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# Cyclotris(paraquat-p-phenylenes)

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Abstract: We report on the synthesis, solid-state characterization and redox properties of a new class of triangular, three-fold symmetric viologen-containing macrocycles. The preparation of cyclotris(paraquat-p-phenylene) (CTPQT<sup>6+</sup>) and cyclotris(paraquat-p-1,4-dimethoxyphenylene) (MCTPQT6+), can be executed by following a three-step protocol. Their X-ray single-crystal (super)structures reveal intricate three-dimensional packing. The crystallization of MCTPQT<sup>6+</sup> results in nanometer-sized channels in contrast with its parent counterpart CTPQT<sup>6+</sup> which crystallizes as a couple of polymorphs in the form of intercalated assemblies. In the solid-state. MCTPQT<sup>3(++)</sup>—the three-electron reduced form of MCTPQT<sup>6+</sup>—exhibits stacks between the 1.4-dimethoxyphenylene and bipyridinium radical cations, providing new opportunities for the manipulation and control of the recognition motif associated with viologen radical cations. These redox-active cyclophanes demonstrate that geometry-matching and weak intermolecular interactions are of paramount importance in dictating the formation of their intricate solid-state superstructures.

Interest in research on macrocycles in the context of supramolecular chemistry<sup>[1]</sup> has spawned numerous examples derived from common building blocks, including cyclodextrins,<sup>[2]</sup> crown ethers,<sup>[3]</sup> cucurbiturils,<sup>[4]</sup> calixarenes,<sup>[5]</sup> pillararenes,<sup>[6]</sup> asararenes<sup>[7]</sup> and several other cyclophanes,<sup>[8]</sup> along with structures incorporating redox-active bipyridinium units.<sup>[9]</sup> Since the original report<sup>[10]</sup> of the synthesis of cyclobis(paraquat-pphenylene) (CBPQT<sup>4+</sup>), the range of bipyridinium-containing cyclophanes has expanded enormously to produce an alluring series of macrocycles that can form well-defined superstructures,<sup>[11]</sup> as well as mechanically interlocked molecules,<sup>[12]</sup> such as rotaxanes and catenanes. Notably, the electrochemical properties of these macrocycles allow access to their corresponding open-shell species following chemical or electrochemical reduction. These additional redox states have broadened their scope considerably, on account of the radicalradical pimerization ( $\pi$ -dimerization) that occurs<sup>[13]</sup> between the viologen radical cations. Their redox chemistry enriches their properties with respect to both the self-organization and hostguest chemistry of these macrocyclic entities.[14] In order to explore extended derivatives of CBPQT4+, whilst retaining access to the rich and varied chemistry of viologen-based

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radicals, it is important to maintain the structural integrity<sup>[15]</sup> of the bipyridinium units so as to allow the convenient generation and isolation of the respective radical cations by chemical means.

Herein, we describe the synthesis of (i) a new 'triangular' cyclophane, cyclotris(paraquat-p-phenylene) hexakis(hexafluorophosphate) (CTPQT-6PF<sub>6</sub>), which incorporates three paraguat units, separated from each other by para-phenylene groups, and (ii) its methoxy-substituted analog, cyclotris-(paraquat-p-1,4-dimethoxyphenylene) hexakis(hexafluorophosphate) (MCTPQT-6PF<sub>6</sub>), in which the phenylene groups are replaced by electron-rich 1.4-dimethoxyphenylene (DMP) units. resulting in a redox-active pillararene-like macrocycle. We have investigated their optical properties, electrochemistry and solidstate properties, in both their hexacationic and triply reduced forms. We have found that the incorporation of DMP units has important repercussions for the self-organization of **MCTPQT**•6PF<sub>6</sub> and its corresponding triply reduced trisradical trication (MCTPQT-3PF<sub>6</sub>) in the solid state that enabled us to obtain single crystals of sufficient quality for X-ray crystal structure analysis.

