

A Three-Pole Supramolecular Switch<sup>†</sup>

Peter R. Ashton,<sup>‡</sup> Vincenzo Balzani,<sup>\*,§</sup> Jan Becher,<sup>#</sup> Alberto Credi,<sup>§</sup> Matthew C. T. Fyfe,<sup>||</sup> Gunter Matternsteig,<sup>||</sup> Stephan Menzer,<sup>⊥</sup> Mogens B. Nielsen,<sup>||</sup> Francisco M. Raymo,<sup>||</sup> J. Fraser Stoddart,<sup>\*,||</sup> Margherita Venturi,<sup>\*,§</sup> and David J. Williams<sup>\*,⊥</sup>

Contribution from The School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT, U.K., Dipartimento di Chimica "G. Ciamician" dell'Università di Bologna, via Selmi 2, I-40126 Bologna, Italy, Department of Chemistry, Odense University, Campusvej 55, DK-5230 Odense M., Denmark, Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90095, and Department of Chemistry, Imperial College, South Kensington, London SW7 2AY, U.K.

Received December 15, 1998

**Abstract:** A supramolecular system that switches reversibly, via three different states, through electrochemical adjustment of the guest properties of tetrathiafulvalene (TTF) has been developed. <sup>1</sup>H NMR, luminescence, and absorption spectroscopies, in conjunction with LSI mass spectrometry, X-ray crystallography, and cyclic/differential pulse voltammetries, established that the  $\pi$ -electron-accepting (EA) tetrathiafulvalenium dication (TTF<sup>2+</sup>) binds strongly within the cavity of the  $\pi$ -electron-donating (ED) macrocyclic polyether 1,5-dinaphtho[38]crown-10 (1/5DN38C10), generating a host–guest complex that is stabilized by, inter alia,  $\pi$ – $\pi$  stacking interactions. Comparable techniques have also demonstrated that neutral tetrathiafulvalene (TTF(0)) acts as an ED guest when it complexes with the EA tetracationic cyclophane cyclobis(paraquat-*p*-phenylene) (CBPQT<sup>4+</sup>). On the other hand, the tetrathiafulvalenium radical cation (TTF<sup>•+</sup>) is not bound by either of the hosts CBPQT<sup>4+</sup> or 1/5DN38C10. Electrochemical experiments revealed that the three-component mixture CBPQT<sup>4+</sup>–1/5DN38C10–TTF behaves as a reversible three-pole supramolecular switch, since, depending on the potential range, TTF can be (1) free (in the TTF<sup>•+</sup> state), (2) included within the cavity of CBPQT<sup>4+</sup> (as TTF(0)), or (3) complexed with 1/5DN38C10 (in the TTF<sup>2+</sup> state). The system's three-pole behavior has interesting implications in relation to the design of electrochromic displays and devices capable of controlling energy- or electron-transfer processes between selected components.

## Introduction

Many examples exist already of supramolecular<sup>1</sup> systems that exhibit two-pole electrochemical switching.<sup>2</sup> These systems rely, for instance, upon (1) hydrogen bond-driven recognition processes,<sup>3</sup> (2) guest encapsulation by cyclodextrins,<sup>4</sup> (3) threading/dethreading of pseudorotaxanes,<sup>5</sup> and (4) translational isomerizations in suitably designed [2]rotaxanes<sup>6</sup> or [2]catenanes.<sup>7</sup> In this article, we describe a supramolecular system that can be switched between three distinct states through electrochemical manipulation of a guest's redox properties in the presence of

two hosts with differing  $\pi$ -donor/ $\pi$ -acceptor capabilities. The new system we report here is comprised (Figure 1) of two hosts—namely,<sup>7b</sup> the  $\pi$ -electron-accepting (EA) tetracationic cyclophane cyclobis(paraquat-*p*-phenylene) (CBPQT<sup>4+</sup>) and the  $\pi$ -electron-donating (ED) macrocyclic polyether 1,5-dinaphtho[38]crown-10 (1/5DN38C10)—and tetrathiafulvalene (TTF), a guest known<sup>8</sup> to exist in three stable forms, specifically, TTF(0),

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<sup>†</sup> Molecular Meccano, Part 53. For Part 52, see: Amabilino, D. B.; Ashton, P. R.; Bravo, J. A.; Raymo, F. M.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *Eur. J. Org. Chem.* Submitted.

\* Corresponding authors. Address correspondence to Prof. J. F. Stoddart at The Department of Chemistry and Biochemistry, University of California, Los Angeles, CA 90095. Tel.: +(310) 206-7078. Fax: +(310) 206-1843. E-mail: stoddart@chem.ucla.edu.

<sup>‡</sup> University of Birmingham.

<sup>§</sup> Università di Bologna.

<sup>#</sup> Odense University.

<sup>||</sup> University of California, Los Angeles.

<sup>⊥</sup> Imperial College.

