

Cite this: *Chem. Commun.*, 2011, **47**, 11023–11025

www.rsc.org/chemcomm

COMMUNICATION

An oxidative coupling route to macrocyclic thiophenes and its application in the synthesis of a donor/acceptor hybrid molecule†

Stefan K. Maier, Stefan-S. Jester, Ute Müller, Walter M. Müller and Sigurd Höger*

Received 29th July 2011, Accepted 26th August 2011

DOI: 10.1039/c1cc14664e

A route towards phenylene-bithiophene macrocycles via oxidative thiophene coupling under pseudo-high dilution conditions is reported. This method is applied to the synthesis of a shape-persistent thiophene macrocycle with extraannularly attached perylenebisimide moieties that forms supramolecular aggregates at the solid/liquid interface.

Macrocycles containing thiophene segments have proven to be fascinating compounds considering their ability to form functionalised self-assembled monolayers at the solid/liquid interface that allow the epitaxial coadsorption of guest molecules such as fullerenes or metallacycles on top of the preformed macrocycle pattern.¹ Furthermore, supramolecular empty nanotubes have been observed for thiophene macrocycles in the liquid crystalline mesophases.² Besides self-assembly, the optoelectronic properties of macrocyclic thiophenes are very interesting as the *syn* configuration of adjacent thiophene units gives rise to unusual properties.³ This might become of special interest as linear oligothiophenes have proven to be prominent electron rich organic semiconductors applied as donor materials in organic solar cells. In the latter, one of the key steps is the photoinduced electron transfer from an electron rich to an electron poor organic semiconductor.⁴ For the conventional case of two-component active layers this electron transfer occurs intermolecularly. Therefore the covalent joint of electron rich and electron poor molecular building blocks towards hybrid molecules leads to one-compound active layers with intramolecular electron transfer which is discussed as a route towards a maximised contact of donor and acceptor materials.⁵

Perylenebisimide (PBI) units are promising candidates for such electron accepting building blocks. Additionally, they are known for their outstanding properties as highly stable fluorescent organic dyes.⁶ They exhibit a pronounced tendency to form stacked arrays which may support the aggregation of PBI-functionalised molecules towards well-defined supramolecular stacks.^{7,8} This is of great importance for functional donor/acceptor hybrid materials, as an ordered structure is

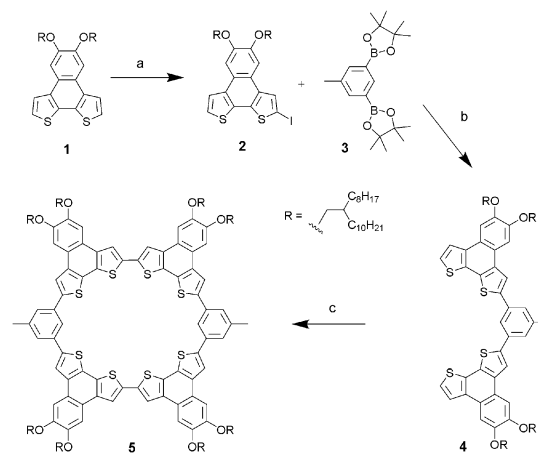
discussed as inevitable for an efficient extraction of charges, which is limited by fast recombination processes in such a solar cell.⁹

Despite some successful reports, the synthesis of thiophene macrocycles is still a challenging task, as reactive functional groups in the 2-position of the thiophene, such as metals or unprotected ethynyls, often do not possess sufficient chemical stability to be coupled without considerable side reactions. Because of these difficulties, the cyclisation reaction is mostly not performed at the thiophene sites,^{1c} or requires a rather lengthy and advanced synthesis.¹⁰

In this work we will present an efficient method to directly connect two thiophene terminated precursor molecules at the 2-positions by oxidative coupling. This allows the synthesis of macrocycles from the respective thiophene-terminated “half-ring” structures in only one synthetic step.¹¹

The synthesis of macrocycle **5** is shown in Scheme 1. The bridged bithiophene building block **1** involves thiophene moieties constrained to planarity.^{1c,12} Furthermore, the bridge between the thiophene units reduces the rotational degrees of freedom and is thus expected to support the cyclisation reaction.¹³ To overcome the general low solubility of rigid structures,¹⁴ long branched alkoxy sidechains were attached to the bithiophene building blocks.

