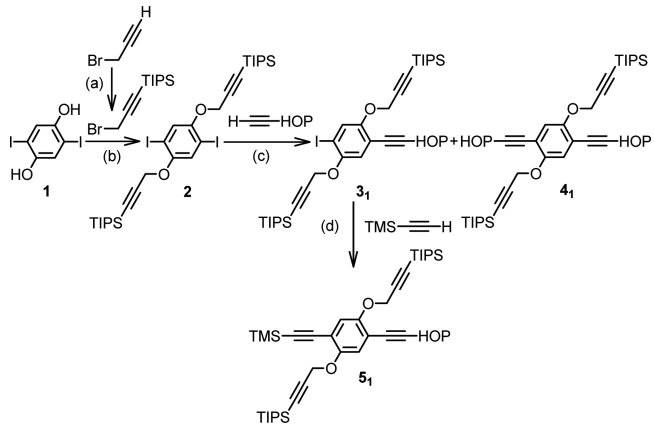


[a]Crucial for success is the orthogonality and the gradual lability of three alkyne protecting groups and the polar tags. The introduction of the final side chains on a late step of the synthesis makes the isolation of the target compounds of the many discrete synthetic steps quite simple. Furthermore, it opens the possibility to adjust side chains to multiple other needs without having to start from the very beginning for each individual type of side chain.

gradient in reactivity toward alkali hydroxide or an alkali alkoxide in an aqueous or alcoholic solution so that the TMS group can be removed without harming the TIPS group.[84] As outlined below, the HOP group is not only an alkyne protecting group orthogonal to the TMS and TIPS groups, but its hydroxy group plays an essential role as a polar tag for simple molecule sorting. This polar tagging strategy has been introduced with the synthesis of oligoPPEs with hexyl groups as side chains[85,86] and has been used in many related syntheses.[87−93]

Synthesis of the Building Blocks. The basic building block to prepare the spacers, monomer $\mathbf{5_1}$, was prepared from diiodo hydroquinone **1** over three steps (Scheme 2): (1) *O*-

Scheme 2. Synthesis of Monomer $\mathbf{5_1}$[a]



[a](a) (1) *n*-BuLi, THF, −78 °C, (2) TIPS-Cl, −78 °C, 41%; (b) K_2CO_3, acetone, 60 °C, 6 h, 91%; (c) $PdCl_2(PPh_3)_2$, CuI, piperidine, THF, room temperature, 42 h; A 1.0:0.6 ratio of diiodobenzene **2** and HOP-acetylene was used. The ratio of $\mathbf{3_1}$:$\mathbf{4_1}$:**2** was ^{1}H NMR spectroscopically determined to be 42:7:51. Isolated yield of $\mathbf{3_1}$: 43%; (d) $PdCl_2(PPh_3)_2$, CuI, piperidine, THF, room temperature, 44 h, 90%.

Alkylation through reaction with TIPS-protected propargyl bromide gave diiodobenzene **2**, (2) Sonogashira−Hagihara coupling with HOP-acetylene provided monoiodobenzene $\mathbf{3_1}$, and (3) Sonogashira−Hagihara coupling with TMS-acetylene gave monomer $\mathbf{5_1}$.

TIPS-protected propargyl bromide, needed in the synthesis of diiodobenzene **2**, was prepared following a published procedure[94] via deprotonation of propargyl bromide with *n*-butyllithium and silylation of the acetylide with TIPS-Cl. After aqueous workup and removal of the volatile components, a mixture of TIPS-protected propargyl bromide, hept-1-ynyltriisopropylsilane, 1,6-bis(triisopropylsilyl)hexa-1,5-diyne, and TIPS-OH in a molar ratio of 100:46:22:85 (determined by ^{1}H NMR spectroscopy) was obtained. TIPS-OH was separated during column chromatography on silica gel with 20:1 pentane/CH_2Cl_2 as the eluent. Under these conditions, all other byproducts have an R_f value of 0.7 and therefore cannot be separated from each other. A distillation at reduced pressure of this mixture gave a mixture of TIPS-protected propargyl bromide and hept-1-ynyltriisopropylsilane in a molar ratio of 1.0:0.47. Byproduct 1,6-bis(triisopropylsilyl)hexa-1,5-diyne remained in the residue of the distillation. The yield of TIPS-protected propargyl bromide was 41%. Fortunately, hept-1-ynyltriisopropylsilane did not interfere with the reaction between diiodo hydroquinone **1** and TIPS-protected propargyl bromide, and, because it is a liquid, it was easily removed from the *O*-alkylation product, diiodobenzene **2**, upon crystallization of diiodobenzene **2**. The Sonogashira−Hagihara coupling of diiodobenzene **2** with HOP-acetylene gave a mixture of monocoupling product $\mathbf{3_1}$, dicoupling product $\mathbf{4_1}$, and starting compound, diiodobenzene **2** (Scheme 2). Because of the pronounced effect of a hydroxy group on the chromatographic behavior on silica gel, the HOP group guarantees a very easy chromatographic separation of starting material **2**, monocoupling product $\mathbf{3_1}$, and dicoupling product $\mathbf{4_1}$. Because

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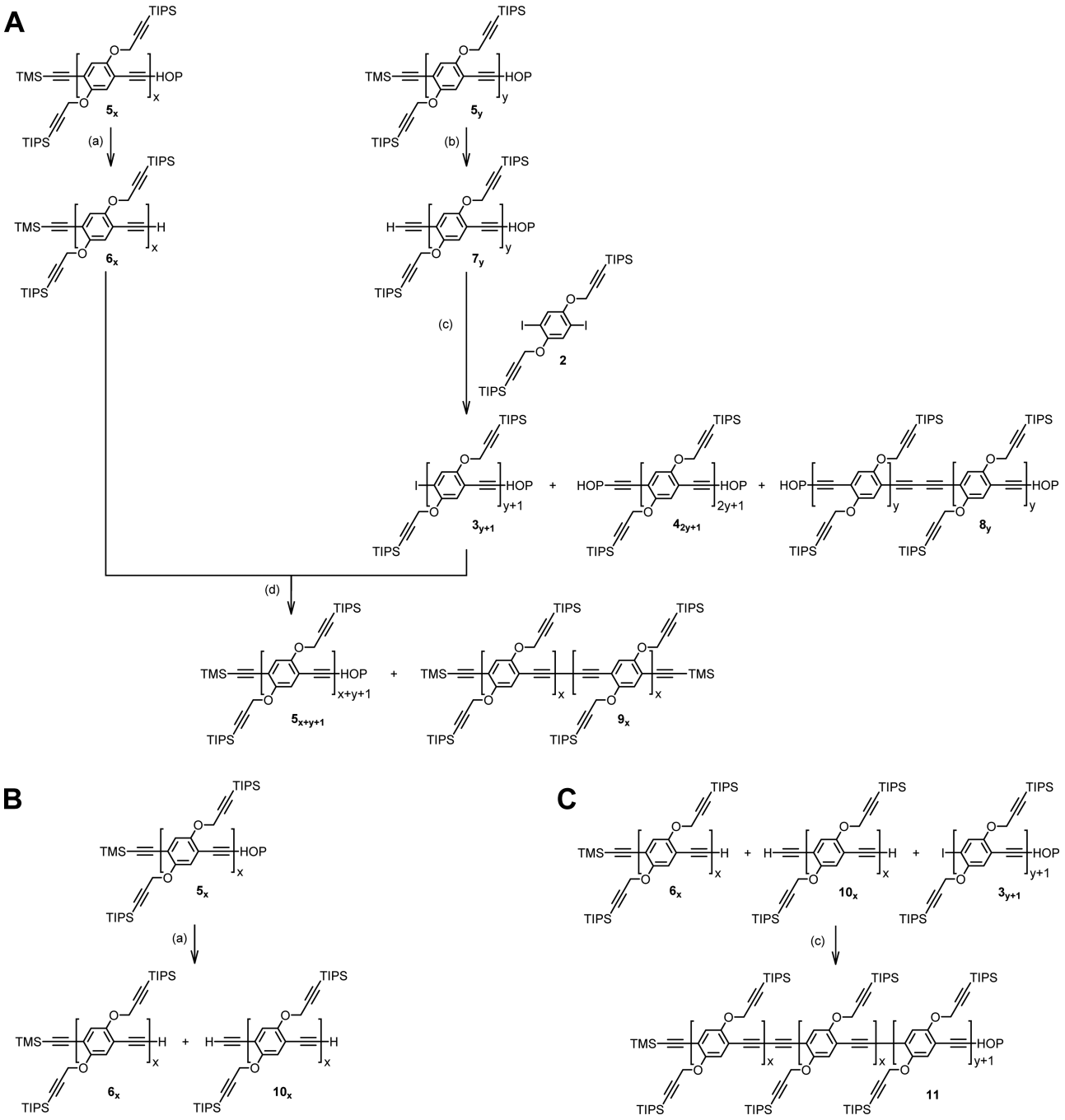
Scheme 3. Synthesis of OligoPPEs 5_n[a]



[a](a) NaOH, toluene, reflux, 54−100%; (b) for y = 1: K_2CO_3, MeOH, 50 °C, 100%; for y = 3: K_2CO_3, $MeOH/CH_2Cl_2$, room temperature, 97%; (c) $PdCl_2(PPh_3)_2$, CuI, piperidine, THF, room temperature, 42−72%; (d) $PdCl_2(PPh_3)_2$ or $Pd(PPh_3)_4$, CuI, piperidine, THF, room temperature, 83−99%.

dicoupling product $\mathbf{4_1}$ is useless for our synthesis, we reduced its percentage by using an excess of diiodobenzene **2**. The results of variations on the ratio of diiodobenzene **2** and HOP-acetylene are summarized in Table S1. The experimentally found product compositions are very close to the ones expected for equal reactivities of diiodobenzene **2** and monoiodobenzene $\mathbf{3_1}$ toward HOP-acetylene. Obviously, the type of substituent in the para position to the iodo substituent does not matter. Using a 1:0.6 ratio of diiodobenzene **2** to HOP-acetylene kept the loss of material in the form of dicoupling product $\mathbf{4_1}$ below 10%. The large amount of residual starting compound in the product mixture did not impede the chromatographic separation even on a large scale, such as 22 g of recovered starting material **2** and 18 g of monoiodobenzene $\mathbf{3_1}$.

With monomer $\mathbf{5_1}$ and diiodobenzene **2** as the building blocks, oligoPPEs $\mathbf{5}_n$ with n = 2−7 were assembled (Scheme 3A) employing selective alkyne deprotection and the alkynyl-aryl coupling. Briefly, with details of the individual steps discussed in the next paragraph, using oligoPPEs $\mathbf{5}_x$ and $\mathbf{5}_y$ as starting building blocks, oligoPPE $\mathbf{5}_n$ with $n = x + y + 1$ was prepared through four simple steps and with trouble-free isolation: removal of the HOP group from oligoPPE $\mathbf{5}_x$ gave

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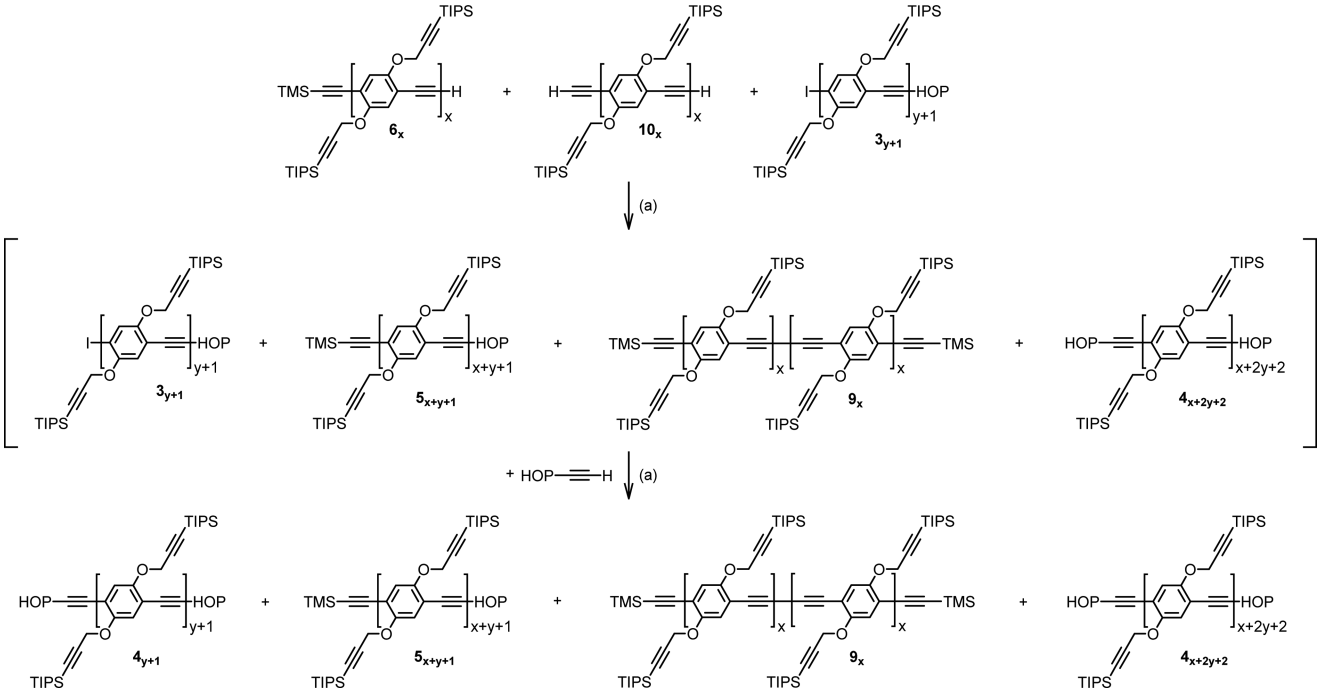
Scheme 4. Products Formed when Using the Mixture of Alkyne 6_x, Dialkyne 10_x, and an Excess of Monoiodo Building Block 3_{y+1} for the Preparation of OligoPPE 5_{x+y+1} and Trapping Residual Monoiodo Building Block 3_{y+1} with HOP-Acetylene[a]



[a]Reaction conditions: (a) $Pd(PPh_3)_4$, CuI, piperidine, THF. The brackets symbolize that no workup was pursued after the first coupling reaction.

alkyne $\mathbf{6}_x$, removal of the TMS group from oligoPPE $\mathbf{5}_y$ provided alkyne $\mathbf{7}_y$. Alkyne $\mathbf{7}_y$ was coupled with diiodobenzene **2**. This gave a mixture of monoiodo building block $\mathbf{3}_{y+1}$, dicoupling product $\mathbf{4}_{2y+1}$, unreacted diiodobenzene **2**, and a small amount of oxidative alkyne dimerization product $\mathbf{8}_y$ (Glaser coupling product). The desired monoiodo building block $\mathbf{3}_{y+1}$ was chromatographically easily isolated due to the HOP group. The coupling of monocoupling product $\mathbf{3}_{y+1}$ with alkyne $\mathbf{6}_x$ provided a mixture of the desired product, oligoPPE $\mathbf{5}_{x+y+1}$, and a small amount of the alkyne dimer $\mathbf{9}_x$. Again, the polar HOP group was decisive for product separation. Throughout the syntheses, it was found that the polar ether moieties of the side chains had only a small impact on the elution of the compounds from a silica gel column. It is the hydroxyl of the HOP group that predominantly dictates the chromatographic behavior. Obviously, the TIPS group shields the polar ether moiety sufficiently from interaction with the silica gel.

The removal of the TMS group of oligoPPEs $\mathbf{5}_y$ using K_2CO_3 and MeOH (Scheme 3A, step b) provided alkynes $\mathbf{7}_y$ in high purity and nearly quantitative yield. With increasing y, the solubility of oligoPPEs $\mathbf{5}_y$ in MeOH decreased drastically.[95] Adding CH_2Cl_2 as a cosolvent or heating the reaction mixture led to complete dissolution of oligoPPEs $\mathbf{5}_y$.

The removal of the HOP group of oligoPPE $\mathbf{5}_x$ while keeping the TMS group unaffected to obtain alkyne $\mathbf{6}_x$ (Scheme 3A, step a) was prone to disappointing results. Reaction conditions are needed in which hydroxide is acting as a base to remove the HOP group while not acting as a nucleophile and therefore not reacting with the TMS group. Thus, all measures were taken to minimize the amount of water in the reaction mixture, such as performing the reaction in a carefully dried reaction vessel using anhydrous toluene and powdered NaOH that was stored under argon. Nevertheless, dialkyne $\mathbf{10}_x$ was found to be a byproduct in nearly all of these reactions (Scheme 3B). For the repeating numbers $x = 1$ and 2, the products alkyne $\mathbf{6}_x$ and dialkyne $\mathbf{10}_x$ can be separated through column chromatography on silica gel, albeit only painfully. For $x > 2$, these two products are inseparable, at least through standard column chromatography. In reactions on a small scale (<500 mg), we found approximately 2−6% of dialkyne $\mathbf{10}_x$ accompanying desired alkyne $\mathbf{6}_x$. In large scale reactions, dialkyne $\mathbf{10}_x$ was formed in a substantially larger percentage of 20−46%. The reason for this different outcome may be that, whereas the ratio of starting material $\mathbf{5}_x$ and NaOH was the same in all reactions, the amount of toluene was not proportionally scaled up with the amount of the reactants. Less toluene was used in the large scale reactions. This must have led to a larger concentration of water in the reaction mixture, as water is formed in the reaction between the deprotected acetylene and NaOH. We reason that this water dissolves some of the NaOH and in this way turns the hydroxide, which is non-nucleophilic as long as it is bound as solid NaOH, into a dissolved and therefore nucleophilic hydroxide. Remarkably, the reaction rate of the HOP group removal decreases with increasing repeating number x. To minimize the loss of the TMS group in the case of oligoPPEs $\mathbf{5}_x$ with $x > 3$, we stopped the reaction before the removal of the HOP group was complete. The chromatographic separation of residual oligoPPEs $\mathbf{5}_x$ and alkynes $\mathbf{6}_x$ is easy because of the polar tagging of oligoPPEs $\mathbf{5}_x$ with the HOP group. In this way, alkynes $\mathbf{6}_x$ with a content of dialkynes $\mathbf{10}_x$ of only 2−6% were obtained, a content percentage that is not of concern as outlined below in the paragraphs on the preparation of oligoPPEs $\mathbf{5}_{x+y+1}$.

In the coupling between alkyne $\mathbf{6}_x$ and monoiodo building block $\mathbf{3}_{y+1}$ giving oligoPPE $\mathbf{5}_{x+y+1}$, a complete conversion of monoiodo building block $\mathbf{3}_{y+1}$ was sought in the beginning because the separation of oligoPPE $\mathbf{5}_{x+y+1}$ and leftover

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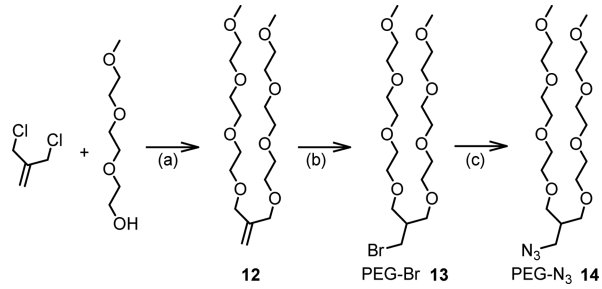
monoiodo building block $\mathbf{3}_{y+1}$ is extremely tedious, if successful at all. The chromatographic behavior of the compounds is essentially determined by the HOP group of which oligoPPE $\mathbf{5}_{x+y+1}$ and monoiodo building block $\mathbf{3}_{y+1}$ both carry one. The complete conversion was achieved by applying an excess of alkyne $\mathbf{6}_x$ (1.02−1.1 equiv). In none of these reactions was alkyne $\mathbf{6}_x$ detected after workup. Instead, alkyne dimer $\mathbf{9}_x$, the oxidative dimerization product (Glaser coupling product) of alkyne $\mathbf{6}_x$, was found. We surmise that the dimerization occurs during workup in air. The chromatographic separation of oligoPPE $\mathbf{5}_{x+y+1}$ and dimer $\mathbf{9}_x$ is easy because of the polar tagging of oligoPPE $\mathbf{5}_{x+y+1}$ with the HOP group.

As mentioned, alkyne $\mathbf{6}_x$ was obtained in a mixture with dialkyne $\mathbf{10}_x$. If this mixture is used for a coupling with monoiodo building block $\mathbf{3}_{y+1}$, there is a chance that, besides oligoPPE $\mathbf{5}_{x+y+1}$, another product with only one HOP group is formed, namely compound **11** (Scheme 3C). This compound results if one ethyne unit of dialkyne $\mathbf{10}_x$ undergoes alkynyl-aryl coupling with monoiodo building block $\mathbf{3}_{y+1}$, and the other ethyne unit undergoes Glaser coupling with alkyne $\mathbf{6}_x$. All other possible products delineated from dialkyne $\mathbf{10}_x$ will have either two HOP groups or none. Because the content of dialkyne $\mathbf{10}_x$ was at most 6%, and the percentage of ethyne units that are not involved in an alkynyl-aryl coupling with monoiodo building block $\mathbf{3}_{y+1}$ but instead are involved in a Glaser coupling reaction was maximum at 14% (this number results from the complete conversion of monoiodo building block $\mathbf{3}_{y+1}$ and the chosen ratio of alkyne $\mathbf{6}_x$ and dialkyne $\mathbf{10}_x$ to the monoiodo building block $\mathbf{3}_{y+1}$), the contamination of oligoPPE $\mathbf{5}_{x+y+1}$ through compound **11** will be below 1%. Indeed, we did not find any hint, in either ^{1}H NMR or MS spectra, of compound **11**.

Nevertheless, because the formation of compound **11** is proportional to the extent of Glaser coupling, today we favor forcing all monosubstituted ethyne units of alkyne $\mathbf{6}_x$ and dialkyne $\mathbf{10}_x$ to undergo an alkynyl-aryl coupling if a mixture of alkyne $\mathbf{6}_x$ and dialkyne $\mathbf{10}_x$ is to be deployed. This goal is achieved by applying an excess of monoiodo building block $\mathbf{3}_{y+1}$ and, instead of the commonly used Pd(II)-complex, a Pd(0)-complex as catalyst to avoid alkyne dimerization by Pd(II) (Scheme 4). This approach was taken for the synthesis of oligoPPEs $\mathbf{5}_4$ and $\mathbf{5}_5$ in which a mixture of alkyne $\mathbf{6}_3$ and dialkyne $\mathbf{10}_3$ was used. Expected was a mixture of leftover monoiodo building block $\mathbf{3}_{y+1}$, oligoPPE $\mathbf{5}_{x+y+1}$, probably a trace of alkyne dimer $\mathbf{9}_x$ (in the most realistic case a trace of oxygen is present during the alkynyl-aryl coupling), and the dicoupling product $\mathbf{4}_{x+2y+2}$, which derives from dialkyne $\mathbf{10}_x$. The formation of compound **11** is rated as highly improbable because of the low content of dialkyne $\mathbf{10}_x$ in combination with the low probability of oxidative dimerization when applying the Schlenk technique properly. As mentioned above, separation of monoiodo building block $\mathbf{3}_{y+1}$ and oligoPPE $\mathbf{5}_{x+y+1}$ is (nearly) impossible. Therefore, before workup, HOP-acetylene was added to convert monoiodo building block $\mathbf{3}_{y+1}$ to oligoPPE $\mathbf{4}_{y+1}$ (Scheme 4). This resulted in a mixture of components of which only the targeted oligoPPE $\mathbf{5}_{x+y+1}$ has one HOP group. All other components have either zero or two HOP groups. Consequently, chromatographic isolation of oligoPPE $\mathbf{5}_{x+y+1}$ was simple. All of the other expected components, dicoupling product $\mathbf{4}_{x+2y+2}$, oligoPPE $\mathbf{4}_{y+1}$, and a trace of alkyne dimer $\mathbf{9}_x$ (1−2% related to alkyne $\mathbf{6}_x$), were found as separate fractions.

