Conjugated Macrocycles

DOI: 10.1002/anie.200900101

Giant Cyclo[*n*]thiophenes with Extended π Conjugation

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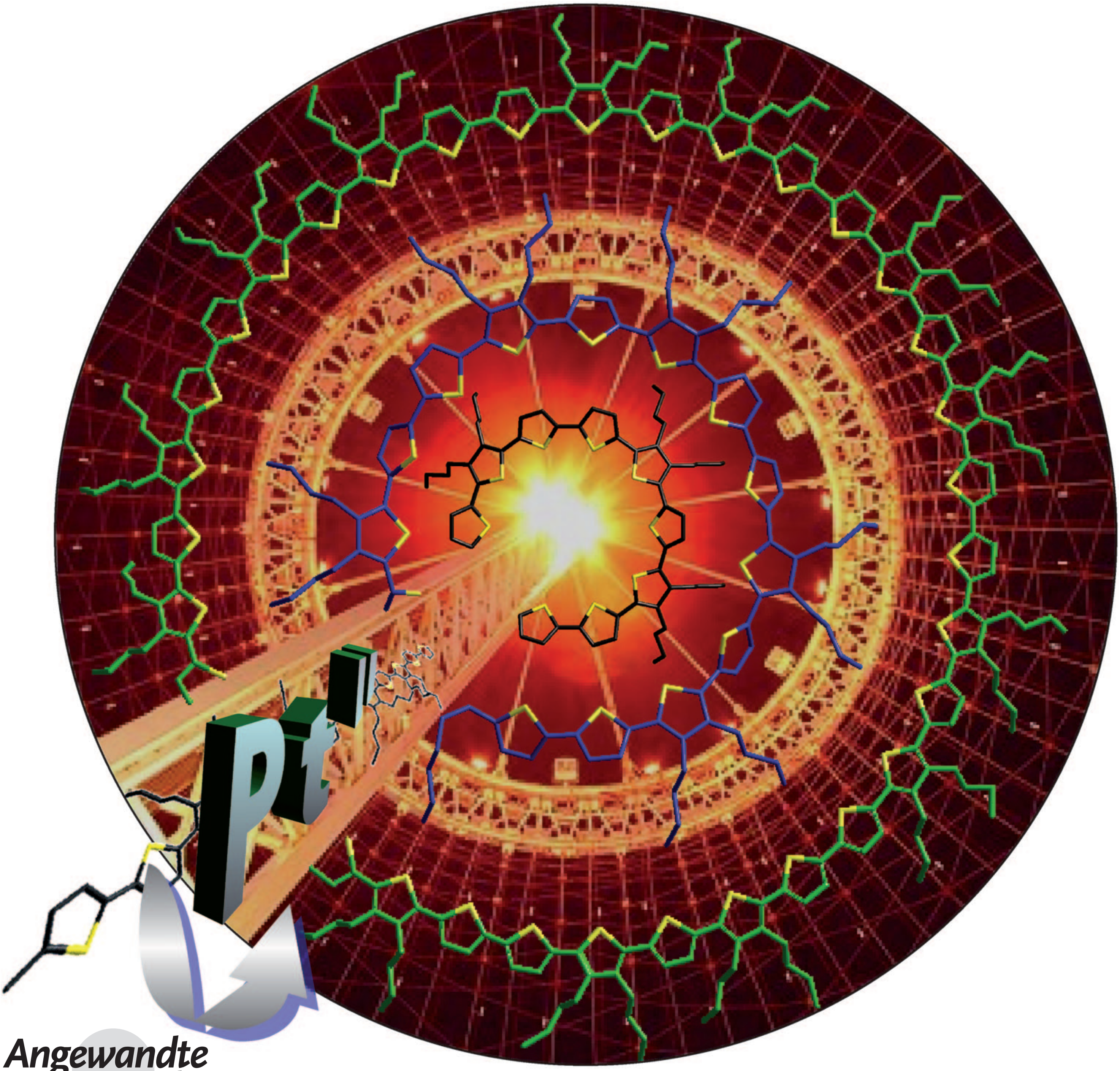

