Chiral molecular tapes from novel tetra(thiafulvalene-crown-ether)-substituted phthalocyanine building blocks†

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A tetra(thiafulvalene-crown-ether) phthalocyanine self-assembles into helical tapes nanometers wide and micrometers long. Formation of these scrolled molecular architectures is a first for phthalocyanine fibres and shows potential as a novel conducting material.

Fundamental to the development of molecular electronic devices is the efficient construction of effective "molecular wires" and conductive architectures. These architectures are synthetic materials of nanometer sized dimensions, capable of directional, long-range electron-transport. While the development of conducting polymers has shown the potential role for such "synthetic metals" in emergent technology, challenging issues such as processability and design flexibility remain.[1] The use of molecular self-assembly to construct functional materials is now well-established and presents one possible direction in the exploration of readily accessible conducting materials. The versatility of chemical synthesis used in forming the individual components for these self-assembled materials provides for an important control over both the electronic and structural features of the resulting materials. Two synthetic components which have attracted above average interest in this field are phthalocyanines (Pcs)[2–4] and tetrathiafulvalenes (TTFs),[5–7] both of which have excellent conductive properties. Pcs appended with crown-ether moities substituted with long alkoxy chains readily self-assemble into long fibres, possessing the multiple potentials of electron conduction, ion transport and liquid crystallinity.[8–11] TTFs have featured prominently in the area of "synthetic metal" research. In order to make functional Pc-based fibres, TTF units have been incorporated into a crown-ether-Pc building block, to give **6**, with the aim of endowing the resulting self-assembled material with potentially interesting electronic and structural properties.

Phthalocyanine **6a** was generated from 4,5-dibromocatechol **1**[8] in a five step procedure (Scheme 1).† Reaction of **1** with bis-2-chloroethyl ether followed by halogen exchange provided the 4,5-dibromobenzo-"half crown" structure **2** in good yield. The coupling of **2** with the bis-protected TTF compound **3**[12] was effected in a one-pot deprotection / coupling step with the 4,5-dibromobenzo-TTF-crown-ether **4** being isolated in pure form. It was found that the penultimate step involving conversion of the aryl dibromide **4** into the phthalonitrile precursor **5** did not proceed as smoothly as could be expected. The isolated yield of **5** (31%) was relatively low in view of the success of the preceding steps and similar complications with molecules of this type have been reported in the past.[13] However, workable quantities were obtained and the phthalonitrile **5** was able to be converted smoothly into the target phthalocyanine **6a**.

Molecular modelling experiments[14] conducted on Pc **6a** predicted an overall planar geometry for the global energy minimised structure, with the crown ether units being able to adopt a boat like conformation. This confirmed the potential for **6a** to form stacked aggregates, through the expected Pc–Pc π–π interactions, as previously observed with other crown-ether Pc analogues.[9] Additional studies, prompted by previous reports of strong intermolecular TTF–Pc interactions,[13] investigated the effect of a competition between intermolecular Pc–Pc, Pc–TTF and TTF–TTF π–π interactions. It appeared that if the latter interactions are fully available, then traditional, columnar Pc stacking should eventuate. However, should this interaction be sterically limited (a possibility indicated by molecular modelling) then Pc–TTF interactions could determine the overall architecture, one potentially different to normal columnar stacks.

Aggregation of **6a** was observed from UV-Vis studies (Fig. 1) in which it was determined that, at 1 : 4 v/v of $CHCl_3$ / MeOH, **6a** could be induced into aggregates as shown by the broadening and blue shifting of the major absorbance bands (Q bands at 663 and 700 nm → 630 nm). More importantly, gelation of **6** was also able to be induced by the slow addition of dioxane to a chloroform solution at 5 °C. In its gelated state **6a** was observed [by transmission electron microscopy (TEM)] to be composed of fibres up to several micrometers in length, which is a length consistent with the stacking of around 100,000 molecules (Fig. 2). This length is also in accordance with previous studies on crown-ether analogues of **6a** which lacked the TTF moieties. These analogues have been previously observed to form fibres and even twisted bundles of fibres driven by the co-facial, linear stacking behaviour of the phthalocyanine moieties.[9]

However, further inspection of the fibres formed from the TTF containing Pc **6a**, revealed additional features indicating a dramatic deviation from the initially expected linear stacking behaviour. The TEM images reveal the presence of unusual, very thin bilayer-type structures (Fig. 2a). The width of these long, tape-like structures formed from **6a** is typically of the order of 20 nm. This width corresponds to approximately 5 times the calculated width of the individual molecule **6a** and is an immediate deviation from all previously observed crown-ether Pc stacking behaviour.