The side chain building block PEG-N_3 **14** was prepared in three steps via PEG-alkene **12** and PEG-Br **13** as shown in Scheme 5. PEG-alkene **12** was obtained from triethylene glycol monomethyl ether and 3-chloro-2-(chloromethyl)prop-1-ene according to a procedure reported for a structurally closely related compound.[96] Hydroboration of PEG-alkene **12** and reaction of the resulting alkylborane with bromine in the presence of NaOMe gave PEG-Br **13**. This one-pot hydroboration-bromination sequence has been described for other alkenes.[97] The already published preparation of PEG-Br **13** from PEG-alkene **12** is more laborious:[98] hydroboration, oxidation of the alkylborane to obtain PEG-OH, and treatment of the isolated PEG-OH with PBr_3. PEG-Br **13** was converted to PEG-N_3 **14** through treatment with NaN_3.

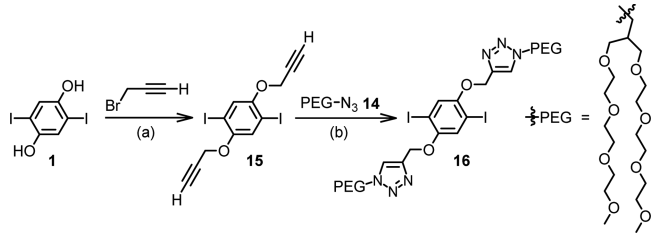
Scheme 5. Synthesis of PEG-N_3 14[a]



[a](a) NaH, THF, 65 °C, 18 h, 93%; (b) (1) BH_3·THF, THF, 0 °C to room temperature, 90 min, (2) MeOH, 10 min, (3) Br_2, NaOMe, 0 °C to room temperature, 120 min, 56%; (c) NaN_3, acetone, 60 °C, 48 h, 97%.

For reasons of simple product isolation, the diiodobenzene that was used to connect two oligoPPEs **B** (Scheme 1) was equipped with PEG side chains. This diiodobenzene **16** was obtained via *O*-alkylation of diiodo hydroquinone **1** with propargyl bromide and subsequent alkyne-azide cycloaddition with PEG-N_3 **14** (Scheme 6).

Scheme 6. Synthesis of Diiodobenzene 16[a]



[a](a) K_2CO_3, acetone, 60 °C, 28 h, 88%; (b) $CuSO_4$·$5H_2O$, sodium L-ascorbate, THF, MeOH, 60 °C, 11 d, 85%.

Assembly of the Gd Rulers. With the building blocks alkynes $\mathbf{6}_x$, diiodobenzene **16**, and 4-iodo-PyMTA ester **17**[99,100] in hand, the first cornerstone on the way to Gd rulers $\mathbf{29}_n$ (Scheme 10) was the preparation of oligoPPEs $\mathbf{20}_x$ (Scheme 7) over three steps: coupling of alkynes $\mathbf{6}_x$ with 4-iodo-PyMTA ester **17**, desilylation of coupling products $\mathbf{18}_x$ to obtain the one-sided functionalized alkynes $\mathbf{19}_x$, and finally linking two molecules of alkynes $\mathbf{19}_x$ via a benzene ring.

When carrying out the coupling of alkyne $\mathbf{6}_x$ with 4-iodo-PyMTA ester **17**, the aspects to be taken into consideration are byproducts formed through Glaser coupling of alkyne $\mathbf{6}_x$, removal of residual starting component, and products derived from dialkyne $\mathbf{10}_x$ that accompanies alkyne $\mathbf{6}_x$ (Scheme 8). The identical situation was met during the formation of the oligomers $\mathbf{5}_{x+y+1}$ (Scheme 3). There, the HOP group acted as

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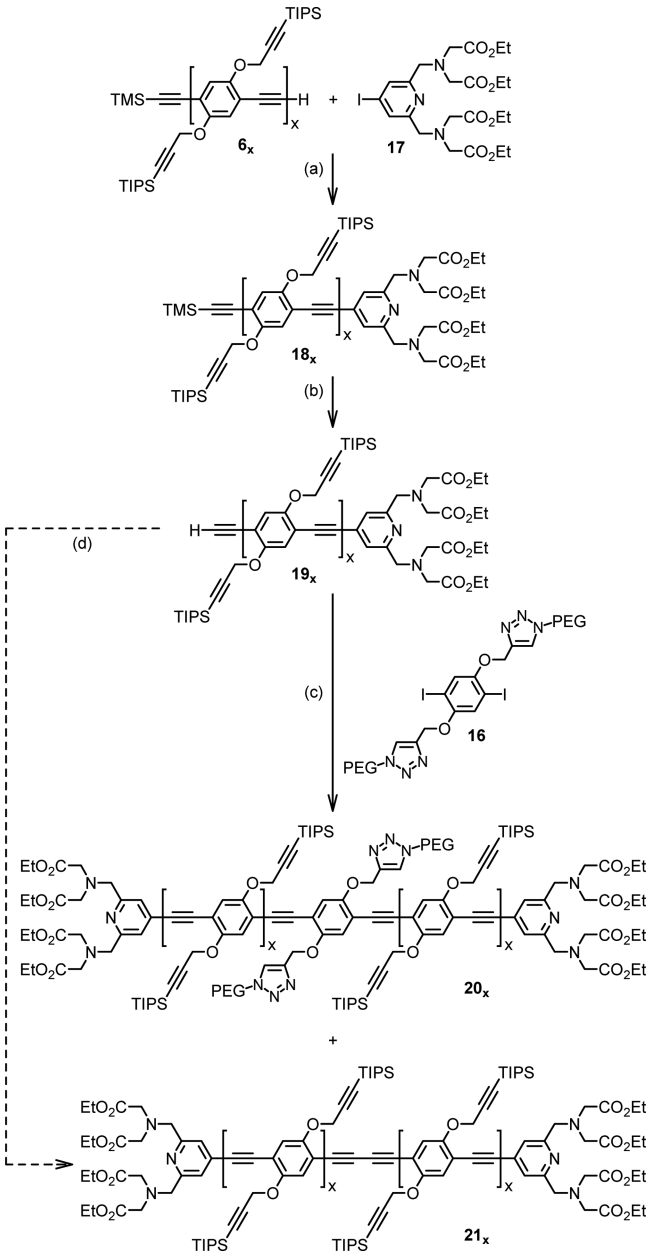
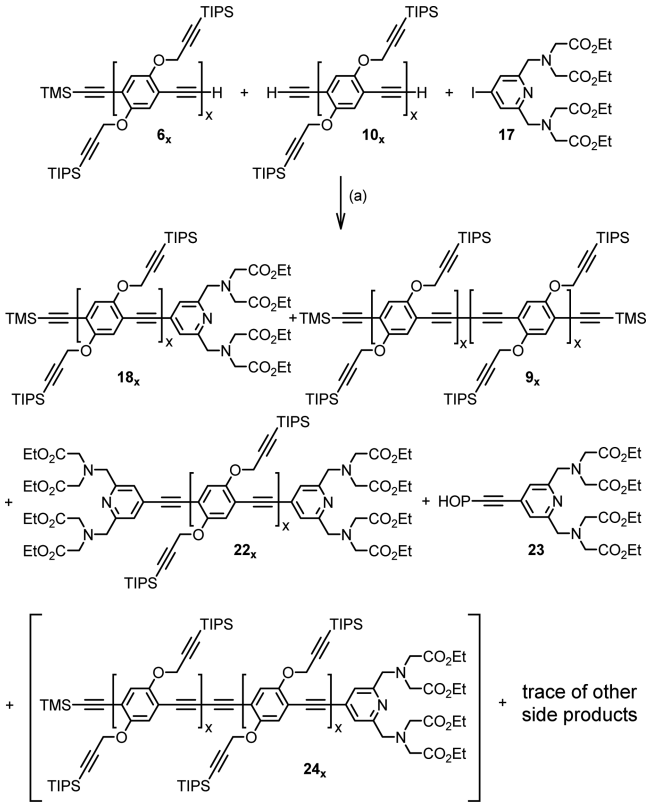
Scheme 7. Synthesis of OligoPPEs 20_x[a]



[a](a) (1) $Pd(PPh_3)_4$, CuI, $^iPr_2NH$, THF, room temperature, (2) HOP-acetylene, (3) metal scavenger, 72−98%; (b) EtOLi or anhydrous K_2CO_3, EtOH or EtOH/THF, room temperature for n = 1−4, 55 °C for n = 5 and 7, 68−100%; (c) (1) $Pd(PPh_3)_4$ or $Pd_2(dba)_3/PPh_3$, CuI, $^iPr_2NH$, THF, (2) metal scavenger, 36−80%; (d) CuCl, tetramethylethylenediamine, THF, air, room temperature.

Scheme 8. Preparation of OligoPPEs 18_x Using the Mixture of Alkyne 6_x, Dialkyne 10_x, and an Excess of 4-Iodo-PyMTA Ester 17[a]



[a]Reaction conditions: (a) (1) $Pd(PPh_3)_4$, CuI, $^iPr_2NH$, THF, room temperature, (2) HOP-acetylene, (3) metal scavenger. A complete conversion of the monosubstituted ethyne moieties of the alkyne 6_x and dialkyne 10_x was achieved through the use of excess 4-iodo-PyMTA ester **17**. The spare 4-iodo-PyMTA ester **17** was converted to compound **23** before workup of the reaction mixture so that the isolation of targeted oligoPPE 18_x was simple. Byproduct 24_x was not detected and is therefore displayed in brackets. As described in the text, its formation is highly unlikely.

a polar tag for simple product isolation, a function overtaken by the PyMTA ester moiety when assembling oligoPPEs 18_x. The probability of the formation of the inseparable byproduct 24_x (Scheme 8), the analogue of compound **11** (Scheme 3C), was minimized through applying an excess of 4-iodo-PyMTA ester **17** and a Pd(0) catalyst (for a detailed discussion of this situation, see the analogous case occurring in the synthesis of oligomers 5_{x+y+1} described in the section "Synthesis of the Building Blocks"). Indeed, we did not obtain any hint that byproduct 24_x was formed. Because 4-iodo-PyMTA ester **17** and oligoPPEs 18_x are nearly inseparable by column chromatography, HOP-acetylene was added before workup, and thus all of the surplus 4-iodo-PyMTA ester **17** was trapped in the form of compound **23**, which is much more polar than oligoPPEs 18_x and therefore chromatographically easily removed. This strategy relies on the complete conversion of excess 4-iodo-PyMTA ester **17** to compound **23**. Therefore, we used 4-iodo-PyMTA ester **17** instead of the more accessible 4-bromo-PyMTA ester.[99] With the latter, we did not achieve complete conversion.[101]

The desilylation of oligoPPEs 18_x (Scheme 7) turned out to be tricky because the ester groups of the PyMTA ester are surprisingly highly susceptible to hydrolysis in the presence of K^+ and Na^+ ions. Exchange of the ethyl ester groups for bulky *tert*-butyl ester groups did not make a sufficient difference here.[102] Obviously, anhydrous conditions are needed. Accordingly, for desilylation we used lithium ethanolate or anhydrous K_2CO_3 as base and performed the reaction in anhydrous EtOH or a mixture of anhydrous EtOH and anhydrous THF, and instead of classical aqueous workup for product isolation, we filtered the reaction mixture through silica gel using diethyl ether or tetrahydrofuran for elution.

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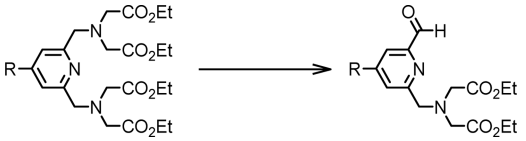
Fast access to Gd rulers was expected through the Glaser coupling of alkynes $\mathbf{19}_x$ to alkyne dimers $\mathbf{21}_x$ (Scheme 7, step d). However, a side reaction blocks this route: the aminomethyl substituent at the pyridine is converted to a formyl group (Scheme 9). The aldehyde is hardly separable from alkyne dimer $\mathbf{21}_x$. Albeit a slow reaction, this oxidation becomes a serious issue when dimerizing alkynes $\mathbf{19}_x$ with $x \geq 2$ because the rate of the Glaser coupling decelerates dramatically with increasing x. Experiments revealed the aldehyde formation to be a copper ion-catalyzed reaction with oxygen. Therefore, instead of connecting two molecules of alkynes $\mathbf{19}_x$ directly with each other, they were linked via a benzene ring in a double Sonogashira–Hagihara coupling of alkyne $\mathbf{19}_x$ with diiodobenzene **16** (Scheme 7, step c), a reaction that still requires the presence of copper ion but not that of oxygen. The two branched PEG substituents of diiodobenzene **16** account for our experience that the Sonogashira–Hagihara coupling is always accompanied by alkyne dimerization, at least to a tiny extent. They act as polar tags for oligoPPE $\mathbf{20}_x$ and thus make the two products, oligoPPE $\mathbf{20}_x$ and alkyne dimer $\mathbf{21}_x$, easily separable. Methoxy or $O(CH_2CH_2O)_2Me$ groups instead of the branched PEG side chains proved to be insufficient for this purpose because the PyMTA ester moieties strongly influence the chromatographic behavior on silica gel.

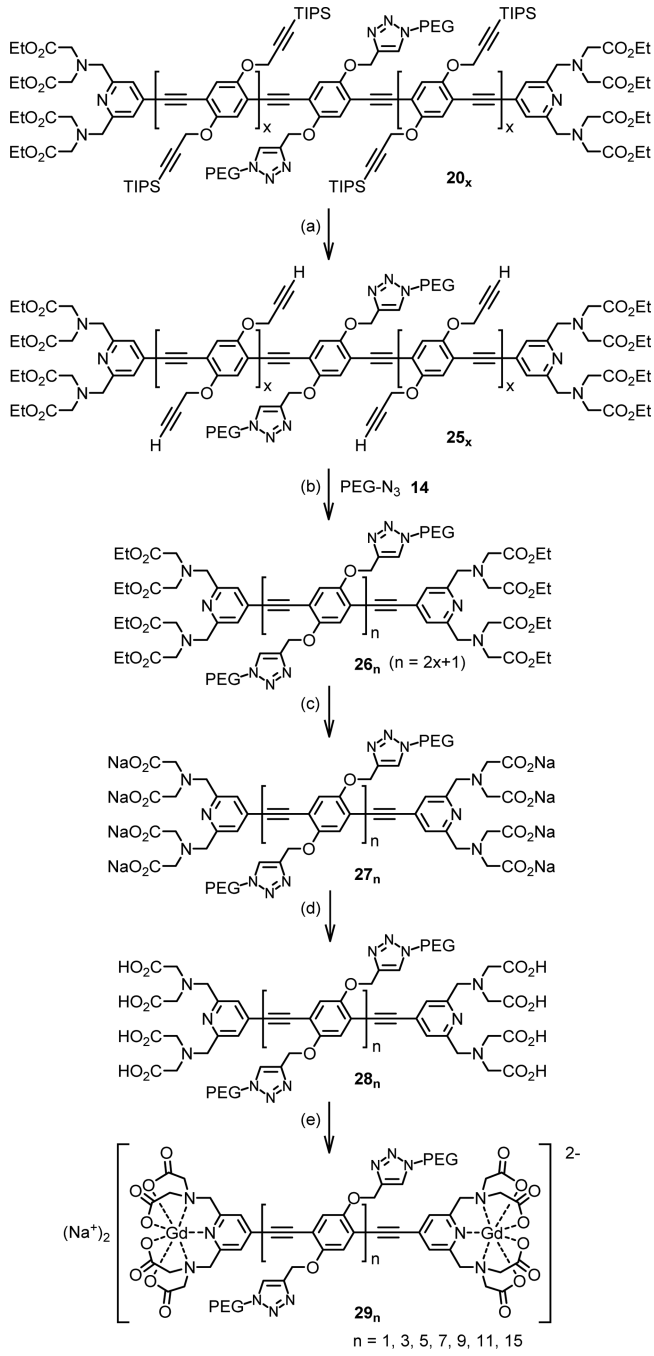
Scheme 9. Oxidation of the Aminomethyl Substituent of the PyMTA Moiety to a Formyl Group in Air in the Presence of Cu(I/II)



During routine workup in air to isolate oligoPPEs $\mathbf{20}_x$, the aforementioned oxidation of the aminomethyl to a formyl substituent (Scheme 9) happened. Therefore, before exposure of the reaction mixture to air, the metal ions were trapped with the thiourea groups of the metal scavenger QuadraPure TU. The solution tested negative for copper ions through the addition of QuadraPure BzA, which becomes green or blue if copper ions are bound to it. The amount of QuadraPure BzA was kept low, and the exposure time of the products to QuadraPure BzA was kept short so as to minimize the potentially occurring aminolysis of the ethyl ester groups of the PyMTA moiety by the benzylamine substituents of QuadraPure BzA. The same procedure was applied to the isolation of oligoPPEs $\mathbf{18}_x$ (Scheme 7). Please note that chromatography on silica gel proved insufficient to remove Cu(I/II) from oligoPPEs $\mathbf{18}_x$ and oligoPPEs $\mathbf{20}_x$.

The last synthetic challenge in the synthesis of the Gd rulers $\mathbf{29}_n$ was to mount the side chains that provide water solubility via alkyne-azide cycloaddition (click reaction) (Scheme 10). The reaction must proceed extremely well to allow for the attachment of up to 30 side chains as is needed for Gd ruler $\mathbf{29}_{15}$. Englert et al.[103] reported a modification of a polyPPE having the same side chains as oligoPPE $\mathbf{20}_x$ through in situ desilylation with tetrabutylammonium fluoride and copper-catalyzed alkyne-azide cycloaddition in the presence of sodium ascorbate. Applying these conditions on oligoPPE $\mathbf{20}_x$, we detected side products. These may be associated with allene formation as indicated from results when treating diiodobenzene **2** with Bu_4NF in THF to remove the TIPS groups, which protect the side chain ethyne units to obtain diiodobenzene **15**. There, we found allenes **30** and **31** as byproducts (Scheme 11). To figure out what causes the isomerization and how to avoid it, we performed a series of reactions. The reaction conditions and the results are listed in Table S2. A comparison of the results of experiments 7–19 reveal that, the longer the reaction time and the higher the concentration of Bu_4NF, the more allene is formed. Because the isomerization of propyne to allene proceeds through a deprotonation-protonation mechanism,[104]

Scheme 10. Synthesis of Gd Rulers $\mathbf{29}_n$[a]



[a](a) Bu_4NF, H_2O, THF, room temperature; (b) (1) $CuSO_4 \cdot 5H_2O$, sodium L-ascorbate, THF, EtOH, H_2O, 60 °C, (2) metal scavenger; (c) EtOH, H_2O, NaOH, rt, 24 h, 100%; (d) H^+-exchange resin, yield 63–87% over 4 steps; (e) (1) $GdCl_3$, D_2O, (2) NaOD, D_2O, 100%.

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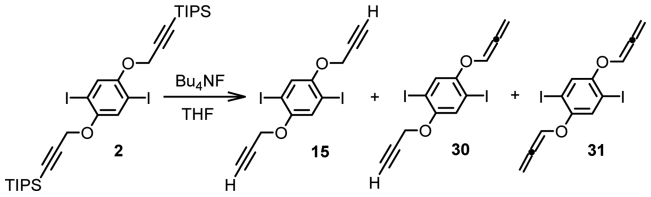
Scheme 11. Allene Formation during Deprotection of Side Chain Ethyne Units



a weak acid was considered to be able to impede the isomerization without reducing the nucleophilicity of the fluoride anion too much. Indeed, the addition of phenol or acetic acid inhibited the isomerization but not the desilylation as the results of the experiments 20−33 prove. Nevertheless, because within a short reaction time no allene is formed, we decided to work without any additives when desilylating oligoPPEs $\mathbf{20}_x$. Besides allene formation, another concern was the high susceptibility of the PyMTA ester groups to hydrolysis. Keeping the ester groups intact during side chain attachment, although they are hydrolyzed in the next step, is essential for simple isolation of ruler precursor $\mathbf{28}_n$, as described below. It appeared wise to avoid the simultaneous presence of sodium ions, coming from sodium ascorbate, and tetrabutylammonium hydroxide, which is formed through the reaction of tetrabutylammonium acetylide with water. Water is an ingredient (5 wt %) of the purchased solution of Bu_4NF in THF. Therefore, desilylation and click reaction of oligoPPE $\mathbf{20}_x$ were performed in separate steps (Scheme 10). Allene formation during desilylation was successfully avoided by applying only a slight excess of Bu_4NF and a short reaction time. According to the ^1H NMR spectra, the click reaction with PEG-N_3 **14** proceeded quantitatively to give oligoPPEs $\mathbf{26}_n$. To avoid oxidative damage of the PyMTA moiety, we trapped the copper ions with metal scavenger QuadraPure TU before the reaction mixture was exposed to air.

The PEG side chains render the oligoPPEs $\mathbf{26}_n$ highly adhesive to silica gel, and therefore standard column chromatography for their isolation is of little suitability. We refrained from isolation of oligoPPEs $\mathbf{26}_n$. Instead, a protocol was developed that provides pure Gd ruler precursors $\mathbf{28}_n$ (Scheme 10 and Figure 1). It capitalizes on the compound specific distribution between an aqueous and an organic phase and the change in this distribution of the target compound upon the conversion of oligoPPEs $\mathbf{26}_n$ to the carboxylates $\mathbf{27}_n$. From oligoPPEs $\mathbf{26}_n$, only the water-soluble compounds were removed through taking up the component mixture of the click reaction into dichloromethane and washing this solution with water (Figure 1). OligoPPEs $\mathbf{26}_n$ are water-soluble but clearly prefer dichloromethane as solvent. The organic phase contained, besides oligoPPE $\mathbf{26}_n$, PEG-N_3 **14**, which had been used in excess, TIPS-OH and/or TIPS-F, and silicone grease. This mixture was subjected to sodium hydroxide in a mixture of water and ethanol, giving carboxylate $\mathbf{27}_n$ in a mixture with PEG-N_3 **14**, TIPS-OH, and silicone grease. Carboxylates $\mathbf{27}_n$ prefer the water phase of a water/CH_2Cl_2 mixture. Thus, PEG-N_3 **14**, TIPS-OH, and silicone grease were removed at this stage through simple washing of the aqueous phase with CH_2Cl_2, and an aqueous solution of carboxylate $\mathbf{27}_n$ and NaOH was obtained. Carboxylates $\mathbf{27}_n$ were converted to the ruler precursors $\mathbf{28}_n$ through the addition of a proton exchange resin to the aqueous solution. Upon this treatment, the sodium ions of NaOH were also exchanged for protons. Treatment of the ruler precursors $\mathbf{28}_n$ with gadoliniumtrichloride and sodium deuteroxide provided the Gd rulers $\mathbf{29}_n$.