Bithiophene **1** was statistically iodinated with *N*-iodosuccinimide (NIS) to give the monoiodinated compound **2**.



Scheme 1 Synthesis of phenylene-bithiophene macrocycle **5** via oxidative coupling. (a) NIS, AcOH, CHCl₃, rt, 12 h, 60%; (b) PEPPSI-IPr,¹⁵ KOH, THF, 60 °C, 40 h, 79%; (c) FeCl₃, CHCl₃, rt, 110 h, 27%.

Universität Bonn, Kekulé-Institut für Organische Chemie und Biochemie, Gerhard-Domagk-Str. 1, 53121 Bonn, Germany.
E-mail: hoeger@uni-bonn.de; Fax: +49 (0)228 73 5662;
Tel: +49 (0)228 73 3495

† Electronic supplementary information (ESI) available: Synthetic procedures, additional STM images and characterisation. See DOI: 10.1039/c1cc14664e

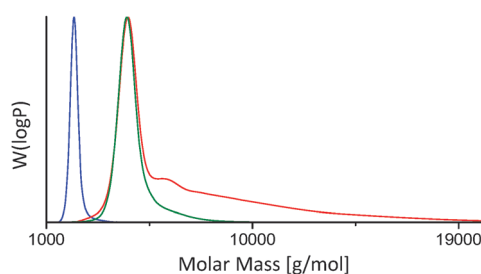


Fig. 1 GPC analysis of the precursor **4** (blue), macrocycle **5** (green) and the crude reaction product (red) of the cyclisation reaction of **4** with FeCl_3 (PS-calibration).

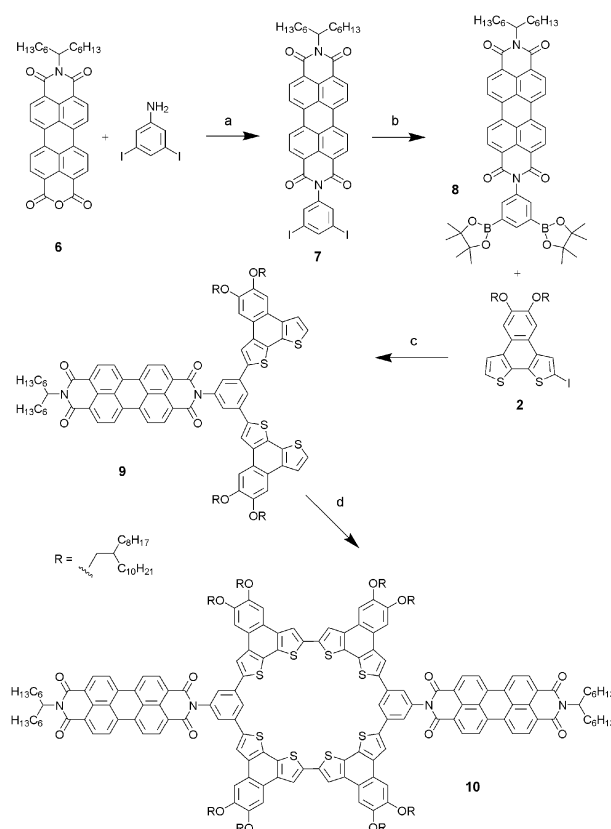
In a twofold Suzuki cross-coupling reaction **4** was obtained in good yield.

The polymerisation of unfunctionalised thiophenes with iron(III) chloride is a well-known and facile route to polythiophenes.¹⁶ Following this pathway, macrocycle **5** was synthesised by slowly adding the precursor molecule **4** to a dispersion of iron(III) chloride in chloroform. The outcome of the cyclisation reaction is shown in Fig. 1. Gel permeation chromatography (GPC) of the crude product shows an elution diagram typical for a cyclisation reaction under pseudo-high dilution conditions.¹⁷ The major component is the cyclic dimer, along with trimer, higher oligomers and polymers. The dimer **5** was purified by recycling GPC (rec GPC), and its cyclic structure was confirmed by high resolution mass spectrometry (MS) as well as high temperature NMR spectroscopy. Room temperature NMR signals were broadened especially in the aromatic region most probably due to strong π - π interactions between the expanded aromatic systems of the molecules (see ESI†).

