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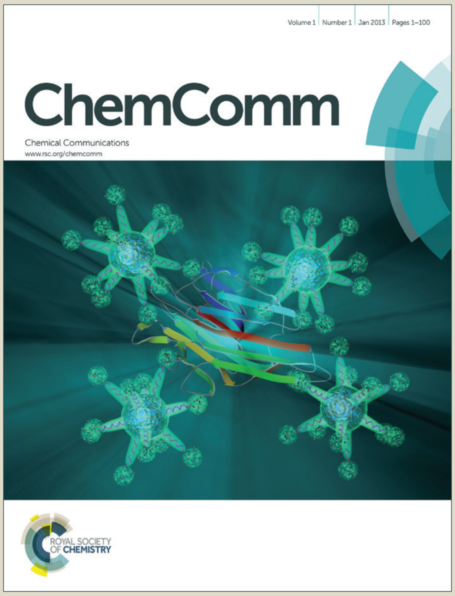

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A Cyclic Octithiophene Containing β,β′-Linkages

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A cyclic octithiophene containing two β,β′-linkages was synthesized. Due to the large structural change in the excited state, this compound exhibited bathochromically shifted fluorescence. It also showed a small difference between the first and second oxidation potentials, indicative of spin delocalization through the β,β′-linkage in the one electron-oxidized state.

Oligothiophenes represent a well-established scaffold for π-electron materials, as they demonstrate great potential for a wide variety of applications in organic electronics, including light-emitting diodes, field-effect transistors, and photovoltaics.[1] Most of the oligothiophenes reported to date contain thiophene units catenated in the α-positions, *i.e. via* α,α′-linkages, mostly because the π-conjugation is effectively extended through these α,α′-linkages. Apart from a number of linear α-oligothiophenes, cyclic α-oligothiophenes[2] and related macrocycles[3] have recently attracted substantial attention due to their intriguing π-conjugation in the circular topology. On the other hand, linkage in the β-positions affords oligothiophenes with swivel-cruciform,[4] twisted,[5] branched,[6] or tubular structures.[7] These characteristic structures are advantageous as they improve the solubility in common organic solvents[4] and afford control over the packing structure in the condensed phase.[6a]

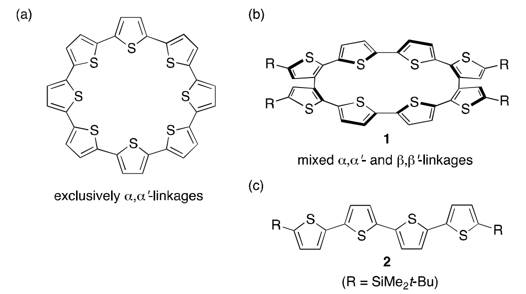
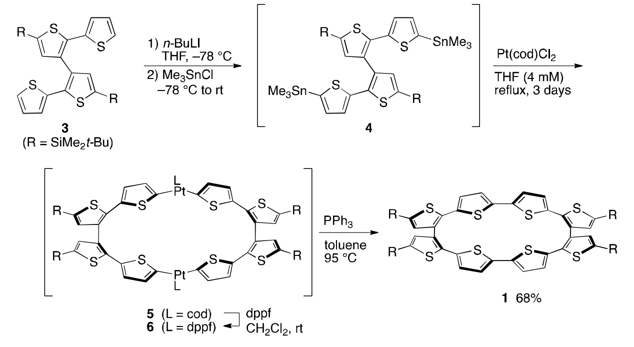


Fig. 1. (a), (b) Connection modes in cyclic oligothiophenes, and (c) a substructure of the cyclic oligothiophene **1**.