Gd rulers $\mathbf{29}_n$ are not only soluble in water, water/glycerol, and aqueous buffers as we expected, but they are also soluble in polar organic solvents such as THF.

Comment on the ^1H NMR Spectra of the OligoPPEs. The ^1H NMR spectra of all compounds with TIPS-protected propargyloxy side chains show additional signals of low intensity. As examples, the spectra of monomer $\mathbf{5}_1$ and oligoPPE $\mathbf{5}_3$ are given in Figure 2. The signals of the methylene protons of the propargyloxy side chains show a shoulder at their high field edge, and each singlet of the aromatic protons is accompanied by a singlet at a slightly higher field. The intensities of the additional singlets are approximately 4% of that of the major singlets. The shoulder shows an intensity that is comparable to that of the additional singlets.

The shoulder of the signal of the methylene protons is interpreted as part of the ^{29}Si satellites because the $^1H-^{29}Si$-HMBC NMR spectrum of monomer $\mathbf{5}_1$ shows a cross signal between the ^{29}Si NMR signal of the TIPS group and the ^1H NMR signal of the methylene protons. We assume also that the additional singlets in the aromatic region are caused by the presence of the isotope ^{29}Si, albeit we have no explanation for this effect of the isotope on the signal shift. However, the relative signal intensity of approximately 4% corresponds to the natural abundance of the ^{29}Si isotope. Moreover, no such

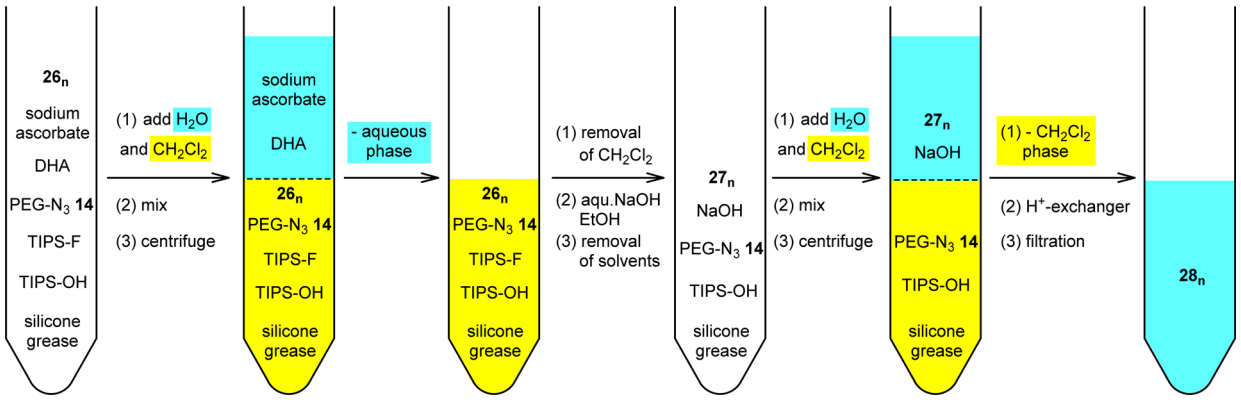


Figure 1. Illustration of the separation procedures of the route to the ruler precursors $\mathbf{28}_n$. The abbreviation DHA stands for dehydroascorbic acid and hydrolysis products thereof.

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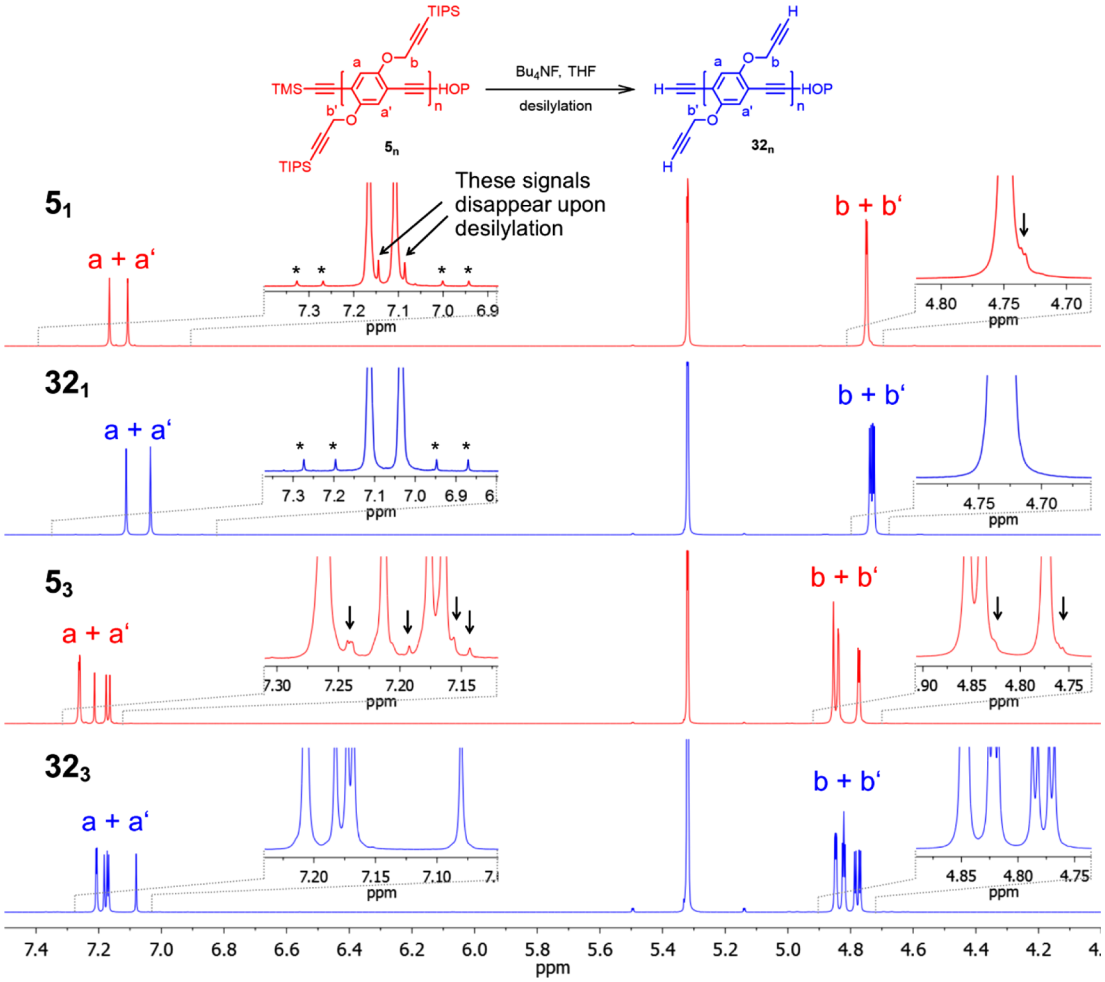

Figure 2. Cutout of the ^{1}H NMR spectra of oligoPPE $\mathbf{5_1}$, $\mathbf{32_1}$, $\mathbf{5_3}$, and $\mathbf{32_3}$ (500 MHz, CD_2Cl_2, room temperature). * = ^{13}C satellite signal.

signals occur in the spectra of the desilylated compounds as exemplified with the spectra of oligoPPE $\mathbf{32_1}$ and $\mathbf{32_3}$.

CONCLUSIONS AND OUTLOOK

A synthesis of monodisperse oligoPPEs that bear the option for on-demand modification of the two termini as well as of the side chains on very late stages in the synthesis has been developed. Playing on the individual reactivities of the three alkyne protecting groups, TMS, TIPS, and HOP, in combination with making use of the HOP group as well as PEG side chains as polar tags for simple molecule sorting on a silica gel column are the essentials of the success. The basic synthesis modules, diiodobenzene **2** and monomer $\mathbf{5_1}$, are accessible on multigram scales. The tailorability of the side chains includes the option to make water compatible and even water-soluble nanorods as demonstrated with the synthesis of water-soluble Gd rulers. The latter are in use for the evaluation of Gd-based EPR techniques. They may furthermore find application in dynamic nuclear polarization (DNP). Only recently have Gd(III) complexes popped up in the context of DNP.[105,106] Whether di-Gd(III) compounds, as described herein as Gd rulers, will be more efficient than mono-Gd(III) compounds, as was found for dinitroxides in comparison to mononitroxides, needs to be explored. The now-established access to water-soluble rulers also opens the door to oligoPPE-based FRET rulers, e.g., for the calibration of chromophore pairs and for a fundamental comparison of DEER and FRET.

EXPERIMENTAL SECTION

General. Unless otherwise stated, reactions were performed in dried glassware under argon using the Schlenk technique and commercial solvents and reagents. The argon was passed through anhydrous $CaCl_2$ prior to use. The solvents used for extraction and chromatography were of technical grade and were distilled prior to their use. The proton-exchange resin (Dowex 50WX4 hydrogen form, 91 g) was subsequently washed with THF (3 × 200 mL), EtOH (2 × 100 mL), H_2O (2 × 150 mL), and EtOH (200 mL) and then dried over P_2O_5 at 0.05 mbar for 5 days to obtain a pure and dry proton-exchange resin (30 g).

The temperature given for the reactions refers to the bath temperature. Solvents were removed at a bath temperature of ∼40 °C and reduced pressure. The products were dried at room temperature at ∼0.05 mbar. The pH/pD values of the solutions were determined using pH indicator strips (resolution: 0.3 pH).

As syringe filters, we used PTFE membranes (13 mm, w/0.45 μm). However, this membrane is not well-suited for aqueous solutions. Therefore, we recommend the use of PDVF membranes for aqueous solutions.

Column chromatography was carried out on silica gel 60 (0.035−0.070 mm) applying slight pressure. In the procedures reported below, the size of the column is given as diameter × length. The material was loaded onto the column dissolved in a small quantity of the eluent. Thin layer chromatography was performed on silica gel 60 containing fluorescent indicator F254. The solid support for the silica gel layer was aluminum foil. Unless otherwise stated, the spots were detected with UV light of λ = 254 and 366 nm. The compositions of solvent mixtures are given in volume ratios.

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For centrifugation, a centrifuge with relative centrifugal force of 4000*g* was used.

NMR spectra were calibrated using the solvent signal as an internal standard [$CDCl_3$: δ (^{1}H) = 7.25, δ (^{13}C{^{1}H}) = 77.0; CD_2Cl_2: δ (^{1}H) = 5.32, δ (^{13}C{^{1}H}) = 53.8; DMSO-d_6: δ (^{1}H) = 2.49, δ (^{13}C{^{1}H}) = 39.5; CD_3OD: δ (^{1}H) = 3.31, δ (^{13}C{^{1}H}) = 49.0; D_2O: δ (^{1}H) = 4.79]. For ^{13}C{^{1}H} NMR experiments in D_2O, a drop of MeOH was added as the internal standard [δ (^{13}C{^{1}H})$_{MeOH}$ = 49.5]. Signal assignments are supported by DEPT-135, COSY, HMBC, and HMQC experiments.

Accurate MS experiments were performed using an FT-ICR mass spectrometer interfaced to an external ESI ion source or using a UHR-TOF mass spectrometer. Unless otherwise stated, the monoisotopic mass of a compound is reported.

The ratio of the components in a mixture was determined by ^{1}H NMR spectroscopy and is given in a molar ratio.

Syntheses. *General Procedure for Alkynyl-Aryl Coupling.* A solution of aryl iodide and terminal alkyne in THF and amine was degassed through three freeze−pump−thaw cycles. The solution was brought to room temperature. Then, the catalysts were added, and the reaction mixture was stirred at the given temperature. Unless otherwise stated, shortly after the addition of the catalysts did the precipitate form.

TIPS-Protected Propargyl Bromide. A solution of *n*-butyllithium in hexanes (1.6 M, 315 mL, 504 mmol) was added to a solution of propargyl bromide (80 wt % solution in toluene, 75.1 g, 504 mmol) in THF (1.2 L) at −78 °C (temperature of the solution) within 100 min. After 30 min of stirring at −78 °C, a solution of TIPS-Cl (104.7 g, 562 mmol) in THF (40 mL) was added at −78 °C within 60 min. Then, the solution was stirred for 9 h at −78 °C. One molar HCl (500 mL) and Et_2O (300 mL) were added to the cold solution; then, the solution was allowed to come to room temperature. The water phase was separated and extracted with Et_2O (200 mL). The combined organic phases were washed with H_2O (300 mL), dried over $MgSO_4$, and filtered. Removal of the solvents gave a yellow oil (130.7 g), which was fractionated by column chromatography (7 cm × 30 cm, pentane/CH_2Cl_2 20:1). The fraction with R_f = 0.7 was collected. Through evaporation of the solvents, a colorless oil (87.2 g) was obtained. It was fractionated by vacuum distillation. In this way, a colorless oil (81.7 g, boiling point 68−73 °C at 0.027−0.040 mbar) consisting of TIPS-protected propargyl bromide and hept-1-ynyltriisopropylsilane in a molar ratio of 68:32 was obtained. The yield of TIPS-protected propargyl bromide was 41%. The residual brown oil in the distillation flask was 1,6-bis(triisopropylsilyl)hexa-1,5-diyne (5.37 g, 5%). ^{1}H NMR signals assigned to TIPS-protected propargyl bromide ($CDCl_3$, 500 MHz): δ 3.93 (s, 2H, CH_2), 1.06 (s, 21H, TIPS). ^{1}H NMR signals assigned to hept-1-ynyltriisopropylsilane ($CDCl_3$, 500 MHz): δ 2.23 (t, ^3J = 7.0 Hz, 2H, $CH_2C{\equiv}C$), 1.52, 1.39, and 1.32 (3 m, 2H each, $(C\underline{H}_2)_3CH_2C{\equiv}C$), 1.05 (s, 21H, TIPS), 0.89 (t, ^3J = 7.3 Hz, 3H, CH_3). ^{13}C NMR signals assigned to TIPS-protected propargyl bromide ($CDCl_3$, 125 MHz): δ 101.8 ($CH_2\underline{C}{\equiv}C$), 89.1 ($CH_2C{\equiv}\underline{C}$), 18.5 ($CH_3$), 14.9 ($\underline{C}H_2C{\equiv}C$), 11.2 (CH). ^{13}C NMR signals assigned to hept-1-ynyltriisopropylsilane ($CDCl_3$, 125 MHz): δ 109.3 ($CH_2\underline{C}{\equiv}C$), 79.9 ($CH_2C{\equiv}\underline{C}$), 30.9, 28.5, 22.1, and 19.8 (CH_2), 18.6 ($CH(\underline{C}H_3)_2$), 14.0 ($\underline{C}H_3CH_2$), 11.3 ($\underline{C}H(CH_3)_2$). MS (EI, 70 eV) of the mixture of TIPS-protected propargyl bromide and hept-1-ynyltriisopropylsilane: *m*/*z* (%) 274.0 (2.7) [TIPS-protected propargyl bromide]$^{+\bullet}$, 252.2 (0.7) [hept-1-ynyltriisopropylsilane]$^{+\bullet}$, 231.0 (50.0) [TIPS-protected propargyl bromide − *i*-Pr]$^+$, 209.1 (50.0) [hept-1-ynyltriisopropylsilane − *i*-Pr]$^+$, 202.9 (11.1), 195.1 (13.1), 181.1 (10.6), 174.9 (12.5), 160.9 (10.7), 153.1 (22.6), 139.1 (22.8), 136.9 (17.0), 123.1 (11.2), 109.0 (20.2), 96.0 (16.0), 95.0 (10.8), 82.0 (15.7), 73.0 (10.7), 69.0 (13.3), 67.0 (38.4), 66.0 (27.6), 59.0 (19.3), 53.0 (10.2), 43.0 (100), 41.0 (84.6), 39.0 (37.0). Analytical data of 1,6-bis(triisopropylsilyl)hexa-1,5-diyne: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.48 (s, 4H, CH_2), 1.04 (s, 42H, TIPS). MS (EI, 70 eV): *m*/*z* (%) 390.4 (0.1) [1,6-bis(triisopropylsilyl)hexa-1,5-diyne]$^{+\bullet}$, 347.3 (49.8) [1,6-bis(triisopropylsilyl)hexa-1,5-diyne − *i*-Pr]$^+$, 305.3 (100.0) [1,6-bis(triisopropylsilyl)hexa-1,5-diyne − 2*i*-Pr + H]$^+$, 263.2 (42.0) [1,6-bis(triisopropylsilyl)hexa-1,5-diyne − 3*i*-Pr + 2H]$^+$, 221.2 (24.6) [1,6-bis(triisopropylsilyl)hexa-1,5-diyne − 4*i*-Pr + 3H]$^+$, 179.1 (16.1), 157.2 (23.3), 96.1 (56.8).

2,5-Diiodohydroquinone **1**. The published procedure[107] was followed with small changes. 1,4-Diiodo-2,5-dimethoxybenzene[108] (15.1 g, 38.7 mmol) was suspended in dry CH_2Cl_2 (120 mL). The light brown suspension was cooled in a dry ice/acetone bath. A solution of BBr_3 (25.0 g, 99.8 mmol) in CH_2Cl_2 (30 mL) was added to the suspension over 12 min. The suspension was stirred, while still in the cooling bath, for 40 min. Then, the dry ice/acetone bath was removed, and the reaction mixture was stirred at room temperature for 20 h. The reaction mixture was poured cautiously onto ice (∼200 g). The precipitate was collected by filtration, washed with water (1 × 100 mL, 5 × 20 mL), and dried at reduced pressure. 2,5-Diiodohydroquinone (**1**) was obtained as light brown crystals (12.2 g, 87%). Mp: 196−197 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.79 (s, 2H, OH), 7.13 (s, 2H, H_{Ar}). ^{13}C NMR (125 MHz, DMSO-d_6): δ 150.4 ($C_{Ar}O$), 123.6 ($C_{Ar}H$), 84.3 ($C_{Ar}I$). MS (EI, 70 eV): *m*/*z* (%) 361.8 (100) [M]$^{+\bullet}$, 234.9 (9) [M − I]$^+$, 126.9 (7) [I]$^+$, 108.0 (17) [M − 2I]$^+$.

Diiodobenzene **2**. Our procedure deviates slightly from the published one.[103] Furthermore, the ^{1}H NMR spectral data and the melting point that we determined differ from the reported data.[103] K_2CO_3 (36.7 g, 165 mmol) was suspended in a solution of 2,5-diiodohydroquinone (**1**) (19.0 g, 52.6 mmol) and a 1.0:0.47 mixture (45.6 g) of TIPS-protected propargyl bromide (115.7 mmol) and hept-1-ynyltriisopropylsilane (54.4 mmol) in anhydrous acetone (250 mL). The suspension was stirred at 60 °C for 7 h. Et_2O (250 mL) and water (250 mL) were added to the suspension, whereupon the precipitate dissolved completely. The phases were separated, and the aqueous phase was extracted with Et_2O (3 × 125 mL). The combined organic phases were washed with a saturated aqueous solution of NaCl (60 mL), and the solvents were removed. Recrystallization of the residual brown solid in EtOH (700 mL) gave diiodobenzene **2** (35.9 g, 91%) as faint brown needles. Mp: 109−110 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46 (s, 2H, H_{Ar}), 4.72 (s, 4H, CH_2), 1.03 (s, 42H, TIPS). ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.1 ($C_{Ar}O$), 124.5 ($C_{Ar}H$), 101.0 ($OCH_2\underline{C}{\equiv}C$), 90.6 ($OCH_2C{\equiv}\underline{C}$), 86.2 ($C_{Ar}I$), 58.7 ($O\underline{C}H_2C{\equiv}C$), 18.6 ($CH_3$), 11.1 (CH). MS (EI, 70 eV): *m*/*z* (%) 750.1 (100) [M]$^{+\bullet}$, 669.0 (11), 580.2 (10), 537.1 (7), 495.1 (9), 385.0 (26), 195.2 (59) [$CH_2C{\equiv}$C-TIPS]$^+$, 157.1 (22), 153.1 (25), 127.9 (10), 125.1 (18), 115.1 (14), 111.1 (21), 96.0 (31), 83.0 (26), 73.0 (26), 67.0 (21), 59.0 (42). Accurate MS (ESI): *m*/*z* calcd for [M + Na]$^+$ $C_{30}H_{48}I_2O_2Si_2Na^+$, 773.11744; found, 773.11957. Elemental analysis calcd (%) for $C_{30}H_{48}I_2O_2Si_2$: C, 48.00; H, 6.44; found: C, 48.17; H, 6.53.

Monoiodobenzene $\mathbf{3_1}$. See the general procedure for alkynyl-aryl coupling. Diiodobenzene **2** (43.9 g, 58.5 mmol), 2-methylbut-3-yn-2-ol (HOP-acetylene, $\mathbf{7_0}$) (2.96 g, 35.2 mmol), piperidine (190 mL, 1.92 mol), THF (300 mL), and catalysts $PdCl_2(PPh_3)_2$ (413 mg, 0.59 mmol) and CuI (223 mg, 1.17 mmol) at room temperature with a reaction time of 42 h. After the reaction, a solution of 37 wt % HCl (185 mL, 2.25 mol) in H_2O (300 mL) was added to the suspension, which was cooled with an ice water bath. The phases were separated, and the aqueous phase was extracted with Et_2O (2 × 150 mL). The combined organic phases were washed with a saturated aqueous solution of NaCl (150 mL), dried over $MgSO_4$, and filtered, and the solvents were removed. The components of the residual brown viscous liquid were separated by column chromatography (7.0 cm × 75 cm). Eluting first with pentane/Et_2O 5:1 gave diiodobenzene **2** (22.1 g, 50%; R_f (pentane/Et_2O 5:1) = 0.70; R_f (pentane/Et_2O 2:1) = 0.82). Then, the eluent was changed to pentane/Et_2O 2:1, and monoiodobenzene $\mathbf{3_1}$ (17.9 g, 43%; R_f (pentane/Et_2O 5:1) = 0.15; R_f (pentane/Et_2O 2:1) = 0.42) was obtained as a red viscous liquid that became an orange-red solid during storage at −24 °C for several months. Finally, pentane/Et_2O 1:1 was used to elute the dicoupling product $\mathbf{4_1}$ (2.56 g, 7%; R_f (pentane/Et_2O 5:1) = 0; R_f (pentane/Et_2O 2:1) = 0.04). Analytical data of monoiodobenzene $\mathbf{3_1}$: Mp 38−39 °C. For ^{1}H NMR and ^{13}C NMR data, see Tables S3 and S4. Accurate MS (ESI): *m*/*z* calcd for [M + Na]$^+$ $C_{35}H_{55}IO_3Si_2Na^+$, 729.26266; found, 729.26239. Elemental analysis calcd (%) for $C_{35}H_{55}IO_3Si_2$: C, 59.47; H, 7.84; found: C, 59.58; H, 7.91. Analytical data of dicoupling

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product $\mathbf{4}_1$: for ^{1}H NMR and ^{13}C NMR data, see Tables S5 and S6. MS (EI, 70 eV): m/z (%) 662.4 (82) $[M]^{+\bullet}$, 644.4 (28) $[M - H_2O]^{+\bullet}$, 626.4 (95) $[M - 2H_2O]^{+\bullet}$, 604.3 (25) [M − acetone]$^+$, 586.3 (16) [M − H_2O − acetone]$^+$, 546.3 (9) [M − 2acetone]$^+$, 431.2 (22) [M − $CH_2C{\equiv}C$-TIPS]$^+$, 389.2 (19), 255.1 (43), 237.1 (19), 195.1 (63) $[CH_2C{\equiv}C$-TIPS]$^+$, 125.1 (43), 111.1 (49), 83.0 (55) $[C{\equiv}C-C(Me)_2OH]^+$, 73.0 (62), 59.0 (100) $[C(Me)_2OH]^+$.

