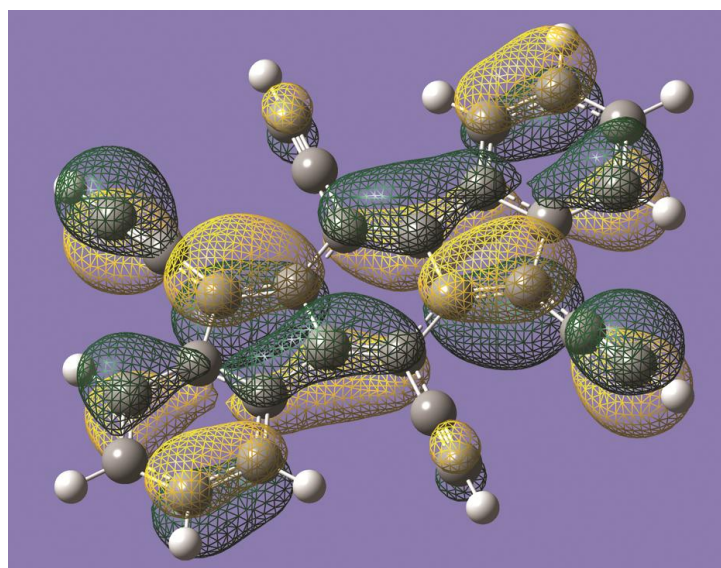# ChemComm

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COMMUNICATION

A rigid donor–acceptor daisy chain dimer†‡

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A functionalised cyclobis(paraquat-*p*-phenylene) attached by a rigid linker to a tetrathiafulvalene unit, which is incapable of self-complexation, forms preferentially a [*c2*]daisy chain which undergoes rapid disassociation and reassociation on the ¹H NMR time-scale above room temperature.

Artificial molecular muscles and actuators have become a source of interest in recent years because of their incorporation into nanoelectromechanical systems (NEMS)[1] in order to transduce nanoscale molecular motions into macroscopic movements.[2] Elastomers,[3] conducting polymers,[4] and carbon nanotubes,[5] capable of actuation, have all been a part of this interest. Simultaneously, mechanically interlocked molecules[2] (MIMs) which mimic protein filaments in biological systems, have generated attention since the discrete relative movements of their components can be controlled by a number of different stimuli. To this end, in addition to electrochemically-stimulated doubly bistable [3]rotaxanes,[6] both acid–base[7] and chemically[8b] actuated bistable [*c2*]daisy chains have been introduced. The latter have been designed and synthesised around metal–ligand coordination,[8] hydrogen bonding,[7,9] hydrophobic,[10] and π-donor/acceptor interactions,[11] as the sources of their mutual recognition units. More often than not, however, daisy chain monomers self-assemble in solution to give[10c–d,11] a mixture of linear and cyclic oligomers, depending on the concentration of the monomer.

In the case of donor–acceptor-based daisy chains, there have been numerous attempts to attach flexible donating units to the electron-deficient cyclobis(paraquat-*p*-phenylene)[12] (CBPQT⁴⁺) ring. These monomers, however, have shown[13] a strong tendency to self-complex, rather than form higher order superstructures, no doubt as a consequence of the considerable entropy penalty associated with the generation of supramolecular polymers, be they cyclic or acyclic. In order to circumvent self-complexation, we envisage that the use of a

rigid spacer of an appropriate length between the donor and the CBPQT⁴⁺ ring might eliminate the possibility for intramolecular interactions altogether, thus favouring the formation of daisy chains. Herein, we report the synthesis and characterisation of a daisy chain-forming compound **1**⁴⁺ which consists (Fig. 1) of a tetrathiafulvalene (TTF) unit joined by rigid aromatic linkers to a CBPQT⁴⁺ ring for the all but exclusive construction of a donor–acceptor [*c2*]daisy chain. Several important considerations were taken into account in designing **1**⁴⁺, including (i) the rigidity of the linker which was enforced by a phenylacetylene-containing spacer whose length (11.6 Å) is greater than the length (9.9 Å) of the CBPQT⁴⁺ cavity, ensuring that self-complexation cannot occur, (ii) the choice of TTF as the electron-rich donor since previously we have noted[14] that 1-ethynyl-5-hydroxynaphthalene derivatives have a low binding affinity for the CBPQT⁴⁺ ring, and (iii) the use of a phthalimide linker in place of one of the xylylene units in the CBPQT⁴⁺ ring because substituents attached to the imide nitrogen are oriented at right angles to the mean plane of the CBPQT⁴⁺ ring, a situation which maintains a plane of symmetry in a perpendicular direction, thus avoiding the generation of isomeric [*c2*]daisy chains.