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† Electronic supplementary information (ESI) available: Synthetic characterisation, general experimental procedures together with a more in depth descriptive analysis of the self-association behaviour of **6**. See http://www.rsc.org/suppdata/cc/b4/b416034g/

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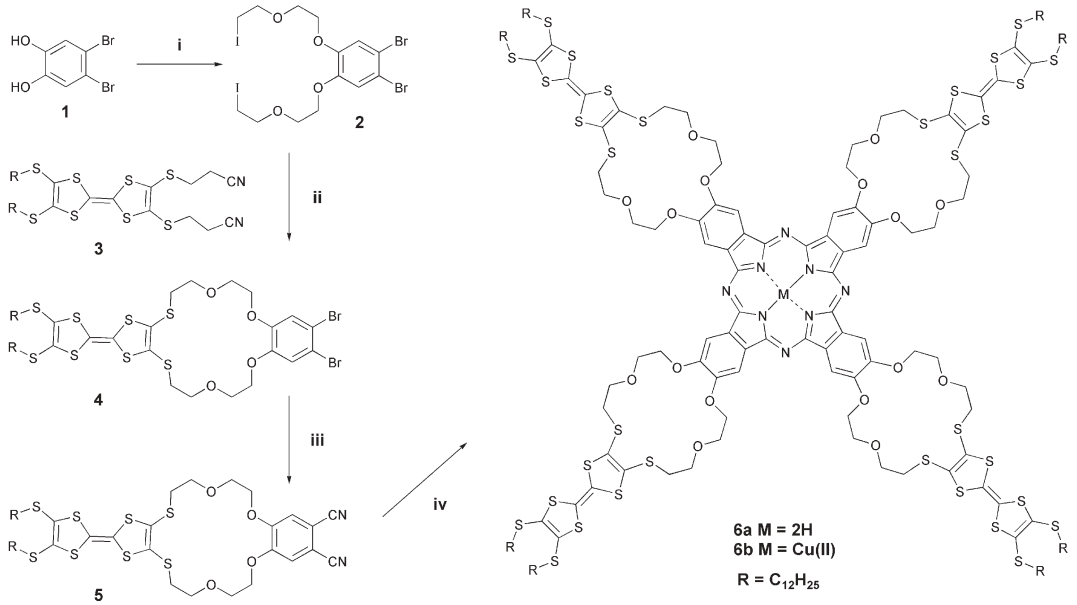

Scheme 1 **i** Bis(2-chloroethyl)ether, K_2CO_3, Δ then NaI, acetone, Δ (two steps, 68% overall). **ii** $CsOH\cdot H_2O$, MeOH, DMF, RT, 53%. **iii** CuCN, DMF, Δ, 31%. **iv** Hexanol, n-butyllithium, Δ, 11%. (**6b** Formed from $CuCl_2$ dimethylaminoethanol, Δ and the diiminoisoindoline derivative of **5**, 9% overall conversion from **5**.)

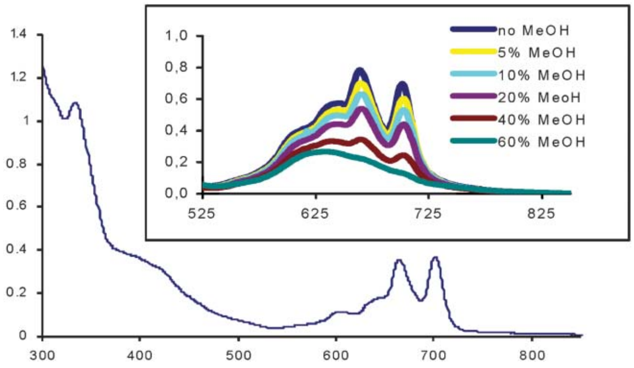

Fig. 1 UV-Vis spectra of **6a** ($CHCl_3$) with the effect of increasing MeOH addition (shown inserted) indicating induced aggegation of the molecule.

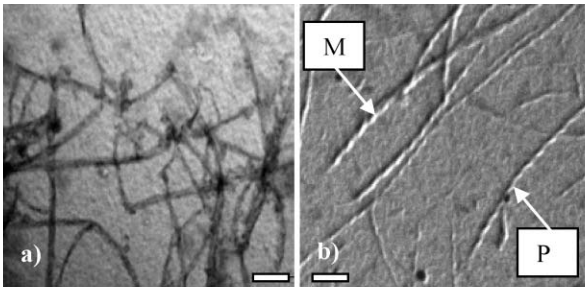

Fig. 2 TEM images of the gelated state of **6a** showing **a)** thin Pc tapes (left) and **b)** an equal distribution of both left and right helical structures, nanometers wide and micrometeres in length (right). Scale bar = 200 nm.

Of even greater interest is that, concurrently observed with these tapes, is a second type of fibre immediately identifiable as possessing a three-dimensional detail to its structure. These fibres appear helical in nature, micrometers in length and have a width of approximately 15–25 nm (Fig. 2b). It was not possible to identify the presence of any of the expected, columnar type Pc fibres in these TEM images. From these observations and initial modelling experiments, it is suggested that an unusual combination of multiple TTF–TTF and TTF–Pc interactions can dominate (over Pc–Pc interactions) in the self-association of Pc **6a** leading to the eventual formation of scrolled molecular architectures (Fig. 3 and Fig. 4). The observed equal distribution of both left and right helices is as expected, given the absence of any chiral bias to the structure of **6a**.

