Pt-Tetraethynylethene Molecular Scaffolding: Synthesis and Characterization of a Novel Class of Organometallic Molecular Rods

Peter Siemsen,[a] Ulrich Gubler,[b] Christian Bosshard,[b] Peter Günter,[b] and François Diederich*[a]

Dedicated to Professor Fred Wudl on the occasion of his 60th birthday

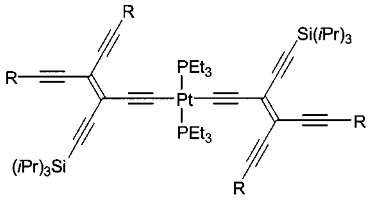
Abstract: The series of monodisperse Pt-bridged TEE oligomers **3a–f** was prepared by oxidative Glaser–Hay oligomerization of monomer **7** under end-capping conditions. These novel molecular rods extend in length from 3.3 nm (monomeric **3a**) to 12.1 nm (hexameric **3f**). Their isolation was achieved by high performance gel permeation chromatography (GPC), and their purification was best monitored by analytical GPC in combination with matrix-assisted laser-desorption-ionization mass spectrometry (MALDI-TOF MS). The mass spectra of each oligomer revealed the molecular ion or its sodium complex as parent ion together with a clean, highly characteristic fragmentation pattern. Delayed addition of the end-capping reagent PhC≡CH to the oligomerization mixture afforded polymer **10** with an average of ≈32 repeat units and a remarkably narrow molecular weight distribution ($M_w/M_n = 1.06$), which is indicative of a living polymerization process. UV/Vis spectral data as well as measurements of the second hyperpolarizability γ by third harmonic generation (THG) revealed a nearly complete lack of π-electron delocalization along the oligomeric backbone. The Pt atoms act as true insulating centers, and the Pt–C(sp) bonds hardly possess any π character. The synthesis of the molecular rods **3a–f** provides another demonstration of the power of oxidative acetylenic homocouplings for the preparation of unusual nanoarchitecture.

Keywords: gel-permeation chromatography · MALDI-TOF mass spectrometry · molecular wires · nonlinear optics · platinum

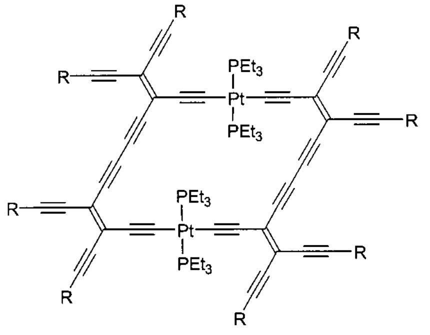
Introduction

Monodisperse, soluble oligomers are well established model compounds for linearly π-conjugated polymers, and their systematic study has enabled the elaboration of useful, predictive structure–property relationships.[1–4] Whereas most of these remarkable molecular architectures feature linear backbones made from carbon atoms, organic–inorganic hybrid oligomers and polymers with backbones consisting of metal σ-bis(acetylide) repeat units[5–7] have also attracted attention as compounds with promising nonlinear optical properties. In particular, platinum(II)-bridged polyynes[8, 9] have been widely studied for third-order nonlinear optical effects.[10, 11]

We have previously shown that tetraethynylethene (TEE, 3,4-diethynylhex-3-ene-1,5-diyne) derivatives[12, 13] act as efficient η^1-ligands and form mono- and dinuclear platinum(II) complexes such as **1a–c** and **2**.[14] X-ray crystal structure data of **1a** and **1b** revealed coplanarity of the TEE moieties, and indicated possible electronic delocalization across the metal center. This notion was further supported by the electronic



1a: R = Si(iPr)3
1b: R = Ph
1c: R = 3,5-di(tBu)phenyl



2: R = 3,5-di(tBu)phenyl

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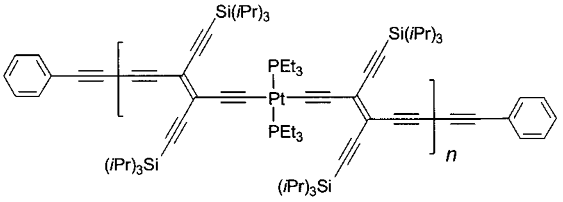
absorption spectra which were dominated by strong metal-to-ligand charge-transfer (MLCT) bands. These observations stimulated our interest in the preparation of a series of Pt-bridged tetraethynylethene oligomers to explore their opto-electronic properties and to determine the rod length at which saturation of these properties occurs. Similar investigations have been extensively conducted over the past years with series of poly(triacetylene) (PTA) oligomers containing π-conjugated all-carbon backbones made from TEE or (*E*)-1,2-diethynylethene (DEE, (*E*)-hex-3-ene-1,5-diyne) repeat units.[15]

Here, we describe the synthesis of a novel series of Pt-bridged TEE oligomers **3a–f** (Figure 1) with the hexameric **3f** with the unprecedented length—for monodisperse rods with metal-acetylenic backbones—of 12.1 nm,[16] and we also examine their optical and nonlinear optical properties.[17–19]



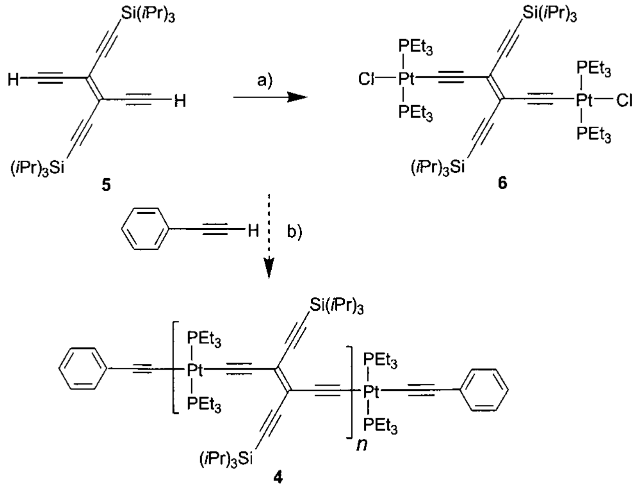
	n	length [nm]
3a	1	3.3
3b	2	5.1
3c	3	6.9
3d	4	8.7
3e	5	10.3
3f	6	12.1

Figure 1. Platinum(II)-bridged TEE oligomers. The lengths calculated by the AM1 semiempirical method[16] include the end-capping phenyl rings.

François Diederich, born in 1952 in the Grand Duchy of Luxembourg, received his Ph.D. degree in 1979 from the University of Heidelberg. Following postdoctoral studies at the University of California at Los Angeles (UCLA) from 1979–1981, he was a research associate at the Max-Planck-Institut für medizinische Forschung in Heidelberg. After his Habilitation in 1985, he joined the Faculty of the Department of Chemistry and Biochemistry at UCLA where he became full professor in 1989. Since April 1992, he is a professor of organic chemistry at ETH Zürich. His research interests encompass the development of covalent fullerene chemistry, the preparation of novel carbon allotropes and acetylenic carbon-rich advanced materials, the exploration of functional dendrimers as models for globular proteins, and molecular recognition studies with synthetic and biological receptors. In 2001, he joined the Editorial Advisory Board of Chemistry – A European Journal.