The synthesis (Scheme 1) of **CTPQT**•6PF<sub>6</sub> and **MCTPQT**•6PF<sub>6</sub> was carried out by heating their corresponding bis(bromomethylaryl)dipyridinium and (aryl-bismethylene)dipyridinium salts under reflux in the presence of TBAI in MeCN, affording **CTPQT**•6PF<sub>6</sub> and **MCTPQT**•6PF<sub>6</sub> in yields of 23% and 19%, respectively. See Scheme S1 for details.



Scheme 1. Synthesis of CTPQT•6PF<sub>6</sub> and MCTPQT•6PF<sub>6</sub>.

**CTPQT**•6PF<sub>6</sub> is a white solid analogous to the PF<sub>6</sub><sup>-</sup> salt<sup>[10]</sup> of **CBPQT**<sup>4+</sup>. In contrast, **MCTPQT**•6PF<sub>6</sub> is yellow in the solid state and in solution, exhibiting a weak absorption (Figure S7) centered on 366 nm (log  $\varepsilon$  = 3.17) in MeCN, indicative of an intramolecular charge-transfer interaction presumably between the methoxy groups and the adjacent bipyridinium units.<sup>[16]</sup>

Colorless crystals of **CTPQT**•6PF<sub>6</sub> were grown by vapor diffusion of  ${}^{i}Pr_{2}O$  into a solution of **CTPQT**•6PF<sub>6</sub> in MeCN, resulting<sup>[17]</sup> in two polymorphs. The molecular dimensions of the triangular cyclophane (Figure 1a) are determined by the lengths of its constituent parts—bipyridinium (~10.0 Å) and xylylene (~5.8 Å)— and the cyclophane exhibits a cavity size of ~10 Å. The solid-state structures, as determined by X-ray crystallography, of the two polymorphs demonstrate a lack of

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#### shape-persistence in **CTPQT**•6PF<sub>6</sub>. In both polymorphs, torsions of the three bipyridinium units of the cyclophane about their 4,4'-C-C bonds range widely from 2° to 62°. In one of the two polymorphs, the unusually low torsion angle of 2°, observed (Figure 1c) in one of the three bipyridinium units, the one in which the bipyridinium unit participates in interactions with PF<sub>6</sub><sup>-</sup> counterions, is presumably a result of packing constraints. The angle between adjacent bipyridinium and xylylene units, linked by bridging methylene groups, was observed to be 107–118° and deviates moderately from the ideal angle for planar truncated triangles (120°) and the characteristic angle (109.5°) between hybrid orbitals with $sp^3$ configuration. As a consequence, X-ray crystal structure analysis revealed four (Figure 1c) and two (Figure 1d) crystallographically equivalent **CTPQT<sup>6+</sup>** molecules in the unit cell of the two respective polymorphs. Their extended superstructures (Figure 1b and

polymorphs. Their extended superstructures (Figure 1b and Figure S11 and S12 in the SI) show a clear offset assembly of **CTPQT<sup>6+</sup>** hexacationic cyclophanes, which are intercalated by  $PF_6^-$  counterions and solvent molecules.



**Figure 1.** X-Ray crystal (super)structure of CTPQT•6PF<sub>6</sub> obtained from MeCN by vapor diffusion of 'Pr<sub>2</sub>O. a) Single CTPQT<sup>6+</sup> hexacation depicting side lengths and cavity size. b) Space-filling model of the CTPQT•6PF<sub>6</sub> superstructure of one of the two polymorphs showing offset-packing. c) Four separate crystallographically equivalent CTPQT<sup>6+</sup> molecules (colored in blue, medium blue, cornflower blue and seafoam green) in the crystal lattice of one polymorph. Top: Side-on angled view. Bottom-left: Top view. Bottom-right: Side-on view. d) Two different crystallographically equivalent CTPQT<sup>6+</sup> molecules (colored in blue and seafoam green) in the crystal lattice of the other polymorph. In a), c) and d) the PF<sub>6</sub><sup>-</sup> counterions and MeCN molecules are omitted for the sake of clarity.