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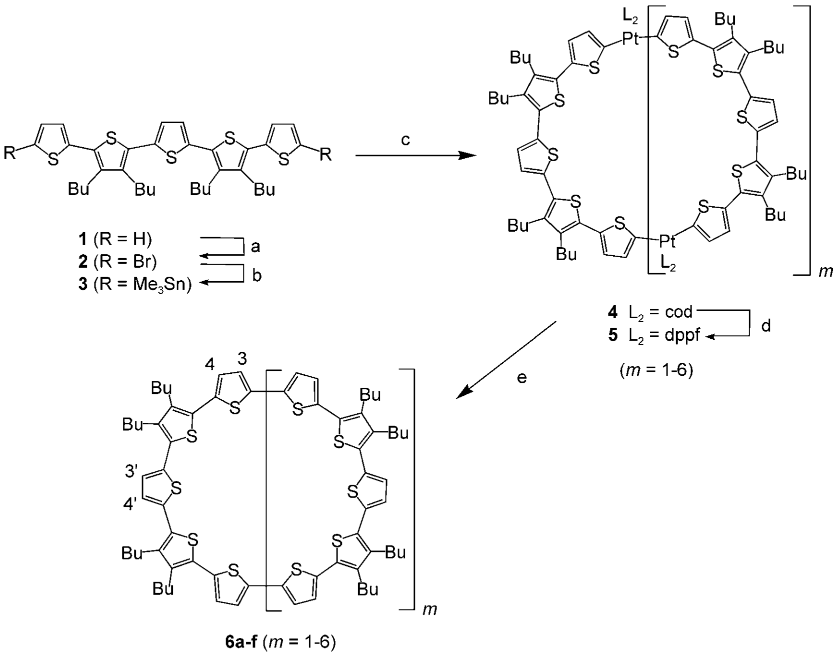
Oligo- and polythiophenes are promising materials for organic electronics because of their outstanding optoelectronic and charge-transport properties.[1] A wealth of thiophene-based molecular architectures of various dimensionalities and shapes have been prepared and extensively studied.[2] Among them, shape-persistent and circularly conjugated cyclo[*n*]thiophenes (C*n*T)[3] are not only theoretically most interesting objects,[4] but also represent a novel class of organic semiconductors with fascinating optical[5] and self-assembling properties.[6] Synthesis however turned out to be a challenge with very limited availability of material, a typical phenomenon for (conjugated) macrocycles.[7]



Scheme 1. a) 2.0 equivalents NBS, DMF, 0 °C to room temperature; b) 1. 2.0 equivalents *n*BuLi, THF, −78 °C, 1 h; 2. 2.0 equivalents Me_3SnCl, −78 °C to room temperature, 2 h; c) 1.0 equivalent $[Pt(cod)Cl_2]$, CH_2Cl_2, reflux for 5 days; d) 1.0 equivalent dppf, CH_2Cl_2, room temperature, 4 h; e) 140 °C in toluene, 8 h. NBS = *N*-bromosuccinimide.

In our first approach, C12T, C16T, and C18T were prepared from terminally ethynylated oligothiophenes but only in low yields and quantities because of a statistical macrocyclization under high-dilution conditions.[3a,c] Reaction of the same ethynylated precursors and Pt^{II} complexes led to stable coordinatively bound diplatinum macrocycles in excellent yields. Oxidatively induced reductive elimination of the Pt^{II} centers under simultaneous formation of C−C bonds gave butadiyne-bridged macrocycles, which, as in the statistical method, had to be transformed to C*n*Ts by reaction with sulfide anions. By this 'metal-template approach' C8T was the smallest member of the series and was obtained in an improved, but still low, overall yield of around 10 % which was limited due to side reactions.[3b,c] A more direct general coupling method was recently developed for stable platinum(II) oligothienyl complexes which undergo controlled reductive elimination and homocoupling to linear oligothiophenes.[8]

This result was now the basis for the development of a novel and highly effective "one-pot" synthesis of cyclo[*n*]thiophenes, furnishing a series of individual macrocycles C*n*T with unprecedented giant sizes up to 35 thiophene rings in an excellent overall yield of around 60 %. For the first time, C*n*Ts are available on a preparative scale, but also members with odd numbers of repeating units can be prepared as well.

