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Synthesis and electronic properties of series of oligothiophene-[1,10]phenanthrolines

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Organic semiconductors containing metal binding sites within their molecular backbones are of a general interest in organic materials chemistry. In this paper, we describe a straightforward synthetic procedure, which gives access to a series of 2-(oligothienyl)-[1,10]phenanthrolines (nT-phen), 2,9-bis(oligothienyl)-[1,10]phenanthrolines (nT-phen-nT) and 2,2′-(oligothienyl)bis-[1,10]phenanthrolines (phen-nT-phen). By a Negishi-type cross coupling of 2-iodo-[1,10]phenanthroline or 2,9-diiodo-[1,10]phenanthroline with *in situ* generated α-zinc derivatives of different mono-, ter-, and quinquethiophenes we were able to synthesize the corresponding oligothienyl-phenanthrolines in medium to excellent yields. Furthermore, characterization of the optical properties of the new materials indicated that the two subunits, oligothiophene and phenanthroline, are in π-conjugation. Characterization of the redox properties revealed additional evidence for the role of [1,10]phenanthroline as a π-bridging unit in the nT-phen-nT series.

Introduction

π-Conjugated oligomers have developed into an important class of organic compounds which in contrast to corresponding polymers are monodisperse and structurally well-defined.[1] In particular, oligothiophenes have been synthesized and investigated to a great extent as they not only represent model compounds establishing valuable structure–property relationships, but also promising materials in their own right.[2] Implementation of oligothiophenes as active components in organic electronic devices such as light emitting diodes,[3] field-effect transistors[4] and more recently solar cells[5] showed that they even might surpass the characteristics of the corresponding polymers and approach those of amorphous silicon-based devices.[6]

New material properties can be achieved when the conjugated backbone is decorated with functional groups.[7] In this respect, it is of great interest to implement coordinative binding sites with the ability to coordinate metals.[8] The incorporation of ligands such as 2,2′-bipyridine (*bpy*), [2,2′:6′,2″]terpyridine (*tpy*) and [1,10]phenanthroline (*phen*) and corresponding metal complexes in a π-conjugated structure allows the fine tuning of important physical properties, *e.g.* redox behaviour or photophysical properties.[9] Further general applications of ligand-functionalized π-conjugated structures are found in metal-templated synthesis of novel supramolecular architectures.[10]

Different copolymers consisting of alternating oligothiophenes and *bpy* units along with their Ru^{II} and Os^{II} complexes had been synthesized and photophysically characterized.[11] Binuclear $Ru^{II}(bpy)_3$-complexes had been studied, where oligothiophene bridging units of different length had been employed.[12] Metal cross-linked oligothiophene–$Ru(bpy)_3^{n+}$ hybrid materials had been reported and were characterized with respect to their metal-centred and thiophene-centered electroactivity and overall conductivity.[13] A very interesting topological approach towards a polyrotaxane ion sensor had been achieved by the use of polythiophene–$Ru(bpy)_3^{n+}$ structures.[14] In the field of thiophene-substituted *tpy* materials, Ziessel and coworkers contributed a class of ditopic *tpy* ligands, bridged with ethynylthiophene moieties.[15] Their use as ligands in multinuclear metal complexes were found to contribute to a significant extent to triplet lifetimes. Electrochemical polymerization and characterization of a bithiophene-substituted $Os^{II}(tpy)_2$ complex have been reported by another team.[16]

Only a few cases of π-conjugated polymers with chelating *phen* subunits are known, despite the more rigid structure and therefore enhanced stability of *phen* chelate complexes. The synthesis and complexation behaviour of a polyphenanthroline and a more soluble dialkoxy derivative had been reported[17] as well as a copolymer consisting of *phen* and dialkoxyphenyl groups, whose emission properties could be fine-tuned by complexation of different metals.[18] At least two examples of π-conjugated polymers are known, in which an interlocking of the polymer strands was induced by a polymerization of preformed pseudotetrahedral $M(phen)_2^{n+}$ complex monomers. *phen*-Bridged pyrroles[19] or *phen*-bridged oligothiophenes[20] had been used as starting materials for these compounds. Beyond this, a polyrotaxane structure based on 3,8-bis(oligothienyl)phenanthroline moieties has been reported.[21]

Despite these most interesting contributions involving *phen*-substituted π-conjugated substrates, the synthesis and characterization of larger series combining *phen* and thiophene units and the subsequent determination of structure–property relationships still remained as a challenge. The first examples of 2,9-bis(oligothienyl)-[1,10]phenanthrolines[20] and 3,8-bis(terthienyl)-[1,10]phenanthrolines[22] have been published only recently. Herein, we now report the efficient synthesis of various series of oligothiophene-phenanthrolines (nT-phen, nT-phen-nT and phen-nT-phen) in which the length of the oligothiophene has been varied systematically (Scheme 1) as well as the ratio of the two subunits. The characterization of their electronic properties results in valuable structure-property relationships which give a basis for the synthesis of more sophisticated oligothiophene-based topologies such as interlocked conjugated macrocycles comprising *phen*-units as complexing moieties.[23]

Result and discussion

Synthesis

Two general ways are known towards the synthesis of 2,9-diarylated [1,10]phenanthrolines. The first method focuses on the ability of [1,10]phenanthroline to undergo a nucleophilic addition of aryl-lithium compounds selectively at the 2- and 9-position. Subsequent oxidative rearomatization results in the desired 2-aryl- or 2,9-diaryl-[1,10]phenanthrolines, depending on the kind of the employed aryl-lithium compound.[24] The

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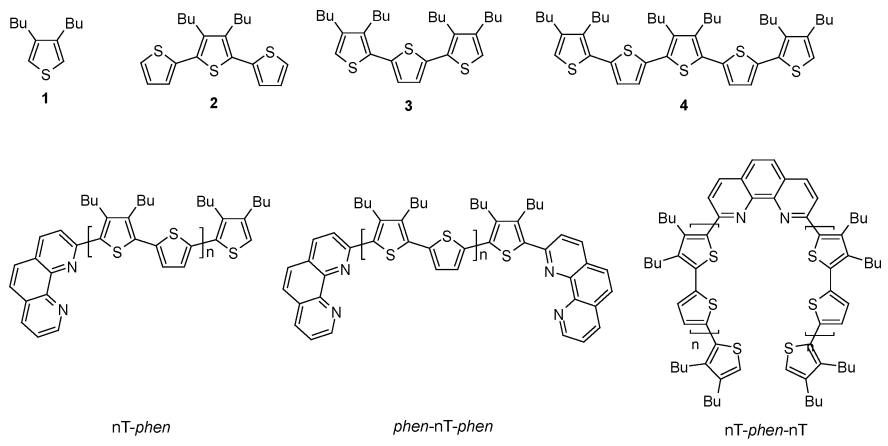
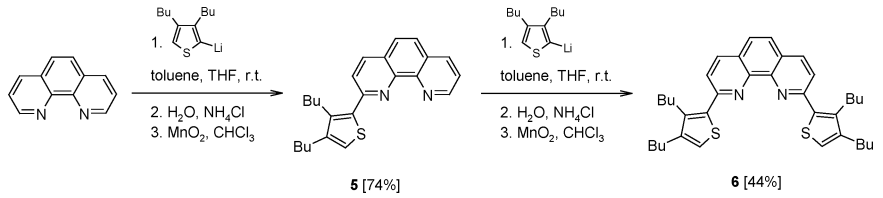


Scheme 1 Oligothiophene building blocks and series of oligothiophene-phenanthrolines.

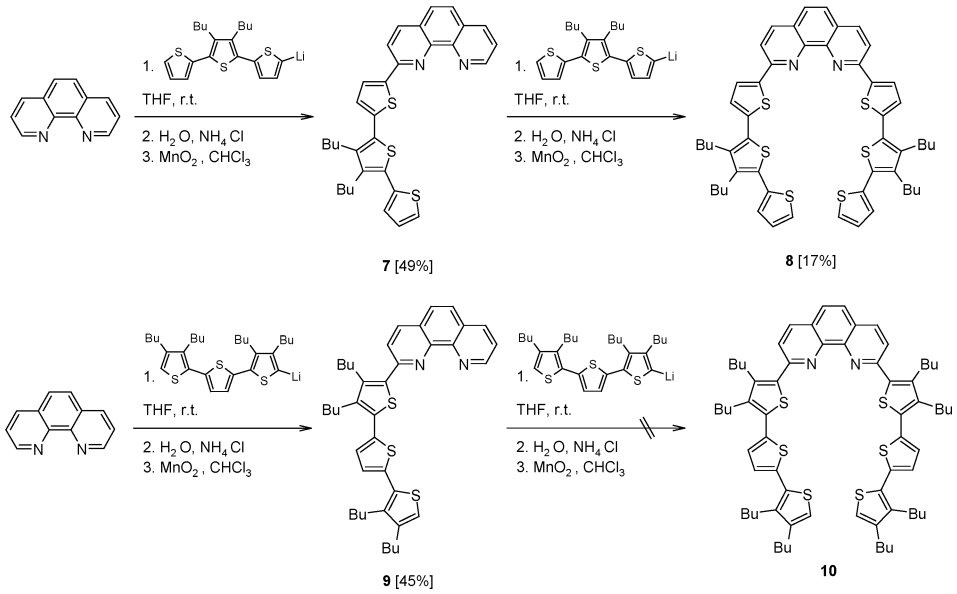
second route utilizes transition metal-catalyzed cross-coupling reactions of halogenated [1,10]phenanthrolines and metalated arylenes. Up to know, attempts utilizing Stille-[21,25] Suzuki-[26] and Negishi-type[27] cross-coupling conditions had been reported.

In our first approach, we started from commercially available [1,10]phenanthroline which was reacted with a twofold excess of the *in situ* prepared 2-lithio-3,4-dibutylthiophene **1**. A comparable method had been described previously along with the use of different thienyllithium reagents and their reaction with [1,10]phenanthroline.[20] In fact, we found similar results as reported in this publication and after aqueous quenching and oxidative rearomatization of the intermediate product we could only isolate the monosubstituted thienyl-phenanthroline **5** in 74% yield. A further addition–oxidation sequence gave dithienyl-phenantholine **6** in 44% yield which corresponds to a moderate overall yield of 33% starting from [1,10]phenanthroline (Scheme 2).