Monoiodo Building Block $\mathbf{3}_2$. See the general procedure for alkynyl-aryl coupling. Diiodobenzene **2** (10.49 g, 14.0 mmol), alkyne $\mathbf{7}_1$ (2.80 g, 4.63 mmol), piperidine (20 mL, 202 mmol), THF (60 mL), and catalysts $PdCl_2(PPh_3)_2$ (19.4 mg, 27.6 μmol) and CuI (12.1 mg, 63.6 μmol) at room temperature with a reaction time of 40 h. After the reaction, the THF and piperidine were removed at room temperature and reduced pressure. Et_2O (100 mL), H_2O (40 mL), and 2 M HCl (30 mL) were added to the residue. The phases were separated, and the aqueous phase was extracted with Et_2O (1 × 15 mL). The combined organic phases were washed with water (15 mL), and the solvents were removed. The components of the residual yellow solid were separated by column chromatography (5 cm × 40 cm). Eluting first with pentane/Et_2O 5:1 gave diiodobenzene **2** (7.57 g, 72%; R_f (pentane/Et_2O 5:1) = 0.70; R_f (pentane/Et_2O 3:1) = 0.80). Then, the eluent was changed to pentane/Et_2O 3:1, and monoiodo building block $\mathbf{3}_2$ (4.09 g, 72%; R_f (pentane/Et_2O 5:1) = 0.15; R_f (pentane/Et_2O 3:1) = 0.38) was obtained as a yellow solid. Finally, pentane/Et_2O 2:1 was used to elute dicoupling product $\mathbf{4}_3$ (770 mg, 10% ; R_f (pentane/Et_2O 5:1) = 0; R_f (pentane/Et_2O 3:1) = 0.08; R_f (pentane/Et_2O 2:1) = 0.53) and a mixture (105 mg; R_f (pentane/Et_2O 3:1) = 0.08; R_f (pentane/Et_2O 2:1) = 0.53 and 0.45) of dicoupling product $\mathbf{4}_3$ and alkyne dimer $\mathbf{8}_1$ in the molar ratio of 6:94. Analytical data of monoiodo building block $\mathbf{3}_2$: for ^{1}H NMR and ^{13}C NMR data, see Tables S3 and S4. Accurate MS (ESI): m/z calcd for $[M + Na]^+$ $C_{67}H_{103}IO_5Si_4Na^+$, 1249.58195; found, 1249.58082. Elemental analysis calcd (%) for $C_{67}H_{103}IO_5Si_4$: C, 65.54; H, 8.46; found: C, 65.55; H, 8.78. Analytical data of dicoupling product $\mathbf{4}_3$: for ^{1}H NMR and ^{13}C NMR data, see Tables S5 and S6. MS (ESI): m/z 1725.9 $[M + Na]^+$.

Monoiodo Building Block $\mathbf{3}_4$. See the general procedure for alkynyl-aryl coupling. Diiodobenzene **2** (3.82 g, 5.09 mmol), alkyne $\mathbf{7}_3$ (2.70 g, 1.64 mmol), piperidine (20 mL, 202 mmol), THF (80 mL), and catalysts $PdCl_2(PPh_3)_2$ (15 mg, 21.4 μmol) and CuI (8 mg, 42 μmol) at room temperature with a reaction time of 40 h. After the reaction, Et_2O and H_2O were added to the reaction mixture, a yellow suspension. The phases were separated, and the aqueous phase was extracted three times with Et_2O. The combined organic phases were washed three times with 2 M HCl and once with a saturated aqueous solution of NaCl, dried over $MgSO_4$, and filtered. The solvents were removed, and the residue was chromatographed (7.5 cm × 16 cm, pentane/CH_2Cl_2 1:1). Monoiodo building block $\mathbf{3}_4$ (1.55 g, 42%; R_f (pentane/CH_2Cl_2 1:1) = 0.11) was obtained as a yellow solid and diiodobenzene **2** (3.09 g, 81%; R_f (pentane/CH_2Cl_2 1:1) = 0.72) as a beige solid. Analytical data of monoiodo building block $\mathbf{3}_4$: for ^{1}H NMR and ^{13}C NMR data, see Tables S3 and S4. Accurate MS (ESI): m/z calcd for $[M + Na]^+$ $C_{131}H_{199}IO_9Si_8Na^+$, 2290.22051; found, 2290.21686.

Monomer (OligoPPE) $\mathbf{5}_1$. See the general procedure for alkynyl-aryl coupling. Monoiodobenzene $\mathbf{3}_1$ (16.7 g, 23.6 mmol), trimethylsilylacetylene ($\mathbf{6}_0$) (5.00 mL, 35.4 mmol), piperidine (117 mL, 1.18 mol), THF (120 mL), and catalysts $PdCl_2(PPh_3)_2$ (332 mg, 0.47 mmol) and CuI (171 mg, 0.90 mmol) at room temperature with a reaction time of 38 h. After the reaction, all volatiles were removed at room temperature and reduced pressure. The residual black solid was suspended in dry Et_2O (50 mL), and the suspension was filtered through silica gel (4.5 cm × 11 cm, rinsing with Et_2O). The eluate was concentrated (final volume: ∼100 mL) and washed with 1 M HCl (100 mL) and then with a saturated aqueous solution of NaCl (100 mL).[109] The aqueous phase was extracted with Et_2O (2 × 50 mL). The combined organic phases were dried over $MgSO_4$ and filtered, and the solvent was removed. Chromatography (7.0 cm × 70 cm, pentane/Et_2O 2:1) of the residual black viscous oil gave monomer $\mathbf{5}_1$ (14.4 g, 90%; R_f (pentane/Et_2O 2:1) = 0.53) as a yellow solid. For ^{1}H and ^{13}C NMR data, see Tables S7 and S8. Accurate MS (ESI): m/z calcd for $[M + Na]^+$ $C_{40}H_{64}O_3Si_3Na^+$, 699.40555; found, 699.40500.

OligoPPE $\mathbf{5}_2$. See the general procedure for alkynyl-aryl coupling. Alkyne $\mathbf{6}_1$ (728 mg, 1.18 mmol), monoiodobenzene $\mathbf{3}_1$ (758 mg, 1.07 mmol), piperidine (4.0 mL, 40.5 mmol), THF (20 mL), and catalysts $PdCl_2(PPh_3)_2$ (6.88 mg, 9.8 μmol) and CuI (3.90 mg, 20 μmol) at room temperature with a reaction time of 45 h. After the reaction, all volatiles were removed at room temperature and reduced pressure. The residual mixture of a yellow viscous oil and a solid was dissolved in a mixture of Et_2O (30 mL), H_2O (20 mL), and 2 M HCl (10 mL). The organic phase was separated, and the aqueous phase was extracted with Et_2O (1 × 10 mL). The combined organic phases were washed with H_2O (1 × 10 mL), and the solvents were removed. Chromatography (4.0 cm × 35 cm, pentane/Et_2O 3:1) of the residual orange solid gave oligoPPE $\mathbf{5}_2$ (1.20 g, 93%; R_f = 0.36) as a yellow solid and alkyne dimer $\mathbf{9}_1$ (63 mg, R_f = 0.85) as an orange solid. Analytical data of oligoPPE $\mathbf{5}_2$: for ^{1}H and ^{13}C NMR data, see Tables S7 and S8. MS (ESI): m/z 1219.6 $[M + Na]^+$, 1197.6 $[M + H]^+$. Accurate MS (ESI): m/z calcd for $[M + Na]^+$ $C_{72}H_{112}O_5Si_5Na^+$, 1219.72483; found, 1219.72184. Elemental analysis calcd (%) for $C_{72}H_{112}O_5Si_5$: C, 72.18; H, 9.42; found: C, 72.51; H, 9.71. Analytical data of alkyne dimer $\mathbf{9}_1$: for ^{1}H NMR data, see Table S13.

OligoPPE $\mathbf{5}_3$. See the general procedure for alkynyl-aryl coupling. Alkyne $\mathbf{6}_1$ (985 mg, 1.59 mmol), monoiodo building block $\mathbf{3}_2$ (1.77 g, 1.44 mmol), piperidine (7.15 mL, 72.4 mmol), THF (15 mL), and catalysts $PdCl_2(PPh_3)_2$ (8.61 mg, 12.3 μmol) and CuI (4.52 mg, 23.7 μmol) at room temperature with a reaction time of 48 h. After the reaction, all volatiles were removed at room temperature and reduced pressure. The residual yellow solid was dissolved in a mixture of Et_2O (30 mL), H_2O (15 mL), and 2 M HCl (10 mL). The organic phase was separated, and the aqueous phase was extracted with Et_2O (2 × 10 mL). The organic phases were combined, and the solvents were removed. Chromatography (5.0 cm × 32 cm, pentane/Et_2O 3:1) of the residual yellow solid gave oligoPPE $\mathbf{5}_3$ (2.43 g, 98%; R_f = 0.40) as a yellow solid. For ^{1}H and ^{13}C NMR data, see Tables S7 and S8. MS (ESI): m/z = 1740.0 $[M + Na]^+$, 1718.1 $[M + H]^+$. Accurate MS (ESI): m/z calcd for $[M + Na]^+$ $C_{104}H_{160}O_7Si_7Na^+$, 1740.04411; found, 1740.04250. Elemental analysis calcd (%) for $C_{104}H_{160}O_7Si_7$: C, 72.67; H, 9.38; found: C, 73.16; H, 9.79.

OligoPPE $\mathbf{5}_4$. See the general procedure for alkynyl-aryl coupling. Alkyne $\mathbf{6}_3$ (200 mg, 120 μmol) accompanied by dialkyne $\mathbf{10}_3$ (4 mg, 2.5 μmol), monoiodobenzene $\mathbf{3}_1$ (107 mg, 151 μmol), piperidine (0.9 mL, 9.1 mmol), THF (3 mL), and catalysts $Pd(PPh_3)_4$ (1.50 mg, 1.30 μmol) and CuI (0.805 mg, 4.23 μmol). The reaction mixture was stirred at room temperature for 70 h. Then, 2-methylbut-3-yn-2-ol (HOP-acetylene, $\mathbf{7}_0$) (12 μL, 123 μmol) was added, and the yellow suspension was stirred at room temperature for another 46 h. Then, all volatiles were removed at room temperature and reduced pressure. The components of the residual yellow solid were separated by column chromatography (3.5 cm × 45 cm). Eluting with pentane/Et_2O 3:1 gave alkyne dimer $\mathbf{9}_3$ (5 mg, 1%, R_f (pentane/Et_2O 3:1) = 0.91; R_f (pentane/Et_2O 1:1) = 0.98) as a yellow solid and oligoPPE $\mathbf{5}_4$ (271 mg, 99%, R_f (pentane/Et_2O 3:1) = 0.45; R_f (pentane/Et_2O 1:1) = 0.80) as a yellow solid. Then, the eluent was changed to pentane/Et_2O 1:1 and a yellow solid (14 mg, R_f (pentane/Et_2O 3:1) = 0.10; R_f (pentane/Et_2O 1:1) = 0.62) consisting of oligoPPE $\mathbf{4}_1$ and oligoPPE $\mathbf{4}_5$ in a molar ratio of 41:59 was obtained. Analytical data of oligoPPE $\mathbf{5}_4$: for ^{1}H and ^{13}C NMR data, see Tables S7 and S8. MS (ESI): m/z 2260.5 $[M + Na]^+$. Accurate MS (ESI): m/z calcd for $[M + 2Na]^{2+}$ $C_{136}H_{208}O_9Si_9Na_2^{2+}$: 1141.67631; found, 1141.67673. Analytical data of alkyne dimer $\mathbf{9}_3$: for ^{1}H NMR data, see Table S13. Accurate MS (ESI): m/z calcd for $[M + 2Na]^{2+}$ $C_{202}H_{306}O_{12}Si_{14}Na_2^{2+}$, 1680.99442; found, 1680.99491. Analytical data of the mixture of oligoPPE $\mathbf{4}_1$ and oligoPPE $\mathbf{4}_5$: for ^{1}H NMR data, see Table S5. MS (ESI): m/z 685.5 $[\mathbf{4}_1 + Na]^+$, 2767.0 $[\mathbf{4}_5 + Na]^+$. Accurate MS (ESI): m/z calcd for $[\mathbf{4}_1 + Na]^+$ $C_{40}H_{62}O_4Si_2Na^+$, 685.40788; found, 685.40824; calcd for $[\mathbf{4}_5 + 2Na]^{2+}$ $C_{168}H_{254}O_{12}Si_{10}Na_2^{2+}$, 1394.83712; found, 1394.83775.

OligoPPE $\mathbf{5}_5$. See the general procedure for alkynyl-aryl coupling. Alkyne $\mathbf{6}_3$ (456 mg, 274 μmol) accompanied by dialkyne $\mathbf{10}_3$ (9 mg, 5.6 μmol), monoiodo building block $\mathbf{3}_2$ (411 mg, 335 μmol),

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piperidine (2.0 mL, 20.2 mmol), THF (10 mL), and catalysts $Pd(PPh_3)_4$ (2.94 mg, 2.55 μmol) and CuI (1.25 mg, 6.56 μmol). The reaction mixture, a yellow suspension, was stirred at room temperature for 70 h. Then, 2-methylbut-3-yn-2-ol (HOP-acetylene, $\mathbf{7_0}$) (25 μL, 256 μmol) was added, and the yellow suspension was stirred at room temperature for another 46 h. Then, all volatiles were removed at room temperature and reduced pressure. Chromatography (4.0 cm × 40 cm, pentane/Et_2O 3:1) of the residual yellow solid gave oligoPPE $\mathbf{5_5}$ (755 mg, 100%, R_f = 0.36) as a yellow solid. For ^1H and ^{13}C NMR data, see Tables S7 and S8. MS (ESI): *m/z* 2780.9 $[M + Na]^+$. Accurate MS (ESI): *m/z* calcd for $[M + 2Na]^{2+}$ $C_{168}H_{256}O_{11}Si_{11}Na_2^{2+}$, 1401.83595; found, 1401.83633.

OligoPPE $\mathbf{5_6}$. See the general procedure for alkynyl-aryl coupling. Alkyne $\mathbf{6_5}$ (190 mg, 70.2 μmol) accompanied by dialkyne $\mathbf{10_5}$ (12 mg, 4.5 μmol), monoiodobenzene $\mathbf{3_1}$ (48 mg, 67.9 μmol), piperidine (1.0 mL, 10.1 mmol), THF (5 mL), and catalysts $Pd(PPh_3)_4$ (1.70 mg, 1.47 μmol) and CuI (0.748 mg, 3.93 μmol). The reaction mixture, a yellow suspension, was stirred at room temperature for 3 d. Et_2O and H_2O were added. The organic phase was separated, and the aqueous phase was extracted with Et_2O. The organic phases were combined and washed with 2 M HCl and a saturated aqueous solution of NaCl and then dried over $MgSO_4$. The solvents were removed. Chromatography (2.0 cm × 30 cm, pentane/CH_2Cl_2 1:2) of the residual yellow solid gave oligoPPE $\mathbf{5_6}$ (171 mg, 83%; R_f = 0.46) as a yellow solid. For ^1H and ^{13}C NMR data, see Tables S7 and S8. Accurate MS (ESI): *m/z* calcd for $[M + 2Na]^{2+}$ $C_{200}H_{304}O_{13}Si_{13}Na_2^{2+}$, 1661.99928; found, 1661.99559.

OligoPPE $\mathbf{5_7}$. See the general procedure for alkynyl-aryl coupling. Alkyne $\mathbf{6_3}$ (780 mg, 470 μmol) accompanied by dialkyne $\mathbf{10_3}$ (24 mg, 15 μmol), monoiodo building block $\mathbf{3_4}$ (998 mg, 440 μmol), piperidine (6.0 mL, 60.6 mmol), THF (24 mL), and catalysts $PdCl_2(PPh_3)_2$ (8.0 mg, 11.4 μmol) and CuI (4.0 mg, 21.0 μmol) at room temperature with a reaction time of 3 d. Et_2O and H_2O were added. The organic phase was separated, and the aqueous phase was extracted first with Et_2O, then with Et_2O/CH_2Cl_2 (1:1), and finally with CH_2Cl_2. The combined organic phases were washed with 2 M HCl and a saturated aqueous solution of NaCl and then dried over $MgSO_4$. The solvents were removed. Chromatography (2.0 cm × 30 cm, pentane/CH_2Cl_2 1:2) of the residual yellow solid gave oligoPPE $\mathbf{5_7}$ (1.57 g, 96%; R_f = 0.56) as a yellow solid. Mp: 182−183 °C. For ^1H and ^{13}C NMR data, see Tables S7 and S8. Accurate MS (ESI): *m/z* calcd for $[M + 2Na]^{2+}$ $C_{232}H_{352}O_{15}Si_{15}Na_2^{2+}$, 1922.15524; found, 1922.15714.

General Procedure for the Removal of the HOP Group. Under argon, a suspension of oligoPPE $\mathbf{5_n}$ and powdered dry NaOH in dry toluene was heated to reflux. The reaction was monitored by thin layer chromatography (pentane/Et_2O 5:1). The suspension was filtered through silica gel, and the silica gel was rinsed with dry Et_2O or dry THF. The solvents of the eluate were removed.

Alkyne $\mathbf{6_1}$. A small scale and a large scale reaction are reported.

Small Scale Reaction. See the general procedure for the removal of the HOP group. OligoPPE $\mathbf{5_1}$ (330 mg, 487 μmol), NaOH (65 mg, 1.63 mmol), toluene (8 mL) with a reaction time of 45 min; the suspension was then filtered through silica gel (2.0 cm × 6.0 cm) and the silica gel was rinsed with dry Et_2O. Alkyne $\mathbf{6_1}$ (299 mg, 99%) was obtained as a pale yellow solid. No dialkyne $\mathbf{10_1}$ was detected.

Large Scale Reaction. See the general procedure for the removal of the HOP group. OligoPPE $\mathbf{5_1}$ (4.05 g, 5.98 mmol), NaOH (256 mg, 6.40 mmol), toluene (30 mL) with a reaction time of 75 min; the suspension was then filtered through silica gel (4.0 cm × 4.0 cm) and the silica gel was rinsed with dry Et_2O. A yellow viscous oil (3.47 g), which contained alkyne $\mathbf{6_1}$ and dialkyne $\mathbf{10_1}$ in the molar ratio of 57:43, was obtained. This crude product was subjected to column chromatography (6.0 cm × 55 cm, pentane/Et_2O 15:1) to isolate alkyne $\mathbf{6_1}$ (1.99 g, 54%; R_f = 0.68) as a colorless solid. Additionally, column chromatography gave a slight yellow solid (442 mg) containing alkyne $\mathbf{6_1}$ and dialkyne $\mathbf{10_1}$ in a molar ratio of 15:85 and dialkyne $\mathbf{10_1}$ (954 mg, 29%; R_f = 0.55) as a colorless solid. Analytical data of alkyne $\mathbf{6_1}$: Mp 33−34 °C. For ^1H NMR and ^{13}C NMR data, see Tables S9 and S10. Accurate MS (ESI): *m/z* calcd for $[M + Na]^+$ $C_{37}H_{58}O_2Si_3Na^+$, 641.36368; found, 641.36378. Elemental analysis calcd (%) for $C_{37}H_{58}O_2Si_3$: C, 71.78; H, 9.44; found: C, 71.76; H, 9.85. Analytical data of dialkyne $\mathbf{10_1}$: for ^1H NMR and ^{13}C NMR data, see Tables S14 and S15. MS (ESI): *m/z* 569.3 $[M + Na]^+$.

Alkyne $\mathbf{6_2}$. See the general procedure for the removal of the HOP group. OligoPPE $\mathbf{5_2}$ (561 mg, 468 μmol), NaOH (49 mg, 1.23 mmol), toluene (9 mL) with a reaction time of 35 min; the suspension was then filtered through silica gel (2.0 cm × 6.0 cm) and the silica gel was rinsed with dry Et_2O. The obtained brown viscous oil consisted of alkyne $\mathbf{6_2}$ and dialkyne $\mathbf{10_2}$ in the molar ratio of 98:2. Column chromatography (3.0 cm × 52 cm, pentane/Et_2O 10:1) of this material gave alkyne $\mathbf{6_2}$ (510 mg, 96%; R_f = 0.55) as a yellow solid and a mixture (14 mg; R_f = 0.46 and 0.55) of $\mathbf{6_2}$ and $\mathbf{10_2}$ in the ratio of 1.0:0.93 as a yellow solid. Analytical data of alkyne $\mathbf{6_2}$: Mp 83−85 °C. For ^1H NMR and ^{13}C NMR data, see Tables S9 and S10. MS (ESI): *m/z* 1161.7 $[M + Na]^+$. Accurate MS (ESI): *m/z* calcd for $[M + Na]^+$ $C_{69}H_{106}O_4Si_5Na^+$, 1161.68297; found, 1161.68126. Elemental analysis calcd (%) for $C_{69}H_{106}O_4Si_5$: C, 72.70; H, 9.37; found: C, 72.62; H, 9.44.

Alkyne $\mathbf{6_3}$. See the general procedure for the removal of the HOP group. OligoPPE $\mathbf{5_3}$ (1.89 g, 1.10 mmol), NaOH (153 mg, 3.83 mmol), and toluene (18 mL) with a reaction time of 35 min; the suspension was then filtered through silica gel (2.0 cm × 6.0 cm) and the silica gel was rinsed with dry Et_2O. The obtained yellow solid contained alkyne $\mathbf{6_3}$ and dialkyne $\mathbf{10_3}$ in the molar ratio of 97:3. Column chromatography (5.0 cm × 55 cm, pentane/Et_2O 10:1) of this material gave a yellow solid (1.79 g; R_f = 0.50) consisting of alkyne $\mathbf{6_3}$ (96% yield) and dialkyne $\mathbf{10_3}$ in the molar ratio of 98:2. Mp: 131−132 °C. Analytical data of alkyne $\mathbf{6_3}$ obtained from the mixture of alkyne $\mathbf{6_3}$ and dialkyne $\mathbf{10_3}$: for ^1H NMR and ^{13}C NMR data, see Tables S9 and S10. Accurate MS (ESI): *m/z* calcd for $[M + Na]^+$ $C_{101}H_{154}O_6Si_7Na^+$, 1682.00225; found, 1682.00101. Elemental analysis calcd (%) for $C_{101}H_{154}O_6Si_7$: C, 73.04; H, 9.35; found: C, 72.99; H, 9.42.