Our synthetic route started from alkylated quinquethiophene **1**[9] which is readily converted into stannylated intermediate **3** via the corresponding dibromo derivative **2** (Scheme 1). Inspired by the report by Eaborn et al. on the interaction of (cycloocta-1,5-diene)platinum dichloride $[Pt(cod)Cl_2]$ and aryltrimethylstannanes,[10] oligothiophene **3** was treated with equimolar amounts of this Pt^{II} complex. After refluxing in dichloromethane a mixture of multinuclear macrocyclic (cod)Pt^{II} oligothienyl complexes **4** were formed in high yield (over 80 %) and studied by ^1H NMR spectroscopy. To facilitate metal elimination, an in situ ligand exchange of the cod ligand in complexes **4** was performed by reaction with 1,1′-bis(diphenylphosphino)ferrocene (dppf) in a 1:1 molar ratio to quantitatively yield corresponding macrocyclic (dppf)Pt^{II} oligothienyl complexes **5**. Without further purification, the solvent was exchanged for toluene and the reaction mixture heated to 140 °C in a sealed tube. By thermal activation, reductive elimination of the platinum corners smoothly proceeded under C−C bond and macrocycle formation. Size-exclusion chromatography of the crude product mixture delivered a full series of pure C*n*Ts **6a–f** in various sizes spanning from smallest cyclodimer C10T to giant C35T, in an overall yield of isolated products of 57 % (see Supporting Information, SI). The macrocycles **6** were eluted in the order: C35T (**6f**; 1.5 %),[11] cyclohexamer C30T (**6e**; 2.6 %), cyclopentamer C25T (**6d**; 8.8 %), cyclotetramer C20T (**6c**; 14.8 %), cyclotrimer C15T (**6b**; 25.3 %) as the major product, and C10T (**6a**; 4 %). As main by-product linear decithiophene (10T) **7** was finally separated in 5.9 % yield (Table 1). Thus, in the critical reaction step, in which the Pt^{II} corners act both as template and angular building block, macrocyclization to Pt^{II} complexes **4** is favored over oligomerization, although the reaction conditions were mild and high dilution was not used.

Structural confirmation of C*n*Ts **6** came from NMR spectroscopy and high-resolution mass spectrometry. In contrast to linear oligomer **7**, ^1H NMR spectra of C*n*Ts show only a few signals owing to the highly symmetrical

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200900101.

Table 1: Yields, optical and redox data of cyclothiophenes **6a–f** and linear decithiophene **7**.

C*n*T	Yield [%]	λ_{max}^{abs} [nm][a]	ε [L mol^{-1} cm^{-1}][a]	λ_{max}^{em} [nm][b]	λ'_{onset} [nm][a,c]	E' [eV][c]	E_1^0 [V][d]
6a	4.0	417 (≈490)[e]	86000	629, 685	471	2.63	0.03
6b	25.3	423	119000	582, 603	510	2.43	0.08
6c	14.8	434	130000	572, 603	528	2.35	0.08
6d	8.8	440	163000	570, 607	533	2.33	0.09
6e	2.6	444	183000	568, 607	538	2.30	0.16
6f	1.5	445	196000	567, 604	550	2.26	0.16
7	5.9	435	51000	553, 587	519	2.39	0.25