In a similar reaction sequence, we prepared terthiophene-substituted [1,10]phenanthrolines. Utilizing an excess of lithiated 3′,4′-dibutyl-terthiophene **2** in both steps, we received mono-substituted terthienyl-phenanthroline **7** in 49% yield and the disubstituted derivative **8** in only 17%, resulting in a poor overall yield of 8% for **8** (Scheme 3). In the synthesis of the higher alkylated terthienyl-phenanthroline **9**, made from lithiated 3,3″,4,4″-tetrabutyl-terthiophene **3** and [1,10]phenanthroline, we observed a large number of by-products after oxidative rearomatization that complicated chromatographic separation. Finally, derivative **9** could be isolated in 45% yield which is comparable to the other terthienyl-phenanthroline **7**. A mixture of by-products could be separated from the main product showing the presence of ^{13}C chemical shifts typical for carbonyl group signals. This led us to the conclusion that oxidative processes at the butyl side chains, most likely in direct proximity to the phenanthroline residue, might occur. Using the



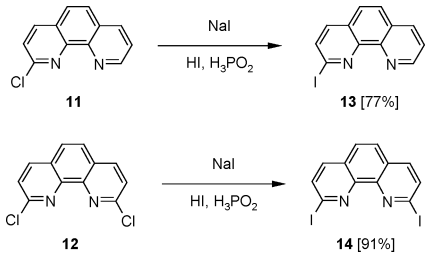
Scheme 2 Monothienyl-phenanthrolines by nucleophilic addition–reoxidation.



Scheme 3 Terthienyl-phenanthrolines by nucleophilic addition–reoxidation.

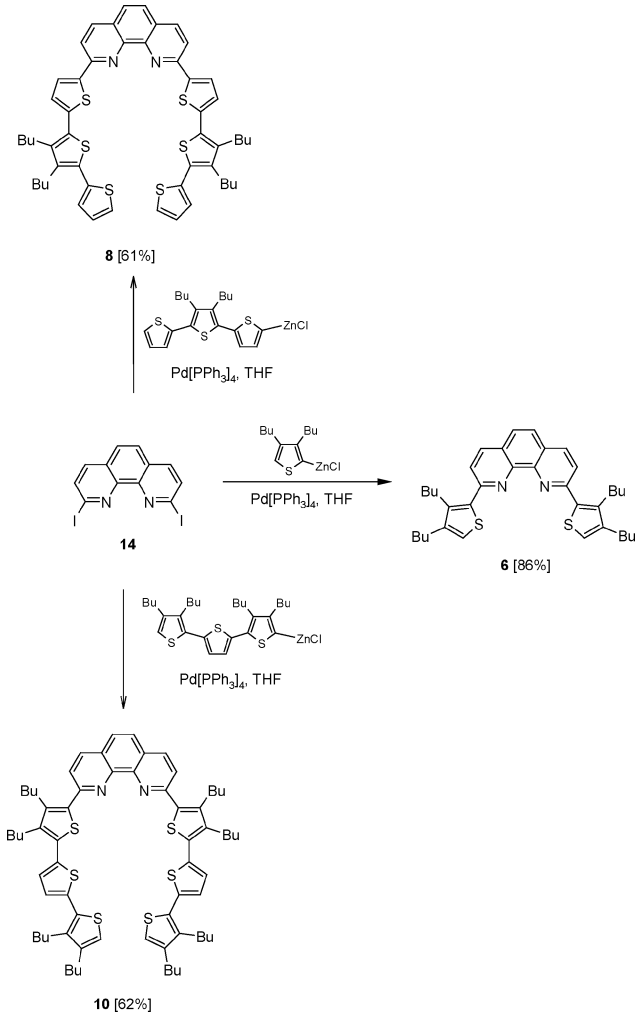
same reaction conditions as for the synthesis of compound **8**, the corresponding 2,9-bis(terthienyl)-phenanthroline **10** could not be successfully prepared from **9**. These experimental results clearly show the difficulty of the nucleophilic addition–rearomatization protocol for the linkage of longer oligothiophenes to [1,10]phenanthroline. In addition, the necessary excess of the terthiophene which had to be used in these preliminary assays is problematic for the synthesis of larger amounts of the desired material.

A different synthetic approach was then developed utilizing transition metal-catalyzed cross-coupling of halogenated phenanthrolines and metalated thiophene derivatives. As iodinated aryl compounds show high reactivity in this type of reaction, we started our approach from 2-iodo-[1,10]phenanthroline **13** and 2,9-diiodo-[1,10]phenanthroline **14**. Both compounds are available from their chlorinated analogues **11** and **12**, which were prepared according to literature procedures.[28] Nucleophilic halogen substitution under acidic conditions was previously reported as a tool for the synthesis of 2,9-diiodo-[1,10]phenanthroline **14**.[26b] We slightly changed the procedure by reacting chlorine derivatives **11** and **12** with an excess of sodium iodide in concentrated hydroiodic acid, which contained a small amount of hypophosphorous acid. Control of the parameters temperature and reaction time evolved to be vital for a successful synthesis procedure. 2-Iodophenanthroline **13** was prepared at 120 °C at a reaction time of 4 hours, while the synthesis of 2,9-diiodophenanthroline **14** led to optimum results after 4 days at 80 °C. Compounds **13** and **14** could finally be isolated in yields of 77% and 91%, respectively (Scheme 4). For the synthesis of the first series of oligothiophene-phenanthrolines, 2,9-diiodophenanthroline **14** was cross-coupled with α-zincates of 3,4-dibutylthiophene **1**, dibutylterthiophene **2** and tetrabutylterthiophene **3**, respectively, and $Pd[PPh_3]_4$ as the catalyst. The zincates were prepared by lithiation of the starting materials with one equivalent *n*-butyllithium (*n*-BuLi) in THF, followed by a subsequent transmetalation with a slight excess of dry zinc chloride in THF (Scheme 5).



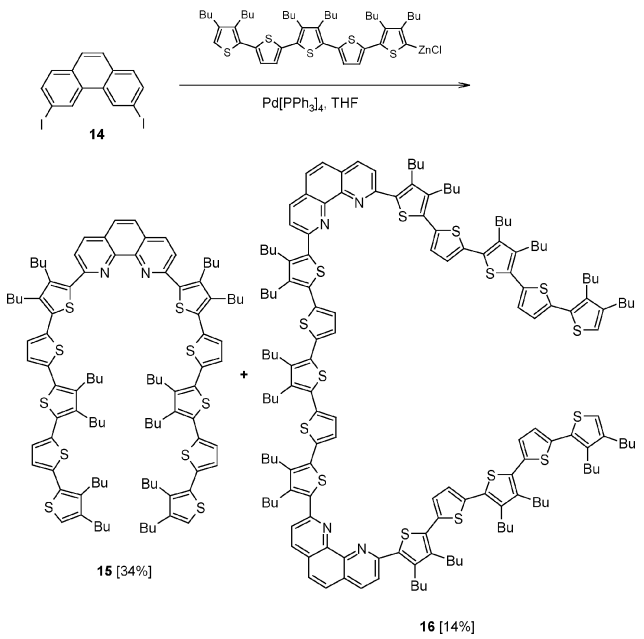
Scheme 4 Synthesis of iodinated phenanthrolines.

All reactions proceeded well at room temperature within several hours, and the reaction mixtures were subsequently quenched with an excess of aqueous ammonia. After chromatographic separation, dithienyl-phenanthroline **6** was obtained in 89% yield, while the corresponding terthiophene derivatives **8** and **10** were available in yields of 61% and 62%, respectively. In mass spectrometric analyses of the crude terthienyl-phenanthrolines, we could observe higher terthienyl-phenanthroline homologues along with starting material. We assume that monolithiation did not occur fully selectively leading to a mixture of unreacted, monometalated and dimetalated species during the lithiation–transmetalation sequence. This general problem which typically occurs in metalations of oligothiophenes was even more evident in the reaction of the longest representative, quinquethiophene **4**. The corresponding zincate was cross-coupled with 2,9-diiodophenanthroline **14** under Pd^0-catalysis to give 34% of bis-quinquethienyl-phenanthroline **15** as the main product, along with 14% of a second product **16**, which was identified to be mixed oligomer 5T-*phen*-5T-



Scheme 5 Oligothienyl-phenanthrolines by Negishi-coupling.

phen-5T which probably had been formed by reaction of 2,9-diiodophenanthroline **14** and a mixture of mono- and dimetalated quinquethiophene **4** (Scheme 6).



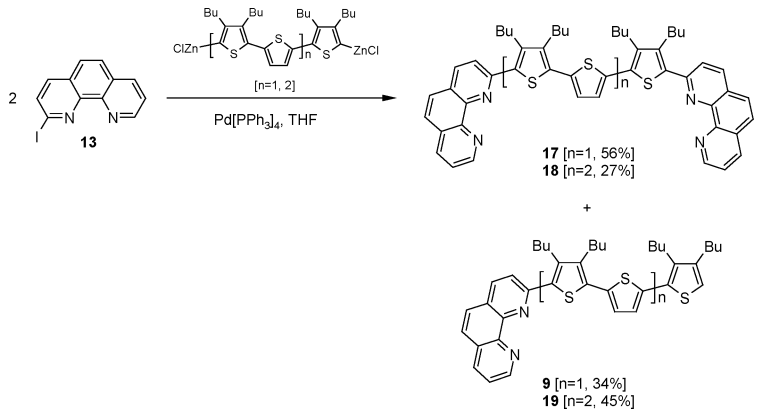
Scheme 6 Quinquethienyl-phenanthrolines by Negishi-coupling.