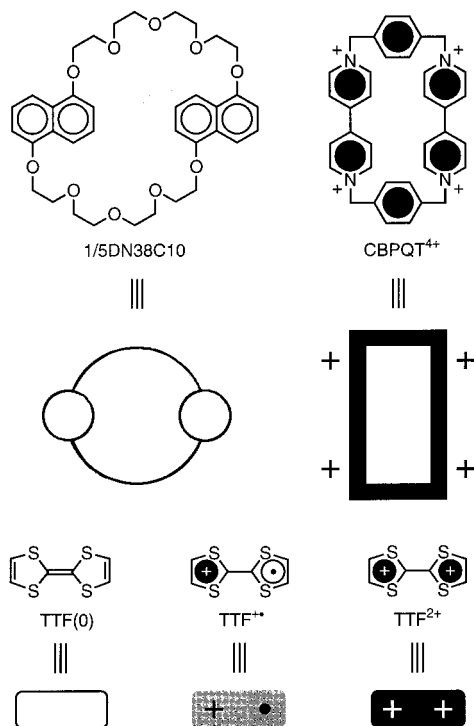
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**Figure 1.** Structural formulas and schematic representations of the components of the three-pole supramolecular switch described here.

TTF<sup>+</sup>, and TTF<sup>2+</sup>. Previous studies<sup>5c,9</sup> have demonstrated that TTF(0), in its role as an ED guest, gives a 1:1 charge-transfer complex with CBPQT<sup>4+</sup>, as evidenced by NMR and UV–vis absorption spectroscopies, X-ray crystallography, and electrochemical experiments. In addition, these investigations established that the components could be reversibly de-/recomplexed by cyclic oxidation/reduction of the TTF moiety. Following these observations, we decided to reverse the role of the TTF component; i.e., we considered that TTF<sup>2+</sup>—generated from the ED guest TTF(0) via oxidation—could play the role of an EA guest in complexes with ED hosts. If this proposal is valid, then it should be possible to use TTF as a switchable ED/EA guest, so that its association with EA/ED hosts can be controlled electrochemically. This article reports that TTF<sup>2+</sup> does, indeed, associate with ED 1/5DN38C10, thereby making it possible to exploit the properties of TTF for the construction of a three-pole supramolecular switch in which electrochemical stimuli can be utilized to shift the system between three states.

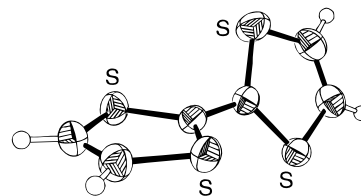
## Results and Discussion

**NMR Spectroscopy/Mass Spectrometry.** The <sup>1</sup>H and <sup>13</sup>C NMR resonances of the uncomplexed TTF<sup>2+</sup> dication (2ClO<sub>4</sub><sup>-</sup> salt<sup>10</sup>) are shifted downfield substantially,<sup>11</sup> with respect to those of its neutral congener TTF(0), by virtue of the deshielding arising from the two sets of cationic 6π-electron aromatic rings. Complex formation between 1/5DN38C10 and the dication was

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**Figure 2.** Thermal ellipsoid plot (50% probability ellipsoids) illustrating the structure of TTF<sup>2+</sup> in the solid state.

indicated from the <sup>1</sup>H NMR spectrum (400 MHz, CD<sub>3</sub>CN–CD<sub>3</sub>NO<sub>2</sub> (5:3), 191 K) of an equimolar mixture of both components. The two signals detected for the protons of complexed TTF<sup>2+</sup>, located at δ 8.89 and 9.37 (relative intensities 1:3), are shifted upfield with respect to the proton resonances found for free TTF<sup>2+</sup> (δ 9.50) under identical conditions. These shifts can be attributed to the creation of two<sup>12</sup> distinct 1/5DN38C10·TTF<sup>2+</sup> complexes that are both stabilized by π–π stacking interactions, the resonances with the larger and smaller shifts being correlated, respectively, to inclusion and alongside face-to-face complexes. The formation of 1/5DN38C10·TTF<sup>2+</sup> was also demonstrated in the gas phase by mass spectrometry; the LSI mass spectrum of an equimolar 1/5DN38C10–TTF<sup>2+</sup>·2ClO<sub>4</sub><sup>-</sup> mixture displays a peak at *m/z* 840, which corresponds to the complex 1/5DN38C10·TTF<sup>+</sup>, i.e., a 1:1 species with an additional electron.

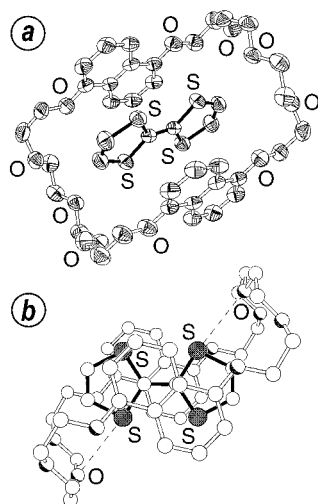
**X-ray Crystallography.** The solid-state structure<sup>13</sup> of TTF<sup>2+</sup> (2ClO<sub>4</sub><sup>-</sup> salt) shows (Figure 2) it to have a twisted gauche-like conformation (mean torsional angle 60°) associated with its two five-membered rings. The S–C bond lengths are in the range 1.660(4)–1.695(5) Å, while the interconnecting C–C bond is 1.467(5) Å in length. The cations and anions are cross-linked by a combination of [C–H···O] hydrogen bonds (ranging from 2.42 to 2.56 Å), involving all four methine hydrogen atoms, and electrostatic interactions between all four sulfur atoms and the oxygen atoms of the ClO<sub>4</sub><sup>-</sup> ions ([S<sup>δ+</sup>···O<sup>δ-</sup>] distances lie in the range 2.97–3.29 Å). We believe that, in all probability, the conformation of TTF<sup>2+</sup> is determined (vide infra) by the multiple interactions that define its supramolecular order.