Results and Discussion

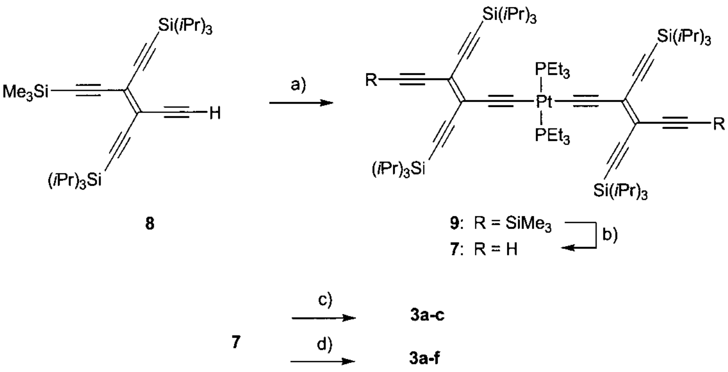
Synthesis: In an initial approach, we planned to prepare platinum(II)-bridged oligomers **4** (Scheme 1) by coupling *trans*-bis-deprotected TEE **5**[12] with the dinuclear complex **6** under end-capping conditions, using the variant of the Hagihara coupling[8] described by Ziessel and co-workers.[9] For that purpose, **5** was transformed with *trans*-[PtCl$_2$(PEt$_3$)$_2$] (3 equiv) in the presence of CuI (catalytic amount) and (*i*Pr)$_2$NH as base into the dinuclear complex **6** which was isolated in 25% yield. This yield could not be improved by variation of the catalyst, reaction temperature, or the nature of the base. All subsequent attempts to couple **5** with **6** in the presence of phenylacetylene, however, failed to give isolable oligomers. Similarly, modified stepwise approaches towards the construction of **4** remained unsuccessful.



Scheme 1. Attempted preparation of oligomers **4**. a) *trans*-[PtCl$_2$(PEt$_3$)$_2$] (3 equiv), CuI (2 mol%), (*i*Pr)$_2$NH, 20°C, 24 h, 25%; b) CuI, (*i*Pr)$_2$NH, 20°C, 20 h.

We subsequently turned to the preparation of the oligomeric series **3a–f** which we hoped to achieve by oxidative coupling[20] of the extended monomer **7** under end-capping conditions. For this purpose, monodeprotected TEE **8**[21] was transformed by Hagihara coupling into the platinum(II) σ-bis(acetylide) complex **9** (52%) which was converted in quantitative yield into **7** by selective removal of the Me$_3$Si protecting groups (Scheme 2). The *trans*-geometry of complex **9** was unambiguously revealed by a X-ray crystal structure, which, however, was too disordered to provide accurate bond-length and bond-angle information.[22]

The subsequent oxidative oligomerization under end-capping conditions was investigated under various conditions. It was rapidly becoming clear that the Glaser–Hay protocol[23] was superior to the Eglinton–Glaser procedure[24] to achieve the desired conversion. The conditions (concentration of reagent and catalyst, solvent, temperature, time of addition of the end-capping reagent) were systematically varied and optimized for both yield and ease of isolation of the individual oligomers. Finally, two sets of conditions were applied to obtain the six oligomers in the amount required for subsequent physical study (Scheme 2). For the preparation of the



Scheme 2. Preparation of the extended monomer **7** and oligomerization to give **3a**–**f**: a) *trans*-[PtCl$_2$(PEt$_3$)$_2$], CuI, (*i*Pr)$_2$NH, THF, 20 °C, 45 h, 52%; b) 1N NaOH, wet THF, MeOH, 20 °C, 3 h; quant; c) CuCl, *N,N,N′,N′*-tetramethylethylenediamine (TMEDA), PhC≡CH (added immediately), CH$_2$Cl$_2$, molecular sieves (4 Å), air, 20 °C, 90 min, 56% (**3a**), 9% (**3b**), 4% (**3c**); d) CuCl, TMEDA, PhC≡CH (added after 10 min), 1,2-dichlorobenzene, molecular sieves (4 Å), air, 80 °C, 1 h, 17% (**3a**), 12% (**3b**), 20% (**3c**), 13% (**3d**), 4% (**3e**), 1% (**3f**).

smaller rods **3a**–**c** (variant A) the oxidative coupling was performed at 20 °C in CH$_2$Cl$_2$, with two equivalents of end-capping reagent directly added at the beginning of the reaction. In contrast, the coupling for the entire series of oligomers **3a**–**f** (variant B) was best conducted in 1,2-dichlorobenzene at 80 °C with the end-capping reagent added only 10 min after the initiation of the reaction. The higher temperature as well as the 10 min delay in the addition of PhC≡CH were crucial for the formation of the higher oligomers in isolable yields. The increase in temperature accelerates the oligomerization, and in the initial absence of end-capping reagent, this favors the formation of longer rods. When the end-capping agent is added after a longer period of time (20 min), longer-chain polymers are mainly formed and isolated (see below).

For the optimization of the reaction conditions, the oligomerizations were conveniently monitored by analytical gel permeation chromatography (GPC, two G2500HHR columns from TosoHaas connected in series; eluent: THF). Figure 2 shows the chromatogram of the mixture of oligomers **3a**–**f** obtained by variant B as described above. Whereas the smaller rods all give resolved peaks, hexameric **3f** was only detected as a shoulder of the peak assigned to pentameric **3e**. Matrix-assisted laser-desorption-ionization mass spectrometry [MALDI-TOF-MS; matrix: 2′,4′,6′-trihydroxyacetophenone (THA)/ammonium citrate (AHC)] revealed that the shoulder fraction not only contained hexameric **3f** but also higher oligomers up to the undecamer.

The separation of the smaller rods **3a**–**c** obtained by oligomerization variant A was conveniently achieved by gravity GPC on polystyrene–divinylbenzene copolymer beads (Bio-Beads S-X1 and S-X3 from Bio-Rad, eluent: CH$_2$Cl$_2$ or PhMe). However, the isolation and purification of the larger oligomers **3d**–**f** from the product mixture obtained by variant B reached the performance limits of currently available analytical and preparative GPC. By analytical GPC (two G2500HHR columns from TosoHaas connected in series), the retention times of pentameric **3e** (11.60 min) and hexameric **3f** (11.59 min) were extremely close (Figure 2). The separation was finally achieved by a multi-step protocol which involved i) separation of the smaller rods **3a**–**c** by gravity GPC as described above and ii) high-performance GPC on two GROM-SDV-Gel 1000 columns connected in series, using up to 80 separation cycles (for the isolation of **3f**) and PhMe as the eluent.

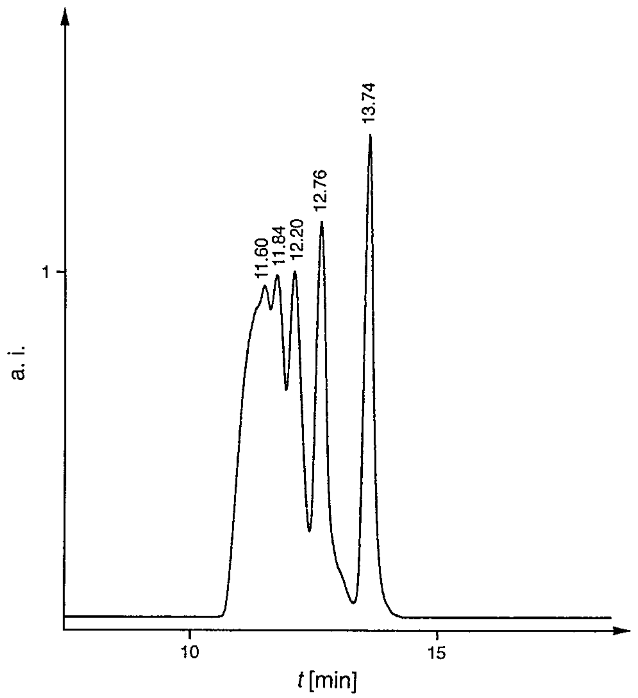
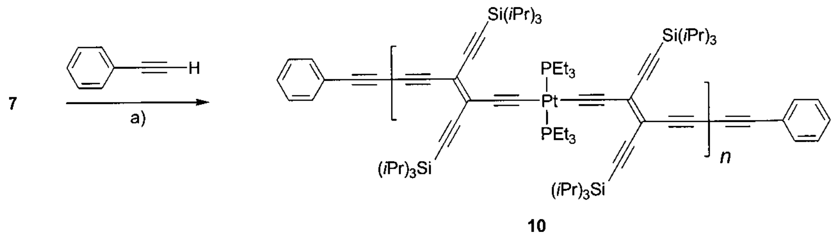