Alkyne $\mathbf{6_4}$. See the general procedure for the removal of the HOP group. OligoPPE $\mathbf{5_4}$ (158 mg, 70.5 μmol), NaOH (6 mg, 150 μmol), and toluene (3 mL). Thin layer chromatographical analysis after a reaction time of 70 min showed an intense spot of oligoPPE $\mathbf{5_4}$. Therefore, additional NaOH (21 mg, 525 μmol) was added to the reaction mixture, and the suspension was heated to reflux for another 55 min; the suspension was then filtered through silica gel (1.0 cm × 9.0 cm) and the silica gel was rinsed with dry Et_2O. The ^1H NMR spectrum of the obtained yellow solid revealed a conversion of ∼30% of oligoPPE $\mathbf{5_4}$ to alkyne $\mathbf{6_4}$. The yellow solid was dissolved in toluene; NaOH (12 mg, 30 μmol) was added, and the reaction mixture was heated to reflux for 190 min. The suspension was then filtered through silica gel and the silica gel was rinsed with dry Et_2O followed by solvent removal. The ^1H NMR spectrum of the yellow solid residue revealed a conversion of ∼65% of oligoPPE $\mathbf{5_4}$ to alkyne $\mathbf{6_4}$ and dialkyne $\mathbf{10_4}$. This material was chromatographed (1.5 cm × 27 cm, pentane/CH_2Cl_2 1:1) giving a yellow solid (100 mg; R_f = 0.80, Mp: 150−151 °C) consisting of alkyne $\mathbf{6_4}$ (61% yield) and dialkyne $\mathbf{10_4}$ in the molar ratio of 96:4. Additionally, oligoPPE $\mathbf{5_4}$ (57 mg, 35%; R_f = 0.20) was isolated. Analytical data of alkyne $\mathbf{6_4}$ obtained from the mixture of alkyne $\mathbf{6_4}$ and dialkyne $\mathbf{10_4}$: for ^1H NMR and ^{13}C NMR data, see Tables S9 and S10. MS (ESI): *m/z* 2202.5 $[M + Na]^+$.

Alkyne $\mathbf{6_5}$. See the general procedure for the removal of the HOP group. OligoPPE $\mathbf{5_5}$ (492 mg, 178 μmol), NaOH (19 mg, 475 μmol), and toluene (7 mL) with a reaction time of 60 min; the suspension was then filtered through silica gel (2.0 cm × 5.0 cm) and the silica gel was rinsed with dry Et_2O. Column chromatography (2.0 cm × 31 cm, pentane/CH_2Cl_2 1:1) of the obtained yellow solid gave a yellow solid (478 mg; R_f = 0.71; Mp: 162−163 °C) consisting of alkyne $\mathbf{6_5}$ (93% yield) and dialkyne $\mathbf{10_5}$ in the molar ratio of 94:6. Additionally, oligoPPE $\mathbf{5_5}$ (20 mg, 4%; R_f = 0.13) was isolated. Analytical data of alkyne $\mathbf{6_5}$ obtained from the mixture of alkyne $\mathbf{6_5}$ and dialkyne $\mathbf{10_5}$: for ^1H NMR and ^{13}C NMR data, see Tables S9 and S10. MS (ESI): *m/z* 2722.5 $[M + Na]^+$.

Alkyne $\mathbf{6_6}$. See the general procedure for the removal of the HOP group. OligoPPE $\mathbf{5_6}$ (160 mg, 48.8 μmol), NaOH (8 mg, 200 μmol),

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and toluene (4 mL) with a reaction time of 150 min. Thin layer chromatographical analysis showed an intense spot of starting material. Additional NaOH (11 mg, 275 μmol) was given to the reaction mixture, and the suspension was heated to reflux for another 340 min; the suspension was then filtered through silica gel and the silica gel was rinsed with dry Et_2O. Column chromatography (1.5 cm × 25 cm, pentane/CH_2Cl_2 1:1) of the obtained yellow solid gave a yellow solid (142 mg, R_f = 0.80; Mp: 158−160 °C) consisting of alkyne **6**$_6$ (88% yield) and dialkyne **10**$_6$ in the molar ratio of 98:2. Additionally, oligoPPE **5**$_6$ (17 mg, 11%; R_f = 0.20) was isolated. Analytical data of alkyne **6**$_6$ obtained from the mixture of alkyne **6**$_6$ and dialkyne **10**$_6$: for ^{1}H NMR and ^{13}C NMR data, see Tables S9 and S10. MS (ESI): m/z 1633.2 $[M + 2Na]^{2+}$.

Alkyne **6**$_7$. See the general procedure for the removal of the HOP group. OligoPPE **5**$_7$ (503 mg, 132 μmol), NaOH (15 mg, 375 μmol), and toluene (13 mL) with a reaction time of 205 min; the suspension was then filtered through silica gel and the silica gel was rinsed with dry Et_2O. Column chromatography (2 cm × 31 cm, pentane/CH_2Cl_2 1:1) of the residual yellow solid gave a yellow solid (341 mg; R_f = 0.83; Mp: 174−176 °C) consisting of alkyne **6**$_7$ (67% yield) and dialkyne **10**$_7$ in the molar ratio of 98:2. Additionally, oligoPPE **5**$_7$ (155 mg, 31%; R_f = 0.21) was isolated. Analytical data of alkyne **6**$_7$ obtained from the mixture of alkyne **6**$_7$ and dialkyne **10**$_7$: for ^{1}H NMR and ^{13}C NMR data, see Tables S9 and S10. MS (ESI): m/z 1893.4 $[M + 2Na]^{2+}$.

Alkyne **7**$_1$. OligoPPE **5**$_1$ (3.99 g, 5.90 mmol) was dissolved in MeOH (200 mL) at 50 °C. K_2CO_3 (0.73 g, 5.30 mmol) was added. During 40 min of stirring at 50 °C, the K_2CO_3 went into solution. The solution was stirred for another 40 min at 50 °C, then cooled to room temperature, and stirred at room temperature for 80 min. The solvent was removed. The residue was suspended in Et_2O (20 mL), and the solution was filtered through silica gel (4.0 cm × 4.0 cm, rinsing with Et_2O). Solvent removal from the eluate provided alkyne **7**$_1$ (3.59 g, 100%) as a brown viscous oil. For ^{1}H NMR and ^{13}C NMR data, see Tables S11 and S12. Accurate MS (ESI): m/z calcd for $[M + Na]^+$ $C_{37}H_{56}O_3Si_2Na^+$, 627.36602; found, 627.36600. Elemental analysis calcd (%) for $C_{37}H_{56}O_3Si_2$: C, 73.45; H, 9.33; found: C, 73.39; H, 9.36.

Alkyne **7**$_3$. OligoPPE **5**$_3$ (3.01 g, 1.75 mmol) was dissolved in MeOH (100 mL) and CH_2Cl_2 (100 mL), and K_2CO_3 (274 mg, 1.98 mmol) was added. The suspension was stirred at room temperature for 80 min. Et_2O and H_2O were added. The organic phase was separated, and the aqueous phase was extracted with Et_2O. The combined organic phases were washed with H_2O and then with a saturated aqueous solution of NaCl, dried over $MgSO_4$, and filtered. The solvents were removed. The ^{1}H NMR spectrum of the residual yellow solid revealed an incomplete removal of the TMS groups. Therefore, this solid was dissolved in MeOH (100 mL) and CH_2Cl_2 (100 mL); K_2CO_3 (297 mg, 2.15 mmol) was added, and the suspension was stirred for 4 h at room temperature. Et_2O and H_2O were added. The same workup procedure as described above gave alkyne **7**$_3$ (2.80 g, 97%) as a yellow solid. Mp: 127−128 °C. For ^{1}H NMR and ^{13}C NMR data, see Tables S11 and S12. MS (ESI): m/z 1668.2 $[M + Na]^+$.

PEG Alkene **12**. The published procedure[96] was followed with small changes. Triethylene glycol monomethyl ether (35.5 g, 216 mmol) was added to a suspension of NaH (60 wt % dispersion in mineral oil, 15.0 g, 375 mmol) and 3-chloro-2-(chloromethyl)prop-1-ene (13.0 g, 100 mmol) in dry THF (140 mL) within 40 min under ice bath cooling. The suspension was stirred at 65 °C for 18 h and then cooled to room temperature. H_2O (5 mL) was added slowly, followed by a saturated aqueous solution of NaCl (20 mL) and Et_2O (30 mL). A precipitate formed in the aqueous phase. As much H_2O was added to the mixture as needed to dissolve the precipitate. The phases were separated, and the aqueous phase was extracted with Et_2O (4 × 30 mL). The combined organic phases were washed with a saturated aqueous solution of NaCl and dried over Na_2SO_4 and filtered, and the solvents were removed. Column chromatography (8.0 cm × 20 cm, Et_2O/EtOH 10:1; iodine vapor was used for staining the spots on the TLC) of the residue gave PEG alkene **12** (35.4 g, 93%; R_f = 0.22) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.17 (s, 2H, $H_2C{=}C$), 4.00 (s, 4H, $H_2C{=}C(C\underline{H}_2)$), 3.67−3.60 and 3.59−3.50 (2 m, 16H and 8H, respectively, OCH_2), 3.36 (s, 6H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 142.2 ($H_2C{=}\underline{C}$), 113.5 ($H_2\underline{C}{=}C$), 71.5, 71.3, 70.2, 70.13, 70.09, and 69.1 (OCH_2), 58.5 (CH_3). Accurate MS (ESI): m/z calcd for $[M + Na]^+$ $C_{18}H_{36}O_8Na^+$, 403.23024; found, 403.23127. Elemental analysis calcd (%) for $C_{18}H_{36}O_8$: C, 56.82; H, 9.54; found: C, 56.71; H, 9.69.

PEG-Br **13**. A solution of BH_3·THF (1.0 M, 29.0 mL, 29.0 mmol) in THF was added dropwise within 45 min to a solution of PEG-alkene **12** (10.0 g, 26.3 mmol) in dry THF (60 mL), which was cooled in an ice bath. The solution was stirred while cooling with an ice bath for 15 min and at room temperature for 90 min. MeOH (5.0 mL, 123 mmol) was added cautiously to the ice-cooled solution to destroy excess borane (***Caution!*** *Strong gas development*). After 10 min of stirring, Br_2 (2.25 mL, 43.9 mmol) and a solution of NaOMe (5.4 M, 6.45 mL, 34.8 mmol) in methanol were separately but simultaneously added to the ice-cooled solution within 25 min at such a rate that the solution stayed a faint yellow. After 20 min, the ice bath was removed, and the suspension was stirred at room temperature for 1 h. To the orange suspension was added an aqueous solution of $Na_2S_2O_3$ (1.0 M) at a volume just enough as was needed to decolorize the suspension. After adding a saturated aqueous solution of NH_4Cl (50 mL), the organic phase was separated, and the aqueous phase was extracted with Et_2O (10 × 20 mL). The organic phases were combined, and the solvents were removed. Column chromatography (6.5 cm × 35 cm, Et_2O/EtOH 10:1; iodine vapor was used for staining the spots on the TLC) of the residue gave PEG-Br **13** (6.75 g, 56%; R_f = 0.40) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.68−3.42 (m, 30H, CH_2), 3.36 (s, 6H, CH_3), 2.25 (m, 1H, CH). ^{13}C NMR (125 MHz, $CDCl_3$): δ 71.7, 70.43, 70.41, 70.33, 70.25, and 69.8 (OCH_2), 58.8 (CH_3), 41.1 (CH), 33.3 ($BrCH_2$). Accurate MS (ESI): m/z calcd for $[M + Na]^+$ $C_{18}H_{37}BrO_8Na^+$, 483.15640; found, 483.15761. Elemental analysis calcd (%) for $C_{18}H_{37}BrO_8$: C, 46.86; H, 8.08; found: C, 46.43; H, 8.24.

PEG-N$_3$ **14**. A solution of PEG-Br **13** (3.53 g, 7.66 mmol), NaN_3 (1.49 g, 23.0 mmol) in acetone (30 mL), and H_2O (3.0 mL) was stirred at 60 °C for 48 h. Because PEG-Br **13** and PEG-N$_3$ **14** have identical R_f values, the reaction was monitored using ^{1}H NMR spectroscopy. The solvents of the solution were removed. The residue, a mixture of a colorless oil and a colorless solid, was dried at reduced pressure and then suspended in Et_2O (20 mL). The suspension was filtered, and the solvents of the filtrate were removed. Column chromatography (3.5 cm × 20 cm, Et_2O/EtOH 10:1; iodine vapor was used for staining the spots on the TLC) of the residue provided PEG-N$_3$ **14** (3.13 g, 97%; R_f = 0.40) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.68−3.38 (m, 30H, CH_2), 3.37 (s, 6H, CH_3), 2.15 (sept-like, 1H, CH). ^{13}C NMR (125 MHz, $CDCl_3$): δ 71.8, 70.49, 70.46, 70.45, 70.39, 70.31, and 69.3 (OCH_2), 58.9 (CH_3), 50.1 (N_3CH_2), 39.7 (CH). Accurate MS (ESI): m/z calcd for $[M + Na]^+$ $C_{18}H_{37}N_3O_8Na^+$, m/z 446.24729; found, 446.24812.

Diiodobenzene **15**. Our procedure deviates slightly from the published one.[110] K_2CO_3 (3.82 g, 27.6 mmol) was suspended in a solution of 2,5-diiodohydroquinone (**1**) (2.01 g, 5.56 mmol) and propargyl bromide (1.98 g of an 80 wt % solution in toluene, 13.3 mmol) in anhydrous acetone (40 mL). The suspension was stirred at 60 °C for 28 h. After cooling to room temperature, the suspension was filtered through silica gel (4 cm × 4 cm, rinsing with Et_2O); the solvents of the eluate were removed, and the residue was recrystallized in MeOH (130 mL) to give diiodobenzene **15** (2.14 g, 88%) as faint yellow needle-like crystals. Mp: 148−149 °C. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.38 (s, 2H, H_{Ar}), 4.71 (d, 4H, ^4J = 2.4 Hz, CH_2), 2.63 (t, 2H, ^4J = 2.4 Hz, C≡CH). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 152.5 ($C_{Ar}O$), 124.3 ($C_{Ar}H$), 86.4 ($C_{Ar}I$), 78.0 ($\underline{C}{\equiv}CH$), 76.6 ($C{\equiv}\underline{C}H$), 58.3 ($O\underline{C}H_2C{\equiv}C$). MS (EI, 70 eV): m/z (%) 437.8 (60) $[M]^{+\bullet}$, 398.8 (78) $[M - CH_2C{\equiv}CH]^+$, 271.9 (66) $[M - CH_2C{\equiv}CH - I]^+$, 243.9 (20), 204.9 (9), 145.0 (27), 89.0 (18), 39.0 (100). Accurate MS (EI, 70 eV): m/z calcd for $[M]^{+\bullet}$ $C_{12}H_8I_2O_2^{+\bullet}$: 437.86082; found, 437.86109.

Diiodobenzene **16**. A solution of diiodobenzene **15** (920 mg, 2.10 mmol) and PEG-N$_3$ **14** (2.23 g, 5.28 mmol) in THF (12 mL) and

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EtOH (6 mL) was degassed through three freeze−pump−thaw cycles. A degassed aqueous solution of $CuSO_4$ (2.1 mL, 0.1 M solution, 0.21 mmol) and a degassed solution of sodium L-ascorbate (419 mg, 2.11 mmol) in H_2O (2.0 mL) were added. The brown suspension was stirred at 60 °C for 5 d. It was cooled to room temperature, and the solvents of the solution were removed. Chromatography (5 cm × 40 cm, CH_2Cl_2/EtOH 15:1; iodine vapor was used for staining the spots of PEG-N_3 **14** on the TLC) of the residue gave diiodobenzene **16** (1.95 g, 72%; R_f = 0.50) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.87 (br s, 2H, $H_{triazole}$), 7.33 (s, 2H, $H_{benzene}$), 5.14 (s, 4H, triazole-C$\underline{H}_2$O), 4.50 (d, ^3J = 6.1 Hz, 4H, NCH_2), 3.68−3.45 (m, 48H, OCH_2CH_2), 3.40−3.30 (m, 8H, OC$\underline{H}_2$CH), 3.30 (s, 12 H, CH_3), 2.47 (sept-like, 2H, CH). ^{1}H NMR (500 MHz, CD_3OD): δ 8.16 (s, 2H, $H_{triazole}$), 7.49 (s, 2H, $H_{benzene}$), 5.20 (s, 4H, triazole-C$\underline{H}_2$O), 4.56 (d, ^3J = 6.4 Hz, 4H, NCH_2), 3.65−3.47 (m, 48H, OCH_2CH_2), 3.41−3.37 (m, 8H, OC$\underline{H}_2$CH), 3.31 (s, 12 H, CH_3), 2.47 (sept-like, 2H, CH). ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.6 (C_{Ar}O), 142.9 (br, low intensity, $\underline{C}_{triazole}CH_2$), 124.8 (br, low intensity, $C_{triazole}$H), 123.8 ($C_{benzene}$H), 86.53 (C−I), 71.8, 70.52, 70.45, 70.39, and 70.25 (OCH_2CH_2), 68.8 (O$\underline{C}$H$_2$CH), 64.4 (triazole-$\underline{C}$H$_2$O), 58.9 (CH_3), 48.5 (NCH_2), 40.3 (CH). ^{13}C NMR (125 MHz, CD_3OD): δ 154.1 (C_{Ar}O), 143.9 ($\underline{C}_{triazole}CH_2$), 127.2 ($C_{triazole}$H), 125.4 ($C_{benzene}$H), 87.8 (C−I), 72.9, 71.53, 71.52, 71.50, 71.35, and 71.30 (OCH_2CH_2), 70.0 (O$\underline{C}$H$_2$CH), 64.9 (triazole-$\underline{C}$H$_2$O), 59.1 (CH_3), 49.8 (NCH_2), 41.8 (CH). MS (ESI): 1307.5 $[M + Na]^+$, 665.3 $[M + 2Na]^{2+}$. Accurate MS (ESI): m/z calcd for $[M + 2Na]^{2+}$ $C_{48}H_{82}I_2N_6O_{18}Na_2^{2+}$: m/z 665.17797; found, 665.17625. Elemental analysis calcd (%) for $C_{48}H_{82}I_2N_6O_{18}$: C, 44.86; H, 6.43; N, 6.54; found: C, 44.99; H, 6.56; N, 6.79.

OligoPPE ***18$_0$***. See the general procedure for alkynyl-aryl coupling. Trimethylsilyl acetylene (**6$_0$**; 267 μL, 1.93 mmol), 4-iodo-PyMTA ester **17** (587 mg, 0.966 mmol), Et_2NH (5.4 mL, 52.2 mmol), THF (5.4 mL), and catalysts $PdCl_2(PPh_3)_2$ (13 mg, 18.5 μmol) and CuI (4 mg, 21 μmol). After stirring at room temperature for 17 h, no precipitate had formed. The ^{1}H NMR spectrum of the reaction mixture showed an incomplete reaction. A solution of trimethylsilyl acetylene (**6$_0$**; 1.0 mL, 7.22 mmol) in THF (1.0 mL) was degassed and added to the reaction mixture. After 21 h of stirring at room temperature, the ^{1}H NMR spectrum of the solution showed a complete reaction. All volatiles were removed. Column chromatography (3.0 cm × 35 cm, pentane/Et_2O 1:2) of the residual oil gave oligoPPE **18$_0$** (509 mg, 91%; R_f = 0.30) as a yellow viscous oil. For ^{1}H and ^{13}C NMR data, see Tables S16 and S17. MS (ESI): m/z 600.4 $[M + Na]^+$, 578.5 $[M + H]^+$. Accurate MS (ESI): m/z calcd for $[M + Na]^+$ $C_{28}H_{43}N_3O_8SiNa^+$, 600.27116; found, 600.26997. Elemental analysis calcd (%) for $C_{28}H_{43}N_3O_8Si$: C, 58.21; H, 7.50; N, 7.27; found: C, 58.08; H, 7.86; N, 7.31.

OligoPPE ***18$_1$***. See the general procedure for alkynyl-aryl coupling. Alkyne **6$_1$** (440 mg, 711 μmol), 4-iodo-PyMTA ester **17** (521 mg, 858 μmol), $^iPr_2NH$ (5.0 mL, 35.7 mmol), THF (8 mL), and catalysts $Pd(PPh_3)_4$ (15.8 mg, 13.7 μmol) and CuI (2.10 mg, 11.0 μmol). After stirring at room temperature for 24 h, 2-methylbut-3-yn-2-ol (HOP-acetylene, **7$_0$**; 148 μL, 1.42 mmol) was added, and the suspension was stirred at room temperature for another 17 h. All volatiles were evaporated. The residue was suspended in CH_2Cl_2/Et_2O 1:1, and the suspension was filtered through silica gel (3.5 cm × 2.5 cm, rinsing with CH_2Cl_2/Et_2O 1:1). The solvent of the eluate was removed. Column chromatography (4.0 cm × 35 cm, CH_2Cl_2/Et_2O/EtOH 100:40:2) of the residual yellow oil gave oligoPPE **18$_1$** (753 mg, 96%; R_f = 0.53) and compound **23** (102 mg; R_f = 0.15), both as yellow oils. Analytical data of oligoPPE **18$_1$**: for ^{1}H and ^{13}C NMR data, see Tables S16 and S17. MS (ESI): m/z 1120.7 $[M + Na]^+$, 1098.7 $[M + H]^+$. Accurate MS (ESI): m/z calcd for $[M + Na]^+$ $C_{60}H_{91}N_3O_{10}Si_3Na^+$, 1120.59045; found, 1120.58689. Elemental analysis calcd (%) for $C_{60}H_{91}N_3O_{10}Si_3$: C, 65.59; H, 8.35; N, 3.82; found: C, 65.69; H, 8.44; N, 3.87. Analytical data of compound **23**: ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.45 (s, 2H, $H_{pyridine}$), 4.13 (q, ^3J = 7.2 Hz, 8H, C$\underline{H}_2$CH$_3$), 3.95 (s, 4H, ArC$\underline{H}_2$), 3.55 (s, 8H, C$\underline{H}_2$CO$_2$Et), 2.20 (br s, 1H, OH), 1.58 (s, 6H, C(C$\underline{H}_3$)$_2$OH), 1.25 (t, ^3J = 7.2 Hz, 12H, CH$_2$C$\underline{H}_3$). MS (ESI): m/z 586.3 $[M + Na]^+$, 564.3 $[M + H]^+$. Accurate MS (ESI): m/z calcd for $[M + Na]^+$ $C_{28}H_{41}N_3O_9Na^+$, 586.27350; found, 586.27225.

