

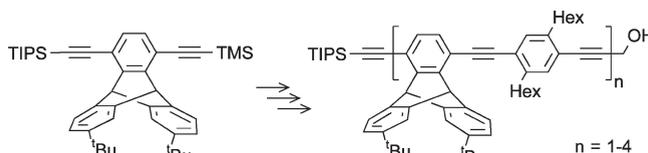
Synthesis of Monodisperse Oligo(1,4-phenyleneethynylene-alt-1,4-triptyceneethynylene)s

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The synthesis of monodisperse oligo(*p*-phenyleneethynylene)s **8a_n** with alternating 2,5-dihexyl-1,4-phenylene and 6,14-di-*tert*-butyl-1,4-triptycene units and orthogonally protected alkyne end groups is reported. Starting from 6,14-di-*tert*-butyl-1-(2-triisopropylsilylethynyl)-4-(2-trimethylsilylethynyl)-triptycene (**5a**), 1,4-dihexyl-2,5-diiodobenzene (**10**), and 1,4-dihexyl-2-iodo-5-(3-hydroxyprop-1-ynyl)-benzene (**9**), oligomers with up to four repeating units, i.e., eight phenyleneethynylene units, were prepared through a partially divergent–convergent route with the alkynyl–aryl (Sonogoshira–Hagihara) coupling as the key reaction. The starting compound **5a** was prepared from triptycenequinone through a sequence of addition of 2-trialkylsilylethynyllithium, reduction and concomitant elimination of water, conversion of the phenol into a triflate, and finally Pd/Cu-catalyzed coupling with trialkylsilylethyne. A similar access to the key compound for a stringent divergent–convergent route, 6,14-di-*tert*-butyl-1-(3-hydroxybut-1-ynyl)-4-(2-triisopropylsilylethynyl)triptycene (**6**), is reported. The optical properties of the oligomers **8a_n** and the corresponding oligo(2,5-dihexyl-1,4-phenyleneethynylene)s in dilute solution are almost identical, whereas they differ significantly for the solid, undiluted compounds.

Introduction

Oligo- and poly(*p*-phenyleneethynylene)s (oligoPPEs, polyPPEs) attract interest as materials for electronic and

optoelectronic devices because of their electrooptical properties,¹ especially their luminescence. Beyond that, they serve as building blocks for nanoscopic molecules^{2,3} on account of their rodlike structure together with their good accessibility. In recent years, much time and effort has been devoted to the development of strategies to retain the optical

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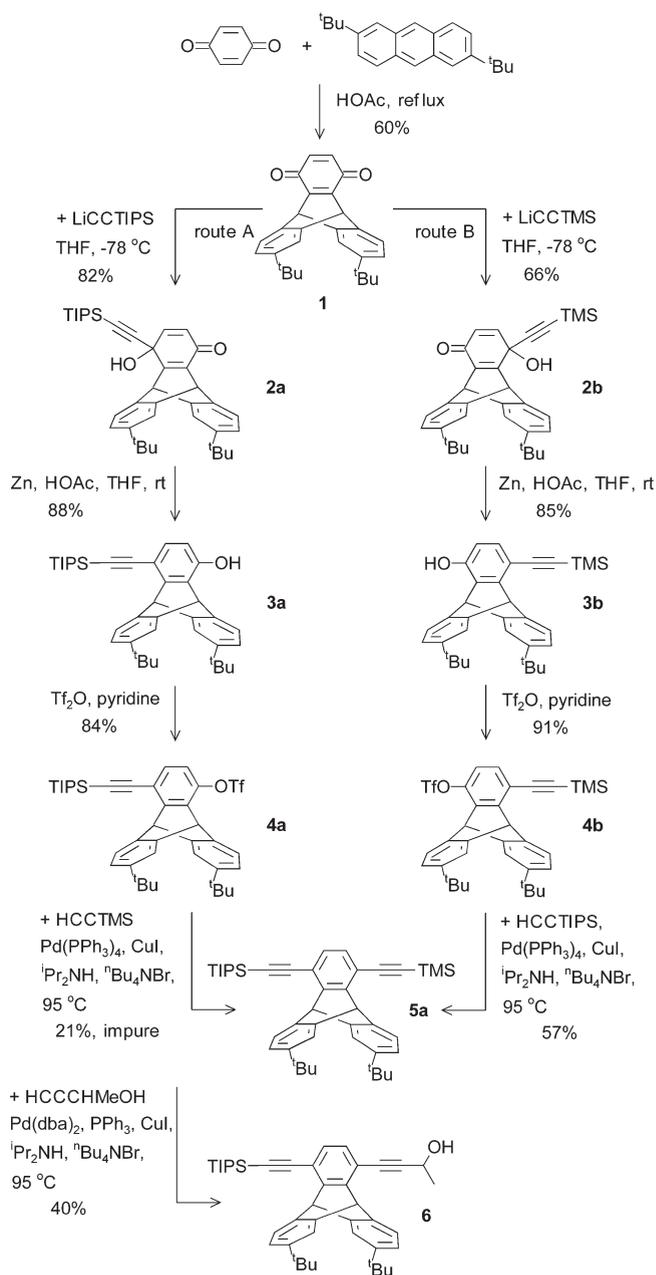
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properties of dilute solutions when going to the undiluted, solid compounds.^{1f,4–8} One of the approaches uses the bulkiness of iptycenes to keep the π -systems of polyPPEs at a distance from each other: Benzene units were substituted for triptycene and/or pentaipitycene ones.⁵ Considering the success of this concept, it is surprising that it was hardly applied to oligomers.^{9,10} We know of only one report on a series of oligomers with iptycene units.¹⁰ It describes the synthesis and properties of “all-pentaipitycene” oligoPPEs, i.e., oligoPPEs with up to four repeating units in which all of the benzene units are substituted for pentaipitycene moieties and with one alkoxy substituent at each of the two termini of the oligomer backbone. Attempts to go beyond four repeating units were unsuccessful. Further fundamental studies on the properties of polyconjugated molecules as well as their use as construction units require an access to even longer, monodisperse iptycene containing oligoPPEs with reactive functional groups at their ends. Herein we describe a strategy for the preparation of monodisperse oligoPPEs **8a_n** in which every second benzene unit is exchanged against a 1,4-triptycene unit. All oligomers **8a_n** have two orthogonally protected, terminal ethynyl groups.¹¹ This allows for selective deprotection and independent use of these two functional groups in further derivatization, e.g., coupling with 1-alkoxy-4-iodobenzene and alkyne dimerization (results not shown).^{3a,12,13}

In the following section, first, the synthesis of the key building block **5a**, a 1,4-diethynyltriptycene with one TIPS and one TMS protecting group, and the preparation of triptycene-containing oligomers **8_n** are described. Second, the key step toward a more rapid oligomer synthesis via a strictly divergent–convergent synthesis with the preparation of triptycene **6** is presented. Triptycene **6** differs from

SCHEME 1. Synthesis of the Key Iptycene Building Blocks **5a** and **6**^a



^aFor simplicity, the compounds are shown as one distinct enantiomer or diastereomer.

5a by the 3-hydroxybut-1-ynyl instead of the TMS-ethynyl substituent. Finally, the optical properties of **8a_n** in solution and solid state are compared with those of the corresponding iptycene-free oligo(2,5-dihexyl-1,4-phenyleneethynylene)s (**11_n**).

Results and Discussion

Synthesis of the Key Building Block 1,4-Diethynyltriptycene 5a. The synthesis of diethynyltriptycene **5a** (Scheme 1) starts with a Diels–Alder reaction between 1,4-benzoquinone and 2,6-di-*tert*-butylanthracene. 1,4-Benzoquinone acts additionally as an oxidant to provide triptycenequinone

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1 directly.¹⁴ Triptycenequinone **1** turned out to be extremely light sensitive. Even the short time needed to set up an experiment is sufficient to produce photoreaction products in amounts detectable by NMR spectroscopy and thin-layer chromatography. The 1,2-addition of 2-trialkylsilylethynyllithium to triptycenequinone **1**¹⁷ gave compounds **2** which were converted into the phenols **3** through treatment with zinc in acetic acid.¹⁰ The corresponding triflates **4**, obtained from the reaction of phenols **3** with triflic anhydride,¹⁸ were coupled with trialkylsilylethyne under Pd/Cu catalysis to yield the diethynyltriptycene **5a**, the key building block for the synthesis of the oligomers **8_n**.

The reaction of 2-trimethylsilylethynyllithium or 2-triisopropylsilylethynyllithium with quinone **1** resulted in a mixture of two diastereomers in a ratio of 1.0:2.3 and 1.0:2.5, respectively. The ratios were constant throughout all of our several experiments. The next step to obtain the phenols **3**, the reduction of the addition products **2** with concomitant elimination of water, proceeded smoothly when zinc in acetic acid¹⁰ was employed. Less successful was the use of SnCl₂^{5g,19} instead of Zn. In the case of **2b**, hardly any phenol **3b** was obtained. Instead, 1-acetyl-6,14-di-*tert*-butyl-4-hydroxytriptycene and 1-ethynyl-6,14-di-*tert*-butyl-4-hydroxytriptycene were obtained together with minor amounts of unidentified products. The former product must have been formed through desilylation of **3b** and subsequent addition of water. This is in agreement with the findings from Fukaminato et al.²⁰ who reported that desilylation occurred when SnCl₂ was used. Desilylation was not reported in another publication where SnCl₂ was applied to similar compounds.^{5g} The conversion of the TIPS analogue **2a** into phenol **3a** with SnCl₂ proceeded cleanly, however, the workup was much more tedious than when applying zinc.