Figure 2. Analytical GPC traces of the oligomeric product mixture **3a**–**f** obtained by Glaser–Hay oligomerization of **7** in 1,2-dichlorobenzene at 80 °C with addition of PhC≡CH after 10 min and a total reaction time of 1 h. Two G2500HHR columns from TosoHaas connected in series, eluent: THF, $T = 40$ °C, UV/Vis detection at $\lambda = 430$ nm. Monomeric **3a** appears at the highest retention time (13.74 min), hexameric **3f** at the lowest retention time (11.59 min) buried under a shoulder to the peak at 11.60 min for pentameric **3e**, together with nonseparable higher oligomers up to the undecamer (MALDI-TOF MS).

Addition of the end-capping reagent after 20 min to the Hay oligomerization mixture in 1,2-dichlorobenzene at 80 °C, the longer-chain polymer **10** was obtained in 62% yield (Scheme 3). Lower molecular weight components were removed by GPC and red-colored **10** was isolated as an air-stable polydisperse compound which only decomposed above 250 °C and was readily soluble in CHCl$_3$, CH$_2$Cl$_2$, PhMe, and even hexane.

Characterization of oligomers 3a–f and polymer 10: The new organometallic rods were characterized by single symmetrical peaks in the analytical GP chromatograms and by IR, UV/Vis, and NMR (^{1}H, ^{13}C, ^{31}P) spectroscopy, as well as MALDI-TOF mass spectrometry. The latter technique was particularly useful to establish purity and monodispersity of the oligomers. Either the protonated molecular ion $[M+\mathrm{H}]^+$ (**3a**–**c**, in THA/AHC) or the $[M+\mathrm{Na}]^+$ ion (**3d**–**f**, in 3-(3-indolyl)acrylic acid (IAA), Figure 3) appeared as the parent ion in the spectra of all oligomers. Characteristic fragmentation patterns were observed as illustrated in Figure 4 for the smaller rods **3a**–**c**.



Scheme 3. Synthesis of polymer **10**: a) CuCl, TMEDA, molecular sieves (4 Å), 1,2-dichlorobenzene, air, end-capping reagent added after 20 min, 80 °C, 2 h, 62 %.

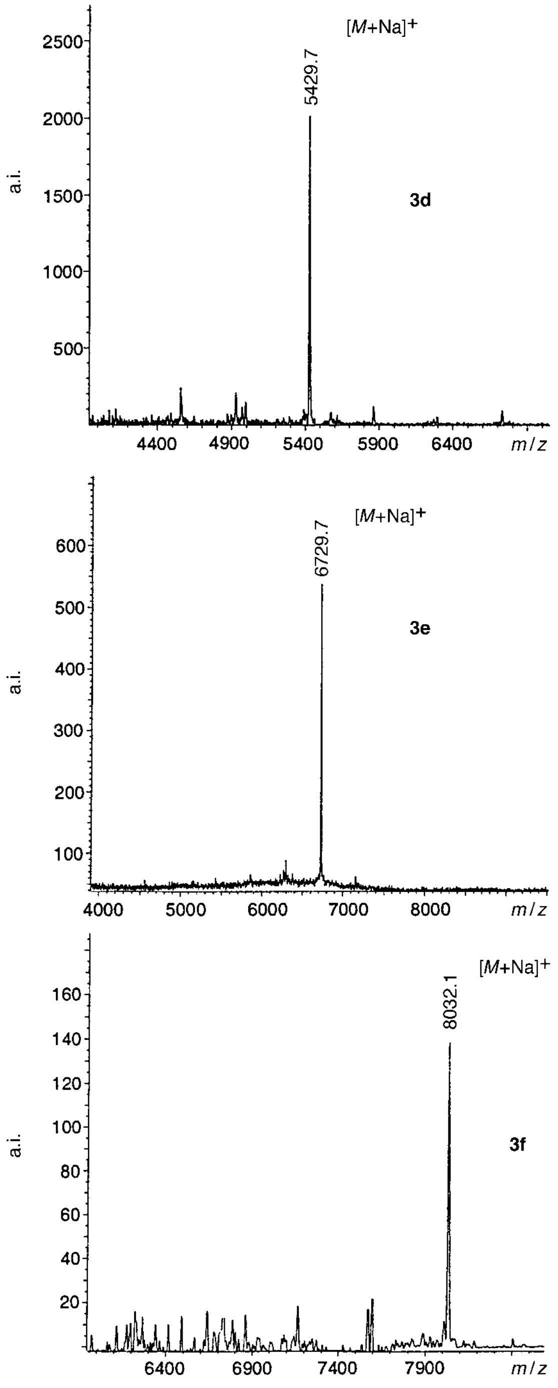


Figure 3. MALDI-TOF mass spectra (matrix: IAA) of oligomers **3d**–**f**.

In the spectrum of monomeric **3a**, the molecular ion 1504 $[M+H]^+$ (100 %) was accompanied by an intense fragment ion at m/z 967 (75 %), formed by loss of one end-capped TEE from the Pt center. In the spectrum of dimeric **3b** ($[M+H]^+ = 2806$, 100 %), the same intense fragment ion (m/z 966, 95 %) was accompanied by a second one (m/z 2269, 30 %) resulting also from cleavage at a Pt center. In the spectrum of **3c** ($[M+H]^+ = 4106$, 100 %), three fragment ions resulting from similar cleavage patterns were observed at m/z 967 (95 %), 2268 (18 %), and 3570 (13 %). Similar cleavage patterns were also observed in the spectra of the higher oligomers **3d**–**f**. The intensity of these fragmentation patterns can be modulated by the choice of matrix and desorption-ionization conditions.

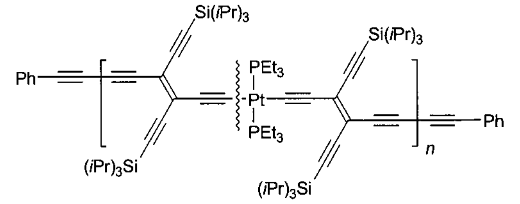


Figure 4. Fragmentation observed in the MALDI-TOF mass spectra (matrix: THA/AHC) of the shorter oligomer **3a**–**c**.

Similar to polymer **10**, oligomers **3a**–**f** were readily soluble in CH_2Cl_2, $CHCl_3$, PhMe, or hexane. They are highly stable both in solution and in the solid state, and storage over 12 months at room temperature under ambient atmosphere did not lead to any noticeable decomposition. Decomposition only starts a few degrees below their melting points which are quite high (e.g. 207 °C for **3a** and 234–238 °C for **3f**).