For this study, we designed a new type of cyclic oligothiophene, namely cyclic octithiophene **1**, containing two β,β′-linkages (Fig. 1). This compound can be regarded as the cyclic dimer of α-quaterthiophenes. In contrast to the cyclic α-oligothiophenes, which serve as model compounds for polythiophene with infinite π-conjugation, compound **1** should furnish the opportunity to investigate the intrinsic nature of the π-conjugation *via* β,β′-linkages. During the course of this study, Sannicolò and co-workers reported similar cyclic oligothiophenes, cyclic oligo(sexithiophene)s connected *via* 3,3′-bi(benzothiophene) units, which represent a new type of chiral macrocycles.[8] A notable difference to the compounds in their study is that compound **1** consists of merely eight thiophene rings. In such a small ring skeleton, the π-conjugation *via* the β,β′-linkages should affect the electronic properties of **1** to a greater extent. Herein, the synthesis of cyclic octithiophene **1**, its crystal structure, and a comparison of its photophysical and electrochemical properties with those of the α-quaterthiophene **2** are reported. The combination of detailed experimental and theoretical studies allows a in-depth description of the π-conjugation through the β,β′-linkages in the excited state as well as in the one electron-oxidized state.



Scheme 1 One-pot synthesis of cyclic octithiophene **1**

The targeted cyclic oligothiophene **1** was obtained from the dimerization of quaterthiophene **3** *via* the formation of a cyclic diarylplatinum complex **5**, followed by a reductive elimination (Scheme 1).[2f,9,10,11] This method is well known as an efficient synthetic route to macrocyclic π-conjugated skeletons, such as cyclic α-oligothiophenes,[2f] cyclic oligo(*p*-phenylene)s,[9] and related compounds.[10,11] Quaterthiophene **3** was chosen as the starting material for the synthesis of **1**, as it already contains a pre-established β,β′-linkage between two thiophene moieties. Compound **3** was dilithiated with *n*-BuLi, followed by treatment with Me_3SnCl. Distannylated quaterthiophene **4** was subsequently treated with $Pt(cod)Cl_2$ in THF under high dilution conditions (4 mM, reflux, 3 d) to produce a precipitate, which contained diarylplatinum complex **5**. This mixture was treated with 1,1′-bis(diphenylphosphino)ferrocene (dppf) in order to substitute the 1,5-cyclooctadiene (cod) ligand. An ensuing treatment with PPh_3[12] successfully promoted a reductive elimination to yield cyclic octithiophene **1** in 68%.

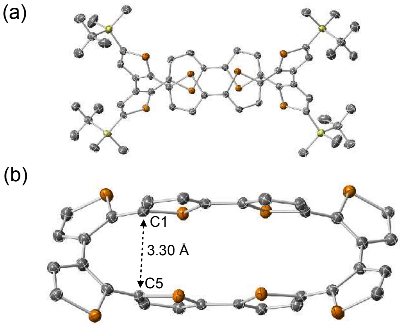


Fig. 2. X-ray crystal structure of **1** (thermal ellipsoids at 50% probability): (a) a top view and (b) a side view; all hydrogen atoms, as well as the silyl groups in (b) are omitted for clarity (colour code: grey = C, orange = S, yellow = Si).

Table 1. Photophysical and electrochemical properties of **1** and **2** in CH_2Cl_2

Cmpd	λ_{abs} [nm]^a	ε [dm^3 mol^{-1}cm^{-1}]^b	λ_{em} [nm]^c	$\Phi_{max}{}^d$	$E_{1/2}{}^{ox}$ [V]^e
1	367	5.27	516	0.02	+0.50 +0.77 +1.01
2	402	3.98	465	0.18	+0.48 +0.82

[a] Maximum absorption wavelengths; [b] molar extinction coefficients; [c] maximum emission wavelengths of the highest energy fluorescence band when exciting **1** (370 nm) and **2** (400 nm); [d] absolute fluorescence quantum yield determined by a calibrated integrating sphere system; [e] oxidation potential vs. Fc/Fc$^+$; CV measurements were conducted in CH_2Cl_2 with Bu_4NPF_6 (0.1 M) as the supporting electrolyte at a scan rate of 0.1 V s^{-1}.

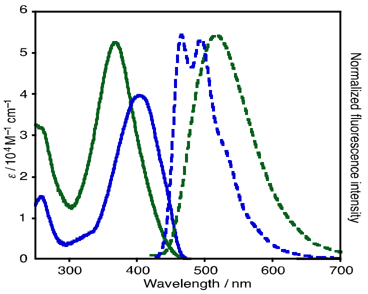


Fig. 3. Absorption (solid line) and fluorescence spectra (dashed line) of **1** (green) and **2** (blue) in CH_2Cl_2.