The last step, the coupling of the triflates **4** with alkynes, turned out to be a high hurdle. To find conditions which gave acceptable to good conversion of the triflates **4a** and **4b**, numerous experiments were necessary in which the type and amount of Pd catalyst [Pd(PPh₃)₂Cl₂, Pd(PPh₃)₄, Pd₂(dba)₃, Pd(dba)₂] the amount of CuI, the type of base (Et₃N, ¹Pr₂NH), solvent (THF, DMF, toluene), and additives (Bu₄NBr, Bu₄NI, KI, PPh₃), and the reaction temperature (60–110 °C) were varied²¹ (Supporting Information, Table S2). Unfortunately, when the reaction was driven to high conversion, the coupling of triflate **4a** with TMS-ethyne is accompanied by the formation of a byproduct, probably a carbometalation product as suggested by mass spectral data. Chromatographic removal of this byproduct was unsuccessful. Accepting lower

conversions in order to avoid the side reaction is no solution to this problem because the starting compound **4a** and the coupling product **5a** are also very difficult to separate through chromatography. Luckily, no such problem occurred in the coupling of triflate **4b** with TIPS-ethyne. The amount of side products was much smaller, and side products as well as residual starting compound, triflate **4b**, could be removed through chromatography. Thus, route B is clearly to be preferred as compared to route A.

An attractive alternative to obtain 1,4-diethynyltriptycene **5a** appears to be a reaction sequence in which first both ethynyl substituents are introduced in one pot by two subsequent 1,2-additions to quinone **1**, followed by the reduction/water elimination procedure as described in the literature for benzoquinone, naphthoquinone, and anthraquinone.^{17,22} The outcome of experiments to obtain **5a** using such a route is discouraging: The second 1,2-addition shows very low conversion (<50%) and additionally the formation of side products.

Synthesis of the Triptycene-Containing Oligomers 8_n. Selective alkyne deprotection and Pd/Cu-catalyzed alkyne-aryl coupling were used to assemble the oligomer series **8a_n** (Scheme 2). The first member of this series, **8a₁**, was obtained through coupling of aryl iodide **9** with alkyne **5b**, the latter being the product of selective desilylation of 1,4-diethynyltriptycene **5a**. The syntheses of the longer oligomers **8a_n** with $n > 1$ is based on alternating desilylation of **8a_n** and coupling of the resulting alkynes **8b_n** with iodo monomer **7**.

Whereas our standard coupling conditions for oligoPPE synthesis,^{11,13} i.e., Pd(PPh₃)₂Cl₂ and CuI in piperidine and THF at room temperature, worked well for the preparation of **8a₁** (88%) and **8a₂** (70%), they gave unsatisfying yields of **8a₃** (40%). An influence of the length of oligoPPEs on the conversion in coupling reactions had been found, too, in the preparation of oligo(2,5-dihexyl-1,4-phenyleneethynylene)s (**11_n**).¹¹ In that case, longer oligoPPEs were obtained in good yields, when Pd(PPh₃)₂Cl₂ was exchanged for Pd₂(dba)₃/PPh₃. For the triptycene-containing oligoPPEs improved yields (89% of **8a₂**, 71% of **8a₃**, 77% of **8a₄**) were finally achieved by using comparatively large amounts of the catalysts Pd(PPh₃)₄ (10 mol %) and CuI (60 mol %) in diisopropylamine and toluene at 60 °C similar to a procedure described by Swager.^{5g} Applying such large amounts of Pd(PPh₃)₄ is not only costly but brings along separation problems: Very careful column chromatography and in the case of **8a₂** a subsequent precipitation with methanol from a solution in CH₂Cl₂ were required to obtain products free of triphenylphosphane oxide.

The iodo monomer **7** was prepared through Pd/Cu-catalyzed coupling of alkyne **5b** with diiodobenzene **10**. Despite a huge excess of diiodobenzene **10** (7 molar equiv), dicoupling product (both iodo substituents of **10** coupled with the alkyne **5b**) was formed. The chromatographic separation of **7** from diiodobenzene **10**, dicoupling product, and the oxidative alkyne dimerization (Glaser coupling) product of alkyne **5b** was facile because the di-*tert*-butyl-substituted triptycene unit influences the chromatographic behavior drastically ($R_f(\mathbf{10}) = 0.68$, $R_f(\mathbf{7}) = 0.49$, R_f (disubstitution product and product of oxidative dimerization of alkyne

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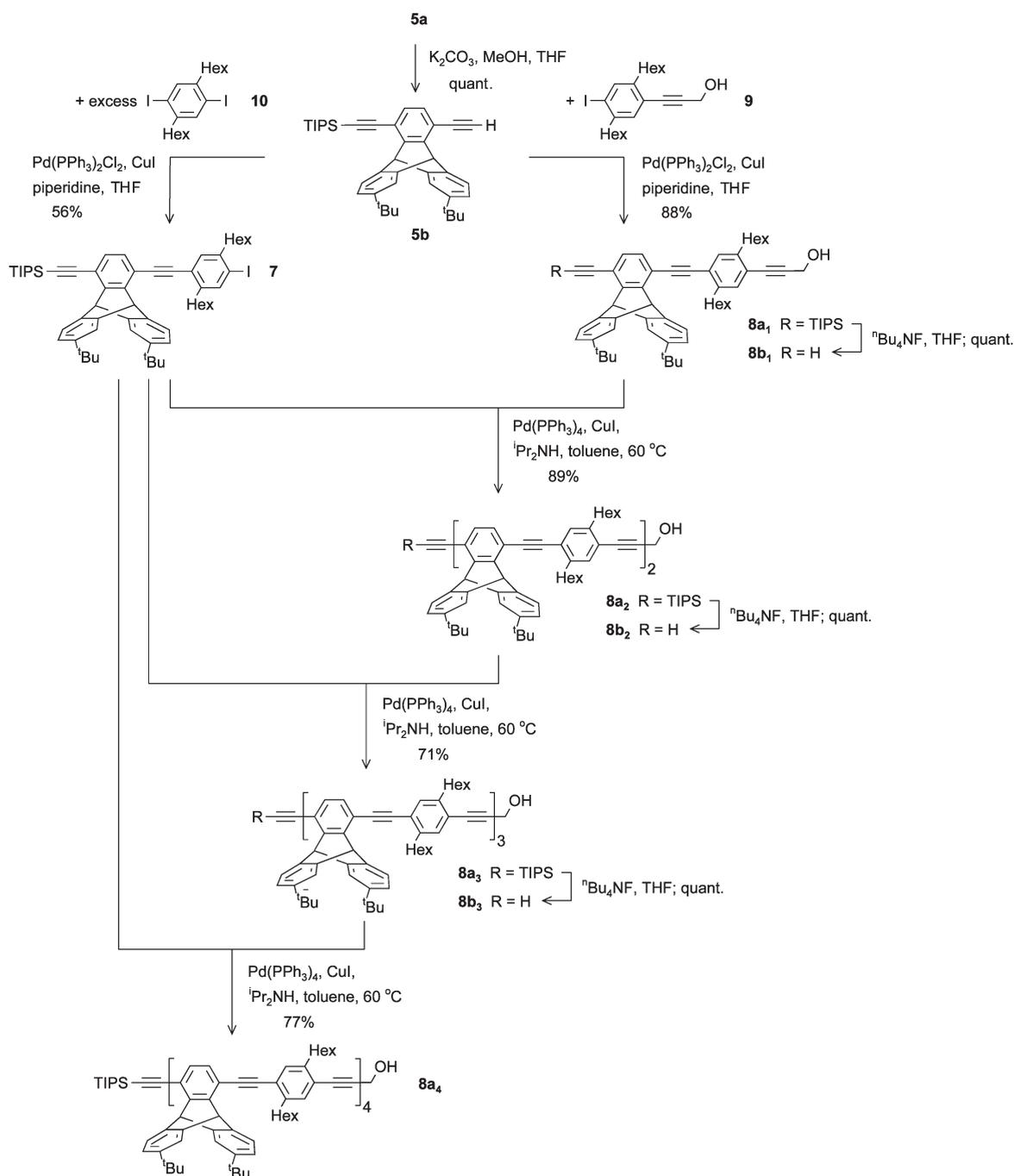
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SCHEME 2. Syntheses of Oligomers $8a_n$ with Alternating 1,4-Phenylene and 1,4-Triptycene Units^a

^aFor simplicity, the compounds are shown as one distinct enantiomer or diastereomer, and the oligomers $8a_n$ and $8b_n$ are presented with only one specific tacticity. All desilylations went to completion according to 1H NMR spectra. The yields of desilylation products are not given because the accompanying trialkylsilyl compounds such as trialkylsilylanol, hexaalkyldisiloxane, and trialkylsilyl fluoride were only partially removed.