OligoPPE ***18$_2$***. See the general procedure for alkynyl-aryl coupling. A mixture of alkyne **6$_2$** and dialkyne **10$_2$** in a molar ratio of 94:6 (568 mg, corresponding to 468 μmol of alkyne **6$_2$**), 4-iodo-PyMTA ester **17** (364 mg, 599 μmol), $^iPr_2NH$ (3.5 mL, 24.9 mmol), THF (8 mL), and catalysts $Pd(PPh_3)_4$ (11.5 mg, 9.92 μmol) and CuI (3.07 mg, 16.1 μmol). After stirring at room temperature for 24 h, 2-methylbut-3-yn-2-ol (HOP-acetylene, **7$_0$**; 97.3 μL, 993 μmol) was added, and the suspension was stirred at room temperature for another 17 h. All volatiles were evaporated. The residue was suspended in CH_2Cl_2/Et_2O 1:1, and the suspension was filtered through silica gel (3.5 cm × 2.5 cm, rinsing with CH_2Cl_2/Et_2O 1:1). The solvent of the eluate was removed. Column chromatography (4.0 cm × 30 cm, CH_2Cl_2/Et_2O/EtOH 100:40:2) of the residual yellow solid gave oligoPPE **18$_2$** (744 mg, 96%; R_f = 0.53) as a yellow solid, compound **22$_2$** (29 mg; R_f = 0.23) as a yellow solid, and compound **23** (52 mg; R_f = 0.15) as a yellow oil. Analytical data of **18$_2$**: for ^{1}H and ^{13}C NMR data, see Tables S16 and S17. MS (ESI): m/z 1640.9 $[M + Na]^+$, 1618.9 $[M + H]^+$. Accurate MS (ESI): m/z calcd for $[M + H]^+$ $C_{92}H_{139}N_3O_{12}Si_5H^+$, 1618.92779; found, 1618.92486. Analytical data of compound **22$_2$**: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.54 (2H, $H_{pyridine}$), 7.35 and 7.29 (2s, $H_{benzene}$, 2H each), 4.88 and 4.87 (2s, 4H each, benzene-OC$\underline{H}_2$), 4.15 (q, ^3J = 7.2 Hz, 16H, C$\underline{H}_2$CH$_3$), 4.01 (s, 8H, PyCH$_2$), 3.59 (s, 16H, C$\underline{H}_2$CO$_2$Et), 1.26 (t, ^3J = 7.2 Hz, 24H, CH$_2$C$\underline{H}_3$), 1.051 and 1.047 (2s, 42H each, TIPS). MS (ESI): m/z 2048.4 $[M + Na]^+$, 2026.4 $[M + H]^+$. For analytical data of compound **23**, see the synthesis of oligoPPE **18$_1$**.

OligoPPE ***18$_3$***. See the general procedure for alkynyl-aryl coupling. A mixture of alkyne **6$_3$** and dialkyne **10$_3$** in a molar ratio of 98:2 (413 mg, corresponding to 244 μmol of alkyne **6$_3$**), 4-iodo-PyMTA ester **17** (184 mg, 303 μmol), $^iPr_2NH$ (1.8 mL, 12.8 mmol), THF (8 mL), and catalysts $Pd(PPh_3)_4$ (6.97 mg, 6.03 μmol) and CuI (1.96 mg, 10.3 μmol). After stirring at room temperature for 24 h, 2-methylbut-3-yn-2-ol (HOP-acetylene, **7$_0$**; 49.5 μL, 506 μmol) was added, and the suspension was stirred at room temperature for another 17 h. All volatiles were evaporated. The residual yellow solid was suspended in CH_2Cl_2/Et_2O 1:1, and the suspension was filtered through silica gel (3.5 cm × 2.5 cm, rinsing with CH_2Cl_2/Et_2O 1:1). The solvents were removed from the filtrate. Column chromatography (3.0 cm × 30 cm, CH_2Cl_2/Et_2O/EtOH 100:40:2) of the residual yellow solid gave oligoPPE **18$_3$** (438 mg, 84%; R_f = 0.53) as a yellow solid and alkyne dimer **9$_3$** (50 mg; R_f = 0.88). OligoPPE **18$_3$** was dissolved under argon in degassed anhydrous CH_2Cl_2. Metal scavenger QuadraPure TU (324 mg) was added. The suspension was stirred at room temperature for 23 h. Metal scavenger QuadraPure BzA (50 mg) was added, and the suspension was stirred for another 4 h at room temperature. The metal scavenger QuadraPure BzA did not change color, which indicated that there had been no free Cu(I/II) left in the solution. The suspension was filtered through silica gel (1.5 cm × 1.5 cm, CH_2Cl_2/Et_2O/EtOH 100:40:2). Removal of the solvent gave metal-free oligoPPE **18$_3$** (423 mg, 82%). Analytical data of **18$_3$**: for ^{1}H and ^{13}C NMR data, see Tables S16 and S17. MS (ESI): m/z 2161.6 $[M + Na]^+$, 2139.6 $[M + H]^+$. Accurate MS (ESI): m/z calcd for $[M + Na]^+$ $C_{124}H_{187}N_3O_{14}Si_7Na^+$, 2161.22901; found, 2161.23330. Analytical data of alkyne dimer **9$_3$**: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.31, 7.279, 7.269, 7.264, 7.256, and 7.17 (6s, 2H each, H_{Ar}), 4.86, 4.84, and 4.78 (3s, 12H, 8H, 4H respectively, CH_2), 1.072, 1.065, 1.059, 1.054, and 1.049 (5s, 42H, 42H, 42H, 84H, 42H respectively, TIPS), 0.26 (s, 18H, TMS).

OligoPPE ***18$_4$***. See the general procedure for alkynyl-aryl coupling. A mixture of alkyne **6$_4$** and dialkyne **10$_4$** in a molar ratio of 96:4 (97 mg, corresponding to 42.6 μmol of alkyne **6$_4$**), 4-iodo-PyMTA ester **17** (33 mg, 54.8 μmol), $^iPr_2NH$ (311 μL, 2.22 mmol), THF (3 mL), and catalysts $Pd(PPh_3)_4$ (1.12 mg, 0.97 μmol) and CuI (0.478 mg, 2.51 μmol). After stirring at room temperature for 24 h, 2-methylbut-3-yn-2-ol (HOP-acetylene, **7$_0$**; 10.0 μL, 102 μmol) was added, and the suspension was stirred at room temperature for another 22 h. All volatiles were evaporated. Under argon, the residue was dissolved in degassed anhydrous CH_2Cl_2, and metal scavenger QuadraPure TU (70

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mg) was added. The suspension was stirred at room temperature for 19 h. Metal scavenger QuadraPure BzA (5 mg) was added, and the suspension was stirred for another 1 h at room temperature. The metal scavenger QuadraPure BzA did not change its color, which indicated that there had been no free Cu(I/II) left in solution. The suspension was filtered through a syringe filter, and the solvent of the filtrate was removed. Column chromatography (2.0 cm × 40 cm, CH_2Cl_2/Et_2O 10:4) of the residual yellow solid gave oligoPPE **18**$_4$ (82 mg, 72%; R_f = 0.48) as a yellow solid. Analytical data of oligoPPE **18**$_4$: for ^{1}H and ^{13}C NMR data, see Tables S16 and S17. MS (ESI): *m*/*z* 2660.1 $[M + H]^+$, 1341.5 $[M + H + Na]^{2+}$, 1330.5 $[M + 2H]^{2+}$. Accurate MS (ESI): *m*/*z* calcd for $[M + 2Na]^{2+}$ $C_{156}H_{235}N_3O_{16}Si_9Na_2^+$, 1352.26876; found, 1352.26813.

OligoPPE ***18*****$_5$**. See the general procedure for alkynyl-aryl coupling. A mixture of alkyne **6**$_5$ and dialkyne **10**$_5$ in a molar ratio of 94:6 (233 mg corresponding to 81 μmol of alkyne **6**$_5$), 4-iodo-PyMTA ester **17** (62.8 mg, 103 μmol), ^{i}Pr$_2$NH (604 μL, 4.30 mmol), THF (6 mL), and catalysts $Pd(PPh_3)_4$ (2.41 mg, 2.09 μmol) and CuI (0.703 mg, 3.69 μmol). After stirring at room temperature for 24 h, 2-methylbut-3-yn-2-ol (HOP-acetylene, **7**$_0$; 16.8 μL, 172 μmol) was added, and the reaction mixture was stirred at room temperature for another 18 h. All volatiles were evaporated. The residue was dissolved under argon in degassed anhydrous CH_2Cl_2, and metal scavenger QuadraPure TU (116 mg) was added. The suspension was stirred at room temperature for 19 h. Metal scavenger QuadraPure BzA (5 mg) was added, and the suspension was stirred at room temperature for another 2 h. The metal scavenger QuadraPure BzA did not change its color, which indicated that there had been no free Cu(I/II) left in solution. The suspension was filtered through a syringe filter, and the solvent of the filtrate was removed. Column chromatography (3.0 cm × 35 cm, CH_2Cl_2/Et_2O 10:4) of the residual yellow solid gave oligoPPE **18**$_5$ (251 mg, 98%; R_f = 0.48) as a yellow solid. Analytical data of oligoPPE **18**$_5$: for ^{1}H and ^{13}C NMR data, see Tables S16 and S17. MS (ESI): *m*/*z* 1612.6 $[M + 2Na]^{2+}$, 1601.6 $[M + H + Na]^{2+}$.

OligoPPE ***18*****$_6$**. See the general procedure for alkynyl-aryl coupling. A mixture of alknye **6**$_6$ and dialkyne **10**$_6$ in a molar ratio of 98:2 (140 mg, corresponding to 42.5 μmol of acetylene **6**$_6$), 4-iodo-PyMTA ester **17** (31.8 mg, 52.3 μmol), ^{i}Pr$_2$NH (304 μL, 2.16 mmol), THF (3 mL), and catalysts $Pd(PPh_3)_4$ (1.10 mg, 0.96 μmol) and CuI (0.372 mg, 1.95 μmol). After stirring at room temperature for 24 h, 2-methylbut-3-yn-2-ol (HOP-acetylene, **7**$_0$; 8.5 μL, 87 μmol) was added, and the suspension was stirred at room temperature for another 19 h. All volatiles were evaporated. The residue was dissolved under argon in degassed anhydrous CH_2Cl_2, and metal scavenger QuadraPure TU (59 mg) was added. The suspension was stirred at room temperature for 19 h. Metal scavenger QuadraPure BzA (5 mg) was added, and the suspension was stirred at room temperature for another 2 h. The metal scavenger QuadraPure BzA did not change its color, which indicated that there had been no free Cu(I/II) left in solution. The suspension was filtered through a syringe filter, and the solvent of the filtrate was removed. Column chromatography (2.0 cm × 38 cm, CH_2Cl_2/Et_2O 10:4) of the residual yellow solid gave oligoPPE **18**$_6$ (137 mg, 87%; R_f = 0.48) as a yellow solid. Analytical data of **18**$_6$: for ^{1}H and ^{13}C NMR data, see Tables S16 and S17. MS (ESI): *m*/*z* 1872.9 $[M + 2Na]^{2+}$, 1861.9 $[M + H + Na]^{2+}$, 1850.9 $[M + 2H]^{2+}$.

OligoPPE ***18*****$_7$**. See the general procedure for alkynyl-aryl coupling. A mixture of alkyne **6**$_7$ and dialkyne **10**$_7$ in a molar ratio of 98:2 (170 mg, corresponding to 44.5 μmol of alkyne **6**$_7$), 4-iodo-PyMTA ester **17** (33.2 mg, 54.6 μmol), ^{i}Pr$_2$NH (318 μL, 2.26 mmol), THF (3 mL), and catalysts $Pd(PPh_3)_4$ (1.06 mg, 0.92 μmol) and CuI (0.460 mg, 2.42 μmol). After stirring at room temperature for 24 h, 2-methylbut-3-yn-2-ol (HOP-acetylene, **7**$_0$) (8.9 μL, 91 μmol) was added, and the suspension was stirred at room temperature for another 18 h. All volatiles were evaporated. The residue was dissolved under argon in degassed and anhydrous CH_2Cl_2, and metal scavenger QuadraPure TU (67 mg) was added. The suspension was stirred at room temperature for 20 h. Metal scavenger QuadraPure BzA (5 mg) was added, and the suspension was stirred for another 2 h at room temperature. The metal scavenger QuadraPure BzA did not change its color, which indicated that there had been no free Cu(I/II) left in solution. The suspension was filtered through a syringe filter, and the solvent of the filtrate was removed. Column chromatography (2.0 cm × 39 cm, CH_2Cl_2/Et_2O 10:4) of the residual yellow solid gave oligoPPE **18**$_7$ (154 mg, 82%; R_f = 0.48) as a yellow solid. Analytical data of oligoPPE **18**$_7$: for ^{1}H and ^{13}C NMR data, see Tables S16 and S17. MS (ESI): *m*/*z* 2132.8 $[M + 2Na]^{2+}$, 2121.8 $[M + H + Na]^{2+}$.

Alkyne ***19*****$_0$**. A solution of *n*-butyllithium in hexanes (1.6 M, 250 μL, 400 μmol) was slowly added to anhydrous EtOH (1.75 mL) at room temperature. Part of this solution of EtOLi (0.90 mL, ∼180 μmol) was added to a solution of oligoPPE **18**$_0$ (321 mg, 556 μmol) in anhydrous EtOH (5 mL). After stirring for 1 h at room temperature, the reaction solution was filtered through silica gel (2.0 cm × 2.0 cm, rinsing with Et_2O). The solvents of the eluate were removed, giving alkyne **19**$_0$ (262 mg, 93%) as a yellow brown oil. For ^{1}H NMR and ^{13}C NMR data, see Tables S18 and S19. MS (ESI): *m*/*z* 528.4 $[M + Na]^+$, 506.5 $[M + H]^+$. Accurate MS (ESI): *m*/*z* calcd for $[M + Na]^+$ $C_{25}H_{35}N_3O_8Na^+$, 528.23164; found, 528.23021. Elemental analysis calcd (%) for $C_{25}H_{35}N_3O_8$: C, 59.39; H, 6.98; N, 8.31; found: C, 58.77; H, 7.45; N, 8.27.

Alkyne ***19*****$_1$**. A solution of *n*-butyllithium in hexanes (1.6 M, 144 μL, 230 μmol) was slowly added to anhydrous EtOH (5.0 mL) at room temperature. The resulting solution was added to a solution of oligoPPE **18**$_1$ (508 mg, 462 μmol) in anhydrous EtOH (10 mL) and anhydrous THF (12 mL). After stirring for 1 h at room temperature, the reaction solution was filtered through silica gel (2.0 cm × 2.0 cm, rinsing with Et_2O). The solvents of the eluate were removed, giving alkyne **19**$_1$ (452 mg, 95%) as a pale yellow oil. For ^{1}H NMR and ^{13}C NMR data, see Tables S18 and S19. MS (ESI): *m*/*z* 1048.6 $[M + Na]^+$, 1026.6 $[M + H]^+$. Accurate MS (ESI): *m*/*z* calcd for $[M + Na]^+$ $C_{57}H_{83}N_3O_{10}Si_2Na^+$, 1048.55092; found, 1048.54849.

Alkyne ***19*****$_2$**. A solution of *n*-butyllithium in hexanes (1.6 M, 90 μL, 144 μmol) was slowly added to anhydrous EtOH (4.0 mL) at room temperature. The resulting solution was added to a solution of oligoPPE **18**$_2$ (475 mg, 293 μmol) in anhydrous EtOH (4 mL) and anhydrous THF (5 mL). After stirring for 1 h at room temperature, the solution was filtered through silica gel (2.0 cm × 2.5 cm, rinsing with CH_2Cl_2/THF/EtOH 15:10:1). Solvent removal of the eluate gave alkyne **19**$_2$ (382 mg, 84%) as a pale yellow oil. For ^{1}H NMR data, see Table S18. MS (ESI): *m*/*z* 1568.7 $[M + Na]^+$, 1546.7 $[M + H]^+$.

Alkyne ***19*****$_3$**. A solution of *n*-butyllithium in hexanes (1.6 M, 40 μL, 64 μmol) was slowly added to anhydrous EtOH (2.5 mL) at room temperature. The resulting solution was added to a solution of oligoPPE **18**$_3$ (251 mg, 117 μmol) in anhydrous EtOH (5 mL) and anhydrous THF (6 mL). After stirring for 2 h at room temperature, the solution was filtered through silica gel (2.0 cm × 4.0 cm, rinsing with Et_2O). Solvent removal of the eluate provided alkyne **19**$_3$ (211 mg, 87%) as a yellow solid. For ^{1}H NMR data, see Table S18. MS (ESI): *m*/*z* 2089.5 $[M + Na]^+$, 2067.5 $[M + H]^+$.

Alkyne ***19*****$_4$**. A solution of *n*-butyllithium in hexanes (1.6 M, 38 μL, 61 μmol) was slowly added to anhydrous EtOH (5.0 mL) at room temperature. Part of the obtained solution (1.0 mL, ∼12 μmol) was added to a solution of oligoPPE **18**$_4$ (65 mg, 24 μmol) in anhydrous EtOH (2 mL) and anhydrous THF (1.5 mL). After stirring for 1 h at room temperature, the solution was filtered through silica gel (2.0 cm × 4.0 cm, rinsing with Et_2O). Solvent removal of the eluate gave a yellow solid (56 mg). The ^{1}H NMR spectrum of this material proved that the removal of the TMS group was incomplete. The yellow solid was dissolved in anhydrous EtOH (1.3 mL) and anhydrous THF (1.5 mL). A freshly prepared EtOLi solution (0.7 mL, ∼12 μmol; the solution had been prepared through addition of *n*-butyllithium in hexanes (1.6 M, 33 μL, 53 μmol) to anhydrous EtOH (3.0 mL) at room temperature) was added. After stirring for 2 h at room temperature, the solution was filtered through silica gel (2.0 cm × 4.0 cm, rinsing with Et_2O). Solvent removal of the eluate gave alkyne **19**$_4$ (42 mg, 68%) as a yellow solid. For ^{1}H NMR data, see Table S18. MS (ESI): *m*/*z* 1316.4 $[M + 2Na]^{2+}$, 1305.4 $[M + Na + H]^{2+}$.

Alkyne ***19*****$_5$**. OligoPPE **18**$_5$ (97 mg, 30 μmol) was dissolved in anhydrous EtOH (2 mL) and anhydrous THF (3 mL). Anhydrous K_2CO_3 (12 mg, 87 μmol) was added. The suspension was stirred at 55 °C for 2.5 h and filtered through silica gel (1.0 cm × 1.0 cm, rinsing

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with THF). The solvents of the eluate were removed, giving a yellow solid (95 mg). The ^{1}H NMR spectrum of the yellow solid showed that the cleavage of the TMS group was incomplete. The yellow solid was dissolved in anhydrous EtOH (2 mL) and anhydrous THF (3 mL). To the solution was added anhydrous K_2CO_3 (12 mg, 87 μmol). The suspension was stirred at 55 °C for 4 h and filtered through silica gel (1.0 cm × 1.0 cm, rinsing with THF). The solvents of the eluate were removed to obtain alkyne **19$_5$** (101 mg, contains a small amount of silicone grease, quantitative yield) as a yellow solid. For ^{1}H NMR data, see Table S18.

*Alkyne **19$_7$**.* OligoPPE **18$_7$** (82 mg, 19 μmol) was dissolved in anhydrous EtOH (2.0 mL) and anhydrous THF (3.2 mL). Anhydrous K_2CO_3 (9 mg, 65 μmol) was added to the solution. The suspension was stirred at 55 °C for 3 h and then filtered through silica gel (1.0 cm × 1.0 cm, rinsing with THF). The solvents of the eluate were removed, giving alkyne **19$_7$** (88 mg, contains a small amount of silicone grease, quantitative yield) as a yellow solid. For ^{1}H NMR data, see Table S18. MS (ESI): *m*/*z* 2096.6 $[M + 2Na]^{2+}$.

*OligoPPE **20$_0$** (**26$_1$**).* See the general procedure for alkynyl-aryl coupling. Alkyne **19$_0$** (103 mg, 204 μmol), diiodobenzene **16** (107 mg, 83.3 μmol), ^{i}Pr$_2$NH (1.2 mL, 8.56 mmol), THF (3 mL), and catalysts $Pd(PPh_3)_4$ (5.42 mg, 4.69 μmol) and CuI (1.81 mg, 9.48 μmol) at room temperature with a reaction time of 44 h. After the reaction, all volatiles were evaporated. Column chromatography (3.0 cm × 43 cm, CH_2Cl_2/EtOH 10:1) of the residual yellow oil gave oligoPPE **20$_0$** (166 mg, 80%; R_f = 0.36) as a pale yellow viscous oil and alkyne dimer **21$_0$** (22 mg, 11%; R_f = 0.55) as a yellow oil. Analytical data of oligoPPE **20$_0$**: for ^{1}H and ^{13}C NMR data, see Tables S20 and S21. MS (ESI): *m*/*z* 2078.1 $[M + K]^+$, 2062.1 $[M + Na]^+$, 2040.2 $[M + H]^+$, 1042.6 $[M + 2Na]^{2+}$, 1031.6 $[M + Na + H]^{2+}$. Accurate MS (ESI): *m*/*z* calcd for $[M + 2Na]^{2+}$ $C_{98}H_{150}N_{12}O_{34}Na_2^{2+}$: 1042.50809; found, 1042.50509. Elemental analysis calcd (%) for $C_{98}H_{150}N_{12}O_{34}$: C, 57.69; H, 7.41; N, 8.24; found: C, 57.35; H, 7.78; N, 8.22. Analytical data of alkyne dimer **21$_0$**: for ^{1}H NMR data, see Table S22. MS (ESI): *m*/*z* 1031.4 $[M + Na]^+$, 1009.4 $[M + H]^+$, 527.2 $[M + 2Na]^{2+}$, 516.2 $[M + Na + H]^{2+}$. Accurate MS (ESI): *m*/*z* calcd for $[M + 2Na]^{2+}$ $C_{50}H_{68}N_6O_{16}Na_2^{2+}$, 527.22381; found, 527.22228.

*Oligo PPE **20$_1$**.* See the general procedure for alkynyl-aryl coupling. Alkyne **19$_1$** (114 mg, 111 μmol), diiodobenzene **16** (64 mg, 50 μmol), ^{i}Pr$_2$NH (595 μL, 4.25 mmol), THF (3.5 mL), and catalysts $PdCl_2(PPh_3)_2$ (0.588 mg, 0.838 μmol) and CuI (0.603 mg, 3.17 μmol) at room temperature with a reaction time of 51 h. Under argon, all volatiles were evaporated, and the residue was dissolved in degassed anhydrous CH_2Cl_2. Metal scavenger QuadraPure TU (80 mg) was added, and the suspension was stirred at room temperature for 16 h. Metal scavenger QuadraPure BzA (10 mg) was added to the suspension. No color change occurred within 2 h of stirring at room temperature. The suspension was filtered through silica gel (1.0 cm × 1.0 cm, rinsing with CH_2Cl_2/EtOH 10:1). The solvents of the filtrate were removed. Column chromatography (3.0 cm × 35 cm, CH_2Cl_2/Et_2O/THF/EtOH 100:13:1.5:7) gave oligoPPE **20$_1$** (126 mg, 74%; R_f = 0.45) as a yellow-green viscous oil and alkyne **19$_1$** (35 mg, ∼30%, contains impurity; R_f = 0.75) and alkyne dimer **21$_1$** (3 mg, 1%; R_f = 0.65) as a yellow oil. Analytical data of oligoPPE **20$_1$**: for ^{1}H and ^{13}C NMR data, see Tables S20 and S21. MS (ESI): *m*/*z* 1563.0 $[M + 2Na]^{2+}$, 1552.0 $[M + Na + H]^{2+}$, 1541.0 $[M + 2H]^{2+}$, 1035.2 $[M + 2H + Na]^{3+}$, 1027.9 $[M + 3H]^{3+}$. Accurate MS (ESI): *m*/*z* calcd for $[M + 3Na]^{3+}$ $C_{162}H_{246}N_{12}O_{38}Si_4Na_3^{3+}$, 1049.54799; found, 1049.55106. Elemental analysis calcd (%) for $C_{162}H_{246}N_{12}O_{38}Si_4$: C, 63.13; H, 8.04; N, 5.45; found: C, 63.03; H, 8.07; N, 5.49. Analytical data of alkyne dimer **21$_1$**: for ^{1}H NMR data, see Table S22.