We have taken note of investigations<sup>[18]</sup> on a triangular pyromellitic diimide (PMDI) macrocycle, which is reminiscent structurally of **CTPQT**•6PF<sub>6</sub>—containing DMP and PMDI units instead of phenylene and bipyridinium units, respectively—but is more rigid and lacks counterions. In contrast to **CTPQT**•6PF<sub>6</sub>, the self-organization of these PMDI-based macrocycles to form nanotubular superstructures is apparent when crystallized in the presence of toluene or [2<sup>3</sup>]paracyclophane.

We have investigated the crystal growth of a derivative of the **CTPQT<sup>6+</sup>** hexacation which incorporates three DMP units into its triangular scaffold, yielding **MCTPQT**•6PF<sub>6</sub>, with the result that an intricate tubular organization in the solid state is achieved. Yellow needle-like crystals of sufficient quality for X-ray crystal (super)structure analysis were obtained from slow vapor

diffusion of  $Pr_2O$  into a solution of the cyclophane in Me<sub>2</sub>CO. After examining different crystalline samples, we found that **MCTPQT**•6PF<sub>6</sub> does not form polymorphs<sup>[19]</sup> under these conditions. The macrocycle shows (Figure 2a) similar side lengths (~10.0 and ~5.8 Å) and cavity size (~10 Å) to its parent counterpart **CTPQT**•6PF<sub>6</sub>.



**Figure 2.** X-Ray crystal (super)structures of **MCTPQT**•6PF<sub>6</sub>. a) Single **MCTPQT**<sup>6+</sup> molecule depicting side lengths, cavity size and angles. b) Angled top view of **MCTPQT**<sup>6+</sup> molecule illustrating C<sub>3</sub>-symmetry and close distances between the methoxyl oxygen atoms and the nitrogen atom and a-carbons of the bipyridinium units. c) Side-on view of tubular assembly of five **MCTPQT**<sup>6+</sup> molecules illustrating van der Waals separations between methoxyl groups. d) Top view of four **MCTPQT**<sup>6+</sup> molecules illustrating noncovalent bonding interactions. Counterions, hydrogen atoms, and Me<sub>2</sub>CO molecules are omitted for the sake of clarity.

The torsion angles of all the bipyridinium units about their 4,4'-C-C bond range from 27° to 43° and the angles between the bipyridinium and the xylylene units that are linked by the methylene groups were found to range between 108 and 112°. It is worth noting that the oxygen atoms of the methoxy groups are positioned (Figure 2b) in close proximity to the nitrogens (2.9-3.3 Å) and  $\alpha$ -carbons (2.8-3.3 Å) of the bipyridinium units, which may contribute to charge-transfer interactions indicated by the UV/Vis absorption spectrum (Figure S8 in the SI) of **MCTPQT**•6PF<sub>6</sub>.

Three crystallographically equivalent **MCTPQT**<sup>6+</sup> hexacationic macrocycles were observed (Figure S13 in the SI) by X-ray crystallography, all of which exhibited local  $C_3$ -symmetry and revealed (Figure 2c) van der Waals separations (3.4–3.6 Å) between the methoxyl groups on the DMP pillars of adjacent triangles, leading to the formation of channel-like architectures. These channels are arranged in a tessellated manner, with interactions (Figure 2d) between each tubular assembly characterized by (i) offset  $\pi$ – $\pi$  interactions (3.3–3.5 Å) between the bipyridinium units and methoxyl groups of the DMP units.