$5b$) = 0.24 for *n*-pentane/ Et_2O 80:1, silica gel). This finding is remarkable in light of our experience with oligoPPEs 11_n . In the latter case, two oligomers are (nearly) inseparable by standard column chromatography, even if they differ by several, e.g., four, repeating units.²³

Synthesis of 1,4-Diethynyltriptycene 6 with Orthogonally Protected Alkyne Groups. Diethynyltriptycene $5a$ is the first

example of a triptycene with two differently protected ethynyl substituents.^{5g,21b,c} Selective removal of the TMS group allows the two alkyne groups to be addressed independently in subsequent reactions, e.g., for the formation of the monodisperse oligomers $8a_n$. However, the growth of the oligomers $8a_n$ starting with diethynyltriptycene $5a$ is slow: One repeating unit after the other is attached. For much more rapid growth via a divergent-convergent process, a 1,4-diethynyltriptycene with orthogonal alkyne

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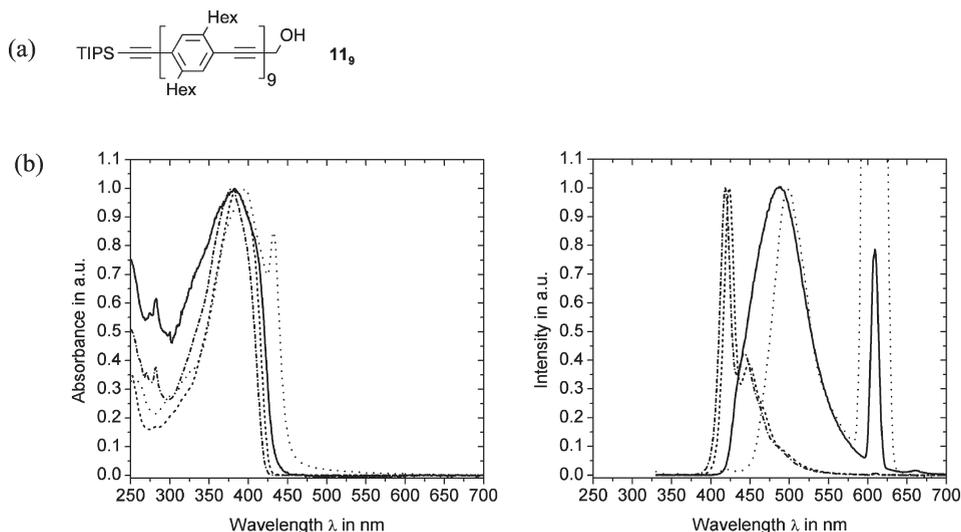


FIGURE 1. (a) Structural formula of oligomer **11_n**. (b) UV/vis (left) and fluorescence spectra (right) (excitation at 305 nm) of **8a₄** in CHCl_3 (···) and in a pristine dropcast film (—) and of **11_n** in CHCl_3 (---) and in a pristine dropcast film (···).

protecting groups, such as triisopropyl and 1-hydroxyethyl (Scheme 1),¹¹ is desired. We selected the 1-hydroxyethyl group instead of the hydroxymethyl group because in comparison to the latter the 1-hydroxyethyl group inhibits or at least drastically reduces the Pd-catalyzed addition of a terminal alkyne to the ethynylene moiety.^{24,25} The 1-hydroxyethyl group can be removed as smoothly as the hydroxymethyl group using $\gamma\text{-MnO}_2$ /powdered KOH.²⁵ Even though the coupling of triflate **4a** with but-3-yn-2-ol proceeded to completion and only a small amount of side product was formed, as judged from the ¹H NMR spectrum of the crude product, repeated chromatography was needed to remove dibenzylideneacetone, the ligand of the Pd catalyst, and two side products, most probably 6,14-di-*tert*-butyl-1-(3-oxobut-1-enyl)-4-(2-triisopropylsilylethynyl)tritycene and 6,14-di-*tert*-butyl-1-(3-oxobut-1-ynyl)-4-(2-triisopropylsilylethynyl)tritycene.²⁶ For the formation of the former, a base-induced isomerization of the 3-hydroxybut-1-ynyl substituent is assumed.²⁸ The difficulties in isolation may have contributed to the disappointingly low yield of 40% of isolated pure product **6**.

(24) Such a side reaction was described for the Pd/Cu-catalyzed coupling of 1,4-dihexyl-5-(3-hydroxyprop-1-ynyl)-2-iodobenzene with TIPS-ethyne in ref 11.

(25) Schulte, M.; Sahoo, D.; Godt, A. Manuscript in preparation.

(26) Neither of these two side products were obtained as pure products. Nevertheless, the following signals in the ¹H NMR spectra from chromatographic fractions containing these products give sufficient hints that these side products were formed. The yields of these side products is estimated to be below 5%. Characteristic signals of 6,14-di-*tert*-butyl-1-(3-oxobut-1-enyl)-4-(2-triisopropylsilylethynyl)tritycene: ¹H NMR (250 MHz, CDCl_3) δ = 8.17 (d, J = 16.0 Hz, 1H, $\text{CH}=\text{CH}-\text{Ac}$), 7.20 and 7.11 (AB spinsystem, J = 8.4 Hz, 1H each, H_c), 6.71 (d, J = 16.0 Hz, 1H, $\text{CH}=\text{CH}-\text{Ac}$), 6.00 and 5.86 (2 s, 1 H each, H_d), 2.45 (s, 3 H, COCH_3). Compare these data with the reported NMR data for dibenzylideneacetone in ref 27. Characteristic signals of 6,14-di-*tert*-butyl-1-(3-oxobut-1-ynyl)-4-(2-triisopropylsilylethynyl)tritycene: ¹H NMR (250 MHz, CDCl_3) δ = 7.11 and 7.07 (AB spinsystem, J = 8.1 Hz, 1H each, H_c), 5.93 and 5.79 (2 s, 1 H each, H_d), 2.56 (s, 3 H, COCH_3).

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Comparison of Optical and Thermal Properties of Oligomers **8a_n and OligoPPEs **11_n**.** The UV/vis and fluorescence spectra of diethynyltritycene **5a** and the oligomers **8a_n** (Figure S1 in the Supporting Information and Figure 1) in dilute solution strongly resemble those of the corresponding oligoPPEs **11_n**.¹¹ The absorption bands of **5a** and **8a₁** show distinct vibrational fine structures, the absorption bands of the longer oligomers **8a_{2–4}** are broad and featureless, and all emission spectra exhibit vibrational fine structures. The longer the backbone the more bathochromic the shift with a linear relation between the absorption energy and the reciprocal number of phenylene moieties (Figure S2 in the Supporting Information).^{11,29}

In order to investigate the effect of the di-*tert*-butyl-substituted triptycene moiety on the intermolecular electronic interaction, the optical spectra of solid films of triptycene containing oligoPPE **8a₄** and triptycene-free oligoPPE **11_n** were recorded (Figure 1). These two compounds have the same end groups and have nearly the same length. The films were drop-cast onto quartz from dilute solutions in chloroform and dried at room temperature. The transition of oligoPPE **11_n** from a dilute solution into the solid state is accompanied by drastic changes in the absorption and emission spectra: A bathochromic shift of the absorption maximum by 13 nm, an additional absorption band at 433 nm, and instead of the narrow emission band with vibrational fine structure that was found for dissolved **11_n**, a broad emission band at long wavelengths ($\lambda_{\text{max}} = 499$ nm). The same type of changes was found for the structurally related poly(2,5-didodecyl-1,4-phenyleneethynylene) (**12**)³⁰ and polyPPEs with other simple alkyl substituents.³¹ A bathochromic shift of 26 nm, an additional absorption band at 450 nm, and a broad emission band ($\lambda_{\text{max}} = 540$ nm).

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Therefore, we consider the explanation for the optical changes of the polymers to be valid for oligoPPE **11₉** and assign the additional absorption band of solid oligoPPE **11₉** to an increased planarization of the conjugated backbone^{30,32} and the broad emission band to excimer formation.^{30,33} Compared with oligoPPE **11₉**, the iptycene-containing oligoPPE **8a₄** behaves quite differently. Upon film formation from solution the absorption maximum is red-shifted by only 4 nm, and no separated, additional absorption band appears. The broadening of the absorption band at the red edge which results in an absorption onset at about 450 nm for the film (compare this with the onset at 430 nm for the solution) and the weakly developed shoulder at around 430 nm indicate that upon film formation the conjugated backbone of **8a₄** is planarized, however, to a much smaller extent than that of **11₉**. The emission spectra of both oligomers **11₉** and **8a₄** display a broad emission band at very long wavelengths ($\lambda_{\text{max}}(\mathbf{8a}_4) = 487 \text{ nm}$; $\lambda_{\text{max}}(\mathbf{11}_9) = 499 \text{ nm}$) and, thus, disclose excimer formation for both compounds. However, there is a striking difference between the emission of **8a₄** and **11₉**. Whereas the red edge of the emission bands of **11₉** and **8a₄** looks essentially identical, below 500 nm the emission band of **8a₄** is broader by about 30 nm. The emission at shorter wavelengths may be the emission of excimers of different structure, such as excimers with larger intermolecular distances³⁴ or with conformationally more twisted backbones. It may also be interpreted as the emission of individual oligomers. The missing of the 0 \rightarrow 0 transition for this emission would be explained with the reabsorption effect in optically dense materials.

Obviously, the di-*tert*-butyltritycene moieties profoundly influence the solid-state optical properties. They largely inhibit packing induced planarization of the conjugated backbone. How strong an influence they exert on the inter-chain electronic interaction, especially in comparison to unsubstituted triptycene and pentyptycene,^{5g,f} cannot be deduced from our study. Swager et al. concluded from a comparative study on polyPPEs with alternating 2,5-dialkoxy-1,4-phenylene and 1,4-tritycene or 1,4-pentyptycene units that the iptycene moieties sequester the conjugated backbones with pentyptycene being the much more effective unit.^{5g,f} Unfortunately, the optical data of those polymers cannot be compared to the ones of oligomers **8_n** because the thin film optical properties of polyPPEs with alkoxy side chains and polyPPEs with alkyl side chains differ significantly.^{1a,35} The “all-pentyptycene” oligoPPEs reported by Yang et al.¹⁰ are not a good reference, either, because the end groups play a distinctive role, too: Terminal, barely substituted benzene rings as in **8_n** can act as electronic mediators between the individual molecules in solid state.^{10,37} Further insight may be gained from oligomers such as **8_n**, but with triptycene units at both ends.