The amount of structural information gained from the ^1H NMR spectra ($CDCl_3$) was quite limited owing to signal overlap. A characteristic quintet-like multiplet around $\delta = 1.90-2.25$ was observed for the CH_2 protons of the phosphane ligands, and results from a complex coupling pattern with $\{^{195}Pt,^1H\}$, $\{^{31}P,^1H\}$ and $\{^1H,^1H\}$ couplings.[25, 26] In the ^{13}C NMR spectra ($CDCl_3$) of the shorter rods **3a**–**c**, all resonances of the vinylic carbon atoms between $\delta = 128$ and 133 were resolved, whereas the acetylenic resonances already overlapped at the stage of trimeric **3c**, which showed 18 out of the theoretically expected 26 resonances. The spectra of the higher oligomers revealed little information due to severe overlap of the resonances. The ^1H- and ^{13}C-broadband-decoupled ^{31}P NMR spectrum ($CDCl_3$) of monomeric **3a** displayed one resonance at $\delta = 12.44$ ($^1J(^{195}Pt,^{31}P) = 2340$ Hz).[27] Correspondingly, two resonances were observed in the spectra of **3b** [$\delta = 12.44$ ($^1J(^{195}Pt,^{31}P) = 2334$ Hz) and 12.93 ($^1J(^{195}Pt,^{31}P) = 2326$ Hz)] and **3c** [$\delta = 12.31$ ($^1J(^{195}Pt,^{31}P) = 2342$ Hz) and 12.94 ($^1J(^{195}Pt,^{31}P) = 2326$ Hz)]. For tetrameric **3d**, the two expected ^{31}P NMR resonances were still clearly discernable [$\delta = 12.54$ ($^1J(^{195}Pt,^{31}P) \approx 2322$ Hz) and 13.58 ($^1J(^{195}Pt,^{31}P) \approx 2324$ Hz)]. However, an increase in the broadening of the peaks—possibly owing to

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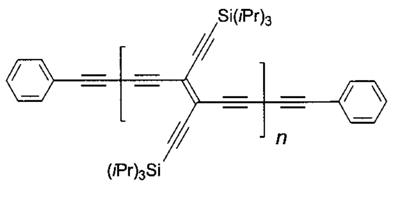
long-range couplings—occurred and prevented spectral interpretation for the next higher oligomer. Owing to the small quantities of isolated hexameric **3f** and the lack of information obtained from the various NMR spectra as a result of severe peak overlap, no NMR spectra were recorded for the longest representative of this series of molecular rods.

Polymer **10** was characterized by IR and ^{1}H NMR spectroscopies, which indicated the absence of residual free terminal alkyne moieties, in agreement with exhaustive end-capping. Analytical GPC on a PL-Gel column (a styrene–divinylbenzene copolymer; THF, 45 °C), with polystyrene standards and laser light-scattering detection, afforded a number-average molecular weight (M_n) of 40100 (number-average degree of polymerization $X_n = 31$) and a weight-average molecular weight (M_w) of 42400 (weight-average degree of polymerization $X_w = 33$).[28] Thus, polymer **10** is characterized by a very narrow molecular weight distribution (polydispersity) $M_w/M_n = 1.06$. Such narrow molecular weight distributions are characteristic for "living polymerizations",[29] and this result is in agreement with the current mechanistic understanding of Cu-catalyzed oxidative alkyne homocoupling reactions.[20]

Linear and nonlinear optical properties: The electronic absorption spectra of the Pt-TEE hybrid oligomers **3a–f** in CH_2Cl_2 are shown in Figure 5. They reveal a strong metal-to-ligand charge-transfer band,[14, 26, 30] with high molar extinction coefficients, and they dominate the longer-wavelength spectral region. Both the maximum of this band and the spectral end-adsorption shift only slightly to longer wavelengths up to the tetramer, after which saturation of the electronic properties occurs. Thus, λ_{MLCT} moves from 436 nm (in monomeric **3a**) to 442 nm (in pentameric **3e**) and remains exactly at this wavelength in hexameric **3f**.[31] In the series of TEE-based oligomers **11a–e**[15a,b] much larger bathochromic changes of the position of the longest wavelength absorption maxima (λ_{max}) and the end-absorption were observed with oligomeric length. Thus, this maximum appeared at 479 nm in **11a** and shifted to 514 nm in pentameric **11e**. These data are a strong indication that, despite efficient MLCT, electronic conjugation along the entire backbone in the Pt-bridged TEE oligomers **3a–f** is quite limited.



11a–e: $n = 1$-5

The similarity of the UV/Vis spectra of all oligomers **3d–f** strongly suggests that throughout the series similar conformations (*s-trans* orientation of neighboring TEE C=C double bonds with respect to the C≡C—Pt—C≡C fragments) and configurations (*trans*-geometry at the Pt centers and in the individual TEE moieties) are maintained.

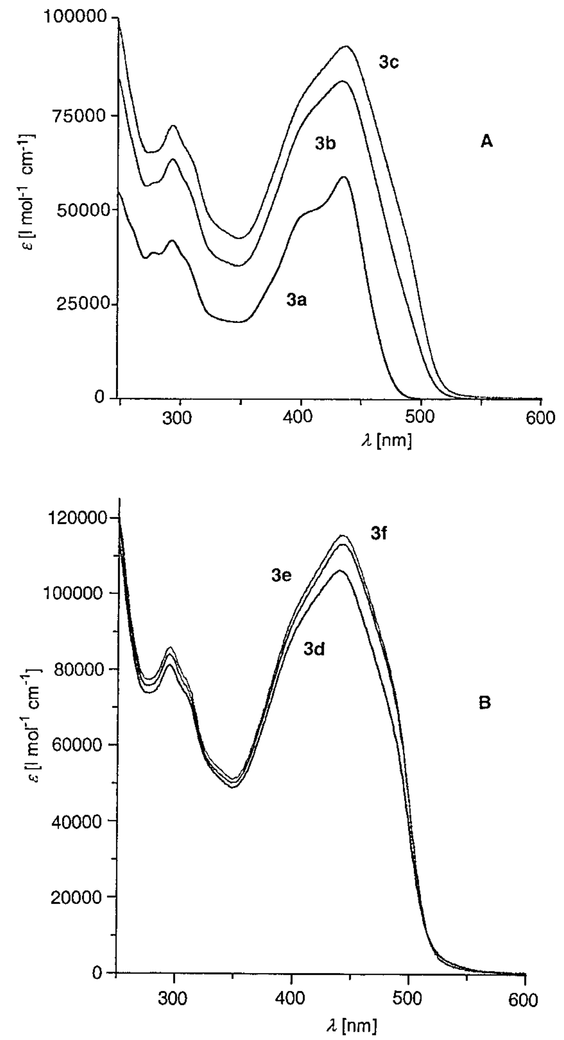


Figure 5. Electronic absorption spectra of A) the lower oligomer **3a–c** and B) the higher oligomers **3d–f** recorded at 20 °C in CH_2Cl_2.

In agreement with inefficient π-electron conjugation along the linear backbone, the UV/Vis spectrum of polymer **10** in CH_2Cl_2 closely resembles the monodisperse oligomers, with λ_{MLCT} appearing at 446 nm.

Measurements of the second hyperpolarizability γ in $CHCl_3$ by third-harmonic generation (THG)[32] further corroborated these results (Table 1). None of the compounds investigated showed an electronic absorption at the third-harmonic frequency 3ω (636 nm), and thus their γ values are not resonantly enhanced.