The modification of **CTPQT**•6PF<sub>6</sub> with DMP pillars creates spacings between the rims of the cyclophanes in which all the  $PF_6^-$  counterions are situated giving rise for a porous architecture (Figure S13 in the SI) with an accessible volume of 33.6 %. The pores are filled with solvent molecules coming from the crystallization procedures. After removing the solvent under vacuum overnight, powder X-ray diffraction analysis was carried

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out to assess whether the structural integrity of the pores is still maintained when devoid of solvent molecules. While the PXRD indicated that the material was still crystalline, it was not consistent with the diffraction pattern for the channel-like superstructure (Figure S15 in the SI) simulated from the single X-ray crystal structure analysis. This observation suggests that the Me<sub>2</sub>CO molecules promote the stabilization of this highly ordered superstructure. The dried microcrystalline sample could not be investigated further by single crystal X-ray structure analysis as a result of the poor diffraction of the sample. Indeed, N<sub>2</sub> isotherm measurements (see SI Figure S16) of the desolvated material confirmed a lack of porosity. We suggest that MCTPQT•6PF<sub>6</sub> undergoes polymorphism upon removal of Me<sub>2</sub>CO molecules.

Cyclic voltammetry of **CTPQT**•6PF<sub>6</sub> and **MCTPQT**•6PF<sub>6</sub> reveal (Figure S10 in SI) two reversible three-electron transfer processes. In the case of **CTPQT**<sup>6+</sup>, the redox waves at -0.74 and -1.17 V (vs. Fc<sup>+</sup>/Fc couple) correspond to the reversible formation of the (i) trisradical trication and (ii) the fully reduced neutral state, respectively. **MCTPQT**<sup>6+</sup> shows similar redox behavior, with small cathodic shifts of the redox waves to -0.79 and -1.22 V, which can be ascribed to the increased electronic density provided by the electron-rich DMP units.

Taking into account the potentials of the redox waves, we employed Zn dust to generate their corresponding trisradical tricationic species in MeCN. After removing the excess of Zn dust by filtration, the filtrate containing CTPQT-3PF<sub>6</sub> was subjected to vapor diffusion with Pr<sub>2</sub>O, resulting in a dark purple polycrystalline or film-like material of insufficient quality to conduct a single crystal structure analysis. In contrast, purplecolored single crystals of MCTPQT-3PF<sub>6</sub> could be grown under the same conditions and were investigated<sup>[20]</sup> by X-ray crystallography. In the solid state, MCTPQT-3PF<sub>6</sub> (Figure 3a) has similar side-lengths and cavity size to those exhibited by CTPQT•6PF<sub>6</sub> and MCTPQT•6PF<sub>6</sub>. The torsion angles present in the bipyridinium radical cations, however, are dramatically decreased to below 5° when compared with those present in bipyridinium dications in the fully cationic state: This observation is not uncommon<sup>[13]</sup> for open-shell viologens. The distances measured between the methoxyl oxygen atoms and the pyridinium nitrogen and α-carbon atoms (Figure 3b) suggests the presence of ion-dipole intramolecular interactions of 2.9-3.4 Å and 2.8-3.5 Å, respectively, between these two groups. The spatial orientation of the DMP pillars does not give rise to  $C_3$ symmetry as was observed (Figure 2b) in the solid-state structure of its fully oxidized form MCTPQT•6PF<sub>6</sub>.

The packing of the **MCTPQT**•3PF<sub>6</sub> trisradical trications in the extended solid-state superstructure (Figure 3c) was found to be predominantly a result of (i) radical-radical interactions, (ii) DMP-viologen interactions and (iii) offset  $\pi$ - $\pi$  stacks between the DMP units. The accessible volume of this superstructure is decreased by more than half to 14.1% when compared with that of its fully oxidized form.

The cyclophanes are paired (Figure 3c) by the inclusion of one of the DMP units of one cyclophane inside the cavity of an adjacent cyclophane, resulting in  $\pi$ - $\pi$  interactions (3.4 Å) between DMP and viologen radical cation units. These radical cationic units are involved in distinctly offset radical-radical interactions (3.3 Å), exhibiting a negligible interaxial angle

(Figure 3c, inset) with a bipyridinium unit that is stacked with the DMP unit of another neighboring cyclophane, resulting in a quadruple  $\pi$ -stack in which an unprecedented  $\pi$ -stack of a viologen radical pimer, sandwiched between two DMP units. The pimer is characterized by a marginal orbital overlap between two  $\alpha$ -carbon and two  $\beta$ -carbon atoms. The remaining bypyridinium units of the respective cyclophane show radical–radical interactions (3.1 Å) with near-planar viologen units with a high interaxial angle of 76° and  $d(\text{HC}^{\bullet\bullet\bullet\pi}\pi)$  interactions (3.4 Å) with DMP units. Furthermore, one DMP unit is paired (3.4 Å) with another DMP unit of an adjacent cyclophane.