[a] In CH_2Cl_2. [b]Highest intensity values are underlined. [c] Taken from the intense ($S_0 \rightarrow S_2$) absorption band. [d] First oxidation potential in TCE/0.1 M $TBAPF_6$ at 295 K, v = 20 mV s^{-1}, potentials versus ferrocene/ferrocenium (Fc/Fc$^+$) couple. TCE: tetrachloroethane, $TBAPF_6$: tetrabutylammonium hexafluorophosphate. [e] Shoulder; weak ($S_0 \rightarrow S_1$) absorption band.

structure of the compounds. The spectra are characterized by the lack of resonances for terminal thiophene α-protons and the presence of two doublets assigned to H-3, H-4 and a singlet for H-3′, H-4′. With the increasing size of the macrocycles, the chemical shifts of the signals approximate to those of linear analogue **7** suggesting increasing conformational flexibility of the ring system. For the smallest member, C10T (**6a**) which has the most rigid structure, signals for H-3′, H-4′, and H4 are shifted upfield by approximately 0.1 ppm (compared to **7**) indicating conformational twists of various thiophenes (see Supporting Information). In agreement, semi-empirical calculations on **6a** showed *syn* conformations of all the thiophene rings with dihedral inter-ring angles of 15.7 to 48.9 degrees so that the required curvature is achieved. The next higher homologue, C15T (**6b**), is rather flat.

In ESI-FTICR mass spectra obtained from dichloromethane solutions of macrocycles **6a–d**, molecular ions were detected in different charge states, in the case of C25T (**6d**) these ranged from a radical cation ($M^{\cdot+}$) up to a radical trication ($M^{\cdot 3+}$; Figure 1). Larger macrocycles tend to stabilize a higher number of charges. Thus, the ionization process is an easy oxidation of C*n*Ts at the tip of the ESI needle. Furthermore, ions for oligomeric aggregates from dimers (M_2^{x+}) to pentamers (M_5^{x+}) were detected in different charge states reaching quite high molecular masses of up to around 16 kDa.

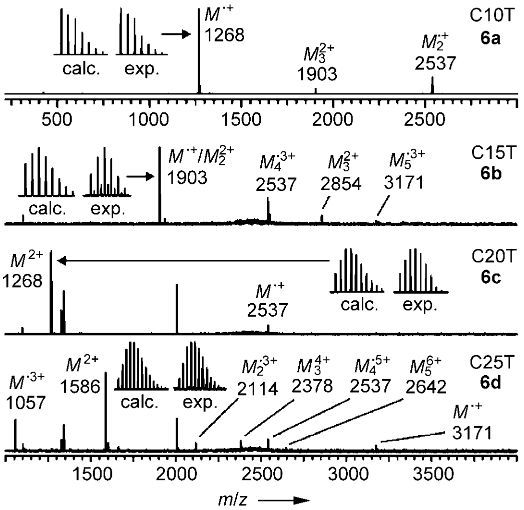

Figure 1. ESI-FTICR mass spectra of **6a–d** (from top to bottom). Insets show calculated and experimental isotope patterns. For C15T (**6b**), a superposition of singly charged monomer and doubly charged dimer is observed.

Dilution as well as tandem MS experiments confirm the noncovalent nature of these ionized oligomeric aggregates. They are formed during the ESI process: After oxidation at the ESI needle, electron-poor cations and electron-rich neutral macrocycles form non-covalent complexes (see Supporting Information). Notably, for linear 10T (**7**) there is only one peak which is at *m*/*z* 1270 and is assigned to the monomer radical cation.

The optoelectronic properties of the novel series of conjugated macrocycles **6** were investigated to obtain structure–property relationships. Absorption and emission maxima, optical energy gaps, and oxidation potentials are given in Table 1 along with those of the linear analogue **7**. The high symmetry of the cyclic structures influences their photophysical properties: the absorption maxima correspond to the $S_0 \rightarrow S_2$ electronic transition[5] and are progressively red-shifted and intensified with increasing ring size (see Supporting Information). The same trend can be observed for the onset absorption (λ'_{onset}), and the calculated optical band gaps ($E' \approx 2.26$–2.63 eV) lie in the range of band gaps for linear semiconducting oligo- and polythiophenes. The emission maxima for **6c–f** are not significantly different whereas the smaller cycles **6a** and **6b** show a much weaker fluorescence band that is shifted to longer wavelengths, as a result of the high ring strain.[12] The distorted conformation of the smallest cycle **6a** is also the origin of the much narrower absorption band and the emergence of a new lower energy transition ($S_0 \rightarrow S_1$), which can be directly correlated with theoretical predictions.[5]