The second hyperpolarizability γ increases linearly with the number n of monomeric repeat units in the molecular rods. In contrast, most oligomers with a linear π-conjugated backbone show a power law increase of the second hyperpolarizability $\gamma a n^{a}$[15e,f, 33, 34] below the effective conjugation length where saturation occurs. THG measurements of the TEE-based oligomer series **11a–c**[34a] showed a superlinear growth of the second hyperpolarizability versus oligomeric length (Table 1), in contrast to the linear increase observed for the Pt-TEE oligomers **3a–c**. The Pt centers in **3a–c** and **10** clearly exert an insulating effect, and we conclude that Pt–C(sp) bonds in these compounds are pure σ-bonds similar to the bonds in alkyl platinum compounds.[35]

Table 1. Second hyperpolarizabilities γ (-3ω, ω,ω,ω) of oligomers **3a–c**, polymer **10** and, for comparison, oligomers **11a–c** in $CHCl_3$. The THG experiments were performed at the fundamental wavelength of $\lambda = 1907$ nm.[a]

Compound	n	$\varepsilon_{3\omega}$ [$M^{-1}cm^{-1}$]	γ [10^{-36} esu]	γ [10^{-48} m^5V^{-2}]	γ/n [10^{-36} esu]	γ/n [10^{-48} m^5V^{-2}]
3a	1	0	200	2.8	200	2.8
3b	2	0	450	6.3	220	3.1
3c	3	0	660	9.2	220	3.1
10	≈32	0	7400	103	230	3.2
11a	1	0	102	1.43	102	1.43
11b	2	0	430	6.0	215	3.0
11c	3	0	1070	15	357	5.0

[a] Reference $\chi^{(3)}_{fs} = 1.6 \times 10^{-22}$ m^2V^{-2} (1.1×10^{-14} esu) experimental error 10%; n = number of monomeric repeat units in the molecular rods.

Conclusion

The synthesis of the monodisperse Pt-bridged TEE oligomers **3a–f**, up to a length of 12.1 nm, provides another example of spectacular molecular architecture accessible by oxidative acetylenic coupling. An increase in oligomeric length beyond hexameric **3f** is actually not limited by the coupling method as shown by the successful preparation of polymer **10** containing an average of ≈32 repeat units and a remarkably narrow molecular weight distribution ($M_w/M_n = 1.06$). Rather, the separation of even longer monodisperse rods from the mixture obtained by end-capping oligomerization of **7** is currently limited by the performance of analytical and preparative GPC. It should be pointed out, however, that progress in the development of these important techniques is extensive and rapid. During the early stages of the doctoral thesis which includes the presented work,[36] oligomer separation was only possible up to the stage of trimeric **3c** but towards the end of the work, new highly efficient GPC columns became available which enabled oligomer separation up to the stage of hexameric **3f**. Besides GPC, MALDI-TOF-MS has been a key technique in this project. Because the signal overlap in the ^1H and ^{13}C NMR spectra increases with extended oligomeric length and the concomitant loss of structural information, the measurement of the molecular ion (or its sodium complex) as the parent ion together with the observation of a clean and highly characteristic fragmentation pattern have been invaluable for the characterization of the organometallic molecular rods **3a–f**. On the other hand, the optical and nonlinear optical properties of these compounds clearly show that these compounds lack any characteristics of molecular wires. The Pt atoms are true insulating centers since the Pt–C(sp) bonds hardly possess any π-character, thereby localizing π-electron conjugation to the dimeric TEE repeat units.

Experimental Section

Materials and general methods: Reagents and solvents were purchased reagent-grade from Aldrich or Fluka and used without further purification. Compounds **5**[12] and **8**[21] were prepared as described in the literature. THF and Et_2O were distilled from sodium/benzophenone. CH_2Cl_2, $CHCl_3$, and 1,2-dichlorobenzene were distilled over CaH_2. Anhydrous $MgSO_4$ was used as the drying agent after aqueous workup. Evaporation and concentration in vacuo were carried out at water aspirator pressure. Flash chromatography (FC): SiO_2-H (40–50 μm) or SiO_2-60 (40–63 μm) from Fluka. Thin-layer chromatography (TLC) was carried out on DURASIL G/UV$_{254}$ glass plates from Macherey–Nagel with visualization by UV light or dipping into a potassium permanganate solution and subsequent heating with a heat gun. Melting points (m.p.) were determined on a Büchi SB-540 apparatus and are uncorrected. UV/Vis spectra (ε [$l\,mol^{-1}cm^{-1}$]) were recorded on a Varian-Cary-5 spectrophotometer at 293 K. Infrared spectra [cm^{-1}] were obtained on a Perkin–Elmer 1600 FTIR spectrometer. NMR spectra (^1H, ^{13}C, ^{31}P, ^{195}Pt) were recorded on a Bruker AMX 500 and Varian Gemini 300 or 200 at 293 K, with solvent peak (^1H, ^{13}C) or Na_2PtCl_6 (^{195}Pt) as reference. ^{31}P NMR spectra were measured with ^1H- and ^{13}C-broadband decoupling, ^{13}C NMR spectra with ^1H-broadband decoupling. All NMR spectra were recorded in $CDCl_3$ unless noted otherwise. Chemical shifts (δ) are reported in parts per million (ppm). Signal multiplicities: s (singlet), d (doublet), t (triplet), q (quartet), quin (quintet), m (multiplet), m_s, m_d, m_{quint} (higher-order multiplets with singlet, doublet, or quintet-type structure). EI-MS spectra were acquired on a VG-Tribrid spectrometer measured at 70 eV. FAB-MS spectra were recorded on a VG-ZAB-2SEQ spectrometer utilizing *m*-nitrobenzyl alcohol (3-NOBA) as the matrix. MALDI-TOF-MS spectra were obtained using a Bruker Reflex instrument with 3-(indol-3-yl)acrylic acid (IAA) or 2′,4′,6′-trihydroxyacetophenone (THA)/ammonium hydrogen citrate (AHC) as matrices; linear positive-ion mode at +15 and 20 kV, respectively. Elemental analyses were carried out by the Mikrolabor in the Laboratorium für Organische Chemie at ETH Zürich.

Analytical GPC: Two TosoHaas TSKgel G2500HHR (5 μm) columns or one Shodex CG KF-802.5 and one Shodex GPC KF-803L column were connected in series. Instrumentation used was as follows (all Merck–Hitachi): HPLC pump L-7100; column oven L-7360; UV detector L-7400 and chromato-integrator D-2500.

Preparative GPC: Lower oligomers **3a–c** and polymer **10** were separated on a glass-column (5 × 180 cm) filled with Bio-Rad Bio-Beads S-X1 or S-X3 beads. The UV/Vis detector was from Knauer and all chromatograms were recorded at ambient temperature with a variable detection wavelength ranging from $\lambda = 300$–600 nm. The solvent used was PhMe or CH_2Cl_2 (technical grade, distilled prior to use) at 20 °C with a flow rate of approximately 10 drops min^{-1} operated with gravity. The styrene/divinylbenzene-copolymer gel was allowed to swell for 24 h prior to use in approximately the seven-fold volume of solvent. Separation of higher oligomers **3d–f** was obtained by high-performance GPC with two GROM-SDV-Gel 1000 columns from GROM Analytik und HPLC GmbH connected in series and PhMe as the eluent, using the Merck–Hitachi instrumentation described above. The columns were first equilibrated with THF (24 h, flow rate 0.5 mL min^{-1}) then with PhMe using a THF/PhMe concentration gradient by increasing the PhMe content by 2% per min, the flow rate was 0.5 mL min^{-1}. The oligomeric mixture ($c = 1$–2.5 mg mL^{-1}) was dissolved in PhMe (2–4 mL) and the solution filtered before injection. Fractions of 2 mL were taken (UV detection at 430 nm) and subjected to analytical GPC. The number of separation cycles required to reach monodispersity was 30 (**3d**), 45 (**3e**), and 80 (**3f**).

Analytical GPC for oligomeric mass determination: Analytical GPC for oligomeric mass determination was carried out on a Knauer GP chromatograph with a KMX-6-LAALS (Low Angle Laser Light Scattering) detector from Chromatix. Data sampling and evaluation were carried out with TriSEC GPC-Software Version 2.7. Column PL-Gel mixed-C5 from Polymer Laboratories (7.5 × 600 mm) was used with calibration by polystyrene standards from Polymer Laboratories. The eluent was THF and the flow rate was 1 mL min^{-1}.