The X-ray analysis of the 1:1 complex [1/5DN38C10·TTF<sup>2+</sup>]<sub>2</sub>[ClO<sub>4</sub><sup>-</sup>]<sub>2</sub> reveals a superstructure with crystallographic inversion symmetry, the essentially planar dication being sandwiched symmetrically between the two 1,5-dioxynaphthalene ring systems (mean interplanar separation 3.52 Å) of the macrocyclic polyether (Figure 3a). The central C–C axis of the dication TTF<sup>2+</sup> is inclined by 47° to the central C–C bond of each of these ring systems, while the central oxygen atom of each polyether loop is folded back so as to lie only 3.25 Å from diametrically opposite sulfur atoms of the dication (Figure 3b).

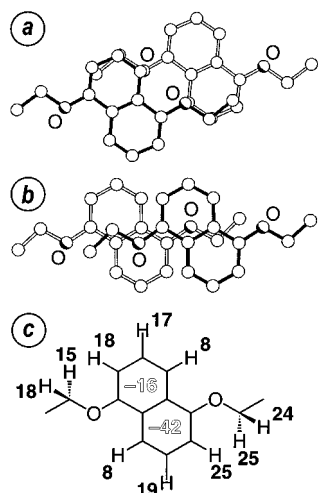
(11) Indeed, the chemical shift values found for the C–H unit of TTF<sup>2+</sup>·2ClO<sub>4</sub><sup>-</sup> are similar to those of Paraquat·2PF<sub>6</sub><sup>-</sup>, another dication that is bound strongly by 1/5DN38C10. See: Ashton, P. R.; Chrystal, E. J. T.; Mathias, J. P.; Parry, K. P.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Williams, D. J. *Tetrahedron Lett.* **1987**, 28, 6367–6370.

(12) Presaturation experiments demonstrate that the TTF<sup>2+</sup> dications of each of the complexes undergo site exchange with one another. It should be noted, however, that this exchange process is slow on the <sup>1</sup>H NMR time scale (400 MHz) at 191 K, as evidenced by the presence of the two signals for complexed TTF<sup>2+</sup>.

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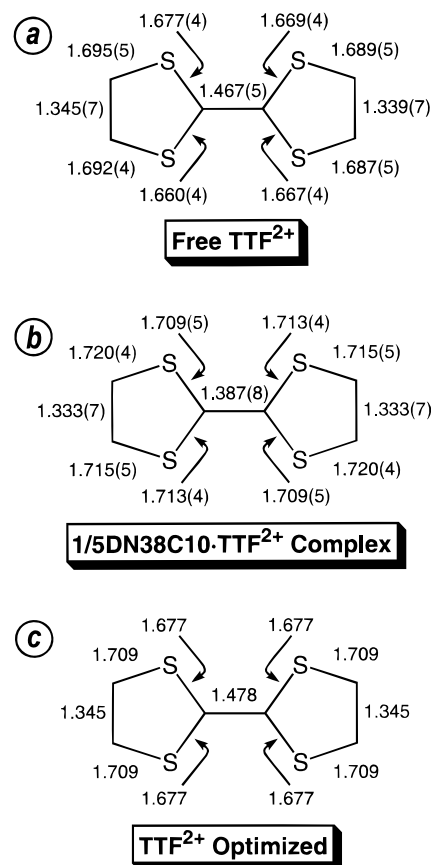
**Figure 3.** Views showing the 1/5DN38C10·TTF<sup>2+</sup> complex in the solid state. (a) Thermal ellipsoid plot (50% probability ellipsoids) highlighting the  $\pi$ - $\pi$  stacking interactions between the crown ether host's 1,5-dioxynaphthalenes and the TTF<sup>2+</sup> guest. (b) Ball-and-stick representation emphasizing the  $[S^{\delta+}\cdots O^{\delta-}]$  interactions that contribute additional stabilization to the complex.



**Figure 4.** Stacking motifs encountered for the 1,5-dioxynaphthalene ring systems in the solid-state structures of (a) 1/5DN38C10·TTF<sup>2+</sup> (intermolecular interaction) and (b) 1/5DN38C10 (intramolecular interaction). (c) Electrostatic potential values (HF/3-21G, kcal mol<sup>-1</sup>) calculated on the van der Waals surfaces of the hydrogen atoms and the aromatic rings.

An inspection of the packing of the complexes reveals (Figure 4a) a parallel offset stacking of the 1,5-dioxynaphthalenes (interplanar separation 3.39 Å). Although the  $\pi$ -systems can be considered to include the phenolic oxygen atoms, this arrangement would not normally be adjudged to be (vide infra) a "conventional"  $\pi$ - $\pi$  stacking interaction. However, an examination of the solid-state structure of uncomplexed 1/5DN38C10, which also has a  $C_i$ -symmetric geometry, reveals (Figure 4b) a very similar intramolecular stacking motif for the 1,5-dioxynaphthalenes (interplanar separation 3.46 Å).

Two particularly interesting features of note emerge with respect to the attributes of the dication TTF<sup>2+</sup> as a function of its complexation by 1/5DN38C10. First, it changes its conformation readily from a twisted to a planar geometry, suggesting (vide infra) minimal energy demands. Second, and perhaps more significantly, there are pronounced changes in the covalent bonding patterns within the dication. In the twisted uncomplexed state, the two five-membered rings have local  $C_{2v}$  symmetry



**Figure 5.** Diagram comparing the covalent bond lengths (Å) within the TTF<sup>2+</sup> unit in its (a) free state, (b) complex with 1/5DN38C10, and (c) optimized (HF/6-31+G\*) geometry. The data for (a) and (b) were obtained from the X-ray analyses, while those for (c) were calculated computationally.