Oligothiophenes end-capped with phenanthroline moieties were available by reacting two equivalents of 2-iodophenanthroline **13** with two-fold zincated tetrabutylterthiophene **3** and quinquethiophene **4**, respectively. In both cases, Pd^0-catalyzed cross-coupling was performed under the same conditions as described above. From the product mixtures, we were able to isolate the expected oligothienyl-bis-phenanthrolines **17** in 56% yield and **18** in 27% yield, along with monosubstituted oligothienyl-phenanthrolines **9** and **19** in 34% and 45% yield, respectively. These results clearly indicate that it is difficult to achieve complete two-fold metalation of terthiophene **3** as well as of quinquethiophene **4**, even when longer reaction times are applied. Nevertheless, in both cases the oligothienyl-phenanthrolines **9** and **19** could be well separated from products **17** and **18** due to their very different chromatographic behaviour (Scheme 7).

Optical properties

Absorption and fluorescence spectra of three series with the general structures nT-*phen* (**5**, **7**, **9**, **19**), nT-*phen*-nT (**6**, **8**, **10**, **15**) and *phen*-nT-*phen* (**17**, **18**) (n = number of thiophene rings) were measured in dichloromethane. The optical properties of the reference oligothiophenes **2**, **3** and **4**[29] and of [1,10]phenanthroline[30] had been investigated previously (Table 1). The maximum absorption wavelengths of terthiophene **3** (λ_{max} = 342 nm) is slightly red-shifted in comparison to terthiophene **2** (λ_{max} = 335 nm) coming from an increasing number of alkyl side chains in **3**. As expected, corresponding the pentamer **4** (λ_{max} = 386 nm) shows a bathochromic shift, which is also accompanied by an increase of the extinction coefficients. [1,10]Phenanthroline as a second parent system absorbs in a regime (λ_{max} = 264 nm) which does not interfere with the π–π* absorption of the oligothiophenes. nT-*phen* Derivatives **5**, **7**, **9** and **19** as well as *phen*-nT-*phen* compounds **17** and **18** throughout show a pronounced bathochromic shift of the longest wavelength absorption and a simultaneous increase of the extinction coefficient compared to the parent oligothiophenes (**7/2**: $\Delta\lambda^{abs}$ = 65 nm, **9/3**: $\Delta\lambda^{abs}$ = 50 nm, **19/4**: $\Delta\lambda^{abs}$ = 22 nm). Therefore, the coupling of a *phen* to an oligothiophene core leads to an increase of the overall conjugation. This effect is even more pronounced when a second phenanthroline residue is attached to the oligothiophene core represented in *phen*-nT-*phen* **17** and **18**. A further red-shift and extension of the effective π-conjugation is evident (**9/17**: $\Delta\lambda^{abs}$ = 19 nm, **19/18**: $\Delta\lambda^{abs}$ = 11 nm). If one compares the absorption maxima of differently alkylated 3T-*phens* **7** and **9** a blue-shift ($\Delta\lambda^{abs}$ = 8 nm) occurs despite the fact that compound **9** bears more alkyl side chains. This indicates that in **9** the *phen* and 3T unit is distorted due to steric hindrance.

The coupling of two oligothiophene residues to a *phen* unit leads to the series nT-*phen*-nT comprising compounds **6**, **8**, **10**, and **15**. In comparison to the *nT-phen* series, in general, a hypsochromic shift of the longest wavelength absorption band is to notice which decreases with increasing oligothiophene chain length (**6/5**: $\Delta\lambda^{abs}$ = −8 nm, **8/7**: $\Delta\lambda^{abs}$ = −4 nm, **10/9**: $\Delta\lambda^{abs}$ = −22 nm, **15/19**: $\Delta\lambda^{abs}$ = −1 nm). This effect seems to be in contrast to a further extension of the conjugated π-system, nevertheless, the emission maxima of the nT-*phen*-nT oligomers are red-shifted compared to the parent nT-*phen* class (**6/5**: $\Delta\lambda^{em}$ = 6 nm, **8/7**: $\Delta\lambda^{em}$ = 22 nm, **10/9**: $\Delta\lambda^{em}$ = 28 nm and **15/19**: $\Delta\lambda^{em}$ = 8 nm). In the nT-*phen*-nT series, steric constraints are evidently dominating the molecular structure in the ground state whereas in the excited state rather rigid planar and quinoid conformations are adopted.



Scheme 7 Synthesis of oligothiophene-bridged phenanthrolines.

Table 1 Spectroscopic data of [1,10]phenanthroline,[30] oligothiophenes **2–4**[29] and oligothienyl-phenanthrolines **5–10**, **15**, **17–19**

	λ_{max}^{abs}/nm	ε/L mol^{-1} cm^{-1}	log (ε)	λ_{max}^{em}/nm	$\Phi_{295\,K}^{em}$ (%)	ΔE_{opt}/eV[a]
phen	264	31000	4.49	358	<1	n.d.
2 (3T*)	335	16000	4.20	n.d.	n.d.	n.d.
3 (3T)	342	18500	4.27	441	5[b]	3.12
4 (5T)	386	26600	4.43	526	22[b]	2.69
5 (1T-*phen*)	305	18400	4.26	417	7[c]	3.41
7 (3T*-*phen*)	400	28300	4.45	503	14[b]	2.74
9 (3T-*phen*)	392	25900	4.41	504	14[b]	2.76
19 (5T-*phen*)	408	39600	4.60	553	28[b]	2.57
17 (*phen*-3T-*phen*)	411	37400	4.57	519, 542	25[b]	2.63
18 (*phen*-5T-*phen*)	419	52300	4.72	551, 581	30[b]	2.52
6 (1T-*phen*-1T)	297	31000	4.49	423	14[c]	3.32
8 (3T*-*phen*-3T*)	396	46700	4.67	512	17[b]	2.76
10 (3T-*phen*-3T)	370	49000	4.69	532	17[b]	2.73
15 (5T-*phen*-5T)	407	67400	4.83	561	23[b]	2.54

[a] Band gaps are determined from the 0→0 transitions in normalized absorption and emission spectra. [b] Relative to standard 9,10-diphenylanthracene. [c] Relative to standard anthracene. n.d. = not determined. 3T* denotes 3′,4′-dibutylterthiophene.

For the various series we also measured fluorescence quantum yields which roughly depend on the oligothiophene chain length. As an example, in the nT-*phen* series emission intensity is stepwise doubled on going from 1T-*phen* **5** (Φ = 7%), to 3T-*phens* **7** and **9** (Φ = 14%), and to 5T-*phen* **19** (Φ = 28%). This is a well-known behaviour found for other oligothiophene series.[31] The influence of the *phen* units on the emission intensities is not significant and is rather subtle. *E.g.*, comparison of 5T-derivatives reveals that coupling of a *phen* unit slightly increases the fluorescence quantum yield (5T **4**: Φ = 22%; 5T-*phen*-5T **23**: Φ = 23%; 5T-*phen* **19**: Φ = 28%; *phen*-5T-*phen* **18**: Φ = 30%). Absorption and corrected emission spectra of the latter 5T-series (**4**, **15**, **18** and **19**) as representative examples are displayed in Fig. 1. Typically, broad and rather non-structured bands are observed.

Electrochemical investigations

Whereas optical measurements provide an estimation of the energy difference of the frontier orbitals which correlate to the (optical) band gap $\Delta E_{opt.}$, the absolute energetic positions of the HOMOs and LUMOs can be derived from redox potentials. Redox potentials of various phenanthroline-oligothiophenes were determined by cyclic voltammetry (CV) in dichloromethane ($c = 1 \times 10^{-3}$ mol l^{-1}) using tetrabutylammonium hexafluorophosphate (TBAHFP, 0.1 M) as supporting salt and are given *versus* the internal standard ferrocene/ferricenium (Fc/Fc^+). For some compounds, reductions were measured in THF–TBAHFP (0.1 M). Comparison of the CVs to those of the reference oligothiophenes **2–4** and that of phenanthroline facilitates the assignment of the individual redox waves in the hybrid systems (Table 2).

With increasing oligothiophene chain length, as a general trend, the number of the redox transitions increases which progressively shift to more negative potentials. In the nT-*phen* series, 1T-*phen* **5** shows a first irreversible redox transition at E^0_1 = 1.06 V which corresponds to the formation of a thiophene radical cation, dialkylated 3T*-*phen* **7** at 0.55 V (Fig. 3) and tetraalkylated 3T-*phen* **9** at 0.46 V reflecting the electron-donating effect of the side chains. Pentamer 5T-*phen* **19** is reversibly oxidized at 0.34 V and shows a second and third redox wave at E^0_2 = 0.57 V and E^0_3 = 0.74 V due to the formation of a di- and trication, respectively (Fig. 3). In comparison to the parent oligothiophenes **2–4**, in the hybrid systems only a marginal effect of the *phen* group is to notice for 3T*-*phen* **7** (ΔE^0_1 = 40 mV) whereas identical potentials are determined for the other compounds in the series. We find the same correlations in the *phen*-nT-*phen* series (**17**/**3**: ΔE^0_1 = 0

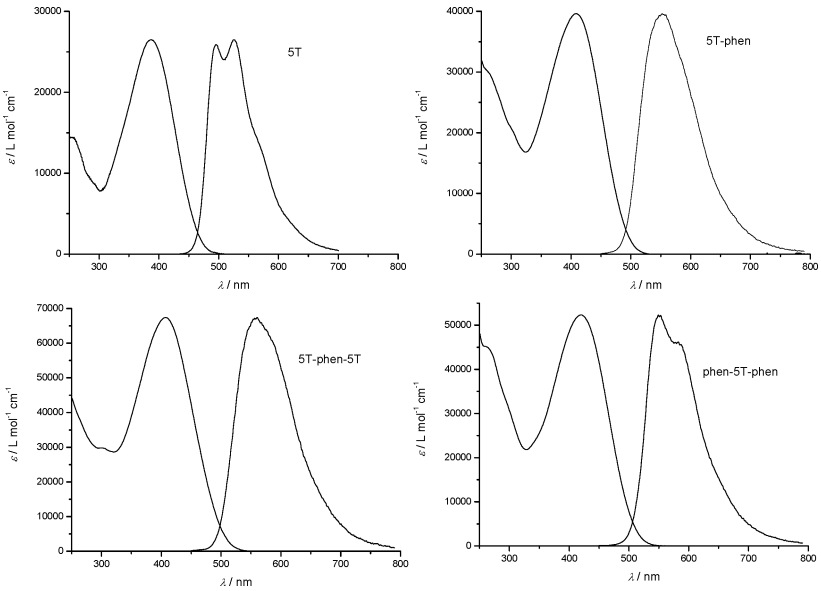


Fig. 1 UV/Vis-absorption and corrected emission spectra (excitation at λ_{max}^{abs}) of oligothiophene **4** and oligothiophene-phenanthrolines **15** (5T-*phen*-5T), **18** (*phen*-5T-*phen*) and **19** (5T-*phen*) in CH_2Cl_2 ($c = 10^{-5}$ mol l^{-1}).