Third-harmonic generation measurements: The laser source was a pulsed Nd/YAG laser ($\lambda = 1.064$ μm, 10 Hz repetition rate, pulse duration of 5 ns) which was used to pump a H_2 gas Raman cell and yielded a frequency shifted wavelength of $\lambda = 1.907$ μm. The *s*-polarized beam was focused onto the sample with a $f = 500$ mm lens. Third-harmonic generation measurements were performed by rotating the 1 mm thick fused silica cuvette with the solution parallel to the polarization to generate well known Maker-fringe interference patterns. The Maker-fringe patterns were analyzed in a manner similar to that described in the literature.[37] All measurements were calibrated against fused silica $\chi^{(3)}_{fs} = 1.6 \times 10^{-22}$ m^2V^{-2} (1.1×10^{-14} esu).[38] A comparison of measurements of fused silica in vacuum and air allowed all subsequent measurements to be performed in air. $CHCl_3$ solutions with initial concentrations of 0.5 to 1.5 weight percent were prepared and later diluted to four lower concentrations. From the concentration series, the molecular second hyperpolarizability of the solute molecules was elucidated.

Molecular modeling of the oligomeric rods: Molecular structures were constructed and energy-minimized using the force field Esff within the molecular modeling package Insight II.[39] X-ray crystallographic data[14] provided constraints for the orientation of the $Si(iPr)_3$ and PEt_3 groups. The force field calculations were stopped when energy changes between minimization steps were below 0.5 kcal mol^{-1}. The structures were subsequently refined using the AM1 method as implemented in the program SPARTAN Version 5.0,[16] providing the oligomeric lengths given in Figure 1.

***trans*-(μ-{(*E*)-3,4-Bis[(triisopropylsilyl)ethynyl]hex-3-ene-1,5-diyne-1,6-diyl})-dichlorotetrakis(triethylphosphane)diplatinum(II) (6)**: *trans*-$[PtCl_2(PEt_3)_2]$ (344 mg, 0.684 mmol), CuI (1 mg, 5 μmol), and $(iPr)_2NH$ (0.5 mL) were added to **5** (100 mg, 0.229 mmol) in dry THF (5 mL) in a Schlenk apparatus (50 mL), and the red-brown mixture was stirred for 24 h at 20 °C under Ar in the dark. Filtration over silica gel and evaporation in vacuo of the solvent gave a dark-brown, highly viscous oil which was purified by FC (silica gel, hexane/CH_2Cl_2 1:1) to provide **6** (80 mg, 25 %) as a dark-yellow solid. M.p. 197 °C; ^1H NMR (300 MHz): $\delta = 2.12 - 1.84$ (m, 24 H), 1.20–0.93 (m, 78 H); ^{31}P NMR (121.5 MHz): $\delta = 15.25$ ($^1J(^{195}Pt,^{31}P) = 2395$ Hz); IR ($CHCl_3$): $\tilde{\nu} = 2944$ (m), 2922 (w), 2867 (m), 2355 (s), 2333 (s), 2100 (m), 2078 (m), 672 (m), 661 (m); FAB-MS: *m*/*z* (%): 1373.5 (10), 1372.5 (22), 1371.5 (36), 1370.5 (60), 1369.5 (81), 1368.5 (100), 1367.5 (98), 1366.5 (84), 1365.5 (47), 1364.5 (19) $[M]^+$.

***trans*-Bis{(*Z*)-3,4-bis[(triisopropylsilyl)ethynyl]-6-(trimethylsilyl)hex-3-ene-1,5-diynyl}bis(triethylphosphane)platinum(II) (9)**: A solution of **8** (295 mg, 0.580 mmol), *trans*-$[PtCl_2(PEt_3)_2]$ (145 mg, 2.89 μmol), CuI (1.0 mg, 0.005 mmol), and $(iPr)_2NH$ in degassed dry THF (5 mL) was stirred in a Schlenk apparatus (20 mL) for 45 h at 20 °C in the dark. Workup in the dark involved filtration of the mixture over silica gel and evaporation in vacuo, and yielded a highly viscous dark-brown oil. FC (silica gel, hexane/CH_2Cl_2 2:1) and recrystallization (CH_2Cl_2/MeCN 2:1) afforded **9** (217 mg, 52 %) as lemon-yellow needles. M.p. > 250 °C (decomp); ^1H NMR (500 MHz): $\delta = 2.04 - 1.98$ (m, 12 H), 1.13–1.05 (m, 102 H), 0.16 (s, 18 H); ^{13}C NMR (125.8 MHz): $\delta = 128.40$, 121.95, 110.15, 110.11, 106.07, 105.92, 103.75, 101.02, 98.75, 97.25, 18.74, 16.48, 11.40, 8.30, −0.16; ^{31}P NMR (202.5 MHz): $\delta = 12.55$ ($^1J(^{195}Pt, ^{31}P) = 2346$ Hz); ^{195}Pt NMR (107.5 MHz): $\delta = -4705.6$ (t, $^1J(^{195}Pt,^{31}P) = 2345$ Hz); IR ($CHCl_3$): $\tilde{\nu} = 3018$ (m), 2963 (w), 2863 (w), 2364 (s), 2065 (m), 1600 (w); UV/Vis ($CHCl_3$): λ_{max} (ε) = 397 (41 700), 298 (sh, 19 700), 285 (20 300); FAB-MS: *m*/*z* (%): 1447 $[M]^+$; $C_{74}H_{132}Si_6P_2Pt \cdot 2CH_2Cl_2$ (1617.29): calcd (%) for: C 56.44, H 8.48; found: C 56.23, H 8.86.

***trans*-Bis{(*Z*)-4-ethynyl-6-(triisopropylsilyl)-3-[(triisopropylsilyl)ethynyl]-hex-3-ene-1,5-diynyl}bis(triethylphosphane)platinum(II) (7)**: NaOH (1 N, 5 mL) was added to **8** (210 mg, 0.145 mmol) in wet THF (10 mL) and MeOH (50 mL), and the mixture was stirred in the dark for 3 h at 20 °C. Workup in the dark involved filtration over silica gel and evaporation in vacuo to give **7** (189 mg, quant. yield) as a dark-yellow, unstable solid which was used without further purification. ^1H NMR (200 MHz): $\delta = 2.13 - 1.93$ (m, 12 H), 1.15–1.00 (m, 102 H); ^{31}P NMR (121.5 MHz): $\delta = 12.38$ ($^1J(^{195}Pt,^{31}P) = 2346$ Hz).

Glaser–Hay oligomerization of 7: Variant A: Compound **7** (189 mg, 0.145 mmol) and PhC≡CH (32 μL, 0.284 mmol) were dissolved in CH_2Cl_2 with molecular sieves (4 Å). A solution of Hay catalyst (prepared by stirring CuCl (16 mg, 162 μmol) and TMEDA (0.7 mL) in CH_2Cl_2 (5 mL) for 30 min at 20 °C under a stream of O_2) was added, and the mixture was stirred in the air for 11 h and turned brownish-yellow. Additional PhC≡CH (32 μL, 0.284 mmol) was added, and stirring was continued for 1 h until TLC (silica gel, CH_2Cl_2/hexane 2:1) and analytical GPC indicated completion of the reaction. CH_2Cl_2 (100 mL) was added, and the suspension was extracted with saturated aqueous NH_4Cl solution (2 ×) and saturated aqueous NaCl solution (1 ×). Filtration over silica gel and evaporation in vacuo yielded a highly viscous, orange-colored oil which, according to TLC (silica gel, CH_2Cl_2/hexane 2:1) contained four products with R_f values of 0.63 (**3c**), 0.70 (**3b**), 0.75 (**3a**), and 0.87 (1,4-diphenylbuta-1,3-diyne). Analytical GPC (eluent: THF) on two G2500HHR columns connected in sequence gave retention times of 13.95 min (**3a**), 12.76 min (**3b**), and 12.20 min (**3c**). GPC (eluent: PhMe) on Bio-Beads S-X1 afforded yellow **3a** (123 mg, 56 %) and orange-colored **3b** (19 mg, 9 %), while GPC (eluent: PhMe) on Bio-Beads S-X3 provided pure light-red **3c** (7 mg, 4 %).