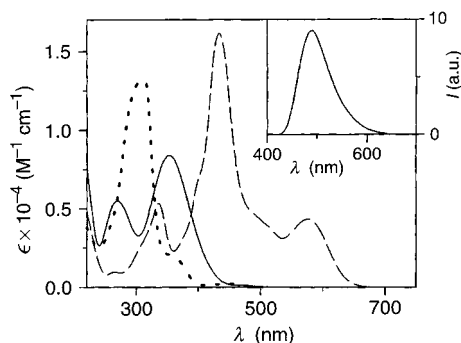
about the C-C bond linking them (Figure 5a). The bonds from each sulfur atom are, in all cases, asymmetric, with those to the terminal olefinic carbon atoms noticeably longer than those to the carbon atoms linking the two ring systems. Overall, there appears to be substantial delocalization within each five-membered ring. The interlinking C-C bond length is typical of a  $C_{sp^2}$ - $C_{sp^2}$  single bond; i.e., the twisting of the two five-membered ring systems with respect to one another inhibits any significant interannular delocalization. Upon complexation, and the adoption of an essentially planar geometry with overall  $D_{2h}$  symmetry, the terminal olefinic bond length is essentially unchanged, but all the C-S bonds equalize and show (Figure 5b) a noticeable increase in their lengths. Accompanying these changes is a marked reduction in the  $C_{sp^2}$ - $C_{sp^2}$  bond length, which is now comparable to that expected for a delocalized C=C bond. Indeed, it is fair to say that, upon complexation, TTF<sup>2+</sup> adopts bond lengths and angles which resemble those of TTF(0).<sup>14</sup>

**Molecular Modeling.** Single-point calculations<sup>15</sup> (MP2/6-31+G\*) of the energies associated with the solid-state geometries of free and complexed TTF<sup>2+</sup> revealed that the "twisted" conformation illustrated in Figure 2 is ca. 5.2 kcal mol<sup>-1</sup> more stable than the "flat" conformation displayed in Figure 3. This energy difference is compensated for by the intracomplex noncovalent bonding interactions present<sup>16</sup> in 1/5DN38C10·

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**Figure 6.** Absorption spectra (MeCN, 298 K) of  $\text{TTF}^{2+}$ ,  $\text{TTF}^{+}$ , and  $\text{TTF}(0)$ , represented by full, dashed, and dotted lines, respectively. Inset: Emission spectrum (MeCN, 298 K,  $\lambda_{\text{exc}} = 352$  nm) of  $\text{TTF}^{2+}$ .

$\text{TTF}^{2+}$ . The optimized (HF/6-31+G\*) geometry of  $\text{TTF}^{2+}$  is “twisted”, with a torsion angle of  $47^\circ$  about the bond linking the two five-membered rings. Remarkable similarities were noted between the bond lengths found (Figure 5) for this optimized geometry and free  $\text{TTF}^{2+}$  in the solid state. Nevertheless, the optimized geometry is more stable than the observed crystal structure geometry by ca.  $59.8$  kcal mol $^{-1}$  (MP2/6-31+G\*); i.e., subtle geometrical changes strongly destabilize the  $\text{TTF}^{2+}$  unit. This destabilization is offset by the intermolecular bonding interactions present in the crystalline state.

An examination of the HF/3-21G electrostatic potential surface of two  $\pi$ -stacked 1,5-dioxynaphthalene ring systems reveals that the parallel offset co-conformation seen in the X-ray analyses is dictated by electrostatic interactions. Indeed, the electron-deficient hydrogen atoms of one ring system can maximize attractive electrostatic interactions with the electron-rich  $\pi$ -surface of the other only when the two ring systems are slightly offset and parallel with respect to one another, i.e., when the hydrogen atoms with positive electrostatic potentials (Figure 4c) from one ring overlay their negative counterpart on the other.

**Absorption Spectra, Luminescence Properties, and Stability Constants.** The absorption spectra (MeCN, 298 K) of  $\text{TTF}(0)$ ,  $\text{TTF}^{+}$ , and  $\text{TTF}^{2+}$  are shown in Figure 6.<sup>8a,b</sup> While  $\text{TTF}(0)$  and  $\text{TTF}^{+}$  do not exhibit any luminescence at all,  $\text{TTF}^{2+}$  displays a fluorescence band with a maximum at 488 nm ( $\Phi = 0.04$ ;  $\tau < 1$  ns).  $\text{CBPQT}^{4+}$  shows<sup>7b</sup> an absorption band whose maximum is located at 260 nm ( $\epsilon^* = 40\,000$  M $^{-1}$  cm $^{-1}$ ), while it does not give rise to an emission band. On the other hand, 1/5DN38C10 gives<sup>7b</sup> an absorption band whose maximum is observed at 295 nm ( $\epsilon^* = 17\,600$  M $^{-1}$  cm $^{-1}$ ), as well as a fluorescence band at 345 nm ( $\Phi = 0.26$ ;  $\tau = 8.5$  ns). In MeCN at 298 K,  $\text{CBPQT}^{4+}$  and  $\text{TTF}(0)$  associate with one another to produce a strong 1:1 complex, with a stability constant<sup>17</sup> ( $K_a$ ) of  $(1.0 \pm 0.1) \times 10^4$  M $^{-1}$ , that exhibits a broad charge-transfer absorption band with a maximum located at 855 nm ( $\epsilon^* = 3000$  M $^{-1}$  cm $^{-1}$ ).<sup>18</sup> Conversely,  $\text{TTF}^{+}$  and  $\text{TTF}^{2+}$  do not interact with  $\text{CBPQT}^{4+}$  under otherwise indistinguishable conditions, as indicated by the absence of any changes to either spectroscopic or electrochemical (vide infra) properties. When  $\text{TTF}^{2+}$  ( $2\text{ClO}_4^-$  salt) was mixed with 1/5DN38C10 in MeCN at 298 K, we