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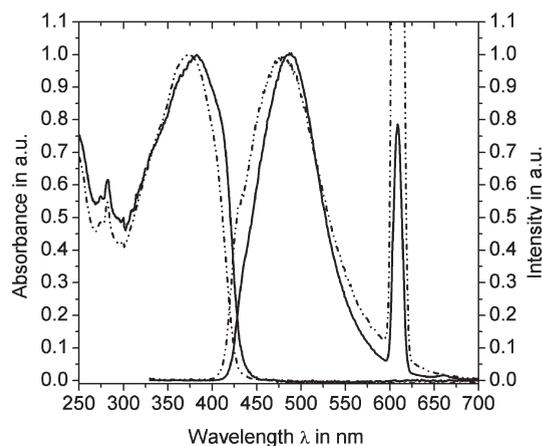


FIGURE 2. UV/vis and fluorescence spectra (excitation at 305 nm) of a drop-cast film of **8a₄** before (—) and after (· · · · ·) annealing at 300 °C.

Bunz et al. showed that the annealing of the spin-cast film of polymer **12** changes the intensity ratio of the two absorption maxima in favor of the “planarization” band at 450 nm, i.e., increases the degree of coplanarity of the phenylene moieties.³⁰ Furthermore, annealing reduces the excimer emission and leads to strong additional emission at shorter wavelengths from individual chains.³⁰ In contrast to these findings,³⁸ annealing a film of oligomer **8a₄** at 300 °C (mp ~ 270 °C) resulted in minute changes (Figure 2): A blue-shift by around 7 nm of the absorption and emission maxima and a vanishing of the red edge shoulder of the absorption band. Both features indicate that annealing leads to an increase of twisted conformations at the expense of coplanar alignment of the backbone forming phenylene units. A driving force for this could be that a better space filling packing is gained. The assumption of different packing in a pristine and an annealed film is corroborated by the thermal behavior of oligomer **8a₄**. Visual inspection reveals that the material sinters at 160 °C (possibly the melting of the hexyl side chains) and melts at 267–270 °C. Corresponding endothermic transitions at 158, 260, and 267 °C were detected with DSC during the first heating run. No thermal transition was detectable by DSC during cooling or heating the same sample a second time. However, the solid/fluid transition at around 270 °C could be repeated several times with the same sample on a heating stage. Most probably, upon cooling the melt, oligomer **8a₄** forms a glass whose T_g stayed undetected by DSC because there is too small a change in heat capacity at T_g . This assumption fits the observation that the melt of **8a₄** is highly viscous, much more viscous than a melt of **11₉**. In stark contrast, DSC curves of oligoPPE **11₉** exhibit an easily

(38) A much better comparison would be with an annealed film of oligoPPE **11₉**, but this material in thin films decomposed when heated. OligoPPE **11₉** shows a reproducible melting and crystallization transition in subsequent DSC runs. Moreover, the ¹H NMR spectrum of a sample that had been used in three consecutive DSC runs, twice up to 200 °C and once up to 300 °C, showed no indication of decomposition. However, annealing a film of oligoPPE **9₉** at 200 °C overnight gave a brownish film which showed very minute fluorescence and was only partially dissolvable in CHCl₃. Solution UV/vis and fluorescence spectra taken from the dissolved part bore no resemblance to the spectra recorded from pristine material. In contrast to this, the film of oligomer **8a₄** proved to be thermally stable, even at much higher temperature (300 vs 200 °C). The emission spectra of the dissolved annealed film—the film was completely dissolvable—and of thermally untreated material were identical.

detectable melting and recrystallization peak, also when repeating the heating/cooling cycle with the same sample. It is not surprising that the bulky, conformationally rigid di-*tert*-butyltritycene units inhibit crystallization of the oligomers **8_n**.

Conclusions and Outlook

A synthesis for monodisperse oligoPPEs with alternating 1,4-phenylene and 1,4-tritycene units has been developed. The two terminal ethynyl groups are orthogonally protected, which allows for an independent derivatization of both terminal groups. Additionally, a way to synthesize the orthogonally protected 1,4-diethynyltritycene **6** was found. In combination with the diiodo compound **10** or 1,4-diiodotritycene³⁹ this 1,4-diethynyltritycene **6** opens the door for a stringent divergent–convergent synthesis of the oligomers **8_n** and “all triptycene” oligoPPEs, respectively, in analogy to the synthesis of oligoPPEs **11_n**.¹¹ The di-*tert*-butyltritycene moieties hamper crystallization from the melt and planarization of the conjugated backbone in solid films. They also impact the electronic interaction between individual oligomers.

Experimental Section

General Methods. THF was dried over sodium/benzophenone. Piperidine was distilled from CaH₂. Pyridine was purchased from Merck in SeccoSolv quality and used as received. γ -MnO₂,⁴⁰ 1,4-dihexyl-2,5-diiodobenzene (**10**),¹¹ and 1,4-dihexyl-2-(3-hydroxyprop-1-ynyl)-5-iodobenzene (**9**)¹¹ were prepared according to the literature.

If not mentioned otherwise, the reactions were carried out under an argon atmosphere using the Schlenk technique. The solvents or solutions were degassed through at least three freeze–pump–thaw cycles.

Thin-layer chromatography was performed with silica gel coated aluminum foils (Merck, 60 F₂₅₄). Spots were detected using a UV lamp ($\lambda = 254$ nm and/or 366 nm). Chromatography was carried out under slight pressure using silica gel (Merck, 40–63 μ m, or Acros, 35–70 μ m). If not mentioned otherwise, the crude product was adsorbed onto a small quantity of silica gel by dissolving it in CH₂Cl₂, adding silica gel to this solution, and removing the solvent (40 °C, reduced pressure). The resulting fine, freely flowing powder was added on top of a silica gel column through pouring it into the small amount of solvent which overlaid the silica gel.

Solvents were removed at 40 °C and reduced pressure using a rotary evaporator. Toward the end of solvent removal, most of the materials form a voluminous solid foam abruptly. In most cases, the material used for analytical purposes was freeze-dried from benzene to remove residual solvent which was tenaciously adhering to the compound.

Melting points were determined in open capillaries and are not corrected. The NMR spectra were recorded at 30 °C (250 MHz instrument) and at 27 °C (500 MHz instrument) using the solvent as an internal standard. Carbon multiplicity was determined by a DEPT-135 experiment, and as mentioned with the individual experiments, HMQC spectra were measured to support signal assignment. For signal assignment, atoms are labeled as shown in Figure 3. The atoms of compounds **1–6** are labeled analogously. If a differentiation is possible, the atoms

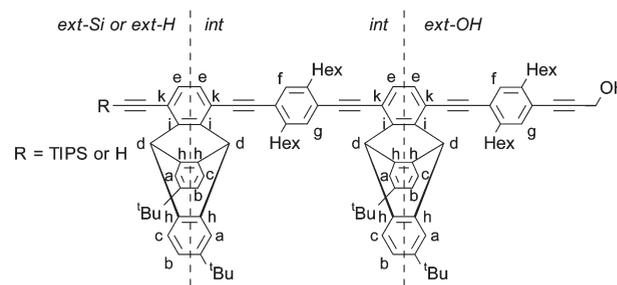


FIGURE 3. Labeling of atoms for the assignment of NMR signals. In this drawing, neither the possibility of isomers differing in their tacticity nor other configurational isomerism is taken into account. The NMR spectra give no hint that the proton or carbon resonances are sensitive to the tacticity.

are assigned to the region *int*, *ext-Si*, and *ext-OH*. For quoting the shifts of the protons H_c, which form an AB spinsystem, the middle position between the two signals of A and the middle position between the two signals of B is given despite the distinct roof effect.

MALDI TOF mass spectra were recorded with a Voyager DE Instrument mounted with a 1.2 m flight tube. Ionization was achieved using a LSI nitrogen laser (337 nm beam wavelength, 3 ns pulse width, 3 Hz repetition rate). Depending on the mass range, the ions were accelerated with 15 to 20 kV. If not mentioned differently, 2-[(2*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile⁴¹ was used as the matrix and THF as solvent to prepare the samples. EI mass spectra were recorded using an Autospec X magnetic sector mass spectrometer with EBE geometry equipped with a standard EI source (70 eV). Ions were accelerated by 8 kV. With both MS-techniques, MALDI TOF, and EI, cations were detected.

The UV/vis spectra and emission spectra were obtained from solutions in CHCl₃ (5–6 μ mol/L). For the recording of UV/vis spectra of drop cast films on quartz an integrating sphere (Ulbricht sphere) was used.

Synthesis of the Triptycene Building Blocks **5b** and **6**.