Table 2 Redox potentials of phenanthroline, oligothiophenes **2–4**[28] and oligothienyl-phenanthrolines **5–10**, **15**, **17–19** in V *vs.* Fc/Fc^+

	Oxid.					Red.			
	E^0_1/V	E^0_2/V	E^0_3/V	E^0_4/V	E^0_5/V	E^0_1/V	E^0_2/V	E^0_3/V	ΔE_{CV}/eV
phen						−2.62			
2 (3T*)	0.59								
3 (3T)	0.46								
4 (5T)	0.34	0.57							
5 (1T-*phen*)	1.06[a]								
7 (3T*-*phen*)	0.55[a]								
9 (3T-*phen*)	0.46	1.13							
19 (5T-*phen*)	0.34	0.57	0.74			−2.33			2.67
17 (*phen*-3T-*phen*)	0.46	0.83							
18 (*phen*-5T-*phen*)	0.32	0.51				−2.26[b]	−2.50	−2.78	2.52
6 (1T-*phen*-1T)	0.94[a]								
8 (3T*-*phen*-3T*)	0.47[a]	0.64[a]							
10 (3T-*phen*-3T)	0.38	0.55	0.67	0.86	1.11				
15 (5T-*phen*-5T)	0.26	0.38	0.49	0.65	0.83	−2.16[a]			2.54

[a] Irreversible wave, E° determined at $I^\circ = 0.855 \times I_p$. [b] Two-electron transfer. 3T* denotes 3′,4′-dibutylterthiophene.

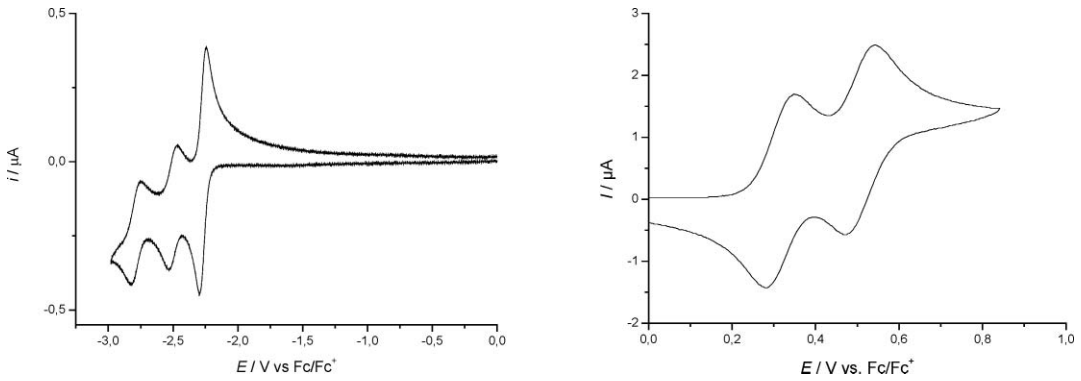


Fig. 2 Cyclic voltammogram of *phen*-5T-*phen* **18** in THF–TBAHPF (0.1 M, left) and in CH_2Cl_2–TBAHPF (0.1 M, right) at 295 K, $V = 100$ mV s^{-1}).

mV; **18/4**: $\Delta E^0{}_1 = -20$ mV), whereas in contrast in the nT-*phen*-nT series, throughout lower oxidation potentials are noticed in comparison to the parent compounds (**8/2**: $\Delta E^0{}_1 = -120$ mV; **10/3**: $\Delta E^0{}_1 = -120$ mV; **15/4**: $\Delta E^0{}_1 = -80$ mV). The same trends are true for the terthiophene series 3T **3**, 3T-*phen* **9** and *phen*-3T-*phen* **17** and 3T-*phen*-3T **10**. Therefore, in the nT-*phen*-nT series the *phen* unit acts as a bridge between the two oligothiophene moieties extending π-conjugation.

This behaviour is further supported by the comparison of CV data obtained for a constant oligothiophene chain length, but varying number of *phen* units. The CV of *phen*-5T-*phen* **18** exhibits two reversible redox waves at $E^0{}_1 = 0.32$ V and $E^0{}_2 = 0.51$ V (Fig. 2) and in shape and position of the potentials fully resembles that of parent 5T **4** ($E^0{}_1 = 0.34$ V, $E^0{}_2 = 0.57$ V). The electrochemical behaviour of 5T-*phen* **19** is very similar, however, a third redox wave arises which we attribute to the formation of a 5T-trication ($E^0{}_1 = 0.34$ V, $E^0{}_2 = 0.57$ V, $E^0{}_3 = 0.74$ V). In the case of 5T-*phen*-5T **15**, however, five separated redox transitions are visible which are correlated with the successive charging of each oligothiophene unit ($E^0{}_1 = 0.26$ V, $5T^{+\bullet}$-*phen*-5T; $E^0{}_2 = 0.38$ V, $5T^{+\bullet}$-*phen*-$5T^{+\bullet}$; $E^0{}_3 = 0.49$ V, $5T^{2+}$-*phen*-$5T^{+\bullet}$; $E^0{}_4 = 0.65$ V, $5T^{2+}$-*phen*-$5T^{2+}$; $E^0{}_5 = 0.83$ V, $5T^{3+}$-*phen*-$5T^{2+}$). The mean values of $E^0{}_1/E^0{}_2$ (0.32 V) and $E^0{}_3/E^0{}_4$ (0.57 V) are in good agreement with the first and second redox potential of *phen*-5T-*phen* **18**, 5T-*phen* **19** and 5T **4** indicating full conjugation and "communication" *via* the *phen* bridge. This finding is very important for the development of conjugated macrocycles and catenanes built from corresponding nT-*phen*-nT subunits.[23]

For various 5T-derivatives CVs were taken in the electrolyte system THF–TBAHFP (0.1 M) in order to analyze reduction processes in the negative potential regime. Whereas parent compound *phen* exhibits a quasireversible reduction at −2.62 V *vs.* Fc/Fc^+, the coupling of *phen* to an oligothiophene in 5T-*phen* **19** results in a decreased reduction potential of −2.33 V ($\Delta E^\circ{}_1 = 0.29$ V) which is further decreased in 5T-*phen*-5T **15** to −2.16 V due to the second electron-donating quinquethiophene unit ($\Delta E^\circ{}_1 = 0.15$ V). The reduction of derivative *phen*-5T-*phen* **18** ($E^\circ{}_1 = -2.26$ V) is only slightly lower in comparison to 5T-*phen* **19** (Fig. 2) These results further support that electronic coupling and conjugation are operative between the donor and acceptor units. In the same line and in accordance with the optical data, band gap ΔE_{CV} which is determined from the difference between the first oxidation and reduction potential and correlates with the HOMO–LUMO gap becomes smaller when the π-system is increased: $\Delta E_{CV} = 2.67$ eV for 5T-*phen* **19**; 2.60 eV for *phen*-5T-*phen* **18** and 2.40 eV for 5T-*phen*-5T **15** (Table 2).

In the case of derivatives containing shorter thiophene blocks, redox waves are irreversible indicating follow-up reactions of the radical cations and dications. In the nT-*phen* series, *e.g.* for 3T*-*phen* **7**, in subsequent scans the formation of a coupling product at more negative potentials is visible which we attribute to the dimer, sexithiophene *phen*-6T*-*phen* (Fig. 3). Repeated scanning on 3T*-*phen*-3T* **8** leads to the formation of a polymer film containing (6T-*phen*) repeating units on the working electrode which is characterized by a broad redox wave at lower potentials.

Conclusion

In summary, we were able to develop an efficient synthesis of a variety of oligothiophene-substituted [1,10]phenanthrolines in good overall yields and purities by Pd-catalyzed Negishi cross-coupling reactions of iodinated phenanthrolines and zincated oligothiophenes. Several series of hybrid systems were generated with varying length of the oligothiophene chain (1T, 3T, 5T) and varying ratio of both components (nT-*phen*, *phen*-nT-*phen*, nT-*phen*-nT). The optical and redox properties were determined and structure–property relationships deduced showing the ability of the 2,9-substituted phenanthroline unit to contribute to the overall conjugation. These new types of π-conjugated materials that contain intrinsic metal chelating moieties[32] serve as model