*OligoPPE **20$_2$**.* See the general procedure for alkynyl-aryl coupling. Alkyne **19$_2$** (138 mg, 89 μmol), diiodobenzene **16** (52 mg, 40 μmol), ^{i}Pr$_2$NH (567 μL, 4.05 mmol), THF (6 mL), and catalysts $PdCl_2(PPh_3)_2$ (1.21 mg, 1.73 μmol) and CuI (0.784 mg, 4.12 μmol)with a reaction time of 17 h at 50 °C. No precipitate formed. $PdCl_2(PPh_3)_2$ (1.27 mg, 1.81 μmol) and CuI (0.657 mg, 3.45 μmol) were added. After stirring at 50 °C for 24 h, still no precipitate had formed. The solution was cooled to room temperature, upon which some precipitate formed. The mixture was heated to 50 °C for 5 min, during which the precipitate dissolved in the solution. The suspension was stirred at room temperature for another 22 h. Under argon, all volatiles were evaporated, and the residue was dissolved in degassed anhydrous CH_2Cl_2. Metal scavenger QuadraPure TU (224 mg) was added, and the suspension was stirred at room temperature for 22 h. Metal scavenger QuadraPure BzA (6 mg) was added to the suspension. No color change occurred within 2 h of stirring at room temperature. The suspension was filtered through a syringe filter. The solvents of the filtrate were removed. Column chromatography (3.0 cm × 36 cm, CH_2Cl_2/Et_2O/EtOH 10:4:0.5) of the residual yellow-brown oil gave oligoPPE **20$_2$** (84 mg, 46%; R_f = 0.33) as a yellow viscous oil and alkyne dimer **21$_2$** (4 mg, 1%; R_f = 0.59) as a yellow-brown oil. Analytical data of oligoPPE **20$_2$**: for ^{1}H and ^{13}C NMR data, see Tables S20 and S21. MS (ESI): because of the high molecular weight of this compound and the insufficient intensity of the signal corresponding to the monoisotopic mass, the most abundant mass of each signal is reported, *m*/*z* 1397.4 $[M + 3Na]^{3+}$, 1390.3 $[M + 2Na + H]^{3+}$, 1382.4 $[M + Na + 2H]^{3+}$. Analytical data of alkyne dimer **21$_2$**: for ^{1}H NMR data, see Table S22. ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.3 (C═O), 159.2 ($C_{pyridine}$ ortho to N), 154.3, 153.1, 152.7, and 152.6 ($C_{benzene}O$), 132.5 ($C_{pyridine}$ para to N), 123.4 ($C_{pyridine}H$), 120.5, 120.0, 119.0, and 118.8 ($C_{benzene}H$), 115.9, 115.4, 113.8, and 113.1 ($C_{benzene}C{\equiv}C$), 102.04, 101.95. 101.89, 101.71, 93.3, 92.2, 91.8, 90.8, 90.7, 89.6, 79.7, and 79.6 (C≡C), 60.8 (CH_2Me), 60.3 (pyridine-CH_2), 58.66, 58.61, 58.37, and 58.35 (benzene-OCH_2), 55.2 (CH_2CO_2Et), 18.693 and 18.686 ($CH(CH_3)_2$), 14.4 (CH_2CH_3), 11.51, 11.49, and 11.47 ($CHMe_2$). MS (ESI): *m*/*z* 1568.0 $[M + 2Na]^{2+}$, 1557.0 $[M + Na + H]^{2+}$, 1546.0 $[M + 2H]^{2+}$. Accurate MS (ESI): *m*/*z* calcd for $[M + 2H]^{2+}$ $C_{178}H_{262}N_6O_{24}Si_8^{2+}$, 1545.88043; found, 1545.88245.

*OligoPPE **20$_3$**.* See the general procedure for alkynyl-aryl coupling. Alkyne **19$_3$** (143 mg, 69 μmol), diiodobenzene **16** (40.2 mg, 31 μmol), ^{i}Pr$_2$NH (370 μL, 2.64 mmol), THF (4 mL), and catalysts $PdCl_2(PPh_3)_2$ (0.967 mg, 1.38 μmol) and CuI (0.527 mg, 2.77 μmol) at room temperature with a reaction time of 18 h. No precipitate formed. The solution was stirred at 50 °C for 5 h. No precipitate formed. $PdCl_2(PPh_3)_2$ (1.18 mg, 1.68 μmol) and CuI (0.690 mg, 3.62 μmol) were added. Two minutes after the addition of the catalysts, a precipitate formed. The suspension was stirred at 50 °C for 23 h. Under argon, all volatiles were evaporated, and the residue was dissolved in degassed anhydrous CH_2Cl_2. Metal scavenger QuadraPure TU (188 mg) was added, and the suspension was stirred at room temperature for 18 h. Metal scavenger QuadraPure BzA (7 mg) was added to the suspension. No color change occurred within 1 h of stirring at room temperature. The suspension was filtered through a syringe filter (0.45 μM, PTFE). The solvents of the filtrate were removed. Column chromatography (2.0 cm × 30 cm, CH_2Cl_2/Et_2O/EtOH 10:4:0.5) of the residual yellow solid gave oligoPPE **20$_3$** (110 mg, 62%; R_f = 0.36) as a yellow solid. Analytical data of oligoPPE **20$_3$**: for ^{1}H and ^{13}C NMR data, see Tables S20 and S21. MS (ESI): because of the high molecular weight of this compound and the insufficient intensity of the signal corresponding to the monoisotopic mass, the most abundant mass of each signal is reported, *m*/*z* 1744.7 $[M + 3Na]^{3+}$, 1737.1 $[M + 2Na + H]^{3+}$, 1730.4 $[M + Na + 2H]^{3+}$, 1722.7 $[M + 3H]^{3+}$, 1314.2 $[M + 4Na]^{4+}$, 1308.8 $[M + 3Na + H]^{4+}$, 1303.5 $[M + 2Na + 2H]^{4+}$.

*OligoPPE **20$_4$**.* See the general procedure for alkynyl-aryl coupling. Alkyne **19$_4$** (42 mg, 16.2 μmol), diiodobenzene **16** (9.5 mg, 7.39 μmol), ^{i}Pr$_2$NH (100 μL, 713 μmol), THF (1.5 mL), and catalysts $PdCl_2(PPh_3)_2$ (0.524 mg, 0.747 μmol) and CuI (0.161 mg, 0.845 μmol) at room temperature with a reaction time of 16 h. No precipitate formed. CuI (0.158 mg, 0.830 μmol) was added to the solution, and the solution was heated to 50 °C and stirred at 50 °C for 23 h. No precipitate formed. $Pd(PPh_3)_4$ (0.489 mg, 0.423 μmol) was added to the solution. The solution was stirred at 50 °C for another 23 h, but still no precipitate formed. Under argon, all volatiles were evaporated, and the residue was dissolved in degassed anhydrous CH_2Cl_2. Metal scavenger QuadraPure TU (58 mg) was added, and the suspension was stirred at room temperature for 14 h. Metal scavenger QuadraPure BzA (4 mg) was added to the suspension. No color

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change occurred within 2 h of stirring at room temperature. The suspension was filtered through a syringe filter (0.45 μM, PTFE). The solvents of the filtrate were removed. Column chromatography (1.5 cm × 36 cm, CH_2Cl_2/Et_2O/EtOH 10:4:0.5) of the residual yellow solid gave oligoPPE **20$_4$** containing a trace of triphenylphosphaneoxide (21 mg, yield ∼46%; R_f = 0.36) as a yellow solid. Analytical data of oligoPPE **20$_4$**: for ^{1}H NMR data, see Table S20. MS (ESI): because of the high molecular weight of this compound and the insufficient intensity of the signal corresponding to the monoisotopic mass the most abundant mass of each signal is reported, *m*/*z* 2084.8 [M + 2Na + H]$^{3+}$, 2077.6 [M + Na + 2H]$^{3+}$, 2069.9 [M + 3H]$^{3+}$, 1569.2 [M + 3Na + H]$^{4+}$, 1563.6 [M + 2Na + 2H]$^{4+}$, 1558.3 [M + Na + 3H]$^{4+}$.

OligoPPE ***20$_5$***. See the general procedure for alkynyl-aryl coupling. Alkyne **19$_5$** (99 mg, ∼30 μmol, containing a small amount of silicone grease), diiodobenzene **16** (14.1 mg, 11 μmol), ^{i}Pr$_2$NH (250 μL, 1.78 mmol), THF (4 mL), and catalysts $Pd_2(dba)_3$ (2.12 mg, 2.32 μmol), PPh_3 (1.67 mg, 6.36 μmol), and CuI (0.815 mg, 4.28 μmol) with a reaction time of 19 h at 50 °C. Under argon, all volatiles were evaporated, and the residue was dissolved in degassed anhydrous CH_2Cl_2 (7 mL). Metal scavenger QuadraPure TU (178 mg) was added, and the suspension was stirred at room temperature for 19 h. Metal scavenger QuadraPure BzA (5 mg) was added. No color change occurred within 2 h of stirring at room temperature. The suspension was filtered through a syringe filter (0.45 μM, PTFE). The solvents of the filtrate were removed. Column chromatography (2 cm × 36 cm, CH_2Cl_2/Et_2O/EtOH 10:4:0.5) of the residue gave oligoPPE **20$_5$** (57 mg, 52%; R_f = 0.36) as a yellow solid. Analytical data of oligoPPE **20$_5$**: for ^{1}H NMR data, see Table S20. MS (ESI): because of the high molecular weight of this compound and the insufficient intensity of the signal corresponding to the monoisotopic mass, the most abundant mass of each signal is reported, *m*/*z* 2432.2 [M + 2Na + H]$^{3+}$, 2424.5 [M + Na + 2H]$^{3+}$, 2417.2 [M + 3H]$^{3+}$, 1824.1 [M + 2Na + 2H]$^{4+}$, 1818.8 [M + Na + 3H]$^{4+}$.

OligoPPE ***20$_7$***. See the general procedure for alkynyl-aryl coupling. Alkyne **19$_7$** (86 mg, ∼19 μmol, containing a small amount of silicone grease), diiodobenzene **16** (11.2 mg, 8.72 μmol), ^{i}Pr$_2$NH (125 μL, 0.89 mmol), THF (3 mL), and catalysts $Pd_2(dba)_3$ (0.814 mg, 0.889 μmol), PPh_3 (1.37 mg, 5.21 μmol), and CuI (0.365 mg, 1.92 μmol) at room temperature with a reaction time of 24 h. Thin layer chromatography (CH_2Cl_2/Et_2O/EtOH 10:4:0.5) demonstrated that the reaction was incomplete. The solution was stirred at 50 °C for 19 h. Thin layer chromatography still showed an incomplete reaction. $Pd_2(dba)_3$ (0.902 mg, 0.781 μmol) and CuI (0.320 mg, 1.68 μmol) were added. The solution was stirred at 50 °C for another 15 h. Under argon, all volatiles were evaporated, and the residue was dissolved in degassed anhydrous CH_2Cl_2 (7 mL). Metal scavenger QuadraPure TU (148 mg) was added, and the suspension was stirred at room temperature for 18 h. Metal scavenger QuadraPure BzA (5 mg) was added. No color change occurred within 4 h of stirring at room temperature. The suspension was filtered through a syringe filter (0.45 μM, PTFE). The solvents of the filtrate were removed. Column chromatography (2 cm × 34 cm, CH_2Cl_2/Et_2O/EtOH 10:4:0.5) of the residual yellow-orange solid gave oligoPPE **20$_7$** (32 mg, 36%; R_f = 0.36) as a yellow solid. Analytical data of oligoPPE **20$_7$**: for ^{1}H NMR data, see Table S20.

General Procedure for the Removal of the TIPS Groups. According to the supplier, the herein used solution of Bu_4NF (1.0 M) in THF contained 5 wt % of water. OligoPPE **20$_n$** was dissolved in THF. A solution of Bu_4NF (1.0 M) in THF was added upon which the reaction solution changed color immediately from yellow to brown. The solution was stirred at room temperature. Afterwards it was filtered through silica gel (1.5 cm × 1.5 cm, rinsing with THF). Solvent removal gave yellow solids that consisted of deprotected oligoPPEs **25$_n$** accompanied by TIPS-F and/or TIPS-OH and silicon grease.

Deprotected OligoPPE ***25$_1$***. See general procedure for the removal of the TIPS groups. OligoPPE **20$_1$** (80 mg, 26.0 μmol), solution of Bu_4NF in THF (1.0 M; 129.8 μL, 129.8 μmol), THF (4 mL) with a reaction time of 1 h. A yellow solid (62 mg) was obtained. For ^{1}H NMR data of deprotected oligoPPE **25$_1$**, see Table S23.

Deprotected OligoPPE ***25$_2$***. See general procedure for the removal of the TIPS groups. OligoPPE **20$_2$** (50 mg, 12.1 μmol), solution of Bu_4NF in THF (1.0 M; 170 μL, 170 μmol), THF (4 mL) with a reaction time of 1 h. A yellow solid (34 mg) was obtained. For ^{1}H NMR data of deprotected oligoPPE **25$_2$**, see Table S23.

Deprotected OligoPPE ***25$_3$***. See general procedure for the removal of the TIPS groups. OligoPPE **20$_3$** (99 mg, 19.2 μmol), solution of Bu_4NF in THF (1.0 M; 270 μL, 270 μmol), THF (5 mL) with a reaction time of 40 min. A yellow solid (67 mg) was obtained. For ^{1}H NMR data of deprotected oligoPPE **25$_3$**, see Table S23.

Deprotected OligoPPE ***25$_4$***. See general procedure for the removal of the TIPS groups. OligoPPE **20$_4$** (18 mg, ∼2.9 μmol, containing a small amount of triphenyphosphaneoxide), solution of Bu_4NF in THF (1.0 M; 55.7 μL, 55.7 μmol), THF (2 mL) with a reaction time of 40 min. A yellow solid (11 mg), which consisted mainly of deprotected oligoPPE **25$_4$** accompanied by triphenyphosphaneoxide, TIPS-F and/or TIPS-OH, and silicon grease, was obtained. For ^{1}H NMR data of deprotected oligoPPE **25$_4$**, see Table S23.

Deprotected OligoPPE ***25$_5$***. See general procedure for the removal of the TIPS groups. OligoPPE **20$_5$** (41 mg, 5.66 μmol), solution of Bu_4NF in THF (1.0 M; 136 μL, 136 μmol), THF (3 mL) with a reaction time of 40 min. A yellow solid (25 mg) was obtained. For ^{1}H NMR data of deprotected oligoPPE **25$_5$**, see Table S23.

Deprotected OligoPPE ***25$_7$***. See general procedure for the removal of the TIPS groups. OligoPPE **20$_7$** (31 mg, 3.32 μmol), solution of Bu_4NF in THF (1.0 M; 103 μL, 103 μmol), THF (3 mL) with a reaction time of 40 min. A yellow solid (17 mg) was obtained. For ^{1}H NMR data of deprotected oligoPPE **25$_7$**, see Table S23.

General Procedure for Alkyne-Azide Cycloaddition. A solution of PEG-N_3 **14** and the material that had been obtained through treatment of oligoPPE **20$_x$** with Bu_4NF in THF and EtOH was degassed through three freeze−pump−thaw cycles. Degassed aqueous solutions of sodium L-ascorbate and $CuSO_4$ were added. A small amount of precipitate formed upon the addition of the sodium L-ascorbate solution. The suspension was heated to 60 °C, whereupon the reaction mixture became an orange-brown suspension. The reaction mixture was stirred for several days at 60 °C. Then, it was cooled to room temperature. Metal scavenger QuadraPure TU was added, and the suspension was stirred at room temperature for several hours. Metal scavenger QuadraPure BzA was added, and the suspension was stirred at room temperature for a few hours. In none of the experiments did a change in color occur. This finding proves that all of the Cu(I/II) ions had been trapped by QuadraPure TU. To this point, the reaction mixture had been kept under argon. The suspension was filtered through silica gel. Solvent removal from the eluate gave a viscous yellow oil. This oil contained oligoPPE **26$_n$**, PEG-N_3 **14**, TIPS-OH and/or TIPS-F, sodium L-ascorbate, dehydroascorbic acid, and silicone grease. It was dissolved in CH_2Cl_2, and the resulting solution was washed several times with water. The washing was performed in a centrifuge tube. The CH_2Cl_2 phase and the aqueous phase were mixed well. Centrifugation of the resulting yellow emulsion at 5000 rpm for 5 min separated the mixture into two phases: a yellow CH_2Cl_2 phase and a colorless aqueous phase. The aqueous phase was removed with the help of a glass pipet. Washing of the CH_2Cl_2 phase was repeated several times. After washing, the solvent of the CH_2Cl_2 phase was removed, giving a mixture of oligoPPE **26$_n$**, PEG-N_3 **14**, TIPS-OH, and silicone grease.

OligoPPE ***26$_1$***. See the synthesis of oligoPPE **20$_0$**.

OligoPPE ***26$_3$***. See the general procedure for alkyne-azide cycloaddition. The material (62 mg, containing ∼26.0 μmol deprotected oligoPPE **25$_1$**) that had been obtained through the desilylation of oligoPPE **20$_1$**, PEG-N_3 **14** (65 mg, 154 μmol), $CuSO_4$ (0.1 M aqueous solution, 50.5 μL, 5.05 μmol), sodium L-ascorbate (3.17 mg dissolved in 100 μL H_2O, 16.0 μmol), THF (1.5 mL), and EtOH (1.0 mL) with a reaction time of 6 d. QuadraPure TU (137 mg) was added and the suspension was stirred for 20 h. QuadraPure BzA (13 mg) was added and the suspension was stirred for 2 h. The suspension was filtered through silica gel (3.0 cm × 1.0 cm, rinsing with CH_2Cl_2/EtOH 3:1). Solvent removal from the eluate gave a viscous yellow oil. This oil was taken up in CH_2Cl_2 (6 mL), and the

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solution was washed with water (4 × 6 mL). The solvent of the CH_2Cl_2 phase was removed, giving a mixture (122 mg) of a viscous yellow oil with small amounts of solid. ^{1}H NMR spectroscopy revealed that this mixture consisted of oligoPPE **26$_3$**, PEG-N_3 **14**, silicone grease, and TIPS-OH. Analytical data of oligoPPE **26$_3$**: for ^{1}H NMR data, see Table S24. MS (ESI): because of the high molecular weight of this compound and the insufficient intensity of the signal corresponding to the monoisotopic mass, the most abundant mass of each signal is reported, *m*/*z* 1416.8 $[M + 2K + Na]^{3+}$, 1411.8 $[M + K + 2Na]^{3+}$, 1406.4 $[M + 3Na]^{3+}$, 1399.1 $[M + 2Na + H]^{3+}$. Accurate MS (ESI): *m*/*z* calcd for $[M + 2Na + 2H]^{4+}$ $C_{198}H_{316}N_{24}O_{70}Na_2^{4+}$, 1049.04196; found, 1049.04301.

OligoPPE **26$_5$**. See the general procedure for alkyne-azide cycloaddition. The material (34 mg, containing ∼12.1 μmol deprotected oligoPPE **25$_2$**) that had been obtained through the desilylation of oligoPPE **20$_2$**, PEG-N_3 **14** (58 mg, 137 μmol), $CuSO_4$ (0.1 M aqueous solution, 48.5 μL, 4.85 μmol), sodium L-ascorbate (3.01 mg dissolved in 120 μL H_2O, 15.2 μmol), THF (1.5 mL), and EtOH (1.0 mL) with a reaction time of 5 d. QuadraPure TU (119 mg) was added and the suspension was stirred for 17 h. QuadraPure BzA (18 mg) was added and the suspension was stirred for 3 h. The suspension was filtered through silica gel (1.5 cm × 1.5 cm, rinsing with CH_2Cl_2/EtOH 4:1). Solvent removal from the eluate provided a yellow viscous oil. This was taken up in CH_2Cl_2 (4 mL), and the solution was washed with water (4 × 4 mL). The solvent of the CH_2Cl_2 phase was removed, yielding a mixture (101 mg) of a yellow viscous oil with a small amount of solid. ^{1}H NMR spectroscopy revealed that this mixture consisted of oligoPPE **26$_5$**, PEG-N_3 **14**, silicone grease, and TIPS-OH. For ^{1}H NMR data of oligoPPE **26$_5$**, see Table S24.

OligoPPE **26$_7$**. See the general procedure for alkyne-azide cycloaddition. The material (67 mg, containing ∼19.2 μmol deprotected oligoPPE **25$_3$**) that had been obtained through the desilylation of oligoPPE **20$_3$**, PEG-N_3 **14** (138 mg, 326 μmol), $CuSO_4$ (0.1 M aqueous solution, 115 μL, 11.5 μmol), sodium L-ascorbate (7.84 mg dissolved in 100 μL H_2O, 39.6 μmol), THF (2 mL), and EtOH (1.5 mL) with a reaction time of 6 d. QuadraPure TU (248 mg) was added and the suspension was stirred for 20.5 h. QuadraPure BzA (15 mg) was added and the suspension was stirred for 2 h. The mixture was filtered through silica gel (2.5 cm × 1.0 cm, rinsing with CH_2Cl_2/EtOH 3:1). Solvent removal from the eluate gave a viscous yellow oil with a small amount of solid. This mixture was taken up in CH_2Cl_2 (6 mL), and the solution was washed with water (4 × 6 mL). The solvent of the CH_2Cl_2 phase was removed, giving a mixture (191 mg) of a yellow viscous oil and a small amount of solid. ^{1}H NMR spectroscopy revealed that this material consisted of oligoPPE **26$_7$**, PEG-N_3 **14**, silicone grease, and TIPS-OH. Analytical data of oligoPPE **26$_7$**: for ^{1}H NMR data, see Table S24. MS (ESI): because of the high molecular weight of this compound and the insufficient intensity of the signal corresponding to the monoisotopic mass, the most abundant mass of each signal is reported, *m*/*z* 2116.3 $[M + 4Na]^{4+}$, 2110.5 $[M + 3Na + H]^{4+}$, 2105.0 $[M + 2Na + 2H]^{4+}$, 1697.6 $[M + 5Na]^{5+}$, 1693.2 $[M + 4Na + H]^{5+}$.

OligoPPE **26$_9$**. See the general procedure for alkyne-azide cycloaddition. The material (11 mg, containing ∼2.9 μmol deprotected oligoPPE **25$_4$**) that had been obtained through the desilylation of oligoPPE **20$_4$**, PEG-N_3 **14** (30 mg, 70.8 μmol), $CuSO_4$ (0.1 M aqueous solution, 25 μL, 2.5 μmol), sodium L-ascorbate (2.26 mg dissolved in 100 μL H_2O, 11.4 μmol), THF (1 mL), and EtOH (0.5 mL) with a reaction time of 5 d. QuadraPure TU (61 mg) was added and the suspension was stirred for 24 h. The suspension was filtered through silica gel (1.5 cm × 1.5 cm, rinsing with CH_2Cl_2/EtOH 3:1). Solvent removal from the eluate gave a mixture of a yellow viscous oil with a small amount of solid. This mixture was taken up in CH_2Cl_2 (3.5 mL) and washed with water (4 × 3.5 mL). The solvent of the CH_2Cl_2 phase was removed, giving a mixture (59 mg) of a viscous yellow oil. The ^{1}H NMR spectrum revealed that this solid consisted of oligoPPE **26$_9$**, PEG-N_3 **14**, triphenylphosphine oxide, silicone grease, and TIPS-OH. For ^{1}H NMR data of oligoPPE **26$_9$**, see Table S24.