1,2-Adduct **2b.** The glassware was flame-dried before use. A solution of *n*-butyllithium in hexane (1.6 M, 22 mL, 35 mmol) was added to a solution of trimethylsilylethyne (4.5 mL, 31 mmol) in THF (60 mL) at –78 °C. After the reaction mixture was stirred at –78 °C for another 15 min, this solution of trimethylsilylethynyllithium was added dropwise over a period of 20 min to a solution of triptycenequinone **1** (10.4 g, 26.2 mmol) in THF (80 mL) at –78 °C. The color of the solution changed immediately from orange to turquoise. After the reaction mixture was stirred at –78 °C for 2 h, Et₂O and water were added to the cold reaction mixture, the phases were separated, the aqueous phase was extracted with Et₂O, and the combined organic phases were washed with a saturated aqueous solution of NH₄Cl and dried over MgSO₄. Removal of solvent gave a beige-orange solid, which was dissolved in a minimum amount of CH₂Cl₂. This solution was applied to a chromatography column. Chromatography (solvent gradient CH₂Cl₂ → CH₂Cl₂/Et₂O 20:1 → CH₂Cl₂/Et₂O 10:1) gave first a mixture of the starting quinone **1** and unidentified byproducts (2.17 g, *R_f*(*n*-pentane/Et₂O 5:2) = 0.58, 0.50), second the 1,2-adduct **2b** (8.55 g, 66%; *R_f*(*n*-pentane/Et₂O 5:2) = 0.27) as a yellow-beige solid, and finally a mixture (1.13 g, *R_f*(*n*-pentane/Et₂O 5:2) = 0.27, 0.19) of the 1,2-adduct **2b** and a product that had resulted from a 1,2-addition of BuLi to starting compound quinone **1**. The product **2b** consisted of two diastereomers D1

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and D2 in a ratio of approximately 2:1. Analytical data of 1,2-adduct **2b**: $^1\text{H NMR}$ (500 MHz, CD_2Cl_2) signals of diastereomer D1: $\delta = 7.48$ and 7.44 (2 d, $^4J = 1.7$ Hz, 1 H each, H_a), 7.332 (d, $^3J = 8$ Hz, 1 H of D1, H_c of D1 and D2), 7.31 (d, $^3J = 8$ Hz, 1 H, H_c), 7.06 (dd, $^3J = 7.7$ Hz, $^4J = 1.8$ Hz, 1 H, H_b), 7.03 (dd, $^3J = 7.7$ Hz, $^4J = 1.8$ Hz, 1 H of D1, H_b of D1 and D2), 6.68 (d, $^3J = 9.9$ Hz, 1 H, H_e), 6.01 (broadened d, $^3J = 9.9$ Hz, 1 H of D1, H_e of D1 and D2), 5.70 (s, 1 H of D1, H_d of D1 and D2), 5.54 (s, 1 H, H_d), 2.52 (s, 1 H of D1, OH of D1 and D2), 1.265 (1 s, 18 H, $\text{C}(\text{CH}_3)_3$), 0.18 (s, 9 H, $\text{Si}(\text{CH}_3)_3$); signals of diastereomer D2: $\delta = 7.46$ and 7.43 (2 d, $^4J = 1.7$ Hz, 1 H each, H_a), 7.332 (d, $^3J = 8$ Hz, 1 H of D2, H_c of D1 and D2), 7.326 (d, $^3J = 8$ Hz, 1 H, H_c), 7.08 (dd, $^3J = 7.7$ Hz, $^4J = 1.8$ Hz, 1 H, H_b), 7.03 (dd, $^3J = 7.7$ Hz, $^4J = 1.8$ Hz, 1 H of D2, H_b of D1 and D2), 6.69 (d, $^3J = 9.9$ Hz, 1 H, H_e), 6.01 (broadened d, $^3J = 9.9$ Hz, 1 H of D2, H_e of D1 and D2), 5.70 (s, 1 H of D2, H_d of D1 and D2), 5.53 (s, 1 H, H_d), 2.52 (s, 1 H of D1, OH of D1 and D2), 1.273 and 1.25 (2 s, 9 H each, $\text{C}(\text{CH}_3)_3$), 0.20 (s, 9 H, $\text{Si}(\text{CH}_3)_3$); HRMS (MALDI) $m/z = 494.26348$, calcd for $\text{C}_{33}\text{H}_{38}\text{O}_2\text{Si}$ (494.26356). Anal. Calcd for $\text{C}_{33}\text{H}_{38}\text{O}_2\text{Si}$ (494.751): C, 80.11; H, 7.74. Found: C, 79.90; H, 7.98.

Phenol 3b. To a solution of 1,2-adduct **2b** (8.55 g, 17.3 mmol) in THF (p.a., 120 mL) cooled with a NaCl/ice bath were added zinc powder (5.66 g, 86.5 mmol) and glacial acetic acid (120 mL). The resulting green-gray suspension was allowed to warm to room temperature. After 17.2 h of stirring the reaction mixture at room temperature, Et_2O and water were added and residual zinc was filtered off. The phases were separated, the aqueous phase was extracted with Et_2O , and the combined organic phases were washed several times with a saturated aqueous solution of NaHCO_3 and dried over MgSO_4 . Removal of the solvent yielded a slightly yellow solid. Column chromatography (*n*-pentane/ Et_2O 3:2) yielded phenol **3b** (7.0 g, 85%; $R_f = 0.33$) as a slightly beige solid. Ahead of this product, a fraction containing unidentified compounds (469 mg) was eluted: mp $138\text{--}140$ °C; $^1\text{H NMR}$ (250 MHz, CD_2Cl_2) $\delta = 7.46$ and 7.44 (2 d, $^4J = 2.0$ Hz, 1 H each, H_a), 7.33 (d with broadened signals, $^3J = 7.8$ Hz, 2 H, H_c), 7.051 and 7.048 (2 dd, $^3J = 7.8$ Hz, $^4J = 2.0$ Hz, 1 H each, H_b), 6.98 and 6.44 (2 d, $^3J = 8.4$ Hz, 1 H each, H_e), 5.82 and 5.74 (2 s, 1 H each, H_d), 5.19 (s, 1 H, OH), 1.274 and 1.268 (2 s, 9 H each, $\text{C}(\text{CH}_3)_3$), 0.37 (s, 9 H, $\text{Si}(\text{CH}_3)_3$); $^{13}\text{C NMR}$ (62.8 MHz, CD_2Cl_2) $\delta = 150.94$ and 150.88 (C_i ortho to $\text{C}\equiv\text{C}$, C_kOH), 149.1 and 149.0 ($\text{C}'\text{Bu}$), 145.4 (C_h para to $\text{t}'\text{Bu}$), 142.6 (C_h meta to $\text{t}'\text{Bu}$), 132.2 (C_i ortho to OH), 129.7 (C_e ortho to $\text{C}\equiv\text{C}$), 123.8 and 123.5 (C_c), 122.4 and 122.3 (C_b), 121.5 and 121.3 (C_a), 113.3 (C_e ortho to OH), 111.7 ($\text{C}_k\text{C}\equiv\text{CSiMe}_3$), 103.3 and 96.5 ($\text{C}\equiv\text{C}$), 52.6 and 47.2 (C_d), 34.90 and 34.85 (CMe_3), 31.63 and 31.62 ($\text{C}(\text{CH}_3)_3$), 0.3 ($\text{Si}(\text{CH}_3)_3$); MS (EI) $m/z = 478.22$ (100) [$\text{M}]^+$, 463.20 (65), 365.09 (16). Anal. Calcd for $\text{C}_{33}\text{H}_{38}\text{OSi}$ (478.750): C, 82.79; H, 8.00. Found: C, 82.62; H, 7.87.

Triflate 4b. The glassware was flame-dried before use. Triflic anhydride (3.2 mL, 18.9 mmol) was added dropwise over a period of 30 min to a solution of phenol **3b** (6.97 g, 14.5 mmol) in pyridine (50 mL), which was cooled with an ice bath. The color of the solution turned from yellow to orange. After the reaction mixture was stirred for 19.5 h at room temperature, Et_2O and 2 N HCl were added, the phases were separated, the aqueous phase was extracted with Et_2O , and the combined organic phases were washed with 2 N HCl and brine and dried over MgSO_4 . Upon solvent removal an orange solid was obtained. Column chromatography (*n*-pentane/ Et_2O 3:2; $R_f = 0.75$) gave triflate **4b** (8.08 g, 91%) as a slightly yellow solid: mp $107\text{--}109$ °C; $^1\text{H NMR}$ (250 MHz, CD_2Cl_2) $\delta = 7.49$ and 7.47 (2 d, $^4J = 1.9$ Hz, 1 H each, H_a), 7.36 (slightly broadened d, $^3J = 7.8$ Hz, 2 H, H_c), 7.17 (d, $^3J = 8.7$ Hz, 1 H, H_e), 7.11 and 7.07 (2 dd, $^3J = 7.8$ Hz, $^4J = 1.9$ Hz, 1 H each, H_b), 6.90 (d, $^3J = 8.7$ Hz, 1 H, H_e), 5.89 and 5.72 (2 s, 1 H each, H_d), 1.28 and 1.27 (2 s, 9 H each, $\text{C}(\text{CH}_3)_3$), 0.39 (s, 9 H, $\text{Si}(\text{CH}_3)_3$); $^{13}\text{C NMR}$ (125.6 MHz, CD_2Cl_2) $\delta = 152.0$ (C_iOTf or C_j), 149.59 and 149.55 ($\text{C}'\text{Bu}$), 144.5 (C_h para to $\text{t}'\text{Bu}$), 144.3

(C_i or C_kOTf), 143.8 (C_h para to $\text{t}'\text{Bu}$), 141.8 and 140.9 (C_h meta to $\text{t}'\text{Bu}$), 138.7 (C_i or C_kOTf), 130.1 (C_e ortho to $\text{C}\equiv\text{C}$), 124.2 and 123.9 (C_c), 122.9 and 122.8 (C_b), 122.1 and 121.7 (C_a), 119.21 ($\text{C}_k\text{C}\equiv\text{CSiMe}_3$), 119.16 (q, $^1J = 321.0$ Hz, CF_3), 118.3 (C_e ortho to OTf), 101.3 and 100.4 ($\text{C}\equiv\text{C}$), 52.4 and 48.5 (C_d), 34.95 and 34.92 (CMe_3), 31.6 ($\text{C}(\text{CH}_3)_3$), 0.1 (SiMe_3); MS (EI) $m/z = 610.16$ (100) [$\text{M}]^+$, 595.13 (74). Anal. Calcd for $\text{C}_{34}\text{H}_{37}\text{F}_3\text{O}_3\text{SSi}$ (610.813): C, 66.86; H, 6.11. Found: C, 66.89; H, 6.13.