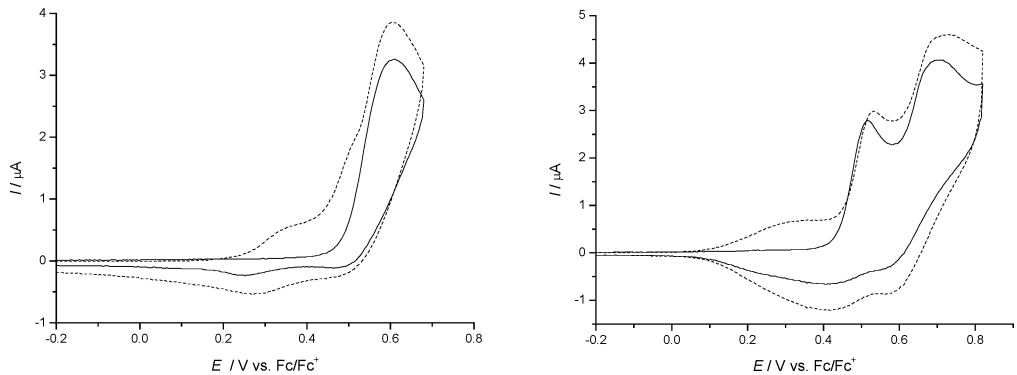
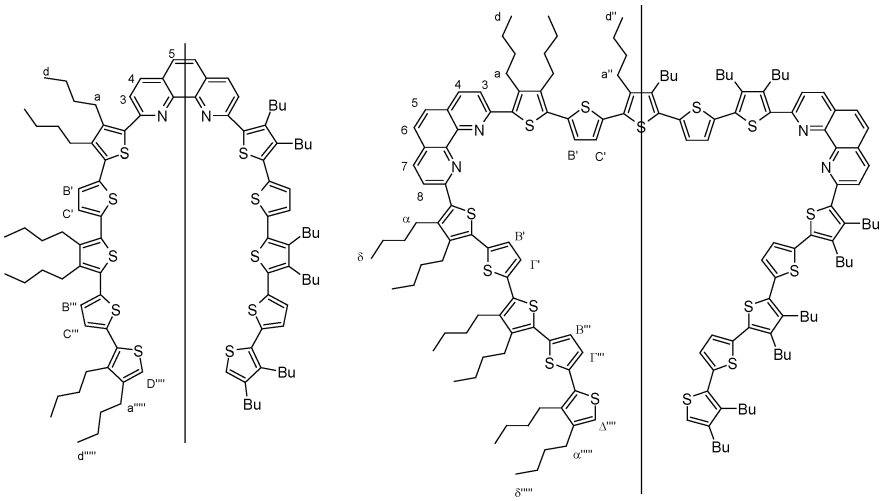


Fig. 3 Cyclic voltammograms and polymerization behaviour of the 3T*-phenanthroline derivatives **7** (left) and **8** (right) (10^{-3} M solutions in CH_2Cl_2–0.1 M $TBAPF_6$ at 295 K, $V = 100$ mV s^{-1}). 3T* denotes 3′,4′-dibutylterthiophene.



Scheme 8 Atom numbering scheme for ^{1}H-NMR assignment.

compounds and precursors in the synthesis of π-conjugated macrocycles and corresponding interlocked catenanes.[23]

Experimental

Solvents and reagents were purchased from Aldrich, Merck and ABCR unless otherwise stated and purified and dried by standard methods prior to use. The following compounds were prepared according to literature procedures: 3,4-dibutylthiophene **1**,[33] 3′,4′-dibutyl-[2,2′:5′, 2″]terthiophene **2**,[34] 3,4,3″,4″-tetrabutyl-[2,2′:5′,2″]terthiophene **3**,[29b,c] 3,4,3″,4″,3‴,4‴-hexabutyl-[2,2′:5′,2″:5″,2‴:5‴,2⁗]quinquethiophene **4**,[29b,c] 2-chloro-[1,10]phenanthroline **11**,[28] 2,9-dichloro-[1,10]phenanthroline **12**.[28] All metal organic reactions were carried out in a dry argon atmosphere using Schlenk techniques. Preparative column chromatography was performed on glass columns packed with silica gel (Merck Silica 60, particle size 0.04–0.063 mm). Thin layer chromatography was carried out on silica gel Si60 F_{254} (Merck). NMR spectra were recorded on a Bruker Avance 400 spectrometer. A general scheme for ^{1}H-NMR atom numbering is outlined in Scheme 8. EI and CI mass spectra were recorded on a Finnigan MAT SSQ-7000, FAB on a Finnigan MAT TSQ-7000 (matrix nitrobenzyl alcohol), ESI on a Waters-Micromass ZMD (samples sprayed from THF–15% water–1% HCOOH solutions) and MALDI-TOF from on a Bruker Daltonics Reflex III (matrix 1,8,9-trihydroxyanthracene). Elemental analysis was performed on an Elementar Vario EL device. Optical measurements were carried out in 1 cm cuvettes with Merck Uvasol grade solvents, absorption spectra recorded on a Perkin Elmer Lambda 19 spectrometer and fluorescence emissions spectra on a Perkin Elmer LS 55 spectrometer.

2-Iodo-[1,10]phenanthroline (13)

Under continuous stirring hypophosporous acid (50%, 0.2 mL) was added to hydroiodic acid (57%, 7 mL) until a colourless solution appeared. 2-Chloro-[1,10]phenanthroline **11** (1.50 g, 7.00 mmol) and sodium iodide (1.57 g, 10.5 mmol) were added and the resulting solution heated for 4 h at 120 °C. After cooling to 0 °C, aqueous ammonia was added until the solution showed alkaline reaction. A precipitate was formed and filtered off, washed several times with water and dried in vacuum. Recrystallization from ethanol containing a small amount of aqueous ammonia gave **13** (1.65 g, 77%) as a buff coloured solid. Mp: 190 °C (decomposition); ^{1}H-NMR ([D]chloroform): $\delta = 9.21$ (dd, $^3J = 4.3$ Hz, $^4J = 1.8$ Hz, 1 H, H-9), 8.21 (dd, $^3J = 8.1$ Hz, $^4J = 1.7$ Hz, 1 H, H-7), 7.97 (d, $^3J = 8.1$ Hz, 1 H, H-4), 7.80 (d, $^3J = 2.4$ Hz, 1 H, H-5), 7.78 (d, $^3J = 3.0$ Hz, 1 H, H-6), 7.70 (d, $^3J = 8.8$ Hz, 1 H, H-3), 7.62 (dd, $^3J = 8.1$ Hz, $^4J = 4.4$ Hz, 1 H, H-8); ^{13}C-NMR ([D]chloroform): $\delta = 151.0$, 147.6, 145.2, 137.0, 136.1, 134.6, 128.9, 127.9, 127.4, 126.2, 123.5, 119.3; MS (FAB): m/z 307 $[M + H]^+$; elemental analysis (%) calcd for $C_{12}H_7IN_2$: C 47.09, H 2.31, N 9.15, found: C 47.12, H 2.39, N 9.12.

2,9-Diiodo-[1,10]phenanthroline (14)

Under continuous stirring hypophosporous acid (50%, 1.2 mL) was added to hydroiodic acid (57%, 44 mL) until a colourless solution appeared. 2,9-Dichloro-[1,10]phenanthroline **12** (5.50 g, 22.1 mmol) and sodium iodide (13.3 g, 88.4 mmol) were added and the resulting solution heated for 4 h at 80 °C. After cooling to 0 °C, aqueous ammonia was added until the solution showed alkaline reaction. A precipitate was formed and filtered off, washed several times with water and dried in vacuum. Recrystallization from CH_2Cl_2–hexane gave **12** (7.95 g, 83%) as a yellowish solid. Mp: 251 °C (decomposition); ^{1}H-NMR ([D]chloroform): $\delta = 8.01$ (d, $^3J = 8.2$ Hz, 2 H, H-3), 7.82 (d, $^3J = 8.4$ Hz, 2 H, H-4), 7.78 (s, 2 H, H-5); ^{13}C-NMR ([D]chloroform): $\delta = 146.4$, 137.0, 135.1, 128.1, 127.0, 119.9; MS (ESI): m/z 455 $[M + Na]^+$, 433 $[M + H]^+$; elemental analysis (%) calcd for $C_{12}H_6I_2N_2$: C 33.36, H 1.40, N 6.48; found: C 33.49, H 1.49, N 6.51.

2-(3,4-Dibutylthien-2-yl)-[1,10]phenanthroline (5)

3,4-Dibutylthiophene **1** (3.93 g, 20.0 mmol) was dissolved in THF (40 mL) and cooled to −78 °C. *n*-BuLi in *n*-hexane (12.6 mL, 20.0 mmol) was slowly added, the resulting solution stirred for 1 h and after removing the cooling bath stirred for an additional hour. The intermediate lithiated thiophene was added at 0 °C to a suspension of [1,10]phenanthroline (1.80 g, 10.0 mmol) in toluene (40 mL). After stirring for 24 h at rt, the reaction was quenched by adding a saturated aqueous NH_4Cl solution. The organic phase was separated and the aqueous residue washed several times with CH_2Cl_2. After drying and evaporation of the solvent, the product was dissolved in $CHCl_3$ (100 mL) and MnO_2 (17.4 g, 200 mmol) was added in small portions over a time of 4 h. Filtration and evaporation of the solvent yielded an oily product, which was purified by flash chromatography (silica, hexane–THF 80:20) to afford **5** (2.79 g, 74%) as a white solid. Mp: 66 °C; ^{1}H-NMR ([D]chloroform): $\delta = 9.18$ (dd, $^3J = 4.4$ Hz, $^4J = 1.8$ Hz, 1 H, H-9), 8.21 (d, $^3J = 8.4$ Hz, 1 H, H-4), 8.20 (dd, $^3J = 8.0$ Hz, $^4J = 1.7$ Hz, 1 H, H-7), 7.86 (d, $^3J = 8.4$ Hz, 1 H, H-3), 7.76 (d, $^3J = 8.8$ Hz, 1 H, H-6), 7.72 (d, $^3J = 8.7$ Hz, 1 H, H-5), 7.59 (dd, $^3J = 8.1$ Hz, $^4J = 4.3$ Hz, 1 H, H-8), 7.06 (s, 1 H, H-D), 3.08 (t, $^3J = 8.1$ Hz, 2 H, H-a), 2.62 (t, $^3J = 7.8$ Hz, 2 H, H-a′), 1.59–1.72 (m, 4 H, H-b,c), 1.37–1.51 (m, 4 H, H-b′,c′), 0.99 (t, $^3J = 7.3$ Hz, 3 H, H-d), 0.89 (t, $^3J = 7.3$ Hz, 3 H, H-d′); ^{13}C-NMR ([D]chloroform): $\delta = 154.5$, 150.4, 146.5, 146.3, 144.1, 141.6, 138.5, 136.4, 135.8,

129.1, 126.9, 126.3, 126.1, 122.9, 122.4, 121.8, 32.9, 32.2, 29.0, 27.6, 23.2, 22.8, 14.2, 14.0; MS (EI): m/z 374 $[M]^+$, 345 $[M - C_2H_5]^+$; elemental analysis (%) calcd for $C_{24}H_{26}N_2S$: C 76.96, H 7.00, N 7.48; found: C 77.00, H 7.08, N 7.47.