The unusual ease with which our macrocycles undergo oxidation and aggregation, which was recently predicted theoretically for C8T,[4e] was confirmed by cyclic voltammetry (CV) of the full series **6a–f** (Table 1). Compared to linear decithiophene **7** all C*n*Ts exhibited a pronounced lower first oxidation potential which increases with increasing ring size and slowly approaches that of the linear analogue **7**. The very low value of 0.03 V for the smallest cycle **6a** is attributed to a raised HOMO level resulting from favorable *syn* conformations of the thiophene units.[4a,13] The complex and symmetrical CV of **6a** is shown in Figure 2 along with that of linear **7** and is characterized by four reversible one-electron oxidation steps E_1^0–E_4^0 (0.03 V, 0.24/0.31 V, 0.76/0.84 V, 1.06 V) indicating the formation of species from stable radical cations to tetracations. Further analysis of the CV revealed preferential formation of equilibria between charged monomeric and dimeric species as a result of favorable intermolecular π–π interactions of the macrocycles which are less pronounced for linear **7** and in excellent agreement with the mass spectrometry measurements.[14] Dimerization of radical cat-

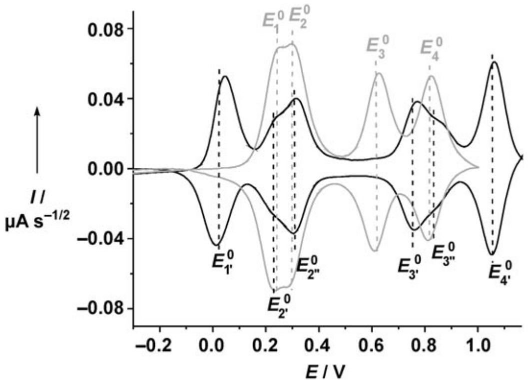

Figure 2. Deconvoluted cyclic voltammogram of **6a** (black line) and **7** (gray line) normalized to the same concentration (($c = 7.8 \times 10^{-4}$ M in TCE/0.1 M TBAPF$_6$, 295 K, v = 20 mV s^{-1}, potential E versus Fc/Fc$^+$.

ions has been reported for a variety of π-conjugated oligomers and was intensively discussed in the frame of charge transport in organic conductors.[15] We ascribe the behavior of the macrocycles to a combination of oxidation and aggregation steps, which concurs with the results in mass spectrometry measurements.

A general new approach to unprecedented giant cyclic oligothiophenes with interesting optoelectronic and supramolecular properties has been developed. The key to the high-yielding reaction sequence was use of Pt^{II} centers playing a decisive dual role as template and angle control in the crucial macrocyclization step and as reactive center in the final reductive elimination and cross-coupling step. In comparison to linear analogue **7**, interesting structure–property relationships were found for the series of cyclothiophenes **6a–f** which clearly depend on ring size. In particular, the pronounced lower oxidation potentials of the cyclic structures and their aggregation tendency in charged states are corroborated by the ease of ionization/oxidation and aggregation detected in the mass spectra. These results indicate promising properties for the use of cyclothiophenes as novel organic electronic materials with increased structural complexity. Macrocyclization reactions involving Pt^{II} complexes of other oligothiophenes and π-conjugated building blocks are currently under investigation to show the generality of the newly developed “one-pot” synthesis.

Received: January 7, 2009
Revised: April 29, 2009

Keywords: conjugation · macrocycles · oligothiophenes · platinum · self-assembly

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