The oblate donor/acceptor hybrid molecule **10** is functionalised with PBI substituents directly attached to the *m*-phenylene corner pieces of the macrocyclic backbone. The synthetic pathway is shown in Scheme 2. Peryleneimide monoanhydride **6**¹⁸ was condensed with 3,5-diiodoaniline¹⁹ to yield the PBI **7** which was subsequently converted to the diboronic ester **8**. The latter was reacted with the monoiodinated bithiophene **2** under Suzuki coupling conditions to yield **9**. If cyclised under similar conditions as applied to the synthesis of **5**, **9** shows a larger tendency to form higher oligomers with a trimeric species as a major product (see GPC data in the ESI†). However, oxidative coupling under even higher diluted conditions yielded up to 23% of cyclodimer **10**. The crude product was again purified by rec GPC and characterised by MS. While **5** could be investigated by high temperature NMR, even at elevated temperature the NMR signals of **10** are significantly broadened.

The UV/Vis spectra of the two macrocycles **5** and **10** as well as of the PBI **11** (*cf.* Fig. 3c, **11** is used as a reference system) are displayed in Fig. 2. The spectrum of the hybrid molecule **10** can be drawn back to a superposition of the spectra of components **5** and **11** indicating weak coupling of the chromophore units. However, despite of **5** and **11** being strong fluorescent dyes, **10** shows no fluorescence. This may be a result of a rapid electron transfer from the macrocycle to the PBI that offers a non-radiative pathway towards the ground state.²⁰

This assumption is supported by cyclic voltammetry (CV) measurements displayed in Fig. 3. Macrocycle **5** is an electron



Scheme 2 Synthesis of the donor/acceptor hybrid macrocycle **10**. (a) *m*-cresol/isoquinoline, 80 \rightarrow 200 $^{\circ}\text{C}$, 9 h, 81%; (b) Bpin_2 , KOAc, $\text{PdCl}_2(\text{dppf})$, DMF, 60 $^{\circ}\text{C}$, 15 h, 84%; (c) PEPPSI-IPr, KOH, THF, 60 $^{\circ}\text{C}$, 24 h, 55%; (d) FeCl_3 , CHCl_3 , rt, 116 h, 23%.

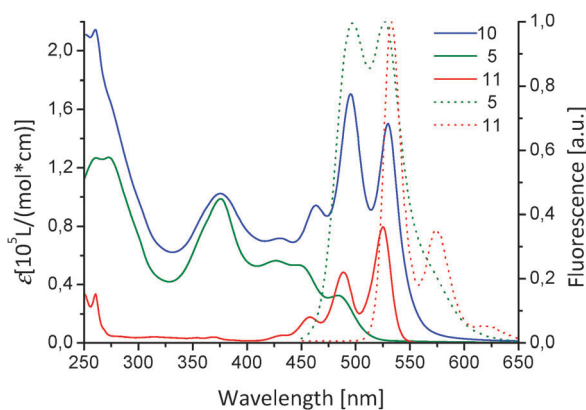


Fig. 2 UV/Vis absorption spectra of the hybrid molecule **10**, the ring **5** and the PBI **11** (solid lines, left axis, all 10^{-5} M in CH_2Cl_2) and normalised fluorescence spectra of **5** and **11** (dotted lines, right axis).

rich compound which can be easily oxidised to the doubly charged cation. The energy of the HOMO (-4.7 eV) was obtained from the onset of the first oxidation step. The LUMO energy (-2.3 eV) was obtained from the bandgap derived from UV/Vis spectroscopy (Fig. 2). With regard to the HOMO/LUMO potentials of the PBI **11** (-3.8 and -6.1 eV respectively), in **10** a photoinduced electron transfer from the macrocyclic backbone to the extraannular PBI moieties is possible after excitation of either one of the chromophores.