(16) The binding energy, determined experimentally from the stability constant (vide infra), is ca.  $4.9$  kcal mol $^{-1}$  in MeCN at 298 K.

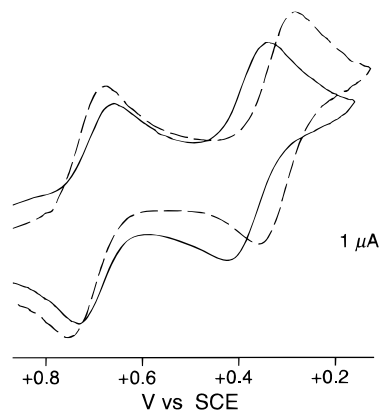
(17) In addition, the  $K_a$  value for the  $\text{CBPQT}^{4+}\text{-TTF}(0)$  complex was determined to be  $1.0 \times 10^4$  M $^{-1}$  ( $\text{CD}_3\text{CN}$ , 300 K) by a  $^1\text{H}$  NMR titration experiment that exploited the correlation between the chemical shift of the tetracation's  $\beta$ -bipyridinium protons and the  $\text{TTF}(0)$  concentration in a nonlinear curve-fitting program. Previously,<sup>9b</sup> on the basis of  $^1\text{H}$  NMR dilution and spectrophotometric titration experiments, a  $K_a$  of ca.  $8.0 \times 10^3$  M $^{-1}$  (MeCN, 298 K) was established for the  $\text{CBPQT}^{4+}\text{-TTF}(0)$  complex.

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**Table 1.** Electrochemical Data for the Redox Processes Involving  $\text{TTF}^a$

system <sup>b</sup>	$E'_{1/2}$ (V vs SCE)	$E''_{1/2}$ (V vs SCE)
free TTF	+0.321	+0.714
$\text{CBPQT}^{4+}\text{-TTF}$	+0.391	+0.714
1/5DN38C10-TTF	+0.321	+0.700
$\text{CBPQT}^{4+}\text{-1/5DN38C10-TTF}$	+0.391	+0.700

<sup>a</sup> Ar-purged MeCN solutions, all processes are reversible and mono-electronic, experimental error  $\pm 2$  mV. <sup>b</sup> The descriptor TTF stands for either  $\text{TTF}(0)$  or  $\text{TTF}^{2+}$ .



**Figure 7.** Cyclic voltammograms (MeCN, 298 K, scan rate 50 mV s $^{-1}$ ) of  $\text{TTF}^{2+}$  (1) by itself (dashed line) and (2) in the presence of excesses of  $\text{CBPQT}^{4+}$  and 1/5DN38C10 (full line).

observed (1) the appearance of a broad, weak absorption band in the near-IR spectral region ( $\epsilon^* = 1700$  M $^{-1}$  cm $^{-1}$  at 840 nm) and (2) the quenching of both components' fluorescence. These results are consistent with the formation of a 1:1 charge-transfer complex, wherein  $\text{TTF}^{2+}$  plays an EA role, and are in agreement with the evidence obtained by NMR spectroscopy, mass spectrometry, X-ray crystallography, and electrochemical experiments (vide infra).<sup>19</sup> The  $K_a$  value associated with the 1/5DN38C10- $\text{TTF}^{2+}$  complex, measured by absorption and emission spectral titrations,<sup>20</sup> is  $(4.1 \pm 0.4) \times 10^3$  M $^{-1}$ . Mixing either  $\text{TTF}(0)$  or  $\text{TTF}^{+}$  with 1/5DN38C10 does not produce any spectral changes, in accord with the absence of association, as also deduced from electrochemical experiments (vide infra).

**Electrochemical Properties.** We have performed systematic electrochemical investigations on (1) the isolated components  $\text{CBPQT}^{4+}$ , 1/5DN38C10, and TTF, (2) the two-component systems  $\text{CBPQT}^{4+}\text{-TTF}$  and 1/5DN38C10-TTF, and (3) the three-component system  $\text{CBPQT}^{4+}\text{-1/5DN38C10-TTF}$ , where, in each case, TTF stands for either  $\text{TTF}(0)$  or  $\text{TTF}^{2+}$ . The results are cataloged in Table 1.