Cyclic voltametry (CV) studies on **6b** showed the redox properties expected for a combination of Pc and TTF moieties. The first ($E_1^{1/2}$) and second ($E_2^{1/2}$) TTF oxidations were slightly raised ($E_1^{1/2} = 0.75$, $E_2^{1/2} = 1.25$ E/V *versus* Ag/AgI, compared to $E_1^{1/2} = 0.65$, $E_2^{1/2} = 1.01$ E/V for **3**) obscuring the expected, weaker Pc oxidation. These oxidation levels are in agreement with other reported Pc–TTF structures which

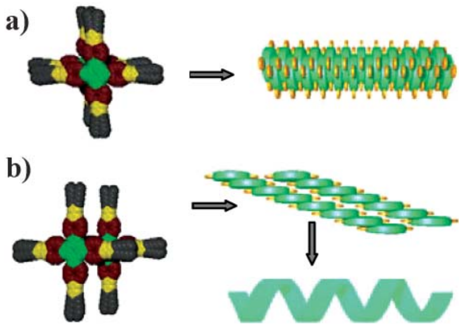

Fig. 3 Molecular models[14] (Pc moiety in green, crown-ether in red, TTF in yellow, alkyl chains in grey) showing the difference between the two modes of stacking of **6a** with schematic of resulting bulk architecture: **a)** TTF–TTF and Pc–Pc interactions dominate resulting in columnar stacks (not observed). **b)** Pc–TTF and TTF–TTF interactions dominate resulting in initial bilayer type structures which scroll into helical tapes (observed).

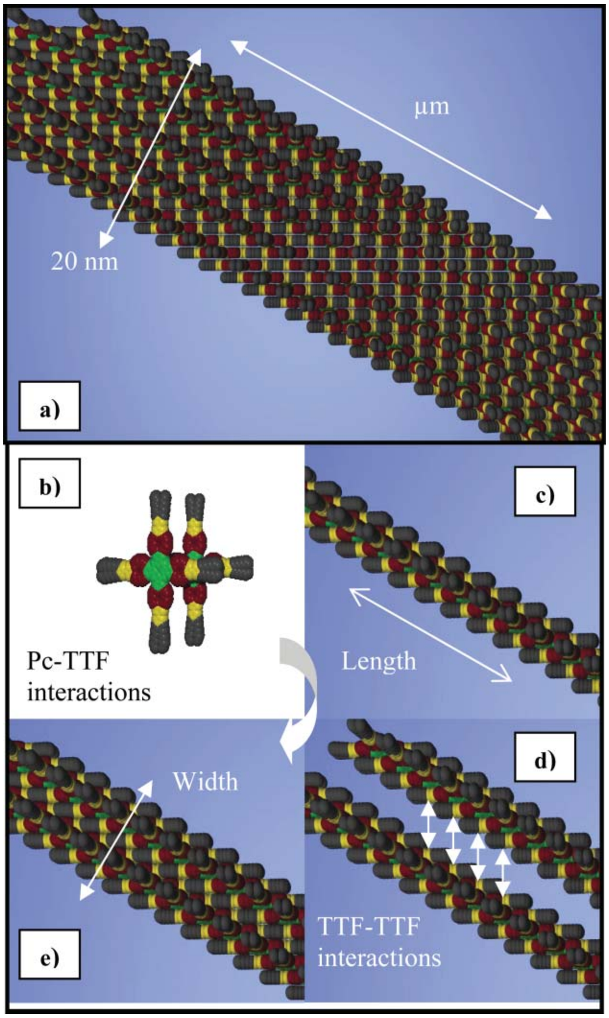

Fig. 4 (a) Proposed arrangement of Pc **6** monomers within the observed thin tape-like structures (colours are as described in Fig. 3). Within the tape, Pc–TTF interactions (b) are the dominant intermolecular interactions within the tape which form offset columns (c) which run lengthwise within the tape. These columns are associated within the tape through weaker TTF–TTF interactions (d). These interactions define the tape width (e). Estimation based on modeling and an observed width of 20 nm suggests approximately five rows of columns within the tapes. The number of columns within the tape is dependent upon the exact offset relationships shown in (b) and (d).

showed little change in the TTF potentials when linked to the Pc macrocycle.[13]

To investigate the potential of these structures to act as a conducting architecture, doping studies on **6b** were conducted using 7,7,8,8-tetra-cyanoquinodimethane (TCNQ) in DMSO. This produced a new absorption band in the UV-Vis spectrum at 750 nm which corresponds to the SOMO–LUMO transition of the cation radical species of the TTF moieties. The formation of a $TCNQ^-$ / TTF^+ charge-transfer complex was confirmed by the FT-IR spectrum which showed the nitrile stretch of the TCNQ radical anion (observed at 2179 cm^{-1} compared to the neutral state of 2223 cm^{-1}). Doping of **6b** in CH_2Cl_2 with I_2 produced a similar effect in the UV-Vis spectrum as with the TCNQ example in DMSO. In this case, an observed lowering of the Q-band absorbances suggests increased aggregation and may indicate a preferred state for the multiple-oxidised species.

Currently, the incorporation of chirality into the basic structure of **6a**, investigations into subsequent controlling effects upon the direction of scroll formation and detailed electrochemical evaluation of these novel, self-assembled structures are underway and will be reported in due course.

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