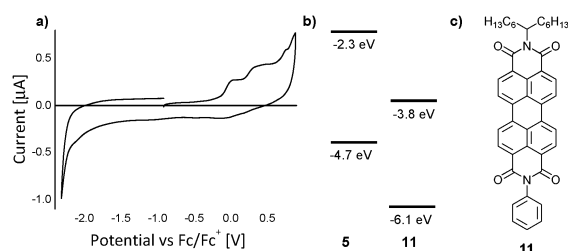


Fig. 3 (a) Cyclic voltammogram of **5** in CH_2Cl_2 at a concentration of 4×10^{-4} M and a sweep rate of 100 mV s^{-1} ; (b) HOMO/LUMO potentials of **5** compared to the HOMO/LUMO energies of the PBI dye **11** shown in (c).

We were able to gain additional structural information of **10** by directly visualising molecular patterns formed by the macrocycles at the interface of 1,2,4-trichlorobenzene (TCB) and highly oriented pyrolytic graphite (HOPG) using scanning tunneling microscopy (STM; see Fig. 4). Stacking between PBI substituents of adjacent molecules leads to the formation of (brightly appearing)²¹ chain-like supramolecular one-dimensional (1D) assemblies with a variable line distance of $w_{1D} \geq 5.5 \text{ nm}$ (cf. Fig. 4b).²² The latter are separated by (darker appearing) intermediate regions covered by the flexible, branched 2-octyldodecyloxy substituents that tend to assemble along the HOPG main axes.²³ From the large distance we assume that all alkoxy substituents are adsorbed and do not interdigitate, which frustrates the interaction of molecules of adjacent lines, so that only 1D order is observed. However, some of the lines form a most dense, two-dimensional (2D) crystalline packing (Fig. 4a, dashed box, and Fig. 4b) with observed line distances of $w_{2D} = 3.5 \pm 0.3 \text{ nm}$, which are consistent with an incomplete adsorption of the branched alkoxy sidechains. It is of interest to note that both packing motifs exist under the imaging conditions used here, indicating

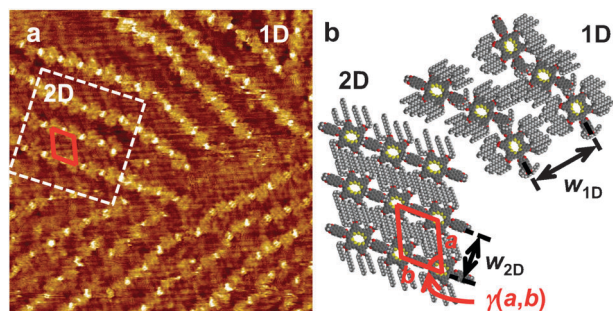


Fig. 4 (a) STM image of **10** at the TCB/HOPG interface. The self-assembly into chains is ascribed to the intermolecular stacking of the extraannular PBI units (bright spots) and consistent with the molecular structure of **10** ($V_S = -0.7 \text{ V}$, $I_t = 30 \text{ pA}$). The molecular models in (b) represent the 1D and 2D ordered adsorbate patterns, as observed in (a). The red lines indicate the unit cell, $a = 3.8 \pm 0.3 \text{ nm}$, $b = 3.2 \pm 0.3 \text{ nm}$, and $\gamma = 66 \pm 3^\circ$.

the structure stabilising effect of the PBI–PBI interaction that leads to robust 1D aggregates at the TCB/HOPG interface.

In conclusion, an oxidative coupling route towards thiophene macrocycles was applied to prepare a shape-persistent electron rich thiophene macrocycle with extraannularly attached electron poor PBI moieties. We have shown that the organisation in one dimension is dominated by the strong attractive forces between the PBI units. The results prove the concept of interaction of PBI substituents applied for supramolecular structure formation of macrocycles.

We gratefully acknowledge the DFG (SFB 813 and SFB 624) for financial support.