2-(3′,4′-Dibutyl-[2,2′:5′,2″]terthien-5-yl)-[1,10]phenanthroline (7)

Terthiophene **2** (9.40 g, 26.1 mmol) was dissolved in THF (260 mL) and cooled to −78 °C. *n*-BuLi in hexane (16.4 mL, 26.1 mmol) was slowly added and after 40 min, the cooling bath was removed and a solution of [1,10]phenanthroline (3.14 g, 17.4 mmol) in THF (25 mL) was added. After 3 d at rt, the reaction was quenched by adding a saturated aqueous NH_4Cl solution. The organic phase was separated and the aqueous residue washed several times with CH_2Cl_2. After drying and evaporation of the solvent, the product was dissolved in $CHCl_3$ (250 mL) and MnO_2 (50.0 g, 575 mmol) was added in small portions over a time of 4 h. Filtration and evaporation of the solvent yielded an oily product, which was purified by flash chromatography (silica, CH_2Cl_2) to afford **7** (4.60 g, 49%) as a gold coloured solid. Mp: 62 °C; ^{1}H-NMR ([D]chloroform): δ = 9.19 (dd, ^3J = 4.3 Hz, ^4J = 1.6 Hz, 1 H, H-9), 8.14 (dd, ^3J = 8.0 Hz, ^4J = 1.7 Hz, 1 H, H-7), 8.09 (d, ^3J = 8.4 Hz, 1 H, H-4), 7.87 (d, ^3J = 8.4 Hz, 1 H, H-3), 7.78 (d, ^3J = 3.9 Hz, 1 H, H-B), 7.64 (d, ^3J = 8.8 Hz, 1 H, H-6), 7.62 (d, ^3J = 8.8 Hz, 1 H, H-5), 7.55 (dd, ^3J = 8.1 Hz, ^4J = 4.3 Hz, 1 H, H-8), 7.29 (dd, ^3J = 5.2 Hz, ^4J = 1.1 Hz, 1 H, H-D″), 7.19 (d, ^3J = 3.9 Hz, 1 H, H-C), 7.16 (dd, ^3J = 3.6 Hz, ^4J = 1.1 Hz, 1 H, H-B″), 7.05 (dd, ^3J = 5.2 Hz, ^3J = 3.6 Hz, 1 H, H-C″), 2.85 (t, ^3J = 8.1 Hz, 2 H, H-a), 2.73 (t, ^3J = 8.2 Hz, 2 H, H-a′), 1.41–1.63 (m, 8 H, H-b,b′,c,c′), 1.00 (t, ^3J = 7.3 Hz, 3 H, H-d), 0.95 (t, ^3J = 7.2 Hz, 3 H, H-d′); ^{13}C-NMR ([D]chloroform): δ = 152.3, 150.4, 146.1, 146.0, 144.4, 140.6, 140.3, 139.6, 136.6, 136.2, 135.9, 130.4, 130.2, 129.1, 127.4, 126.7, 126.5, 126.2, 125.9, 125.4, 122.9, 119.1, 32.9, 32.7, 28.0, 27.9, 23.1, 23.0, 14.0, 13.9; MS (CI): m/z 539 $[M + H]^+$; elemental analysis (%) calcd for $C_{32}H_{30}N_2S_3$: C 71.34, H 5.61, N 5.20; found: C 71.27, H 5.70, N 5.15.

2-(3,4,3″,4″-Tetrabutyl-[2,2′:5′,2″]terthien-5-yl)-[1,10]phenanthroline (9)

Diisopropylamine (1.65 mL, 11.3 mmol) was dissolved in THF (40 mL) and cooled to −78 °C. After addition of *n*-BuLi in hexane (7.38 mL, 11.8 mmol), stirring for 15 min at −78 °C and 30 min at 0 °C, the solution was cooled to −78 °C again. The LDA solution was added to terthiophene **3** (4.71 g, 9.96 mmol) in THF (100 mL). The reaction mixture was stirred for 30 min at −78 °C and subsequently added to a solution of [1,10]phenanthroline (1.28 g, 7.12 mmol) in THF (40 mL) at rt. After 6 d, the reaction was quenched by adding a saturated aqueous NH_4Cl solution. The organic phase was separated and the aqueous residue washed several times with CH_2Cl_2. After drying and evaporation of the solvent, the product was dissolved in $CHCl_3$ (200 mL) and MnO_2 (40.0 g, 460 mmol) was added in small portions over a time of 2 h. Filtration and evaporation of the solvent yielded an oily product, which was purified by flash chromatography (silica, CH_2Cl_2) to afford **9** (2.10 g, 45%) as a yellow solid. Mp: 90 °C; ^{1}H-NMR ([D]chloroform): δ = 9.20 (dd, ^3J = 4.3 Hz, ^4J = 1.7 Hz, 1 H, H-9), 8.22 (d, ^3J = 8.5 Hz, 1 H, H-4), 8.21 (dd, ^3J = 8.0 Hz, ^4J = 1.7 Hz, 1 H, H-7), 7.89 (d, ^3J = 8.4 Hz, 1 H, H-3), 7.76 (d, ^3J = 8.8 Hz, 1 H, H-5 or 6), 7.73 (d, ^3J = 8.8 Hz, 1 H, H-5 or 6), 7.60 (dd, ^3J = 8.0 Hz, ^4J = 4.3 Hz, 1 H, H-8), 7.21 (d, ^3J = 3.8 Hz, 1 H, H-B′), 7.09 (d, ^3J = 3.8 Hz, 1 H, H-C′), 6.88 (s, 1 H, H-D″), 3.11 (t, ^3J = 8.1 Hz, 2 H, H-a), 2.84 (t, ^3J = 8.2 Hz, 2 H, H-a′), 2.76 (t, ^3J = 8.1 Hz, 2 H, H-a″), 2.56 (t, ^3J = 7.5 Hz, 2 H, H-a‴), 1.43–1.67 (m, 16 H, H-b to H-b‴, H-c to H-c‴), 0.90–1.01 (m, 12 H, H-d to H-d‴); ^{13}C-NMR ([D]chloroform): δ = 153.8, 150.5, 146.5, 146.3, 143.7, 142.9, 140.6, 139.4, 139.0, 137.3, 137.0, 136.4, 135.9, 132.8, 131.0, 129.1, 127.0, 126.4, 126.3, 126.2, 126.1, 123.0, 122.2, 119.2, 33.2, 33.1, 32.9, 32.0, 29.0, 28.0, 27.7, 23.3, 23.2, 23.1, 22.8, 14.2, 14.1, 14.0; MS (CI): m/z 651 $[M + H]^+$; elemental analysis (%) calcd for $C_{40}H_{46}N_2S_3$: C 73.80, H 7.12, N 4.30; found: C 73.90, H 7.18, N 4.25.

2,9-Bis(3,4-dibutyl-thien-2-yl)-[1,10]phenanthroline (6)

Dibutylthiophene **1** (5.75 g, 29.3 mmol) was dissolved in THF (60 mL) and the solution cooled to −78 °C. *n*-BuLi in hexane (18.4 mL, 29.3 mmol) was slowly added and the reaction stirred for 1 h at −78 °C and an additional hour after removing the cooling bath. After cooling again to −78 °C, dry $ZnCl_2$ (4.39 g, 32.2 mmol) in THF (25 mL) was added and the reaction mixture stirred for 30 min and additional 30 min after removing the cooling bath. In a second flask, 2,9-diiodophenanthroline **14** (4.21 g, 9.75 mmol) and $Pd[PPh_3]_4$ (488 μmol, 565 mg) were stirred in THF (20 mL) and the zinc organic solution was transferred to this slurry by means of a double ended needle technique. After 24 h at rt, the reaction was quenched by adding aqueous ammonia. The organic phase was separated and the aqueous residue washed several times with CH_2Cl_2. After drying and evaporation of the combined organic phases, the oily product was purified by flash chromatography (silica, petroleum ether–CH_2Cl_2 65 : 35) yielding **6** (4.79 g, 86%) as a white solid. Mp: 84 °C; ^{1}H-NMR ([D]chloroform): δ = 8.18 (d, ^3J = 8.4 Hz, 2 H, H-4), 7.87 (d, ^3J = 8.3 Hz, 2 H, H-3), 7.68 (s, 2 H, H-5), 7.09 (s, 2 H, H-D), 3.27 (t, ^3J = 7.9 Hz, 4 H, H-a), 2.63 (t, ^3J = 7.5 Hz, 4 H, H-a′), 1.35–1.74 (m, 16 H, H-b,b′,c,c′), 1.00 (t, ^3J = 7.3 Hz, 6 H, H-d), 0.84 (t, ^3J = 7.3 Hz, 6 H, H-d′); ^{13}C-NMR ([D]chloroform): δ = 154.2, 146.1, 144.2, 141.5, 139.2, 136.3, 127.2, 125.6, 122.2, 121.5, 32.9, 32.2, 29.1, 27.4, 23.0, 22.8, 14.2, 14.1; MS (EI): m/z 568 $[M]^+$, 539 $[M - C_2H_5]^+$; elemental analysis (%) calcd for $C_{36}H_{44}N_2S_2$: C 76.01, H 7.80, N 4.92; found: C 76.07, H 7.87, N 4.85.