The synthesis (Scheme 1) of **1**·4PF₆ begins[15] with a Diels–Alder reaction between 2,5-dimethylfuran and maleic anhydride. Subsequent elimination of H₂O from the adduct under strongly acidic conditions yields the anhydride **2** which, when condensed with 4-iodoaniline, yields **3**. Dibromide **4**, generated by the NBS bromination of **3**, was hydrolysed to afford the diol **5** in order to "protect" the benzylic bromides during the subsequent Sonogashira coupling. The TTF derivative **6**[16] was then coupled to **5** to yield the intermediate **7**. Since standard PBr₃ bromination to regenerate the dibromide proved to be too harsh, mesylation of the diol followed by chloride substitution was used to generate the dichloride **8** which was
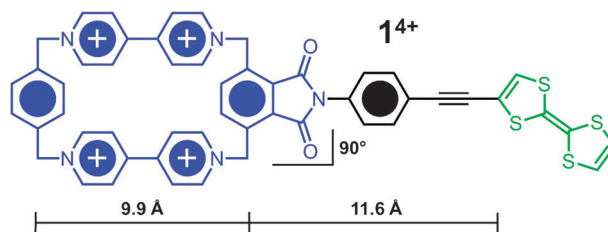
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Fig. 1 The structural formula of **1**⁴⁺ which contains a TTF unit linked to a CBPQT⁴⁺ ring by means of a phenylacetylene spacer.
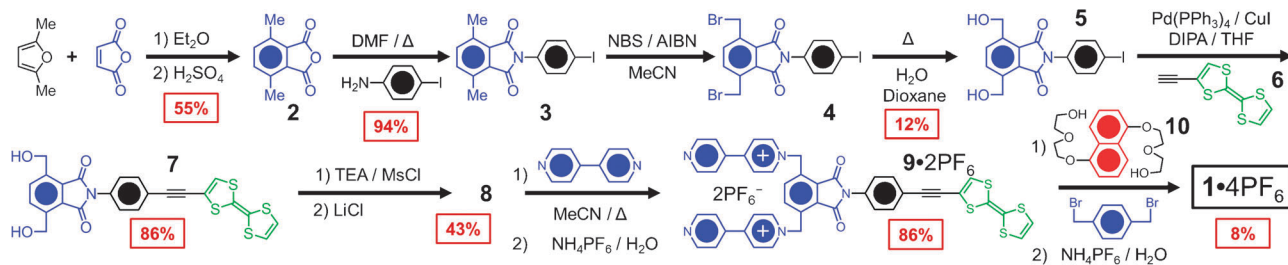
Scheme 1 Synthesis of **1**·4PF$_6$.

reacted in MeCN with an excess of 4,4′-bipyridine to yield **9**·2PF$_6$ after counterion exchange. Finally, 1,4-bis(bromomethyl)-benzene was reacted with **9**·2PF$_6$ in the presence of template **10** to yield **1**·4PF$_6$ after counterion exchange and purification by high-performance liquid chromatography. High resolution electrospray ionization mass spectrometry of a 3 mM solution of **1**·4PF$_6$ revealed peaks at m/z = 1326.0789 and 2797.1162 Da, corresponding to the loss of one PF$_6^-$ counterion from the monomer and dimer of **1**$^{4+}$, respectively.