Notes and references

- (a) G.-B. Pan, X.-H. Cheng, S. Höger and W. Freyland, *J. Am. Chem. Soc.*, 2006, **128**, 4218; (b) E. Mena-Osteritz and P. Bäuerle, *Adv. Mater.*, 2006, **18**, 447; (c) T. Chen, G.-B. Pan, H. Wettach, M. Fritzsche, S. Höger, L.-J. Wan, H.-B. Yang, B. H. Northrop and P. J. Stang, *J. Am. Chem. Soc.*, 2010, **132**, 1328.
- M. Fritzsche, A. Bohle, D. Dudenko, U. Baumeister, D. Sebastiani, G. Richardt, H. W. Spiess, M. R. Hansen and S. Höger, *Angew. Chem., Int. Ed.*, 2011, **50**, 3030.
- (a) M. Bednarz, P. Reineker, E. Mena-Osteritz and P. Bäuerle, *J. Lumin.*, 2004, **110**, 225; (b) F. Zhang, G. Götz, E. Mena-Osteritz, M. Weil, B. Sarkar, W. Kaim and P. Bäuerle, *Chem. Sci.*, 2011, **2**, 781.
- B. C. Thompson and J. M. J. Fréchet, *Angew. Chem., Int. Ed.*, 2008, **47**, 58.
- (a) A. Cravino and N. S. Sariciftci, *J. Mater. Chem.*, 2002, **12**, 1931; (b) J. Roncali, *Chem. Soc. Rev.*, 2005, **34**, 483; (c) G. Bottari, G. de la Torre, D. M. Guldi and T. Torres, *Chem. Rev.*, 2010, **110**, 6768.
- T. Weil, T. Vosch, J. Hofkens, K. Peneva and K. Müllen, *Angew. Chem., Int. Ed.*, 2010, **49**, 9068.
- F. Würthner, *Chem. Commun.*, 2004, 1564.
- L. Zang, Y. Che and J. S. Moore, *Acc. Chem. Res.*, 2008, **41**, 1596.
- (a) Y. Ie, T. Uto, N. Yamamoto and Y. Aso, *Chem. Commun.*, 2009, 1213; (b) N. Tchegotareva, X. Yin, M. D. Watson, P. Samori, J. P. Rabe and K. Müllen, *J. Am. Chem. Soc.*, 2003, **125**, 9734; (c) S. Campidelli, R. Deschenaux, J.-F. Eckert, D. Guillon and J.-F. Nierengarten, *Chem. Commun.*, 2002, 656.
- F. Zhang, G. Götz, H. D. F. Winkler, C. A. Schalley and P. Bäuerle, *Angew. Chem., Int. Ed.*, 2009, **48**, 6632.
- D. Zhao and J. S. Moore, *Chem. Commun.*, 2003, 807.
- J. D. Tovar, A. Rose and T. M. Swager, *J. Am. Chem. Soc.*, 2002, **124**, 7762.
- P. Knops and F. Vögtle, *Chem. Ber.*, 1991, **124**, 1223.
- W. Kern, M. Seibel and H. O. Wirth, *Makromol. Chem.*, 1959, **29**, 164.
- M. G. Organ, G. A. Chass, D.-C. Fang, A. C. Hopkinson and C. Valente, *Synthesis*, 2008, **17**, 2776.
- M. Leclerc, F. M. Diaz and G. Wegner, *Makromol. Chem.*, 1989, **123**, 5651.
- S. Höger, A.-D. Meckenstock and S. Müller, *Chem.-Eur. J.*, 1998, **4**, 2423.
- H. Kaiser, J. Lindner and H. Langhals, *Chem. Ber.*, 1991, **124**, 529.
- S. Höger, K. Bonrad, A. Mourran, U. Beginn and M. Möller, *J. Am. Chem. Soc.*, 2001, **34**, 31.
- J. L. Segura, N. Martin and D. M. Guldi, *Chem. Soc. Rev.*, 2005, **34**, 31.
- R. Lazzaroni, A. Calderone, J. L. Brédas and J. P. Rabe, *J. Chem. Phys.*, 1997, **107**, 99.
- F. Würthner, Z. Chen, V. Dehm and V. Stepanenko, *Chem. Commun.*, 2006, 1188.
- T. Yang, S. Berber, J.-F. Liu, G. P. Miller and D. Tománek, *J. Chem. Phys.*, 2008, **128**, 124709.