2,9-Bis(3′,4′-dibutyl-[2,2′:5′,2″]terthien-5-yl)-[1,10]phenanthroline (8)

Terthiophene **2** (1.44 g, 4.00 mmol) in THF (40 mL) was reacted with *n*-BuLi in hexane (2.52 mL, 4.00 mmol) at −78 °C. After stirring for 1 h, dry $ZnCl_2$ (600 mg, 4.40 mmol) in THF (5 mL) was added and stirred for 30 min at −78 °C and an additional 30 min after removing the cooling bath. In a second flask, 2,9-diiodophenanthroline **14** (864 mg, 2.00 mmol) and $Pd[PPh_3]_4$ (116 mg, 100 μmol) were stirred in THF (5 mL) and the zinc organic solution was transferred to this slurry by means of the double ended needle technique. After stirring for 20 h at rt, the reaction was quenched by adding aqueous ammonia. The organic phase was separated, the aqueous residue washed several times with CH_2Cl_2. After drying and evaporation of the combined organic phases, the oily product was purified by flash chromatography (silica, hexane–THF 70 : 30) yielding **8** (1.10 g, 61%) as a yellow solid. ^{1}H-NMR ([D]chloroform): δ = 8.18 (d, ^3J = 8.5 Hz, 2 H, H-4), 7.95 (d, ^3J = 8.4 Hz, 2 H, H-3), 7.89 (d, ^3J = 3.9 Hz, 2 H, H-B), 7.68 (s, 2 H, H-5), 7.31 (dd, ^3J = 5.1 Hz, ^4J = 1.2 Hz, 2 H, H-D″), 7.25 (d, ^3J = 3.8 Hz, 2 H, H-C), 7.17 (dd, ^3J = 3.5 Hz, ^4J = 1.1 Hz, 2 H, H-B″), 7.07 (dd, ^3J = 5.2 Hz, ^4J = 3.5 Hz, 2 H, H-C″), 2.86 (t, ^3J = 8.1 Hz, 4 H, H-a), 2.73 (t, ^3J = (.2 Hz, 4 H, H-a′), 1.39–1.67 (m, 16 H, H-b,b′,c,c′), 0.88–0.97 (m, 12 H, H-d,d′); ^{13}C-NMR ([D]chloroform): δ = 152.3, 145.9, 145.0, 144.9, 140.8, 140.4, 139.6, 136.8, 136.4, 130.4, 128.0, 127.5, 127.1, 126.6, 126.1, 125.8, 125.5, 119.0, 33.1, 33.0, 28.1, 28.0, 23.2, 23.1, 14.1, 14.0; MS (EI): m/z 896 $[M]^+$; elemental analysis (%) calcd for $C_{52}H_{52}N_2S_6$: C 69.60, H 5.84, N 3.12; found: C 69.30, H 5.75, N 2.93.

2,9-Bis(3,4,3″,4″-tetrabutyl-[2,2′:5′,2″]terthien-5-yl)-[1,10]phenanthroline (10)

Terthiophene **3** (8.00 g, 16.9 mmol) in THF (90 mL) was reacted with *n*-BuLi in hexane (10.6 mL, 16.9 mmol) at −78 °C. After stirring for 1 h, dry $ZnCl_2$ (2.53 g, 18.6 mmol) in THF

(20 mL) was added and stirred for 30 min and an additional 30 min after removing the cooling bath. In a second flask, 2,9-diiodophenanthroline **14** (3.65 g, 8.45 mmol) and $Pd[PPh_3]_4$ (976 mg, 845 μmol) were stirred in THF (20 mL) and the zinc organic solution was transferred to this slurry by means of the double ended needle technique. After stirring for 40 h at rt, the reaction was quenched by adding aqueous ammonia. The organic phase was separated, the aqueous residue washed several times with CH_2Cl_2. After drying and evaporation of the combined organic phases, the oily product was purified by flash chromatography (silica, hexane–THF 90 : 10) to give **10** (5.84 g, 62%) as an orange coloured resin. ^{1}H-NMR ([D]chloroform): $\delta = 8.20$ (d, $^3J = 8.5$ Hz, 2 H, H-4), 7.90 (d, $^3J = 8.4$ Hz, 2 H, H-3), 7.69 (s, 2 H, H-5), 7.26 (d, $^3J = 3.8$ Hz, 2 H, H-B′), 7.08 (d, $^3J = 3.8$ Hz, 2 H, H-C′), 6.88 (s, 2 H, H-D″), 3.36 (t, $^3J = 8.0$ Hz, 4 H, H-a), 2.88 (t, $^3J = 8.1$ Hz, 4 H, H-a′), 2.77 (t, $^3J = 8.1$ Hz, 4 H, H-a″), 2.57 (t, $^3J = 7.8$ Hz, 4 H, H-a‴), 1.43–1.70 (m, 32 H, H-b to H-b‴, H-c to H-c‴), 0.85–1.02 (m, 24 H, H-d to H-d‴); ^{13}C-NMR ([D]chloroform): $\delta = 153.5$, 146.0, 143.7, 143.1, 140.7, 139.0, 137.9, 136.9, 136.7, 136.4, 133.1, 131.1, 127.1, 126.1, 126.0, 125.6, 121.3, 119.2, 33.2, 33.1, 32.9, 32.0, 29.1, 28.1, 27.9, 27.7, 23.2, 23.1, 23.0, 22.8, 14.1, 14.0; MS (MALDI-TOF): m/z 1121 $[M + H]^+$. The resinous product was dissolved in CH_2Cl_2 and precipitated as hydrochloride upon addition of a solution of HCl in diethyl ether. Elemental analysis (%) calcd for $C_{68}H_{84}N_2S_6 \cdot HCl$: C 70.52, H 7.40, N 2.42; found: C 70.58, H 7.67, N 2.34.

2,9-Bis(3,4,3″,4″,3⁗,4⁗-hexabutyl-[2,2′:5′,2″:5″,2‴:5‴,2⁗]-quinquethien-5-yl)[1,10]phenanthroline (15) and 2,2′-(3,4,3″,4″,3⁗,4⁗-hexabutyl-[2,2′:5′,2″:5″,2‴:5‴,2⁗]-quinquethien-5,5⁗-diyl)bis[9-(3,4,3″,4″,3⁗,4⁗-hexabutyl-[2,2′:5′,2″:5″,2‴:5‴,2⁗]-quinquethien-5-yl)-[1,10]phenanthroline (16)

Quinquethiophene **4** (2.16 g, 2.88 mmol) in THF (30 mL) was reacted with *n*-BuLi in hexane (1.81 mL, 2.88 mmol) at −78 °C. After stirring for 1 h, dry $ZnCl_2$ (432 mg, 3.17 mmol) in THF (4 mL) was added and stirred for 30 min and an additional 30 min after removing the cooling bath. In a second flask, 2,9-diiodophenanthroline **14** (622 mg, 1.44 mmol) and $Pd[PPh_3]_4$ (83.2 mg, 72.0 μmol) were stirred in THF (10 mL) and the zinc organic solution was transferred to this slurry by means of the double ended needle technique. After stirring for 24 h at rt, the reaction was quenched by adding aqueous ammonia. The organic phase was separated, the aqueous residue washed several times with CH_2Cl_2. After drying and evaporation of the combined organic phases, the oily product was purified by flash chromatography (silica, hexane–THF 90 : 10) to gave **15** (810 mg, 34%) as a orange coloured solid. ^{1}H-NMR ([D]chloroform): $\delta = 8.21$ (d, $^3J = 8.5$ Hz, 2 H, H-4), 7.91 (d, $^3J = 8.4$ Hz, 2 H, H-3), 7.70 (s, 2 H, H-5), 7.28 (d, $^3J = 3.7$ Hz, 2 H, H-B′), 7.13 (d, $^3J = 3.8$ Hz, 2 H, H-C′), 7.09 (d, $^3J = 3.8$ Hz, 2 H, H-B‴), 7.05 (d, $^3J = 3.8$ Hz, 2 H, H-C‴), 6.88 (s, 2 H, H-D‴), 3.37 (t, $^3J = 8.1$ Hz, 4 H, H-a), 2.90 (t, $^3J = 8.3$ Hz, 4 H, H-a′), 2.77 (m, 12 H, H-a″,a‴,a⁗), 2.56 (t, $^3J = 7.8$ Hz, 4 H, H-a′′′′′), 1.57 (m, 48 H, H-b to H-b′′′′′, H-c to H-c′′′′′), 0.95 (m, 36 H, H-d to H-d′′′′′); ^{13}C-NMR ([D]chloroform): $\delta = 153.5$, 146.0, 143.7, 143.2, 140.8, 140.3, 140.2, 139.0, 138.1, 136.88, 136.86, 136.4, 136.1, 135.9, 133.0, 131.0, 130.1, 130.0, 127.3, 126.20, 126.18, 126.1, 126.0, 125.7, 121.3, 119.2, 33.2, 33.10, 33.07, 33.0, 32.8, 32.0, 31.6, 30.4, 29.8, 29.1, 28.1, 27.9, 27.7, 23.2, 23.13, 23.09, 22.83, 22.79, 14.14, 14.12, 14.07, 14.05, 14.03, 14.0; MS (MALDI-TOF): m/z 1675 $[M + H]^+$; elemental analysis (%) calcd for $C_{100}H_{124}N_2S_{10}$: C 71.72, H 7.46, N 1.67; found: C 71.95, H 7.58, N 1.59.

Purging of the column with hexane–THF 60 : 40 and subsequent flash chromatography (silica, petroleum ether–CH_2Cl_2 45 : 55) gave by-product **16** (346 mg, 14%) as a red solid. Mp: 74 °C; ^{1}H-NMR ([D]chloroform): $\delta = 8.21$ (d, $^3J = 8.4$ Hz, 2 H, H-4), 8.20 (d, $^3J = 8.4$ Hz, 2 H, H-7), 7.91 (d, $^3J = 8.4$ Hz, 2 H, H-3), 7.90 (d, $^3J = 8.4$ Hz, 2 H, H-8), 7.70 (s, 4 H, H-5 and H-6), 7.28 (d, $^3J = 3.8$ Hz, 2 H, H-B′), 7.27 (d, $^3J = 3.8$ Hz, H-C′), 7.14 (d, $^3J = 3.8$ Hz, 2 H, H-B′), 7.13 (d, $^3J = 3.8$ Hz, 2 H, H-Γ′), 7.09 (d, $^3J = 3.8$ Hz, 2 H, H-B‴), 7.06 (d, $^3J = 3.9$ Hz, 2 H, H-Γ‴), 6.86 (s, 2 H, H-δ⁗), 3.35–3.43 (m, 8 H, H-a and H-α), 2.88–2.92 (m, 8 H, H-a′ and H-α′), 2.73–2.81 (m, 16 H, H-a″ and H-α″ to H-α⁗), 2.54 (t, $^3J = 7.7$ Hz, 4 H, H-α′′′′′), 1.43–1.70 (m, 72 H, H-b to b″, H-c to c″, H-β to β′′′′′, H-γ to γ′′′′′), 0.84–1.04 (m, 54 H, H-d to d″, H-δ to δ′′′′′); ^{13}C-NMR ([D]chloroform): $\delta = 153.54$, 153.47, 146.0, 143.7, 143.4, 143.2, 140.84, 140.80, 140.3, 140.2, 139.0, 138.0, 137.8, 136.9, 136.8, 136.4, 136.2, 135.9, 133.0, 132.96, 131.0, 130.1, 130.0, 127.3, 126.2, 126.1, 126.0, 125.7, 121.4, 121.3, 119.2, 33.23, 33.20, 33.1, 33.07, 32.8, 32.0, 29.0, 28.1, 27.9, 27.7, 23.2, 23.12, 23.08, 22.8, 14.12, 14.07, 14.03, 14.0; MS (MALDI-TOF): m/z 2600 $[M + H]^+$; elemental analysis (%) calcd for $C_{156}H_{188}N_4S_{15}$: C 72.06, H 7.29, N 2.15; found: C 71.97, H 7.34, N 2.06.