**Figure 3.** X-Ray crystal (super)structures of trisradical trication **MCTPQT**•3PF<sub>6</sub>. a) Single **MCTPQT**<sup>3(•+)</sup> molecule depicting side lengths, cavity size and angles. b) Angled top view of **MCTPQT**<sup>3(•+)</sup> molecule illustrating close distances between the methoxyl oxygen atoms and the nitrogen atom and  $\alpha$ -carbons of the bipyridinium units. c) Top view of eight **MCTPQT**<sup>3(•+)</sup> molecules illustrating predominant noncovalent bonding interactions and torsion angles between pairs of bipyridinium units. Counterions, hydrogen atoms, and MeCN molecules are omitted for the sake of clarity.

In comparison with previously reported<sup>[14]</sup> bipyridiniumcontaining cyclophanes in their radical states, the dramatic differences in the recognition motif associated with the bipyridinium radical cations presented by this system—as determined by X-ray crystallography—demonstrate the tunability<sup>[13]</sup> of these radical–radical interactions, that can prove effective when incorporated in macrocyclic scaffolds involving DMP units. These findings may have implications for, and may open up new opportunities in, the design of bipyridinium-based materials,<sup>[21]</sup> particularly from the point of view of their conductive and magnetic properties.

In summary, we have synthesized a new class of paraquatcontaining cyclophanes—incorporating three bipyridinium units separated by three xylylene groups— that adopt a triangular arrangement. In contrast to the polymorphic and less-intricate self-organization of the parent cyclotris(paraquat-*p*-phenylene) (**CTPQT**<sup>6+</sup>), the assembly of a porous superstructure in the case of cyclotris(paraquat-*p*-1,4-dimethoxyphenylene) (**MCTPQT**<sup>6+</sup>) was achieved by replacing the phenylene units with electron-rich 1,4-dimethoxyphenylene (DMP) units, highlighting the effective tunability of their solid-state superstructures. The triangular shape and orientation of the DMP pillars represent an increase in structural complexity when compared with cyclic paraquat dimeric analogs reported previously.<sup>[11]</sup> The intermolecular

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interactions involved in the solid-state superstructure are not characterized by interactions between  $\pi$ -electron rich and  $\pi$ electron poor units, but rather established by offset  $\pi-\pi$ interactions between DMP units, d(CH ••• O) interactions and van der Waals interactions involving the methoxyl groups of the pillars. The radical form, MCTPQT-3PF<sub>6</sub>, has been synthesized and obtained as high-quality single crystals for X-ray crystal (super)structural analysis. Notably, a quadruple stack composed of a radical cationic pimer, sandwiched between two DMP units, demonstrates the disruptive impact of the electron-rich pillars on the radical cation recognition motif. In particular, the marginal overlap between the radical cationic bipyridinium units by only two α-carbons and two β-carbons is unprecedented and may provide new insights into the manipulation and control of the self-assembly behavior of viologen radical cations. We envision cyclotris(paraquat-p-phenylene) and its derivatives as a fruitful entry point into the fabrication of advanced mechanically interlocked molecules and supermolecules with intricate threedimensional features.<sup>[21]</sup> Their redox properties also provide access to their corresponding radical forms which open the doors to further possibilities including spintronics applications.<sup>[22]</sup>