OligoPPE **26$_{11}$**. See the general procedure for alkyne-azide cycloaddition. The material (25 mg, containing ∼5.66 μmol deprotected oligoPPE **25$_5$**) that had been obtained through the desilylation of **20$_5$**, PEG-N_3 **14** (70 mg, 165 μmol), $CuSO_4$ (0.1 M aqueous solution, 57 μL, 5.7 μmol), sodium L-ascorbate (3.87 mg dissolved in 100 μL H_2O, 19.5 μmol), THF (1.5 mL), and EtOH (0.75 mL) with a reaction time of 5 d. QuadraPure TU (119 mg) was added and the suspension was stirred for 19 h. The suspension was filtered through silica gel (1.8 cm × 1.3 cm, rinsing with CH_2Cl_2/EtOH 3:1). Solvent removal from the eluate gave a yellow viscous oil. This was taken up in CH_2Cl_2 (3.5 mL), and the solution was washed with water (4 × 3.5 mL). The solvent of the CH_2Cl_2 phase was removed, giving a yellow-green fluorescent viscous oil (85 mg). The ^{1}H NMR spectrum revealed that this oil consisted of oligoPPE **26$_{11}$**, PEG-N_3 **14**, silicone grease, and TIPS-OH. For ^{1}H NMR data of oligoPPE **26$_{11}$**, see Table S24.

OligoPPE **26$_{15}$**. See the general procedure for alkyne-azide cycloaddtion. The material (17 mg, containing ∼3.32 μmol deprotected oligoPPE **25$_7$**) that had been obtained through the desilylation of oligoPPE **20$_7$**, PEG-N_3 **14** (60 mg, 142 μmol), $CuSO_4$ (0.1 M aqueous solution, 47 μL, 4.7 μmol), sodium L-ascorbate (3.69 mg dissolved in 100 μL H_2O, 18.6 μmol), THF (1.5 mL), and EtOH (0.75 mL) with a reaction time of 5 d. QuadraPure TU (113 mg) was added and the suspension was stirred for 19 h. The suspension was filtered through silica gel (1.5 cm × 1.0 cm, rinsing with CH_2Cl_2/EtOH 3:1). Solvent removal from the eluate gave a yellow viscous oil. This was taken up in CH_2Cl_2 (3.5 mL), and the solution was washed with water (4 × 3.5 mL). The solvent of the CH_2Cl_2 phase was removed, giving a yellow-green fluorescent viscous oil (87 mg). The ^{1}H NMR spectrum revealed that this oil consisted of oligoPPE **26$_{15}$**, PEG-N_3 **14**, silicone grease, and TIPS-OH. For ^{1}H NMR data of oligoPPE **26$_{15}$**, see Table S24.

General Procedure for Ester Hydrolysis of OligoPPEs **26$_n$**. The material containing oligoPPE **26$_n$**, i.e., the material that had been obtained through the reaction of deprotected oligoPPE **25$_x$** with PEG-N_3 **14**, was dissolved in EtOH. An aqueous solution of NaOH (2.0 M) and H_2O were added. The solution was stirred at room temperature for several hours.

Washing Process. The aqueous solution was transferred to a centrifuge tube. CH_2Cl_2 was added, and the two phases were mixed well. The resulting emulsion, which in some cases contained a solid phase, was centrifuged at 5000 rpm for 5 min. The mixture separated into two phases, or if a solid was contained, three phases: a yellow aqueous phase at the top, a flocculent solid in the middle, and a colorless CH_2Cl_2 phase at the bottom. Carboxylate **27$_n$** was in the water phase and in the solid. The solid dissolved quite slowly in the aqueous phase. We did not wait until the solid had completely dissolved. The CH_2Cl_2 phase was removed using a syringe. The water phase and the flocculent solid were washed several times with CH_2Cl_2 using the aforementioned procedure. If the solid had not been dissolved at this stage, MeCN was added. To the well-washed aqueous solution was added proton-exchange resin. In this way, the pH of the solution was lowered to ∼3.0. The solution was separated from the resin through filtration through a syringe filter. Removal of the solvent through freeze-drying and drying over P_2O_5 at reduced pressure provided ruler precursor **28$_n$**.

Ruler Precursor **28$_1$**. See the general procedure for ester hydrolysis of oligoPPEs **26$_n$**. OligoPPE **26$_1$** (**20$_0$**) (84 mg, 41.2 μmol), EtOH (2.0 mL), aqueous solution of NaOH (2.0 M, 206 μL, 412 μmol), and H_2O (2.0 mL) with a reaction time of 22 h. The washing process was omitted because no PEG-N_3 **14**, TIPS-OH, or silicone grease had to be removed. Through the addition of proton-exchange resin (300 mg), the pH of the solution was lowered to ∼3.5. The resin was removed through centrifugation. The resin was washed with H_2O (3 × 1 mL). The aqueous solution and the wash solutions were combined and filtered through a syringe filter. The solvent was removed from the filtrate through freeze-drying, giving ruler precursor **28$_1$** (65 mg, 87%) as a yellow solid. For ^{1}H and ^{13}C NMR data, see Tables S25 and S26. MS (ESI): *m*/*z* 1813.9 $[M - H]^-$, 925.2 $[M - 3H + K]^{2-}$, 917.2 [M

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− 3H + Na]$^{2-}$, 906.3 [M − 2H]$^{2-}$, 616.6 [M − 4H + K]$^{3-}$, 611.2 [M − 4H + Na]$^{3-}$, 603.9 [M − 3H]$^{3-}$.

Ruler Precursor $\mathbf{28_3}$. See the general procedure for ester hydrolysis of oligoPPEs $\mathbf{26}_n$. Material (117 mg, containing ∼24.2 μmol of oligoPPE $\mathbf{26_3}$) that had been obtained through the reaction of deprotected oligoPPE $\mathbf{25_1}$ with PEG-N_3 **14**, EtOH (3.0 mL), aqueous solution of NaOH (2.0 M,194 μL, 388 μmol), and H_2O (2.0 mL) with a reaction time of 18 h. H_2O (15 mL) was added, and the solution was frozen. The solvents were removed from the frozen solution at reduced pressure, leaving behind a yellow solid (168 mg) that was taken up in H_2O (3.5 mL). The resulting solution was washed with CH_2Cl_2 (4 × 3.5 mL) as described in the general procedure for the ester hydrolysis of oligoPPEs $\mathbf{26}_n$. Addition of proton-exchange resin (160 mg) lowered the pH of the aqueous solution to ∼3.0. The suspension was filtered through a syringe filter. Removal of the solvent from the filtrate using freeze-drying and drying the residue over P_2O_5 at reduced pressure provided ruler precursor $\mathbf{28_3}$ (81 mg, 83% over 4 steps starting with oligoPPE $\mathbf{20_1}$) as a yellow-orange solid. For ^{1}H and ^{13}C NMR data, see Tables S25 and S26. MS (ESI): *m*/*z* 1961.4 [M − 2H]$^{2-}$, 1307.2 [M − 3H]$^{3-}$.

Ruler Precursor $\mathbf{28_5}$. See the general procedure for ester hydrolysis of oligoPPEs $\mathbf{26}_n$. Material (101 mg, containing ∼12.1 μmol of oligoPPE $\mathbf{26_5}$) that had been obtained through the reaction of deprotected oligoPPE $\mathbf{25_2}$ with PEG-N_3 **14**, EtOH (0.7 mL), aqueous solution of NaOH (2.0 M, 96.9 μL, 194 μmol), and H_2O (1.5 mL) with a reaction time of 19.5 h. H_2O (2.8 mL) was added, and the mixture was washed with CH_2Cl_2 (4 × 4.0 mL) as described in the general procedure for the ester hydrolysis of oligoPPEs $\mathbf{26}_n$. Then, MeCN (1 mL) was added to the mixture of the aqueous phase, whereupon the solid went into solution. Addition of the proton-exchange resin (133 mg) reduced the pH of the aqueous solution to ∼3.0. The resin was removed through filtration through a syringe filter. Removal of the solvent from the filtrate through freeze-drying and drying the residue over P_2O_5 at reduced pressure provided ruler precursor $\mathbf{28_5}$ (46 mg, 63% over 4 steps starting from oligoPPE $\mathbf{20_2}$) as a yellow-orange solid. For ^{1}H and ^{13}C NMR data, see Tables S25 and S26.

Ruler Precursor $\mathbf{28_7}$. See the general procedure for ester hydrolysis of oligoPPEs $\mathbf{26}_n$. Material (183 mg, containing ∼18.4 μmol oligoPPE $\mathbf{26_7}$) that had been obtained through the reaction of deprotected oligoPPE $\mathbf{25_3}$ with PEG-N_3 **14**, EtOH (3 mL), aqueous solution of NaOH (2.0 M, 147 μL, 294 μmol), and H_2O (2 mL) with a reaction time of 18 h. H_2O (15 mL) was added, and the reaction solution was frozen. The solvents were removed from the frozen solution at reduced pressure. The residual yellow solid (177 mg) was dissolved in H_2O (5.5 mL). The aqueous solution was washed with CH_2Cl_2 (3 × 4.0 mL) as described in the general procedure for the ester hydrolysis of oligoPPEs $\mathbf{26}_n$. Addition of proton-exchange resin (180 mg) reduced the pH of the aqueous solution to ∼3.0. The suspension was filtered through a syringe filter. Removal of the solvent from the filtrate through freeze-drying and drying the residue over P_2O_5 at reduced pressure provided ruler precursor $\mathbf{28_7}$ (108 mg, 72% over 4 steps starting from oligoPPE $\mathbf{20_3}$) as a yellow-orange solid. For ^{1}H and ^{13}C NMR data, see Tables S25 and S26. MS (ESI): *m*/*z* 1652.2 [M + 5Na]$^{5+}$.

Ruler Precursor $\mathbf{28_9}$. See the general procedure for ester hydrolysis of oligoPPEs $\mathbf{26}_n$. Material (59 mg, containing ∼2.90 μmol oligoPPE $\mathbf{26_9}$) that had been obtained through the reaction of deprotected oligoPPE $\mathbf{25_4}$ with PEG-N_3 **14**, EtOH (0.7 mL), aqueous solution of NaOH (2.0 M, 40 μL, 80 μmol), and H_2O (1.5 mL) with a reaction time of 22 h. H_2O (5 mL) was added, and the reaction solution was frozen. The solvents were removed from the frozen solution at reduced pressure. The residual yellow solid was dissolved in H_2O (3.5 mL). The mixture was washed with CH_2Cl_2 (4 × 3.5 mL) as described in the general procedure for the ester hydrolysis of oligoPPEs $\mathbf{26}_n$. After washing, MeCN (1 mL) was added. Addition of proton-exchange resin (180 mg) reduced the pH of the aqueous solution to ∼3.0. The suspension was filtered through a syringe filter. Removal of the solvent from the filtrate through freeze-drying provided ruler precursor $\mathbf{28_9}$ (22.6 mg, 76% over 4 steps starting from oligoPPE $\mathbf{20_4}$) as an orange solid. For ^{1}H NMR data, see Table S25.

Ruler Precursor $\mathbf{28_{11}}$. See the general procedure for ester hydrolysis of oligoPPEs $\mathbf{26}_n$. Material (85 mg, containing ∼5.66 μmol oligoPPE $\mathbf{26_{11}}$) that had been obtained through the reaction of deprotected oligoPPE $\mathbf{25_5}$ with PEG-N_3 **14**, EtOH (0.6 mL), aqueous solution of NaOH (2.0 M, 71 μL, 142 μmol), and H_2O (1.5 mL) with a reaction time of 18 h. H_2O (5 mL) was added, and the mixture was washed with CH_2Cl_2 (4 × 4 mL) as described in the general procedure for the ester hydrolysis of oligoPPEs $\mathbf{26}_n$. After washing, MeCN (1 mL) was added. Addition of proton-exchange resin (128 mg) lowered the pH of the aqueous solution to ∼3.0. The suspension was filtered through a syringe filter. Removal of the solvent from the filtrate through freeze-drying and drying the residue over P_2O_5 at reduced pressure provided ruler precursor $\mathbf{28_{11}}$ (48 mg, 69% over 4 steps starting from oligoPPE $\mathbf{20_5}$) as a yellow-orange solid. For ^{1}H NMR data, see Table S25.

Ruler Precursor $\mathbf{28_{15}}$. See the general procedure for ester hydrolysis of oligoPPEs $\mathbf{26}_n$. Material (87 mg, containing ∼3.32 μmol oligoPPE $\mathbf{26_{15}}$) that had been obtained through the reaction of deprotected oligoPPE $\mathbf{25_7}$ with PEG-N_3 **14**, EtOH (0.7 mL), aqueous solution of NaOH (2.0 M, 45 μL, 90 μmol), and H_2O (1.5 mL) with a reaction time of 19.5 h. H_2O (5 mL) was added, and the reaction solution was frozen. The solvents were removed from the frozen solution at reduced pressure. The residual yellow solid was dissolved in H_2O (3.5 mL). The mixture was washed with CH_2Cl_2 (4 × 3.5 mL) as described in the general procedure for the ester hydrolysis of oligoPPEs $\mathbf{26}_n$. After washing, MeCN (1 mL) was added. Addition of proton-exchange resin (90 mg) reduced the pH of the aqueous solution to ∼3.0. The suspension was filtered through a syringe filter. Removal of the solvent from the filtrate through freeze-drying and drying the residue over P_2O_5 at reduced pressure provided ruler precursor $\mathbf{28_{15}}$ (38.0 mg, 69% over 4 steps starting from oligoPPE $\mathbf{20_7}$) as an orange viscous oil. For ^{1}H NMR data, see Table S25.

Gd Ruler $\mathbf{29_1}$. Ruler precursor $\mathbf{28_1}$ (46 mg, 25 mmol) was dissolved in D_2O (0.7 mL), and the solution was diluted to 1.0 mL with D_2O. A solution of $GdCl_3$ in D_2O (0.1 M, 487.1 μL, 48.71 μmol) and a solution of NaOD in D_2O (0.50 M, 372.2 μL, 186 μmol) were added successively. The solution was diluted with D_2O to a total volume of 2500 μL to obtain a 10.0 mM yellow solution of Gd ruler $\mathbf{29_1}$ in D_2O. The pD value of the solution was ∼8.0. Accurate MS (ESI) of Gd ruler $\mathbf{29_1}$ (Figure S223): *m*/*z* calcd for [M − 2Na]$^{2-}$ $C_{82}H_{110}Gd_2N_{12}O_{34}^{2-}$, 1061.28702; found, 1061.28674.

Gd Ruler $\mathbf{29_3}$. Ruler precursor $\mathbf{28_3}$ (73 mg, 18.59 μmol) was dissolved in D_2O (1.0 mL). A solution of $GdCl_3$ in D_2O (0.1 M, 362.5 μL, 36.25 μmol) and a solution of NaOD in D_2O (1.0 M, 120 μL, 120 μmol) were added successively. A solution of NaOD in D_2O (1.0 M, 20 μL, 20 μmol) was added as much as was needed to inrease the pD to 8.0. The solution was diluted with D_2O to a total volume of 1859 μL to obtain a 10.0 mM solution of Gd ruler $\mathbf{29_3}$ in D_2O. The pD value of the solution was ∼8.0. MS (ESI) of Gd ruler $\mathbf{29_3}$: *m*/*z* 2116.5 [M − 2Na]$^{2-}$. Accurate MS (ESI) of Gd ruler $\mathbf{29_3}$ (Figure S224): *m*/*z* calcd for [M − 2Na + Cl]$^{3-}$ $C_{182}H_{274}Gd_2N_{24}O_{70}Cl^{3-}$, 1422.22685; found, 1422.22560.

Gd Ruler $\mathbf{29_5}$. Ruler precursor $\mathbf{28_5}$ (29 mg, 4.80 μmol) was dissolved in D_2O (0.5 mL). A solution of $GdCl_3$ in D_2O (0.1 M, 93.7 μL, 9.37 μmol) and a solution of NaOD in D_2O (1.0 M, 38.4 μL, 38.4 μmol) were added successively. The solution was diluted with D_2O to a total volume of 960 μL to obtain a 5.0 mM solution of Gd ruler $\mathbf{29_5}$ in D_2O. The pD value of the solution was ∼8.0. Accurate MS (ESI) of Gd ruler $\mathbf{29_5}$ (Figure S225): *m*/*z* calcd for [M − 2Na + Cl]$^{3-}$ $C_{282}H_{438}Gd_2N_{36}O_{106}Cl^{3-}$, 2125.27256; found, 2125.27888.

Gd Ruler $\mathbf{29_7}$. Ruler precursor $\mathbf{28_7}$ (72 mg, 8.84 μmol) was dissolved in D_2O (1.0 mL). A solution of $GdCl_3$ (0.1 M, 172.2 μL, 17.22 μmol) and a solution of NaOD in D_2O (1.0 M, 60 μL, 60 μmol) were added successively. A solution of NaOD in D_2O (1.0 M, 20 μL, 20 μmol) was added to increase the pD of the solution to 8.0. The solution was diluted with D_2O to a total volume of 1767 μL to obtain a 5.0 mM solution of Gd ruler $\mathbf{29_7}$ in D_2O. The pD value of the solution was ∼8.0. Accurate MS (ESI) of Gd ruler $\mathbf{29_7}$ (Figure S226): *m*/*z*

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calcd for $[M - 2Na + Cl]^{3-}$ $C_{382}H_{602}Gd_2N_{48}O_{142}Cl^{3-}$, 2828.31827; found, 2828.31467.

Gd Ruler **29$_9$**. Ruler precursor **28$_9$** (21.6 mg, 2.10 μmol) was dissolved in D_2O (0.5 mL). A solution of $GdCl_3$ in D_2O (0.1 M, 41.0 μL, 4.10 μmol) and a solution of NaOD in D_2O solution (1.0 M, 168 μL, 168 μmol) were added successively. A solution of NaOD in D_2O solution (1.0 M, 75 μL, 75 μmol) was added to increase the pD of the solution to 8.0. The solution was diluted with D_2O to a total volume of 1052 μL to obtain a 2.0 mM solution of Gd ruler **29$_9$** in D_2O. The pD value of the solution was ∼8.0. Accurate MS (ESI) of Gd ruler **29$_9$** (Figure S227): because of the high molecular weight of this compound and therefore the broad isotopic distribution, the most abundant mass is reported instead of the monoisotopic mass, *m*/*z* calcd for $[M + 4Na + 4H]^{6+}$ $C_{482}H_{768}Gd_2N_{60}Na_6O_{178}^{6+}$, 1784.0152; found, 1784.0198.

Gd Ruler **29$_{11}$**. Ruler precursor **28$_{11}$** (38 mg, 3.07 μmol) was dissolved in D_2O (0.75 mL). A solution of $GdCl_3$ in D_2O (0.1 M, 59.9 μL, 5.99 μmol) and a solution of NaOD in D_2O (1.0 M, 240 μL, 240 μmol) were added successively. The solution was diluted with D_2O to a total volume of 1535 μL to obtain a 2.0 mM solution of Gd ruler **29$_{11}$** in D_2O. The pD value of the solution was ∼7.5. Accurate MS (ESI) of Gd ruler **29$_{11}$** (Figure S228): because of the high molecular weight of this compound and therefore the broad isotopic distribution, the most abundant mass is reported instead of the monoisotopic mass, *m*/*z* calcd for $[M + Na + 6H]^{7+}$ $C_{582}H_{936}Gd_2N_{72}Na_3O_{214}^{7+}$, 1821.3276; found, 1821.3342.

Gd Ruler **29$_{15}$**. Ruler precursor **28$_{15}$** (36.5 mg, 2.20 μmol) was dissolved in D_2O (0.5 mL). A solution of $GdCl_3$ (0.1 M, 42.9 μL, 4.29 μmol) and a solution of NaOD in D_2O (1.0 M, 176 μL, 176 μmol) were added successively. A solution of NaOD in D_2O (1.0 M NaOD in D_2O, 90 μL, 90 μmol) was added to increase the pD of the solution to 8.0. The solution was diluted with D_2O to a total volume of 1100 μL to obtain a 2.0 mM solution of Gd ruler **29$_{15}$** in D_2O. The pD value of the solution was ∼8.0. Accurate MS (ESI) of Gd ruler **29$_{15}$** (Figure S229): because of the high molecular weight of this compound and therefore the broad isotopic distribution, the most abundant mass is reported instead of the monoisotopic mass, *m*/*z* calcd for $[M + 8H]^{8+}$ $C_{782}H_{1266}Gd_2N_{96}Na_2O_{286}^{8+}$, 2118.7002; found, 2118.7024.

Allene **30**. A solution of Bu_4NF (1.0 M solution in THF, this solution contains 5 wt % of water; 8.0 mL, 8.0 mmol) was added to a colorless solution of diiodobenzene **2** (2.01 g, 2.68 mmol) in THF (20 mL). The color of the solution changed from colorless to brown-black. The solution was stirred at room temperature for 70 min. All volatiles were evaporated at 33 °C and reduced pressure. Column chromatography (5.0 cm × 23 cm, pentane/Et_2O/CH_2Cl_2 1:1:0.2) gave two fractions: fraction A (39 mg, containing **15**, **30**, **31**, and TIPS-OH in a molar ratio of 1.00:0.23:0.024:1.91) and fraction B (1.53 g, containing **15**, **30**, and TIPS-OH in a molar ratio of 1.00:0.042:1.96). Recrystallization of fraction B in EtOH (38 mL) gave brown crystals (583 mg, containing **15** and **30** in a molar ratio of 1.00:0.019). Fraction A of the column chromatography and the mother liquor of the recrystallization were combined and chromatographed twice (1st: 2.5 cm × 50 cm, pentane/Et_2O 2:1; second: 2.0 cm × 35 cm, pentane/Et_2O 2:1). This gave allene **30** (24 mg with a small amount of other components) and alkyne **15** (290 mg with a small amount of other components), which were both slightly yellow solids. Analytical data of allene **30**. ^1H NMR (500 MHz, $CDCl_3$): δ 7.45 and 7.33 (2s, 1H each, H_{Ar}), 6.77 (t, ^4J = 5.9 Hz, 1H, C<u>H</u>=C=CH_2), 5.44 (d, ^4J = 5.9 Hz, 2H, CH=C=C<u>H</u>$_2$), 4.70 (d, ^4J = 2.4 Hz, 2H, C<u>H</u>$_2$-C≡CH), 2.56 (t, ^4J = 2.4 Hz, 1H, CH_2–C≡C<u>H</u>). ^{13}C NMR (125 MHz, $CDCl_3$): δ 201.9 (CH=<u>C</u>=CH_2), 153.0 and 151.7 ($C_{Ar}O$), 127.7 and 123.3 ($C_{Ar}H$), 119.2 (<u>C</u>H=C=CH_2), 91.1 (CH=C=<u>C</u>H$_2$), 86.8 and 86.0 ($C_{Ar}I$), 77.4 (CH_2–<u>C</u>≡CH), 76.6 (CH_2–C≡<u>C</u>H), 57.8 (<u>C</u>H$_2$–C≡CH).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00125.

Tables containing ^1H and ^{13}C NMR data, NMR spectra, and ESI-MS spectra (PDF)

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Notes

The authors declare no competing financial interest.

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