Single crystals of **1** suitable for X-ray crystallographic analyses were obtained by recrystallization from 1-methylnaphthalene. In the crystal structure, **1** adopts an elliptical shape with two α-quaterthiophene substructures along the major axis (Fig. 2). The molecular framework of **1** has a symmetry center and therefore no axial chirality exists in this system in contrast to the similar macrocyclic oligothiophenes.[8] Notably, both of the α-quaterthiophene substructures assume an all-*s*-cis conformation, in which the central 2,2′-bithiophene moieties exhibit high degrees of planarity, reflected in dihedral angles of 8.7(2)° between the two mean thiophene planes. Conversely, the outer 2,2′-bithiophene moieties are highly twisted, as evident from dihedral angles of 50.5(1)° and 57.9(1)° between the two mean thiophene planes. These α-quaterthiophene substructures are connected to each other *via* β□β′-linkages, whereby the 3,3′-bithiophene moieties adopt a highly twisted conformation with dihedral angles of 55.1(1)°. As a consequence of this connecting motive, the central planar 2,2′-bithiophene moieties within the α-quaterthiophene substructures are fixed in a close face-to-face fashion. The interatomic distance between the C1 and C5 atoms is only 3.30 Å, which is shorter than the sum of the van der Waals radii of two carbon atoms (3.40 Å). The variable-temperature ^1H NMR spectra of **1** showed a pair of doublet peaks for the central 2,2′-bithiophene moiety at 130 °C, whereas one of the doublet peak broadened at 40 °C (Fig. S41). This result suggests that the free rotation of the thiophene rings within this ellipsoid cyclic skeleton is partly hindered at ambient temperature.

The UV-vis absorption spectrum of **1** in CH_2Cl_2 showed an intense absorption band (λ_{abs} = 367 nm), which is by ca. 35 nm hypsochromically shifted relative to planar quaterthiophene **2**, reflecting the twisted conformation of the α-quaterthiophene substructure in **1** (Table 1 and Fig. 3). In contrast to that, the fluorescence spectra of **1** showed a significantly bathochromically shifted fluorescence band (λ_{em} = 516 nm; green) relative to that of quaterthiophene **2** (λ_{em} = 465 nm; blue). Correspondingly, the Stokes shift is significantly larger for cyclic oligothiophene **1** (7870 cm^{-1}) than for **2** (3370 cm^{-1}). The fluorescence quantum yield of **1** in CH_2Cl_2 is 0.02, and the fluorescence spectra of **1** did not show any significant solvent dependence ($\lambda_{em/toluene}$ = 518 nm; $\lambda_{em/THF}$ = 515 nm).

To gain an insight into the origin of the large Stokes shift observed for **1**, we carried out DFT calculations on model compound **1′**, where the $SiMe_2$*t*-Bu groups were substituted with $SiMe_3$ groups. Geometry optimizations at the PBE0/6-31G(d) level of theory revealed that the energetically most favourable conformation is not the one observed in the crystal structure, but one adopting a 1.5 kcal mol^{-1} more stable *s*-cis,*s*-trans,*s*-cis conformation within the α-quaterthiophene substructure. On the basis of the geometry of this conformer, TD-DFT calculations were carried out at the same level of theory. According to these, the absorption band observed for **1** at 367 nm should be assigned to the excited singlet state S_4 and is predominantly due to a HOMO–1→LUMO+1 transition, which is associated with a high oscillator strength (f = 1.67; see Table S4 and Fig. S10). On the other hand, the lowest excited singlet state (S_1) resulting from of a HOMO→LUMO+1 transition is forbidden, which is reflected in a very low f value (0.0531). Geometry optimization in S_1 was conducted at the PBE0/6-31G(d) level of theory (Fig. 4). Most notably, both of the α-quaterthiophene moieties and the 3,3′-bithiophene moieties become flattened upon changing from S_0 to S_1, which is reflected in the decrease of the dihedral angles of the two mean thiophene planes in the 3,3′-bithiophene moieties (S_0 = 55.1°, S_1 = 45.3°) (Fig. 4). In S_1, the α-quaterthiophene moieties exhibit a more pronounced quinoidal character relative to S_0. Moreover, the bond length of the β,β′-linkages in the 3,3′-bithiophene moieties is slightly contracted in S_1