Free TTF exhibits (Figure 7, dashed line) two reversible one-electron processes.<sup>8</sup> For a  $1 \times 10^{-4}$  M  $\text{TTF}(0)$  solution (MeCN) containing a 20-fold excess of  $\text{CBPQT}^{4+}$  (in order that more than 90% of the  $\text{TTF}(0)$  guest may be obtained as its complex

(19) Additional proof that  $\text{TTF}^{2+}$  can be included within the cavity of 1/5DN38C10 was provided from an extraction experiment in  $(\text{CH}_2\text{Cl})_2$ . Although  $\text{TTF}^{2+}\cdot 2\text{ClO}_4^-$  is completely insoluble in this solvent alone, it can be dissolved in  $(\text{CH}_2\text{Cl})_2$  in 1/5DN38C10's presence, as shown by the appearance of the typical  $\text{TTF}^{2+}$  band at 352 nm, together with the broad band in the near-IR spectral region that is attributable to a  $\text{TTF}^{2+}$  charge-transfer complex. Likewise, electrochemical experiments demonstrated that the first reduction process of  $\text{TTF}^{2+}$  is reversible in the macrocyclic polyether's presence and irreversible in its absence.

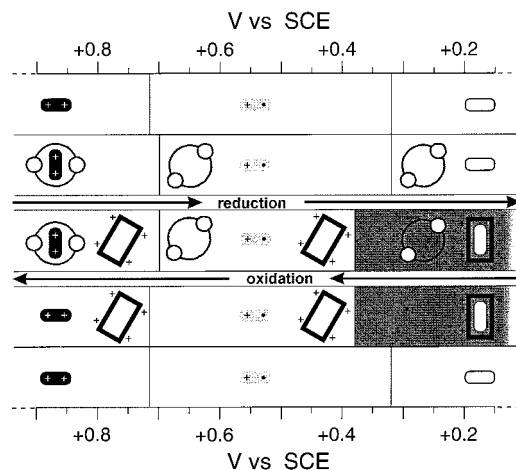
(20) In addition, the  $K_a$  for the 1/5DN38C10- $\text{TTF}^{2+}$  complex was found to be  $2.6 \times 10^3$  M $^{-1}$  through the use of  $^1\text{H}$  NMR titration experiments that employed the correlation between the chemical shift of the proton on the macrocyclic polyether's 4-naphthyl position and the  $\text{TTF}^{2+}\cdot 2\text{ClO}_4^-$  concentration.

with the tetracationic host), the first oxidation process is displaced by 70 mV to more positive potentials, while the second is unaffected.<sup>5c</sup> The current intensity of both processes is about 40% less than that for free TTF(0) as a result of the smaller diffusion coefficient for the electroactive CBPQT<sup>4+</sup>·TTF(0) complex. As expected for reversible electrochemical processes, the same potential values are obtained by replacing TTF(0) with TTF<sup>2+</sup>. Under such conditions, the current intensities of the processes involving TTF are unaffected by the presence of CBPQT<sup>4+</sup>, as the electroactive species is TTF<sup>2+</sup> in both this cyclophane's absence and presence. To summarize, these results indicate that TTF(0) is engaged as an ED guest in the CBPQT<sup>4+</sup>·TTF(0) complex and that this complex rapidly and reversibly decomplexes when the TTF(0) guest experiences its first electron loss.

For a  $1 \times 10^{-4}$  M TTF<sup>2+</sup> solution containing a 50-fold excess of 1/5DN38C10 (to ensure that more than 90% of this dication is complexed by the macrocyclic polyether), the first reduction process is moved to less positive potentials by 14 mV, while the second remains the same. For both processes, the current intensity is about 15% less than that for free TTF<sup>2+</sup> because of the smaller diffusion coefficient of the electroactive 1/5DN38C10·TTF<sup>2+</sup> complex. As expected for reversible electrochemical processes, the same potential values are obtained by replacing TTF<sup>2+</sup> with TTF(0). Under these circumstances, the current intensities associated with the processes involving TTF are unaffected by 1/5DN38C10's presence, as the electroactive species is TTF(0). In short, these results indicate that TTF<sup>2+</sup> acts as an EA guest in the 1/5DN38C10·TTF<sup>2+</sup> complex and that the complex undergoes a fast, reversible decomplexation when the TTF<sup>2+</sup> guest is first reduced.<sup>21</sup>

When respective 20- and 50-fold excesses of CBPQT<sup>4+</sup> and 1/5DN38C10 were both<sup>22</sup> added to a  $1 \times 10^{-4}$  M MeCN solution of TTF (regardless of its oxidation state), we discovered that the potential of the TTF<sup>+</sup>/TTF(0) couple moves (Figure 7, full line) to *more* positive values (70 mV), whereas that of the TTF<sup>2+</sup>/TTF<sup>+</sup> couple moves to *less* positive values (14 mV). This behavior corresponds exactly to that observed for the CBPQT<sup>4+</sup>·TTF(0) and 1/5DN38C10·TTF<sup>2+</sup> complexes, respectively. These results show (1) that the TTF guest interchanges between the two hosts upon altering its oxidation state from 0 to +2, and (2) that the TTF<sup>+</sup> species does not interact with either host. The current intensities for the processes observed are those anticipated on the basis of the electroactive species, which depend (vide supra) on the starting oxidation state of TTF.

It is also worth noting that the CBPQT<sup>4+</sup>–1/5DN38C10–TTF mixture exhibits electrochromic behavior, since its three stable states (free TTF, TTF complexed with the EA host, and TTF complexed with the ED host) have different colors and can be interconverted by changing the potential in an easily accessible range (from +0.3 to +0.8 V vs SCE). An additional two differently colored states can be obtained<sup>23</sup> by reversible



**Figure 8.** Fields of electrochemical stability of the states that are available to the various systems described here.

reduction (from  $-0.2$  to  $-0.8$  V vs SCE) of the CBPQT<sup>4+</sup> cyclophane. Exploitation of these properties for the construction of electrochromic display systems is being explored currently.