Diethynyltriptycene 5a Starting from Triflate 4b. To a degassed yellowish solution of triflate **4b** (4.01 g, 6.56 mmol) and triisopropylsilyl ethyne (2.2 mL, 9.7 mmol) in (*i*-Pr) $_2\text{NH}$ (100 mL) were added $\text{Pd}(\text{PPh}_3)_4$ (0.38 g, 0.33 mmol), CuI (1.25 g, 6.56 mmol), and *n*-Bu $_4\text{NBr}$ (6.35 g, 19.7 mmol). The brown reaction mixture was stirred at 95 °C for 19 h, and then most of the solvent (about 90 mL) was distilled off (125 °C, 1 atm) and Et_2O , CH_2Cl_2 , and water were added to the residue. The phases were separated, the aqueous phase was extracted with a mixture of $\text{Et}_2\text{O}/\text{CH}_2\text{Cl}_2$, and the combined organic phases were washed with 2 N HCl and brine, and dried over MgSO_4 . Removal of the solvent gave a brown solid containing the starting material triflate **4b** and diethynyltriptycene **5a** in a ratio of 1.0:2.4 ($^1\text{H NMR}$ spectroscopically determined). Column chromatography (*n*-pentane/ CH_2Cl_2 10:1) gave diethynyltriptycene **5a** (2.39 g, 57%; $R_f = 0.39$) and triflate **4b** (1.14 g, 28%; $R_f = 0.25$), contaminated with a small amount of diethynyltriptycene **5a** as beige solids.

Comment: Gaseous diisopropylamine was found to dissolve the highly viscous silicon grease which was used to grease the glass joints. To keep the sealing with silicon grease intact, either a rather large flask or a flask with a long neck was used, minimizing the contact between gaseous diisopropylamine and silicon grease.

Analytical data: mp $116\text{--}117$ °C; $^1\text{H NMR}$ (250 MHz, CD_2Cl_2) $\delta = 7.48$ and 7.45 (2 d, $^4J = 1.8$ Hz, 1 H each, H_a), 7.37 and 7.33 (2 d, $^3J = 7.9$ Hz, 1 H each, H_c), 7.10 and 7.07 (2 m, 4 H, H_b , H_e), 5.97 and 5.87 (2 s, 1 H each, H_d), 1.30 (s, 30 H, $\text{C}(\text{CH}_3)_3$ and $\text{CH}(\text{CH}_3)_2$), 1.28 (s, 9 H, $\text{C}(\text{CH}_3)_3$), 0.41 (s, 9 H, $\text{Si}(\text{CH}_3)_3$); $^{13}\text{C NMR}$ (125.6 MHz, CD_2Cl_2) $\delta = 149.2$ ($\text{C}'\text{Bu}$), 148.6 and 148.3 (C_i), 145.0 and 144.9 (C_h para to $\text{t}'\text{Bu}$), 142.24 and 142.15 (C_h meta to $\text{t}'\text{Bu}$), 128.1 and 128.0 (C_e), 123.8 and 123.7 (C_c), 122.6 and 122.5 (C_b), 121.5 and 121.4 (C_a), 119.1 and 118.7 ($\text{C}_k\text{C}\equiv\text{C}$), 104.7 and 96.3 ($\text{C}\equiv\text{CTIPS}$), 102.7 and 100.0 ($\text{C}\equiv\text{CTMS}$), 52.4 and 52.3 (C_d), 34.9 (CMe_3), 31.61 and 31.58 ($\text{C}(\text{CH}_3)_3$), 19.0 ($\text{CH}(\text{CH}_3)_2$), 11.8 (CHMe_2); $^{13}\text{C NMR}$ signal assignment in agreement with HMQC; MS (EI) $m/z = 642.32$ (78) [$\text{M}]^+$, 600.27 (56), 599.27 (100); UV/vis λ (ϵ [10^6 cm 2 mol $^{-1}$]) = 273 (sh, 29.59), 281 (49.12), 297 (61.88), 322 (5.00) nm. Anal. Calcd for $\text{C}_{44}\text{H}_{58}\text{Si}_2$ (643.116): C, 82.18; H, 9.09. Found: C, 82.13; H, 8.96.

Diethynyltriptycene 5b. A suspension of diethynyltriptycene **5a** (4.77 g, 7.43 mmol) and K_2CO_3 (1.24 g 8.97 mmol) in THF (20 mL) and methanol (60 mL) was stirred at room temperature for 1.5 h. Et_2O and water were added, the phases were separated, the aqueous phase was extracted with Et_2O , and the combined organic phases were washed with brine and dried over MgSO_4 . Removal of the solvent gave a beige solid (4.25 g) containing diethynyltriptycene **5b** and TMSOH and/or TMS_2O . The material was used for the following reactions without further purification. For analytical purposes, the accompanying TMS containing products were removed from a sample through freeze-drying from benzene: $^1\text{H NMR}$ (250 MHz, CD_2Cl_2) $\delta = 7.49$ and 7.42 (2 d, $^4J = 2.0$ Hz, 1 H each, H_a), 7.36 and 7.30 (2 d, $^3J = 7.8$ Hz, 1 H each, H_c), 7.08 and 7.05 (2 m, 4 H, H_b , H_e), 5.95 and 5.88 (s, 1 H each, H_d), 3.51 (s, 1 H, $\text{C}\equiv\text{C}-\text{H}$), 1.274 and 1.271 and 1.25 (3 s, overall 39 H, $\text{CH}(\text{CH}_3)_2$, $\text{C}(\text{CH}_3)_3$); MS (EI) $m/z = 571.38$ (39), 570.38 (76) [$\text{M}]^+$, 528.32 (47), 527.32 (100); $\text{C}_{41}\text{H}_{50}\text{Si}$ (570.934).

Assembling of the Oligomers 8a_n and 8b_n.
General Procedure for the Removal of the TIPS Group. A

solution of *n*-Bu₄NF in THF (1 M, 2 equiv) was added to a solution of the TIPS-protected alkyne in THF. After the reaction mixture was stirred for 2.5–3.5 h at room temperature, Et₂O and water were added, the phases were separated, the aqueous phase was extracted with Et₂O, and the combined organic layers were washed with brine and dried over MgSO₄. Removal of solvent gave the deprotected alkynes containing TIPSOH and/or TIPSF and/or TIPS₂O, which give rise to ¹H NMR signals at 0.95–1.15 ppm in CDCl₃. Freeze-drying from benzene diminishes the amount of these products. The deprotected alkynes were used as obtained, i.e., without freeze-drying, for further reactions. The quantities of deprotected oligomers **8b_n** used in the coupling reactions were calculated as if the material consisted only of deprotected oligomers **8b_n**.

General Workup Procedure for the Alkynyl–Aryl Coupling Reactions. Et₂O and water were added, the phases were separated, and the aqueous phase was extracted with Et₂O. The combined organic layers were washed with 2 N HCl and brine and finally dried over MgSO₄. The solvent was removed.

Iodo Monomer 7. To a degassed yellow solution of 1,4-dihexyl-2,5-diiodobenzene (16.4 g, 32.9 mmol) and diethynyltritycene **5b** (2.76 g, max 4.84 mmol; the material contained TMS derivatives) in THF (150 mL) and piperidine (30 mL) were added Pd(PPh₃)₂Cl₂ (34 mg, 0.05 mmol) and CuI (18 mg, 0.09 mmol). After the reaction mixture was stirred for 22 h at room temperature, Et₂O and water were added, the phases were separated, the aqueous phase was extracted with Et₂O, and the combined organic layers were washed with 2 N HCl and brine and finally dried over MgSO₄. The solvent was removed. Column chromatography (*n*-pentane/Et₂O 100:1) of the yellowish residue provided 1,4-dihexyl-2,5-diiodobenzene (13.7 g, 84%; *R_f* = 0.68), iodo monomer **7** (2.57 g, 56%; *R_f* = 0.49) as a colorless solid, and a mixture (1.15 g, *R_f* = 0.24) of the di-substitution product and the Glaser coupling product (i.e., the oxidative dimerization product) of diethynyltritycene **5b** was obtained in a ratio of ca. 2:1 (¹H NMR spectroscopically determined). Analytical data of iodo monomer **7**: mp 78 °C (sintering), 100–103 °C (melting); ¹H NMR (250 MHz, CD₂Cl₂) δ = 7.81 (s, 1H, H_g), 7.50 (d, ⁴*J* = 1.8 Hz, 1H, H_{a,ext-I}), 7.48 (s, 1H, H_f), 7.46 (d, ⁴*J* = 1.8 Hz, 1H, H_{a,ext-Si}), 7.37 and 7.34 (2 d, ³*J* = 8.2 Hz, 1H each, H_c), 7.14 and 7.13 (AB spinsystem, ³*J* = 8.1 Hz, 2H, H_e), 7.09 and 7.08 (2 dd, ³*J* = 7.8 Hz, ⁴*J* = 1.9 Hz, 1H each, H_b), 5.99 and 5.94 (2 s, 1H each, H_d), 2.99 and 2.75 (2 t-like, 2H each, ArCH₂), 1.20–2.00 (m, 16H, CH₂), 1.30 (s, 21H, CH(CH₃)₂), 1.281 and 1.275 (2 s, 9H each, C(CH₃)₃), 0.84 and 0.86 (2 t-like, 3H each, CH₂CH₃); HRMS (MALDI) *m/z* = 940.48409; calcd for C₅₉H₇₇ISi (940.48337). Anal. Calcd for C₅₉H₇₇ISi (941.256): C, 75.29; H, 8.25. Found: C, 75.20; H, 8.34.