(1.457 Å) compared to S_0 (1.475 Å). Consequently, the bond alternation in the entire π-conjugated skeleton in the cyclic octithiophene framework decreases in S_1, despite including the β,β′-linkages. This substantial structural change is most likely responsible for the bathochromically shifted fluorescence of **1** relative to **2**. Similar observations have been reported for other highly strained cyclic oligoarenes.[3e,13]

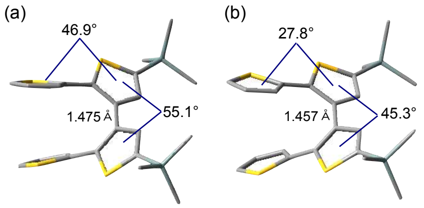


Fig. 4. Structural changes in the quaterthiophene substructures of **1′** (R = $SiMe_3$) between (a) S_0 and(b) S_1; all geometry optimizations at the PBE0/6-31G(d) level of theory.

Cyclic voltammetry (CV) measurements between –1.0 V and 1.5 V showed three-step redox waves with $E_{1/2}$ at 0.50 V, 0.77 V, and 1.01 V for **1**. For α-quaterthiophene **2**, a two-step redox wave was observed at $E_{1/2}$ = 0.48 V and 0.82 V (Fig. 5). Differential pulse voltammogram of **1** also shows three distinct peaks corresponding to the redox waves in CV (Fig S4), demonstrating that each wave is attributable to a one-electron process. The difference between the first and second oxidation potentials in **1** (0.27 V) is smaller than that in **2** (0.34 V), indicating that the π-conjugation in the radical cation $\mathbf{1}^{•+}$ is not confined within one α-quaterthiophene moiety, but extends, at least in part, over the two α-quaterthiophene moieties.

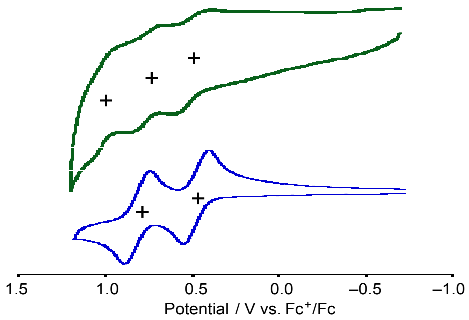


Fig. 5. Cyclic voltammograms of **1** (green) and **2** (blue) at a scan rate of 0.1 V s^{-1} in CH_2Cl_2 with Bu_4NPF_6 as the supporting electrolyte. All oxidation potentials are referenced vs. Fc/Fc^+.

To experimentally examine the π-conjugation in radical cation $\mathbf{1}^{•+}$, cyclic octithiophene **1** and quaterthiophene **2** were chemically oxidized using tris(*p*-bromophenyl)aminium hexachloroantimonate[14] and their EPR spectra were compared (Fig. 6). Upon addition of 1.1 equivalents of the oxidant to **2** in CH_2Cl_2 at ambient temperature, **2** exhibited strong absorption bands at 673 nm and 1115 nm, which seems feasible for a hitherto known quaterthiophene radical cation.[15] Compound **1** also featured emerging broad absorption bands at 659 nm and 1248 nm upon addition of 1.1 equivalents of the oxidant. These characteristic absorption bands are almost identical to those of the corresponding radical cations generated by the electrochemical oxidation (Fig. S5). As the products of the chemical oxidation of **1** and **2** are both EPR active, we concluded that the corresponding radical cations $\mathbf{1}^{•+}$ and $\mathbf{2}^{•+}$ were generated *in situ* under these conditions.[16] While the EPR spectrum of $\mathbf{2}^{•+}$ displayed a distinct hyperfine structure (*g* = 2.0023), that of $\mathbf{1}^{•+}$ exhibited a broad signal (*g* = 2.0023). The simulation of the latter EPR signal, taking account of the spin densities derived from DFT calculations (Fig. S22), gave the hyperfine coupling constants $|a_H|$ of 0.126 mT (4H) as a major contribution together with two minor coupling constants, which are much smaller than the line width of the simulated signal (0.12 mT). Since these values are relatively smaller than those of $\mathbf{2}^{•+}$ (0.26 mT, 0.23 mT 0.11 mT and 0.08 mT), the unpaired electron spin of $\mathbf{1}^{•+}$ is likely delocalized over the entire cyclic π-conjugated skeleton.