UV-Vis spectrophotometric investigations on a model TTF compound (**S1**‡) and CBPQT^{4+} (**S2**$^{2+}$‡) confirm that the TTF units functionalized with a rigid linker bind to the CBPQT^{4+} ring. Indeed, when handling **1**·4PF$_6$, it was noticeable immediately that the colour of the solution is dependent on the concentration (Fig. 2) and the temperature. At higher concentrations, the green colour resulting from the charge transfer (CT) between TTF and CBPQT^{4+} persists while, at lower concentrations, the yellow colour corresponding to a characteristic absorption band appears to dominate. A serial dilution of a solution of **1**·4PF$_6$ in MeCN from 2.7 mM down to 0.1 mM reveals (see SI‡) a CT band at 780 nm for the interaction between TTF and the CBPQT^{4+} ring. The intensity of the band decreases as the concentration is lowered. Applying the Benesi–Hildebrand method (see SI‡) reveals a non-linear relationship between the inverse concentration and the inverse change in absorption intensity, an observation which suggests that the formation of the CT complex is most likely the result of dimerisation rather than as a consequence of self-complexation or oligomerisation.

The equilibrium (Fig. 3a) between the monomer and dimeric [c2]daisy chain can be followed by variable temperature (VT) ^{1}H NMR spectroscopy. At low temperatures, relatively sharp resonances corresponding to the cyclic dimer can be observed. With the assistance of ^{1}H-^{1}H-g-DQF-COSY and ^{1}H-^{1}H ROESY NMR (see SI‡), the resonances for all the protons in **1**$^{4+}$ can be assigned (Fig. 3b) at 233 K. The resonances corresponding to the TTF protons are shifted upfield and well
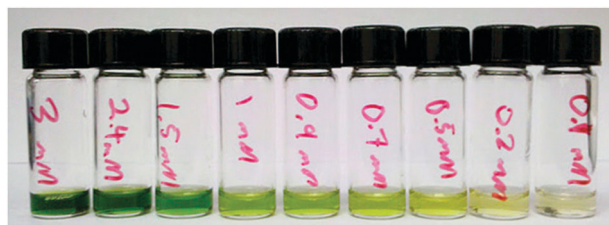
separated from each other, while the peaks for the methylene protons closest to the phthalimide unit separate into an AX system. We hypothesize that this AX system is a result of the stable nature of the [c2]daisy chain at low temperatures where the imide functionality sits exclusively on one side of the CBPQT^{4+} face, imposing diastereotopism upon the H$_{MTD}$ protons on opposite sides of the CBPQT^{4+} ring. As a consequence of the sidedness of the CBPQT^{4+} ring in the dimeric [c2]daisy chain, the resonances corresponding to the bipyridinium protons, H$_{\alpha D1}$, H$_{\alpha D2}$, H$_{\beta D1}$, and H$_{\beta D2}$, as well as to the phenylene protons, H$_{PBD}$, also divide up into four and two sets of resonances, respectively. Upon increasing the temperature of a CD$_3$CN solution of **1**·4PF$_6$ from 233 to 323 K, changes occur (Fig. 4) in the ^{1}H NMR spectra. The resonances corresponding to H$_{\alpha D1}$, H$_{\alpha D2}$, H$_{\beta D1}$, H$_{\beta D2}$, and H$_{PBD}$ coalesce between 248 and 263 K, indicating that the rotations of the pyridinium and phenylene rings become fast on the NMR time-scale. The peaks for the protons employed to probe the energy barriers for rotation, using the coalescence method, results[17] in very similar energies of activation $\Delta G^{\ddagger}$, namely 13.8–14.5 kcal mol^{-1} from the bipyridinium and phenylene protons, indicating that we are looking at a situation involving numerous probes and realizing they reflect the same mechanism—removal of TTF units from inside CBPQT^{4+} rings followed by pyridinium and phenylene ring rotations. At around 293 K, whereas the H$_{TTF2D}$ and H$_{TTF3D}$ resonances essentially spread out into the baseline, between 293 and 323 K, some of the peaks begin to shift while the H$_{TTF2D}$ and H$_{TTF3D}$ resonances reappear at around 6.3 ppm, similar to the TTF resonances in the free model compound **S1**
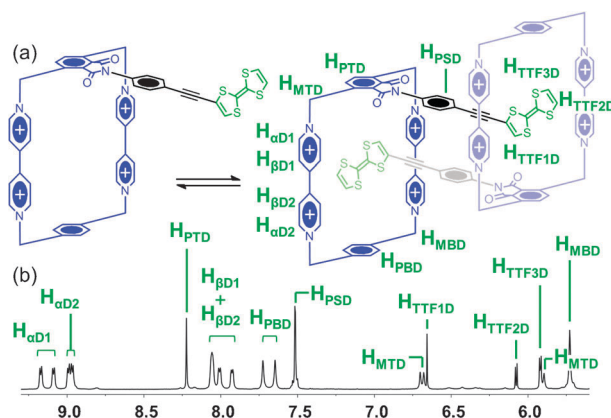

Fig. 2 Solutions of **1**$^{4+}$ in MeCN demonstrating the change in colour as a function of concentration.