Protected Monomer 8a₁. To a degassed solution of 1,4-dihexyl-5-(3-hydroxyprop-1-ynyl)-2-iodobenzene (**9**) (990 mg, 2.32 mmol) and diethynyltritycene **5b** (1.42 g, 2.49 mmol) in THF (60 mL) and piperidine (20 mL) were added Pd(PPh₃)₂Cl₂ (16 mg, 0.02 mmol) and CuI (9 mg, 0.05 mmol). Fifteen minutes later, a precipitate had formed. The reaction mixture was stirred for 23 h at room temperature. Standard workup gave a beige solid which was dissolved in a minimum amount of *n*-pentane/CH₂Cl₂ (1:2). This solution was applied to a chromatography column. Chromatography (*n*-pentane/CH₂Cl₂ 1:2) gave protected monomer **8a₁** (1.78 g, 88%, *R_f* = 0.46) as a beige solid. Ahead of the product, Glaser coupling product, i.e., the oxidative dimer of diethynyltritycene **5b**, was eluted (*R_f* = 0.75). Analytical data of protected monomer **8a₁**: mp 121–124 °C; ¹H NMR (250 MHz, CD₂Cl₂) δ = 7.51 (slightly broadened s, 2H, H_f, H_{a,ext-OH}), 7.47 (d, ⁴*J* = 1.9 Hz, 1H, H_{a,ext-Si}), 7.40 (s, 1H, H_g), 7.39 and 7.35 (2 d, ³*J* = 7.8 Hz, 1H each, H_c), 7.17 and 7.13 (AB spinsystem, ³*J* = 8.1 Hz, 2H, H_e), 7.10 and 7.08 (2 dd, ³*J* = 7.8 Hz, ⁴*J* = 1.9 Hz, 1H each, H_b), 6.00 and 5.96 (2 s, 1H each,

H_d), 4.56 (d, ³*J* = 6.1 Hz, 2H, CH₂OH), 3.04 and 2.82 (2 t-like, 2H each, ArCH₂), 1.20–2.00 (m, 17H, CH₂, OH), 1.30 (s, 21H, CH(CH₃)₂), 1.29 and 1.28 (2 s, 9H each, C(CH₃)₃), 0.94 and 0.87 (2 t-like, 3H each, CH₂CH₃); HRMS (MALDI) *m/z* = 868.56966, calcd for C₆₂H₈₀OSi (868.59730); UV/vis λ (ε [10⁶ cm² mol⁻¹]) = 316 (45.93), 328 (58.73), 333 (sh, 49.96), 351 (54.98) nm; emission (λ_{excitation} = 305 nm) λ = 357, 375, 385 (sh), 406 (sh) nm. Anal. Calcd for C₆₂H₈₀OSi (869.407): C, 85.65; H, 9.28. Found: C, 85.61; H, 9.32.

Deprotected Monomer 8b₁. Starting from protected monomer **8a₁** (1.19 g, 1.37 mmol) in THF (40 mL), an orange solid (1.03 g) was obtained containing deprotected monomer **8b₁** and TIPS derivatives: ¹H NMR (250 MHz, CD₂Cl₂) δ = 7.51 (d, ⁴*J* = 1.9 Hz, 1H, H_{a,ext-OH}), 7.49 (d, ⁴*J* = 1.9 Hz, 1H, H_{a,ext-H}), 7.49 (s, 1H, H_f), 7.39 (s, 1H, H_g), 7.39 and 7.37 (2 d, ³*J* = 7.8 Hz, 1H each, H_c), 7.13 and 7.17 (AB spinsystem, ³*J* = 8.3 Hz, 2H, H_e), 7.08 and 7.07 (2 dd, ³*J* = 7.9 Hz, ⁴*J* = 1.9 Hz, 1H each, H_b), 5.95 and 5.91 (2 s, 1H each, H_d), 4.55 (s, 2H, CH₂OH), 3.54 (s, 1H, C≡CH), 3.01 and 2.80 (2 t-like, 2H each, ArCH₂), 1.20–2.00 (m, 17H, CH₂, OH), 1.28 and 1.27 (2 s, 9H each, C(CH₃)₃), 0.92 and 0.84 (2 t-like, 3H each, CH₂CH₃); MS (MALDI-TOF, 20 kV) *m/z* = 714.81 [M + 2H]⁺, 713.81 [M + H]⁺, 712.80 [M]⁺; C₅₃H₆₀O (713.069).

Protected Dimer 8a₂. Pd(PPh₃)₄ (132 mg, 0.114 mmol) and CuI (137 mg, 0.72 mmol) were added to a degassed yellow solution of iodo monomer **7** (1.08 g, 1.15 mmol) and deprotected monomer **8b₁** (950 mg, max 1.33 mmol; the material contained TIPS derivatives) in (*i*-Pr)₂NH (40 mL) and toluene (60 mL). Upon addition of the catalyst, the color of the solution turned to orange and a colorless solid formed. The suspension was heated to 60 °C for 16 h. Standard workup yielded an orange solid which was dissolved in a minimum amount of *n*-pentane/CH₂Cl₂ (1:2). This solution was applied to a chromatography column. Chromatography (*n*-pentane/CH₂Cl₂ 1:2) gave protected dimer **8a₂** (1.55 g, 89%; *R_f* = 0.55) as a yellow-orange solid which contained a small amount of triphenylphosphane oxide (identified through ¹H NMR spectroscopy). This solid was used in the following reactions without further purification. For analytical purposes, protected dimer **8a₂** (103 mg) was dissolved in CH₂Cl₂ (0.5 mL), and methanol (1.5 mL) was added. A yellow soft wax separated. The overlaying solution was removed, and the residue was dissolved in CH₂Cl₂ (0.5 mL). Upon addition of methanol (1.5 mL) again a second waxlike phase formed, which was transformed into a fine-grained solid by stirring the emulsion for 15 min. The suspension was filtered, and the solid was washed with methanol and dried under vacuum giving protected dimer **8a₂** free of triphenylphosphane oxide as a beige powder (91 mg, 79%; the calculation of the yield takes into account that only a part of the obtained material was treated as described): mp 170 °C (solid turns red), 172–174 °C (melting); ¹H NMR (250 MHz, CD₂Cl₂) δ = 7.649 and 7.646 (2 s, 1H each, H_{g,int}, H_{f,int}), 7.56, 7.55, and 7.54 (3 d, ⁴*J* = 1.9 Hz, 1H each, H_{a,int}, H_{a,ext-OH}), 7.54 (s, 1H, H_{f,ext}), 7.48 (d, ⁴*J* = 1.9 Hz, 1H, H_{a,ext-Si}), 7.44 and 7.43 (2 d, ³*J* = 7.8 Hz, 1H and 2H, respectively, H_{c,int}, H_{c,ext-OH}), 7.41 (s, 1H, H_{g,ext}), 7.37 (d, ³*J* = 7.8 Hz, 1H, H_{c,ext-Si}), 7.27 and 7.24 (AB spinsystem, ³*J* = 8.3 Hz, 2H, H_{e,ext-OH}, H_{e,int}), 7.21 and 7.16 (AB spinsystem, ³*J* = 8.1 Hz, 2H, H_{e,ext-Si}, H_{e,int}), 7.13, 7.12, 7.11, and 7.10 (4 dd, ³*J* = 7.8 Hz, ⁴*J* = 2.0 Hz, 1H each, H_b), 6.04, 6.02, and 6.01 (3 s, 1H, 1H, and 2H, respectively, H_d), 4.57 (d, ³*J* = 6.2 Hz, 2H, CH₂OH), 3.14, 3.06, and 2.83 (3 t-like, 4H, 2H, and 2H, respectively, ArCH₂), 1.05–2.05 (m, 32H, CH₂), 1.79 (t, ³*J* = 6.3 Hz, 1H, OH), 1.25–1.35 (m, 57H, CH(CH₃)₂, C(CH₃)₃), 0.84–0.99 (m, 12H, CH₂CH₃); MS (MALDI-TOF, 20 kV) *m/z* = 1526.59 [M + H]⁺, 1525.69 [M]⁺; UV/vis λ (ε [10⁶ cm² mol⁻¹]) = 358 (95.32) nm; emission (λ_{excitation} = 305 nm) λ = 402, 425, 437 (sh) nm. Anal. Calcd for C₁₁₂H₁₃₆OSi (1526.397): C, 88.13; H, 8.98. Found: C, 87.81; H, 9.05.