**Supramolecular Switching Aspects.** Quite a number of two-state supramolecular switches have been described recently.<sup>24</sup> Although supramolecular systems that are capable of existing in more than two states are less common,<sup>7c,25</sup> they may be expected to handle the processing of molecular-level information more effectively. From the standpoint of molecular association, the three-component mixture CBPQT<sup>4+</sup>–1/5DN38C10–TTF behaves as a *three-pole system* since, depending on the potential range, TTF can be (1) uncomplexed, in its TTF<sup>+</sup> state, (2) complexed with the EA host, in its TTF(0) state, or (3) complexed with the ED host, in its TTF<sup>2+</sup> state. The reversibility of the electrochemical processes shows that the complexations/decomplexations and, consequently, guest exchanges between both hosts are occurring rapidly compared to the time scale of the electrochemical experiments.

Figure 8 portrays schematically the fields of electrochemical stability associated with the states available to the supramolecular system CBPQT<sup>4+</sup>–1/5DN38C10–TTF. This system's three-pole nature is clearly apparent when compared to the two-pole nature (free/complexed guest) of the two-component (CBPQT<sup>4+</sup>–TTF and 1/5DN38C10–TTF<sup>2+</sup>) systems and of some other recently reported<sup>3,18,26</sup> three-component systems.

We would also like to draw attention to the fact that the mechanical movements taking place in the present supramolecular system, wherein a "free" molecule can be driven to associate with either one of two different receptors by electrochemical means, might pave the way to applications of a futuristic nature in the field of molecular-level signal processors.<sup>27</sup> One can envision second-generation three-pole systems in which the electrochemically driven movements can control

(21) The electrochemical behavior of 1/5DN38C10 in the presence of TTF<sup>2+</sup> or TTF(0) leads to the same conclusion (Table 1). Whereas the free macrocyclic polyether shows two, not fully reversible, one-electron oxidation processes at +1.050 and +1.150 V, a not fully reversible two-electron oxidation process is observed at +1.120 V in the presence of TTF<sup>2+</sup> or TTF(0). This observation is consistent with the displacement of the macrocyclic polyether's first oxidation process toward more positive potentials when it hosts TTF<sup>2+</sup> within its cavity; after the first oxidation process, dissociation of the complex takes place so that the second oxidation process occurs on the free macrocyclic polyether.

(22) The interaction between CBPQT<sup>4+</sup> and 1/5DN38C10 ( $K_a < 400$  M<sup>-1</sup>) can be neglected under the experimental conditions employed.

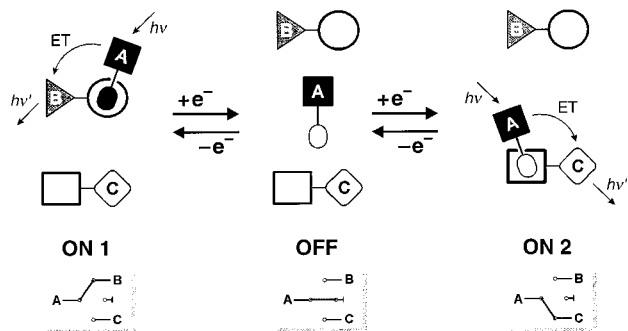
(23) A further state, originating from the oxidation of 1/5DN38C10, is less important, because such a process is not totally reversible.

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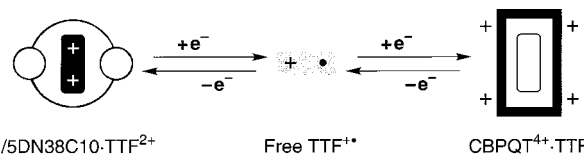


**Figure 9.** Schematic diagram illustrating how the electrochemically driven motions of a three-pole supramolecular switch may be used to influence energy transfer (ET) processes.

the occurrence of, *and* the selection of the partner in, energy- or electron-transfer processes. Consider, for instance, a system (Figure 9) in which the potential guest is appended to a chromophoric group **A**, while the potential hosts are appended, respectively, to the chromophoric groups **B** and **C**, whose lowest excited states are lower than that of **A**. Depending on the potential value selected by the operator in such a system, light excitation of **A** could lead to one of three possibilities, viz., no energy transfer (OFF), energy transfer to **B** (ON 1), or energy transfer to **C** (ON 2). Admittedly, the donor–acceptor-based molecular-level connection poses severe limitations with respect to the choice of the chromophoric groups that can be used if energy transfer has to proceed through the charge-transfer connections. Nevertheless, it does not seem unlikely that systems can be designed wherein molecular association (1) only plays the role of holding the two chromophoric groups together at a suitable distance for through-space energy transfer or (2) relies on a different kind of interaction, e.g., hydrogen bonding.<sup>28</sup> Similar switching processes relating to electron transfers could also be performed. More complex energy- and/or electron-transfer patterns are also conceivable.