Fig. 3 (a) The proposed equilibrium between the monomer and dimer of **1**$^{4+}$. (b) ^{1}H NMR spectrum (600 MHz, 2 mM, 233 K, CD$_3$CN) of **1**·4PF$_6$ and assignment of the resonances.
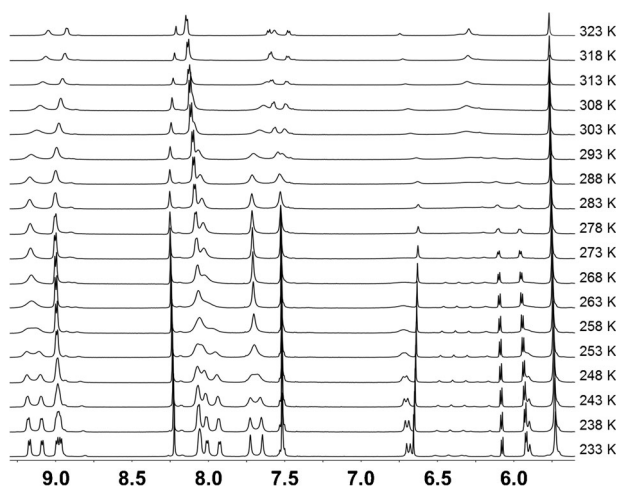
Fig. 4 VT ^{1}H NMR spectra (600 MHz, 2 mM, CD$_3$CN) of 1^{4+}.

(see SI‡), indicating that above room temperature there is a fast equilibrium occurring between the monomer and [c2]daisy chain dimer which begins to favour the free species at 323 K. Indeed, when the NMR tube was removed from the spectrometer at 323 K, the solution was yellow, and only returns to green upon cooling to room temperature. Going higher in temperature than 323 K results in the decomposition of the compound.

We have demonstrated the preferential formation of a [c2]daisy chain as a consequence of the rigidity in the monomer unit which rules out intramolecular interactions leading to self-complexation. The supramolecular complex undergoes rapid disassociation and reassociation on the ^{1}H NMR timescale above RT as indicated by the fact that certain protons on the CBPQT^{4+} ring undergo fast exchange. The next challenge is to design and synthesize rigid donor–acceptor daisy chains with bistability.

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17 The rate constants, k_c, at the coalescence temperatures, T_c, were determined using the approximate expression, $k_c = \pi(\Delta\nu)/(2)^{\frac{1}{2}}$, in which $\Delta\nu$ is the limiting chemical shift (in Hz) between the exchanging proton resonances. The Eyring equation, $\Delta G^{\ddagger}_c = -RT\ln(k_c\hbar/k_B T_c)$ was used to calculate the $\Delta G^{\ddagger}_c$ value at the lower limit of the T_c value for the H$_{\alpha D1}$ ($\Delta\nu = 49.8$ Hz, $k_c = 110.6$, $T_c = 263$ K, $\Delta G^{\ddagger}_c = 14.0 \pm 0.1$ kcal mol^{-1}), (ii) H$_{\alpha D2}$ ($\Delta\nu = 14.6$ Hz, $k_c = 32.5$, $T_c = 248$ K, $\Delta G^{\ddagger}_c = 14.5 \pm 0.4$ kcal mol^{-1}), (iii) H$_{\beta D}$ ($\Delta\nu = 48.6$ Hz, $k_c = 108.0$, $T_c = 263$ K, $\Delta G^{\ddagger}_c = 14.0 \pm 0.1$ kcal mol^{-1}), and (iv) H$_{PBD}$ ($\Delta\nu = 47.5$ Hz, $k_c = 105.4$, $T_c = 258$ K, $\Delta G^{\ddagger}_c = 13.8 \pm 0.1$ kcal mol^{-1}) resonances. See: I. O. Sutherland, *Annu. Rep. NMR Spectrosc.*, 1972, **4**, 71–235.