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[17] (*i*) Polymorph 1 Crystal Parameters.  $C_{126}H_{123}F_{72}N_{21}P_{12}$ , Monoclinic, space group  $P_{21}/n$  (no. 14), a = 31.3397(9), b = 13.9653(5), c = 35.0975(10) Å,  $\beta = 91.751(2)^{\circ}$ , V = 15353.9(8) Å<sup>3</sup>, Z = 4, T = 100 K,  $\mu$ (CuK $\alpha$ ) = 2.54 mm<sup>-1</sup>,  $D_{calc} = 1.59$  g/mm<sup>3</sup>, 83372 reflections measured (3.84  $\leq 2\Theta \leq 130.31$ ), 25551 unique ( $R_{int} = 0.05$ ,  $R_{sigma} = 0.05$ ) which were used in all calculations. The final  $R_1$  value was 0.06 ( $l > 2\sigma(l)$ ) and  $wR_2$  was 0.18 (all data). CCDC 1914248.

*Refinement Details.* Rigid bond restraints were imposed on the displacement parameters as well as restraints on similar amplitudes separated by less than 1.7 Å on the disordered fluorine atoms. Distance restraints were imposed on the disordered  $PF_6^-$  counterions.

(*ii*) Polymorph 2 Crystal Parameters.  $C_{57}H_{52.5}F_{36}N_{7.5}P_6$ , Monoclinic, space group  $P2_1$  (no. 4), a = 18.0524(16), b = 29.672(2), c = 27.797(3) Å,  $\beta = 101.125(5)^\circ$ , V = 14609(2) Å<sup>3</sup>, Z = 8, T = 100.0 K,  $\mu$ (CuK $\alpha$ ) = 2.61 mm<sup>-1</sup>, *Dcalc* = 1.56 g/mm<sup>3</sup>, 54005 reflections measured (3.24  $\leq 20 \leq 101.12$ ), 29733 unique ( $R_{int} = 0.21$ ,  $R_{sigma} = 0.22$ ) which were used in all calculations. The final  $R_1$  value was 0.12 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.36 (all data). CCDC 1914249.

Refinement Details. The enhanced rigid-bond restraint (SHELX keyword RIGU) was applied globally. The solvent masking procedure, as implemented in Olex2 was used to remove the electronic contribution of solvent molecules from the refinement. Since the exact solvent content is not known, only the atoms used in the refinement model are reported in the formula here. Total solvent accessible volume / cell = 1211.4 Å<sup>3</sup> [8.3%]. Total electron count / cell = 297.8.

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Refinement Details. Distance restraints were imposed on the disordered PF<sub>6</sub><sup>-</sup> counterion as well as the enhanced rigid-bond restraint (SHELX keyword RIGU). The solvent masking procedure, as implemented in Olex2 was used to remove the electronic contribution of solvent molecules from the refinement. As the exact solvent content is not known, only the atoms used in the refinement model are reported in the formula here. Total solvent accessible volume / cell = 3354.5 Å<sup>3</sup> [33.6%]. Total electron count / cell = 719.0.

[20] Crystal Parameters. C<sub>60</sub>H<sub>60</sub>F<sub>18</sub>N<sub>6</sub>O<sub>6</sub>P<sub>3</sub>, Monoclinic, space group  $P_{2t/n}$ (no. 14), a = 18.4214(12), b = 10.9307(8), c = 32.7544(16) Å,  $\beta = 93.482(4)^{\circ}$ , V = 6583.2(7) Å<sup>3</sup>, Z = 4, T = 100.0 K,  $\mu$ (CuK $\alpha$ ) = 1.76 mm<sup>-1</sup>, Dcalc = 1.41 g/mm<sup>3</sup>, 22423 reflections measured (5.37  $\leq 20 \leq 124.77$ ), 9924 unique ( $R_{int} = 0.08$ ,  $R_{sigma} = 0.10$ ) which were used in all calculations. The final  $R_1$  was 0.09 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.28 (all data). CCDC 1914256.

Refinement Details. The solvent masking procedure as implemented in Olex2 was used to remove the electronic contribution of solvent molecules from the refinement. As the exact solvent content is not known, only the atoms used in the refinement model are reported in the formula here. Total solvent accessible volume / cell = 927.8 Å<sup>3</sup> [14.1%]. Total electron count / cell = 171.6.

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