Deprotected Dimer 8b₂. Starting from protected dimer **8a₂** (800 mg, 0.524 mmol) in THF (20 mL), an orange solid (778 mg) was obtained containing deprotected dimer **8b₂** and TIPS derivatives: ¹H NMR (250 MHz, CD₂Cl₂): 7.632 and 7.630 (2 s, 1 H each, H_{g,int}, H_{f,int}), 7.55 (d, ⁴J = 1.8 Hz, 1 H, H_{a,ext-OH}), 7.52–7.54 (m, 4 H, H_{a,ext-H}, H_{a,int}, H_{f,ext}), 7.44–7.43, and 7.41 (3 d, ³J = 7.8 Hz, 1 H, 2 H, and 1 H, respectively, H_{c,int}, H_{c,ext-OH}), 7.40 (s, 1 H, H_{g,ext}), 7.25 and 7.21 (AB spinsystem, ³J = 8.1 Hz, 2 H, H_{e,ext-OH}, H_{e,int}), 7.21 and 7.16 (AB spinsystem, ³J = 8.1 Hz, 2 H, H_{e,ext-Si}, H_{e,int}) 7.08–7.14 (m, 4 H, H_b), 6.02, 6.00, and 5.94 (3 s, 1 H, 2 H, and 1 H, respectively, H_d), 4.56 (d, ³J = 5.9 Hz, 2 H, CH₂OH), 3.55 (s, 1 H, C≡C–H), 3.12, 3.04, and 2.82 (3 t-like, 4 H, 2 H, and 2 H, ArCH₂), 1.25–1.35 (m, 33 H, CH₂, OH), 1.25–1.32 (m, 36 H, C(CH₃)₃), 0.80–1.00 (m, 12 H, CH₂CH₃); MS (MALDI-TOF, 20 kV) *m/z* = 1369.69 [M + H]⁺, C₁₀₃H₁₁₆O (1370.053).

Protected Trimer 8a₃. Pd(PPh₃)₄ (53 mg, 0.05 mmol) and CuI (55 mg, 0.29 mmol) were added to a degassed, orange solution of iodo monomer **7** (430 mg, 0.457 mmol) and deprotected dimer **8b₂** (725 mg, max. 0.529 mmol; the material contained TIPS derivatives) in (*i*-Pr)₂NH (20 mL) and toluene (30 mL). After addition of the catalyst, a colorless solid formed. The suspension was heated to 60 °C for 16 h. Standard workup gave an orange solid, which was dissolved in a minimum amount of *n*-pentane/CH₂Cl₂ (1:1). This solution was applied to a chromatography column. Through chromatography (*n*-pentane/CH₂Cl₂ 1:1) protected trimer **8a₃** (705 mg, 71%; *R_f* = 0.47) was obtained as a yellow solid: mp 150 °C (sintering), 182–185 °C (melting); ¹H NMR (250 MHz, CH₂Cl₂) δ = 7.68 and 7.67 (2 broadened s, 4 H, H_{g,int}, H_{f,int}), 7.52–7.63 (m, 6 H, H_{a,int}, H_{a,ext-OH}, H_{f,ext}), 7.41–7.52 (m, 7 H, H_{a,ext-Si}, H_{c,int}, H_{c,ext-OH}, H_{g,ext}), 7.38 (d, ³J = 7.8 Hz, 1H, H_{c,ext-Si}), 7.29 (apparent s, probably AB spinsystem, 2 H, H_{e,int}), 7.27 and 7.25 (AB spinsystem, ³J = 8.2 Hz, 2 H, H_{e,ext-OH}, H_{e,int}), 7.23 and 7.16 (AB spinsystem, ³J = 8.1 Hz, 2H, H_{e,ext-Si}, H_{e,int}), 7.07–7.18 (m, 6 H, H_b), 6.09, 6.07, and 6.03 (3s, 2 H, 1 H, and 3 H, respectively, H_d), 4.58 (d, ³J = 6.2 Hz, 2 H, CH₂OH), 3.18 and 3.08 and 2.85 (3 t-like, 8 H, 2 H, and 2 H, respectively, ArCH₂), 1.20–2.20 (m, 49 H, CH₂), 1.80 (t, *J* = 6.2 Hz, 1 H, OH), 1.25–1.37 (m, 75 H, CH(CH₃)₂, C(CH₃)₃), 0.80–1.00 (m, 18 H, CH₂CH₃); MS (MALDI-TOF, 20 kV) *m/z* = 2182.65 [M + H]⁺; UV/vis λ (ε [10⁶ cm² mol⁻¹]) = 374 (147.34) nm; emission (λ_{excitation} = 305 nm) λ = 414, 438 nm. Anal. Calcd for C₁₆₂H₁₉₂OSi (2183.391): C, 89.12; H, 8.86. Found: C, 89.15; H, 8.83.

Deprotected Trimer 8b₃. Starting from protected trimer **8a₃** (300 mg, 0.137 mmol) in THF (10 mL), a yellow solid (312 mg) was obtained containing deprotected trimer **8b₃** and TIPS derivatives: ¹H NMR (250 MHz, CD₂Cl₂) δ = 7.70–7.60 (m, 4 H, H_{g,int}, H_{f,int}), 7.49–7.60 (m, overall 7 H, H_{a,ext-OH}, H_{a,int}, H_{a,ext-H}, H_{f,ext}), 7.35–7.49 (m, 7 H, H_c, H_{g,ext}), 7.27 (apparent s, probably AB spinsystem, 2 H, H_{e,int}), 7.25 and 7.22 (AB spinsystem, ³J = 8.0 Hz, 2 H, H_{e,ext-OH}), 7.21 and 7.17 (AB spinsystem,

³J = 8.0 Hz, 2 H, H_{c,int}), 7.05–7.18 (m, 6 H, H_b), 6.04, 6.03, 6.00, and 5.94 (4 s, 2 H, 1 H, 2 H, and 1 H, respectively, H_d), 4.56 (d, ³J = 6.1 Hz, 2 H, CH₂OH), 3.56 (s, 1 H, C≡C–H), 3.14, 3.05, and 2.82 (3 t-like, 8 H, 2 H, 2 H, respectively, ArCH₂), 1.20–2.10 (m, 49 H, CH₂, OH), 1.25–1.35 (m, 54 H, C(CH₃)₃), 0.80–1.00 (m, 18 H, CH₂CH₃); MS (MALDI-TOF, 20 kV) *m/z* = 2026.61 [M + H]⁺; C₁₅₃H₁₇₂O (2027.048).

Protected Tetramer 8a₄. Pd(PPh₃)₄ (13 mg, 0.01 mmol) and CuI (13 mg, 0.07 mmol) were added to a degassed yellow solution of iodo monomer **7** (103 mg, 0.109 mmol) and deprotected trimer **8b₃** (282 mg, max. 0.139 mmol; the material contained TIPS-derivatives) in (*i*-Pr)₂NH (5 mL) and toluene (9.5 mL). Upon addition of the catalyst, the color of the solution turned orange and a colorless solid formed. The suspension was heated to 60 °C for 14.5 h. Standard workup gave a yellow solid which was dissolved in a minimum amount of *n*-pentane/CH₂Cl₂ (1:1). This solution was applied to a chromatography column. Chromatography (*n*-pentane/CH₂Cl₂ 1:1) afforded protected tetramer **8a₄** (239 mg, 77%; *R_f* = 0.59) as a yellow solid: mp 160 °C (sintering), 267–270 °C (melting); ¹H NMR (250 MHz, CD₂Cl₂) δ = 7.70, 7.69, and 7.67 (3 s, the middle one is slightly broadened, overall 6 H, H_{g,int}, H_{f,int}), 7.54–7.64 (m, 8 H, H_{a,int}, H_{a,ext-OH}, H_{f,ext}), 7.42–7.54 (m, 10 H, H_{a,ext-Si}, H_{c,int}, H_{c,ext-OH}, H_{g,ext}), 7.39 (d, ³J = 7.8 Hz, 1H, H_{c,ext-Si}), 7.29 (apparent s, probably 2 AB spinsystems, 4 H, H_{e,int}), 7.26 (apparent s, probably AB spinsystem, 2 H, H_{e,ext-OH}, H_{e,int}), 7.08–7.23 (m, 10 H, H_b, H_{e,ext-Si}, H_{e,int}), 6.09 and 6.08 and 6.04 (4 s, 1 and 3 H, respectively, H_d), 4.58 (d, ³J = 6.1 Hz, 2 H, CH₂OH), 3.17 (m, 12H, ArCH₂), 3.08 and 2.85 (2 t-like, 2 H each, ArCH₂), 1.22–2.10 (m, 65 H, CH₂, OH), 1.22–1.38 (m, 93 H, CH(CH₃)₂, C(CH₃)₃), 0.80–1.05 (m, 24 H, CH₂CH₃); MS (MALDI-TOF, 20 kV) *m/z* = 2838.89 [M + H]⁺; UV/vis λ (ε [10⁶ cm² mol⁻¹]) = 379 (194.79) nm; emission (λ_{excitation} = 305 nm) λ = 418, 443 nm. Anal. Calcd for C₂₁₂H₂₄₈OSi (2840.386): C, 89.65; H, 8.80. Found: C, 89.40; H, 8.66.

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Supporting Information Available: Experimental procedures for the synthesis of 2,6-di-*tert*-butylanthracene, triptycenequinone **1**, diethynyltriptycene **5a** via route A, and diethynyltriptycene **6** including the analytical data. ¹³C NMR data of iodo monomer **7** and the oligomers **8a_n**. UV/vis and emission spectra of **5a** and **8a_n**. ¹H and ¹³C NMR spectra of all compounds of which the synthesis is described in this publication. This material is available free of charge via the Internet at <http://pubs.acs.org>.