Variant B: Compound **7** (261 mg, 0.200 mmol) was dissolved in 1,2-dichlorobenzene (8.12 mL) with molecular sieves (4 Å), and the mixture was heated to 80 °C. Hay-catalyst (prepared by stirring CuCl (22.0 mg, 0.223 mmol) and TMEDA (99 μL) in 1,2-dichlorobenzene (4.06 mL) for 30 min at 20 °C under a stream of O_2) was added and, after stirring for 10 min at 80 °C, PhC≡CH (176 μL, 1.56 mmol) was added. Stirring was continued for 50 min at 80 °C, then PhMe (100 mL) was added and the mixture was extracted with saturated aqueous NH_4Cl solution (2 × 50 mL) and saturated aqueous NaCl solution (50 mL). Filtration over silica gel and evaporation gave a red-brown precipitate (291 mg) which was purified first by GPC (PhMe) on Bio-Beads S-X1 to give **3a** (51 mg, 17 %) and **3b** (34 mg, 12 %), then on Bio-Beads S-X3 to give **3c** (55 mg, 20 %). Analytical GPC (two G2500HHR columns connected in series, eluent: THF) showed the higher oligomers at retention times of 11.84 min (**3d**), 11.60 min (**3e**), and 11.59 min (**3f**). High-performance GPC on two GROM-SDV-Gel 1000 columns (2 × 60 cm; eluent: PhMe) using multiple separation cycles gave pure **3d** (35 mg, 13 %), **3e** (10 mg, 4 %), and **3f** (1 mg, 1 %).

***trans*-Bis{(*Z*)-8-phenyl-3,4-bis[(triisopropylsilyl)ethynyl]oct-3-ene-1,5,7-triynyl}bis(triethylphosphane)platinum(II) (3a)**: M.p. > 207 °C (decomp > 195 °C); ^1H NMR (200 MHz): $\delta = 7.55 - 7.46$ (m, 4 H), 7.41–7.31 (m, 6 H), 2.23–1.91 (m_{quint}, 12 H), 1.25–1.05 (m, 102 H); ^{13}C NMR (50.3 MHz): $\delta = 132.41$, 132.31, 129.01, 128.60, 128.50, 122.47, 106.06, 104.09, 99.55, 98.22, 84.06, 81.34, 80.26, 75.08, 18.72, 16.42, 11.23, 8.20; ^{31}P NMR (121.5 MHz): $\delta = 12.44$ ($^1J(^{195}Pt,^{31}P) = 2340$ Hz); IR ($CHCl_3$): $\tilde{\nu} = 2944$ (m), 2867 (m), 2356 (w), 2077 (s), 1600 (m), 1467 (m), 678 (m); UV/Vis ($CHCl_3$): λ_{max} (ε) = 436 (58 800), 406 (sh, 49 400), 305 (sh, 36 900), 294 (41 900), 278 (38 700); MALDI-TOF-MS (THA/AHC): *m*/*z* (%): 1526 (30) $[M+Na]^+$, 1504 (100) $[M+H]^+$, 967 (75) $[M - C_{36}H_{47}Si_2]^+$; $C_{84}H_{124}Si_4P_2Pt$ (1503.27): calcd (%) for: C 67.12, H 8.31; found: C 67.08, H 8.45.

***trans,trans*-Bis{(*Z*)-8-phenyl-3,4-bis[(triisopropylsilyl)ethynyl]oct-3-ene-1,5,7-triynyl}[*μ*-((*Z*,*Z*)-dodeca-3,9-diene-1,5,7,11-tetrayne-1,12-diyl)]tetrakis(triethylphosphane)diplatinum(II) (3b)**: M.p. > 213 °C (decomp > 203 °C); ^1H NMR (500 MHz): $\delta = 7.49 - 7.44$ (m, 4 H), 7.36–7.29 (m, 6 H), 2.19–1.98 (m, 24 H), 1.16–1.05 (m, 204 H); ^{13}C NMR (125.8 MHz): $\delta = 132.31$, 132.23, 128.91, 128.52, 128.41, 125.20, 124.63, 122.43, 109.24, 106.09, 105.95, 104.08, 99.53, 99.49, 99.47, 98.75, 98.34, 98.13, 98.07, 84.06, 81.42, 81.16, 80.25, 75.11, 18.95–18.60 (m), 16.75–16.20 (m), 11.55–11.30 (m), 8.55–8.20 (2 m); ^{31}P NMR (121.5 MHz): $\delta = 12.93$ ($^1J(^{195}Pt,^{31}P) = 2326$ Hz), 12.44 ($^1J(^{195}Pt,^{31}P) = 2334$ Hz); IR ($CHCl_3$): $\tilde{\nu} = 2944$ (m), 2867 (m), 2067 (s), 1600 (s), 1467 (m); UV/Vis ($CHCl_3$): λ_{max} (ε) = 434 (84 100), 416 (sh, 78 800), 305 (sh, 57 200), 294 (63 400), 278 (sh, 57 100); MALDI-TOF-MS (THA/AHC): *m*/*z* (%): 2805 (100) $[M+H]^+$, 2269 (30) $[M - C_{36}H_{47}Si_2]^+$, 966 (95) $[M - C_{104}H_{161}Si_6P_2Pt]^+$; $C_{152}H_{238}Si_8P_4Pt_2 \cdot 3C_6H_5CH_3$ (3080.77): calcd (%) for: C 67.45, H 8.57; found: C 67.57, H 8.75.

***trans,trans,trans*-Bis[*μ*-((*Z*,*Z*)-dodeca-3,9-diene-1,5,7,11-tetrayne-1,12-diyl]bis{(*Z*)-8-phenyl-3,4-bis[(triisopropylsilyl)ethynyl]oct-3-ene-1,5,7-triynyl}hexakis(triethylphosphane)triplatinum(II) (3c)**: M.p. 217–219 °C (decomp > 210 °C); ^1H NMR (500 MHz): $\delta = 7.49 - 7.44$ (m, 4 H), 7.36–7.29 (m, 6 H), 2.18–1.91 (m, 36 H), 1.18–1.03 (m, 306 H); ^{13}C NMR (125.8 MHz): $\delta = 132.50$, 132.31, 132.23, 128.92, 128.52, 128.41, 127.95, 125.13, 124.63, 122.41, 111.54, 111.04, 109.55, 109.24, 106.09, 104.08, 99.49, 98.73, 98.34, 98.29, 98.13, 84.05, 83.82, 81.45, 81.35, 80.22, 75.10, 18.91–18.68 (m), 16.50–16.36 (m), 11.51–11.33 (m), 8.43–8.27 (2 m); ^{31}P NMR (121.5 MHz): $\delta = 12.94$ ($^1J(^{195}Pt,^{31}P) = 2326$ Hz), 12.31 ($^1J(^{195}Pt,^{31}P) = 2342$ Hz); IR ($CHCl_3$): $\tilde{\nu} = 3022$ (m), 2867 (w), 2067 (s), 1600 (s), 1467 (w); UV/Vis ($CHCl_3$): λ_{max} (ε) = 485 (sh, 54 000), 437 (93 300), 416 (sh, 86 500), 305 (sh, 66 200), 295 (72 300); MALDI-TOF-MS (THA/AHC): *m*/*z* (%): 4106 (100) $[M+H]^+$, 3570 (13) $[M - C_{36}H_{47}Si_2]^+$, 2268 (18) $[M - C_{104}H_{161}Si_6P_2Pt]^+$, 967 (95) $[M - C_{172}H_{275}Si_{10}P_4Pt_2]^+$.