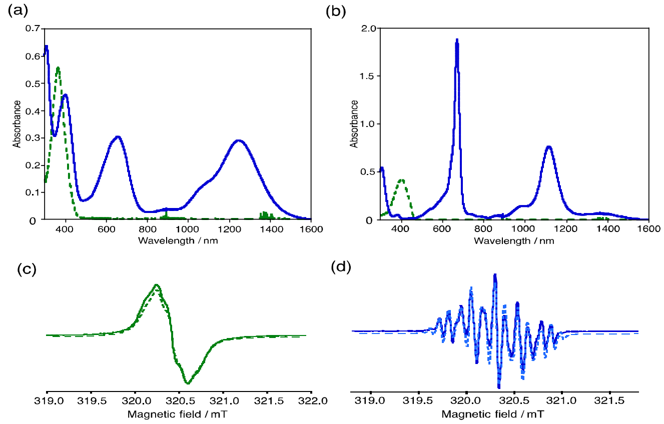


Fig. 6. UV-vis-NIR absorption spectra of (a) **1** and (b) **2** before (dashed line) and after (solid line) the addition of 1.1 equivalents of (p-$BrC_6H_4)_3N^{•+}SbCl_6^-$ in CH_2Cl_2. EPR spectra of (c) **1** and (d) **2** in CH_2Cl_2 after addition of 1.1 equivalents of (p-$BrC_6H_4)_3N^{•+}SbCl_6^-$ (solid line) and simulated spectra (dashed line).

To gain an insight into the structural features of $\mathbf{1}^{•+}$, we performed DFT calculations on model compound $\mathbf{1}'^{•+}$, whose geometry was optimized at the UB3LYP/6-31G(d) level of theory. The bond length of the β,β′-linkages in the 3,3′-bithiophene moiety (1.475 Å) was observed to be shorter than that of neutral **1′** (1.483 Å). Concomitant with this change, the degree of bond alternation in the entire cyclic π-conjugated skeleton also decreased relative to uncharged **1**. This result indicates a significant contribution of a quinoidal resonance structure to the radical cation. Indeed, the calculations demonstrated that the spin densities on the peripheral carbon atoms in $\mathbf{1}'^{•+}$ are smaller than those in $\mathbf{2}'^{•+}$. Specifically, the unpaired electron in $\mathbf{1}'^{•+}$ is delocalized over the entire cyclic skeleton. This result is in good agreement with the observation of a broad signal in the EPR spectrum.

In summary, we have successfully synthesized a cyclic octithiophene containing β,β′-linkages. Macrocycle **1** can be regarded as the dimer of α□quaterthiophenes connected *via* highly twisted 3,3′-bithiophene moieties. The change from the ground into the excited state is accompanied by a large structural change of the nonplanar cyclic structure. As a consequence, **1** exhibited a bathochromically shifted fluorescence relative to the corresponding linear α-quaterthiophene. In the radical cation state, the π-conjugation is extended through the β,β′-linkages, resulting in extensive spin delocalization. Compound **1** moreover features an intriguing elliptical structure, which is different from previously reported cyclic α-oligothiophenes. This structural particularity may ultimately lead to various interesting solid-state properties. Further studies pursuing this research avenue are currently in progress in our laboratory and their results will be disseminated in due course.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental procedures, characterization data for all new compounds, additional spectra, results of theoretical calculations and crystallographic information file (CIF) for **1**. CCDC 1043632. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c000000x/

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16 The spin concentration upon the addition of the oxidant into a 1.0 mM solution of **1** in CH_2Cl_2 was determined to be 0.53 mM by EPR measurements using the standard curve of TEMPO solution in CH_2Cl_2 (Figs. S6 and S7, and Table S3 in ESI). Since the addition of 2.0 equivalents of the oxidant resulted the increase of spin concentration to 0.9 mM, the addition of 1.1 equivalents of oxidant does not produce the over-oxidized dicationic species but likely produces the mixture of $\mathbf{1}^{\bullet+}$ and unreacted **1**.