2,2′-(3,4,3″,4″-Tetrabutyl-[2,2′:5′,2″]terthien-5,5″-diyl)bis-[1,10]phenanthroline (17)

Terthiophene **3** (473 mg, 1.00 mmol) in THF (5 mL) was reacted with *n*-BuLi in hexanes (1.26 mL, 2.00 mmol) at −78 °C. After stirring for 2 h, dry $ZnCl_2$ (300 mg, 2.20 mmol) in THF (3 mL) was added at −78 °C and stirred for 30 min at −78 °C and an additional 30 min after removing the cooling bath. Iodophenanthroline **13** (612 mg, 2.00 mmol) and $Pd[PPh_3]_4$ (116 mg, 100 μmol) were stirred in THF (5 mL) in a second flask and the zinc organic solution was transferred to this slurry by means of the double ended needle technique. After 24 h at rt, the reaction was quenched by adding aqueous ammonia. The organic phase was separated, the aqueous residue washed several times with CH_2Cl_2. After drying and evaporation, the oily product was purified by flash chromatography (silica, hexanes–THF 65 : 35) and gave two major products **17** (464 mg, 56%) as an orange coloured solid and **9** (222 mg, 34%) as a yellow solid. For **17**: Mp: 154 °C; ^{1}H-NMR ([D]chloroform): $\delta = 9.19$ (dd, $^3J = 4.3$ Hz, $^4J = 1.7$ Hz, 2 H, H-9), 8.21 (d, $^3J = 8.4$ Hz, 2 H, H-4), 8.19 (dd, $^3J = 8.0$ Hz, $^4J = 1.7$ Hz, 2 H, H-7), 7.88 (d, $^3J = 8.3$ Hz, 2 H, H-3), 7.74 (d, $^3J = 8.8$ Hz, 2 H, H-6), 7.71 (d, $^3J = 8.7$ Hz, 2 H, H-5), 7.59 (dd, $^3J = 8.1$ Hz, $^4J = 4.3$ Hz, 2 H, H-8), 7.25 (s, 2 H, H-B′), 3.12 (t, $^3J = 8.2$ Hz, 4 H, H-a), 2.86 (t, $^3J = 8.1$ Hz, 4 H, H-a′), 1.62–1.71 (m, 8 H, H-b,b′), 1.42–1.56 (m, 8 H, H-c,c′), 1.00 (t, $^3J = 7.3$ Hz, 6 H, H-d), 0.92 (t, $^3J = 7.3$ Hz, 6 H, H-d′); ^{13}C-NMR ([D]chloroform): $\delta = 153.8$, 150.4, 146.4, 146.3, 143.0, 140.7, 137.4, 136.7, 136.4, 136.0, 132.8, 129.1, 126.9, 126.5, 126.3, 126.2, 123.0, 122.2, 33.2, 33.1, 28.0, 23.2, 23.17, 14.1, 14.0; MS (MALDI-TOF): m/z 829 $[M + H]^+$; elemental analysis (%) calcd for $C_{52}H_{52}N_4S_3$: C 75.32, H 6.32, N 6.76; found: C 75.31, H 6.34, N 6.64.

2,2′-(3,4,3″,4″,3⁗,4⁗-Hexabutyl-[2,2′:5′,2″:5″,2‴:5‴,2⁗]-quinquethien-5,5⁗-diyl)bis-[1,10]phenanthroline (18) and 2-(3,4,3″,4″,3⁗,4⁗-Hexabutyl-[2,2′:5′,2″:5″,2‴:5‴,2⁗]-quinquethien-5-yl)-[1,10]phenanthroline (19)

Quinquethiophene **4** (995 mg, 1.33 mmol) in THF (10 mL) was reacted with *n*-BuLi in hexane (1.67 mL, 2.66 mmol) at −78 °C. After stirring for 3 h, dry $ZnCl_2$ (399 mg, 2.93 mmol) in THF (4 mL) was added and stirred for 30 min and an additional 30 min after removing the cooling bath. In a second flask, 2-iodophenanthroline **13** (814 mg, 2.66 mmol) and $Pd[PPh_3]_4$ (76.8 mg, 66.5 μmol) were stirred in THF (5 mL) and the zinc organic solution was transferred to this slurry by means of the double ended needle technique. After stirring for 20 h at rt, the reaction was quenched by adding aqueous ammonia. The organic phase was separated, the aqueous residue washed several times with CH_2Cl_2. After drying and evaporation of the combined organic phases, the oily product was purified by flash chromatography (silica, hexane–THF 65 : 35) to give **18** (401 mg,

27%) as a red solid. Mp: 166 °C; ^{1}H-NMR ([D]chloroform): δ = 9.20 (dd, ^3J = 4.3 Hz, ^4J = 1.8 Hz, 2 H, H-9), 8.21 (d, ^3J = 8.6 Hz, 2 H, H-4), 8.20 (dd, ^3J = 8.1 Hz, ^4J = 1.8 Hz, 2 H, H-7), 7.88 (d, ^3J = 8.4 Hz, 2 H, H-3), 7.75 (d, ^3J = 8.8 Hz, 2 H, H-6), 7.71 (d, ^3J = 8.8 Hz, 2 H, H-5), 7.60 (dd, ^3J = 8.0 Hz, ^4J = 4.3 Hz, 2 H, H-8), 7.23 (d, ^3J = 3.8 Hz, 2 H, H-B′), 7.15 (d, ^3J = 3.6 Hz, 2 H, H-C′), 3.10 (t, ^3J = 8.1 Hz, 4 H, H-a), 2.78–2.87 (m, 8 H, H-a′ and H-a″), 1.60–1.70 (m, 12 H, H-b to b″), 1.41–1.55 (m, 12 H, H-c to c″), 0.98–1.02 (m, 12 H, H-d and H-d′), 0.90–1.02 (t, ^3J = 7.3 Hz, 6 H, H-d″); ^{13}C-NMR ([D]chloroform): δ = 153.7, 150.4, 146.3, 146.2, 142.8, 140.6, 140.3, 137.4, 136.5, 136.4, 136.1, 135.9, 132.7, 130.0, 129.1, 126.9, 126.4, 126.3, 126.2, 126.1, 125.4, 122.2, 33.15, 33.07, 28.1, 28.0, 23.19, 23.18, 23.15, 14.05, 14.0; MS (MALDI-TOF): m/z 1105 [M + H]$^+$; elemental analysis (%) calcd for $C_{68}H_{72}N_4S_5$: C 73.87, H 6.56, N 5.07; found: C 73.85, H 6.60, N 4.99.

Repeated chromatography of the preliminary eluted material (silica, CH_2Cl_2) gave **19** (556 mg, 45%) as an orange coloured solid. ^{1}H-NMR ([D]chloroform): δ = 9.21 (dd, ^3J = 4.3 Hz, ^4J = 1.8 Hz, 1 H, H-9), 8.20 (d, ^3J = 8.3 Hz, 1 H, H-4), 8.19 (dd, ^3J = 8.1 Hz, ^4J = 1.8 Hz, 1 H, H-7), 7.88 (d, ^3J = 8.6 Hz, 1 H, H-3), 7.73 (d, ^3J = 8.8 Hz, 1 H, H-6), 7.70 (d, ^3J = 8.8 Hz, 1 H, H-5), 7.59 (dd, ^3J = 8.1 Hz, ^4J = 4.3 Hz, 1 H, H-8), 7.24 (d, ^3J = 3.8 Hz, 1 H, H-B′), 7.15 (d, ^3J = 3.8 Hz, 1 H, H-C′), 7.12 (d, ^3J = 3.8 Hz, 1 H, H-B‴), 7.08 (d, ^3J = 3.8 Hz, 1 H, H-C‴), 6.88 (s, 1 H, H-D⁗), 3.12 (t, ^3J = 8.1 Hz, 2 H, H-a), 2.87 (t, ^3J = 8.1 Hz, 2 H, H-a′), 2.74–2.82 (m, 6 H, H-a″ to a⁗), 2.56 (t, ^3J = 7.8 Hz, 2 H, H-a′′′′′), 1.43–1.70 (m, 24 H, H-b to b′′′′′ and H-c to c′′′′′), 0.92–1.03 (m, 18 H, H-d to d′′′′′); ^{13}C-NMR ([D]chloroform): δ = 153.6, 150.4, 146.3, 146.2, 143.6, 142.8, 140.6, 140.2, 140.1, 138.9, 137.4, 136.8, 136.5, 136.4, 136.1, 135.83, 135.80, 132.7, 130.9, 130.0, 129.9, 129.1, 126.9, 126.3, 126.2, 126.14, 126.08, 126.0, 125.9, 122.9, 122.1, 119.2, 33.1, 33.04. 33.02, 33.0, 32.8, 31.9, 29.0, 28.1, 28.0, 27.6, 23.2, 23.13, 23.07, 22.8, 14.1, 14.01, 13.99, 13.97; MS (MALDI-TOF): m/z 927 [M + H]$^+$; elemental analysis (%) calcd for $C_{56}H_{66}N_2S_5$: C 72.52, H 7.17, N 3.02; found: C 72.52, H 7.23, N 2.98.

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