(Inclusion of large non-stoichiometric solvent amounts prevented accurate elemental analyses of **3c–f**).

***trans,trans,trans,trans*-Bis{(*Z*)-8-phenyl-3,4-bis[(triisopropylsilyl)ethynyl]-oct-3-ene-1,5,7-triynyl}octakis(triethylphosphane)tris[*μ*-((*Z*,*Z*)-dodeca-3,9-diene-1,5,7,11-tetrayne-1,12-diyl]tetraplatinum(II) (3d)**: M.p. 222–225 °C (decomp > 218 °C); ^1H NMR (500 MHz): $\delta = 7.49 - 7.42$ (m, 4 H), 7.38–7.27 (m, 6 H), 2.20–1.95 (m, 48 H), 1.17–1.05 (m, 408 H); ^{13}C NMR (125.8 MHz):

$\delta = 132.32$ (several quaternary C-atoms are lacking due to weakness of resonances at small material quantities), 132.23, 128.47, 128.41, 110.42, 105.51, 103.99, 99.53, 84.08, 81.17, 18.85 – 18.64 (m), 16.75 – 16.07 (m), 11.74 – 11.33 (m), 8.53 – 7.99 (m); ^{31}P NMR (162.0 MHz): $\delta = 13.58$ ($^1J(^{195}\text{Pt},^{31}\text{P}) > 2324$ Hz), 12.54 ($^1J(^{195}\text{Pt},^{31}\text{P}) \approx 2322$ Hz); IR (CHCl$_3$): $\tilde{\nu} =$ 3033 (m), 2944 (w), 2867 (w), 2355 (s), 2339 (m), 2067 (m), 1600 (s), 1467 (w), 683 (m); UV/Vis (CHCl$_3$): $\lambda_{\max}$ (ε) = 486 (sh, 65200), 439 (106500), 423 (sh, 101200), 305 (sh, 75100), 294 (81300); MALDI-TOF-MS (IAA): m/z (%): 5430 (100) $[M+\text{Na}]^+$, 5407 (81) $[M+\text{H}]^+$, 4873 (10) $[M - \text{C}_{36}\text{H}_{47}\text{Si}_2]^+$, 3572 (38) $[M - \text{C}_{104}\text{H}_{161}\text{Si}_6\text{P}_2\text{Pt}]^+$, 2270 (95) $[M - \text{C}_{172}\text{H}_{275}\text{Si}_{10}\text{P}_4\text{Pt}_2]^+$.

***trans,trans,trans,trans,trans*-Bis{(*Z*)-8-phenyl-3,4-bis[(triisopropylsilyl)ethynyl]oct-3-ene-1,5,7-triynyl}decakis(triethylphosphane)tetrakis[*μ*-(*Z,Z*)-dodeca-3,9-diene-1,5,7,11-tetrayne-1,12-diyl]pentaplatinum(II) (3e)**: M.p. 228 – 231 °C (decomp > 224 °C); ^{1}H NMR (500 MHz): $\delta = 7.49 - 7.42$ (m, 4H), 7.37 – 7.29 (m, 6H), 2.19 – 1.98 (m, 60H), 1.17 – 1.05 (m, 510H); IR (CHCl$_3$): $\tilde{\nu} =$ 3010 (w), 2867 (w), 2148 (w), 2067 (s), 1602 (s), 1467 (w), 996 (w), 917 (w), 850 (w), 699 (m), 682 (m); UV/Vis (CHCl$_3$): $\lambda_{\max}$ (ε) = 486 (sh, 74300), 442 (113600), 423 (105900), 305 (sh, 77300), 294 (81400); MALDI-TOF-MS (IAA): m/z (%): 6730 (100) $[M+\text{Na}]^+$, 6708 (86) $[M+\text{H}]^+$, 6171 (13) $[M - \text{C}_{36}\text{H}_{47}\text{Si}_2]^+$, 4872 (23) $[M - \text{C}_{104}\text{H}_{161}\text{Si}_6\text{P}_2\text{Pt}]^+$, 3573 (33) $[M - \text{C}_{172}\text{H}_{275}\text{Si}_{10}\text{P}_4\text{Pt}_2]^+$, 2271 (85) $[M - \text{C}_{240}\text{H}_{389}\text{Si}_{14}\text{P}_6\text{Pt}_3]^+$.

***trans,trans,trans,trans,trans,trans*-Bis{(*Z*)-8-phenyl-3,4-bis[(triisopropylsilyl)ethynyl]-oct-3-ene-1,5,7-triynyl}dodecakis(triethylphosphane)pentakis[*μ*-(*Z,Z*)-dodeca-3,9-diene-1,5,7,11-tetrayne-1,12-diyl]hexaplatinum(II) (3f)**: M.p. 234 – 238 °C (decomp > 230 °C); IR (CHCl$_3$): $\tilde{\nu} = 3022$ (w), 2944 (w), 2867 (w), 2355 (m), 2322 (w), 2067 (m), 1600 (s), 1467 (w), 1006 (w), 917 (w), 706 (m), 689 (m); UV/Vis (CHCl$_3$): $\lambda_{\max}$ (ε) = 486 (sh, 75800), 442 (116000), 423 (sh, 108300), 305 (sh, 79100), 294 (86000); MALDI-TOF-MS (IAA): m/z (%): 8032 (100) $[M+\text{Na}]^+$, 808 (89) $[M+\text{H}]^+$.

***α,ω*-Bis[phenylethynyl]poly[trans-bis{(*Z*)-4-ethynyl-6-(triisopropylsilyl)-3-[(triisopropylsilyl)ethynyl]hex-3-ene-1,5-diynyl}bis(triethylphosphane)-platinum(II)] (10)**: A mixture of **7** (100 mg, 77 μmol) and molecular sieves (4 Å) in 1,2-dichlorobenzene was heated to 80 °C. Under a stream of O$_2$, a solution of Hay catalyst (prepared by stirring CuCl (8.4 mg, 85 μmol) and TMEDA (99 μL) in 1,2-dichlorobenzene (2 mL) under a stream of O$_2$ for 30 min at 20 °C) was added. After stirring for 20 min at 80 °C, PhC≡CH (176 μL, 1.56 mmol) was added and the mixture stirred for 2 h at that temperature. PhMe (50 mL) was added, and the mixture was extracted with saturated aqueous NH$_4$Cl solution (2 × 25 mL) and saturated aqueous NaCl solution (50 mL). Filtration over silica gel and evaporation gave a red-brown precipitate which was purified by GPC (Bio-Beads S-X1, PhMe) on Bio-Beads S-X1 to give **10** (62 mg, ≈62 %) as a solid with traces of 1,4-diphenylbuta-1,3-diyne which could not be removed even after three GPC separations. ^{1}H NMR (500 MHz): $\delta = 7.49 - 7.46$ (m), 7.44 – 7.27 (m), 2.14 – 1.91 (br m), 1.35 – 0.83 (br s); IR (CHCl$_3$): $\tilde{\nu} = 3011$ (w), 2944 (m), 2867 (m), 2356 (w), 2322 (w), 2067 (s), 1600 (s), 1489 (m), 1461 (m), 1183 (m), 1017 (w), 917 (w), 883 (w), 700 (s), 689 (s); UV/Vis (CHCl$_3$): $\lambda_{\max}$ (ε) = 489 (sh, 90100), 446 (127300), 423 (105900), 305 (sh, 77300), 294 (81400). (ε calculated for polymer with 32 monomeric repeat units).

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