## Conclusions

Augmenting our earlier discovery<sup>5c,9</sup> that TTF(0) acts as an ED guest when it complexes with the EA host CBPQT<sup>4+</sup>, we have ascertained that the EA dicationic guest TTF<sup>2+</sup> forms a host–guest complex with the ED host 1/5DN38C10 (1) in the solid state (by X-ray crystallography), (2) in solution (by <sup>1</sup>H NMR, luminescence, and absorption spectroscopies, together with cyclic/differential pulse voltammetries), and (3) in the gas phase (by LSI mass spectrometry). Thus, we have shown that, by virtue of the facile electrochemically promoted transformation between its 0 and +2 oxidation states, TTF is a versatile guest for the construction of complexes with either EA or ED macrocyclic hosts. This unique supramolecular Umpolung<sup>29</sup> (polarity reversal) process almost certainly has important implications for synthetic supramolecular chemistry.<sup>1b</sup> However, for the present, we have utilized it, along with the fact that TTF<sup>+</sup> is not bound by either CBPQT<sup>4+</sup> or 1/5DN38C10, for the development of the reversible three-pole supramolecular switch constituted by the CBPQT<sup>4+</sup>–1/5DN38C10–TTF trio. This three-component mixture functions (Figure 10) as a three-pole system inasmuch as, depending on the potential range, TTF can



**Figure 10.** Cartoon displaying the electrochemically reversible three-pole supramolecular switch based on the three-component mixture CBPQT<sup>4+</sup>–1/5DN38C10–TTF. The three poles of the switch are characterized by the three different states that the TTF unit may be in, i.e., (1) free (TTF<sup>+</sup>), (2) bound with CBPQT<sup>4+</sup> (TTF(0)), or (3) complexed with 1/5DN38C10 (TTF<sup>2+</sup>).

(1) be free, when present as the radical cation TTF<sup>+</sup>, (2) form a complex with CBPQT<sup>4+</sup>, in its TTF(0) state, or (3) be complexed by 1/5DN38C10, when it exists as TTF<sup>2+</sup>. The fact that the three states have different colors, coupled with the ease of their electrochemical interconversion, suggests that the three-component mixture CBPQT<sup>4+</sup>–1/5DN38C10–TTF could form the basis of an electrochromic display system. Finally, the proposal that second-generation three-pole systems can be conceived—wherein the occurrence of, in addition to the choice of the partner in, energy- or electron-transfer processes can be coordinated by electrochemically driven molecular motions—may lead to applications pertaining to molecular-level signal processors. Experiments are underway currently in our laboratories to establish the viability of this proposal.

## Experimental Section

**Tetrathiafulvalenium Bis(perchlorate) (TTF<sup>2+</sup>·2ClO<sub>4</sub><sup>-</sup>).** This compound was prepared using a previously reported<sup>10</sup> procedure from the literature: <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN, 300 K) δ 9.51 (4H, s); <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>CN, 300 K) δ 151.1 (C–H), 175.6 (S<sub>2</sub>C–CS<sub>2</sub>). X-ray quality single crystals of TTF<sup>2+</sup>·2ClO<sub>4</sub><sup>-</sup> were obtained when *i*-Pr<sub>2</sub>O vapor was allowed to diffuse into a MeCN solution of the compound.

**1,5-Dinaphtho[38]crown-10 (1/5DN38C10).** We have described the synthesis of this macrocyclic polyether previously.<sup>11</sup> Single crystals, suitable for X-ray analysis, were acquired from liquid diffusion of *i*-Pr<sub>2</sub>O into a MeNO<sub>2</sub>–CHCl<sub>3</sub> (1:1) solution of 1/5DN38C10.

**1,5-Dinaphtho[38]crown-10–tetrathiafulvalenium Bis(perchlorate) Complex ([1/5DN38C10·TTF<sup>2+</sup>][ClO<sub>4</sub><sup>-</sup>]<sub>2</sub>).** 1/5DN38C10 (6.4 mg, 10 μmol) and TTF<sup>2+</sup>·2ClO<sub>4</sub><sup>-</sup> (4.0 mg, 10 μmol) were mixed in anhydrous, degassed MeCN (3 mL) to furnish a dark orange solution of the title 1:1 complex. Single crystals of the complex were obtained by vapor diffusion of *i*-Pr<sub>2</sub>O–PhH into this solution: <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN–CD<sub>3</sub>NO<sub>2</sub> (5:3), 191 K) δ 3.59–4.07 (32H, br m), 6.42–7.38 (12H, br m), 8.89 (1H, br), 9.37 (3H, br); MS (LSI) *m/z* 840 [*M* – 2ClO<sub>4</sub>]<sup>+</sup>. Anal. Calcd for C<sub>42</sub>H<sub>48</sub>Cl<sub>2</sub>O<sub>18</sub>S<sub>4</sub>: C, 48.5; H, 4.7; S, 12.3. Found: C, 48.5; H, 4.5; S, 12.5.

**X-ray Crystallography.** Table 2 provides a summary of the crystal data, data collection, and refinement parameters for compounds TTF<sup>2+</sup>·2ClO<sub>4</sub><sup>-</sup> and 1/5DN38C10, as well as for complex [1/5DN38C10·TTF<sup>2+</sup>][ClO<sub>4</sub><sup>-</sup>]<sub>2</sub>. The structures were solved by direct methods and were refined by full-matrix least-squares based on *F*<sup>2</sup>. One of the ClO<sub>4</sub><sup>-</sup> ions in both TTF<sup>2+</sup>·2ClO<sub>4</sub><sup>-</sup> and [1/5DN38C10·TTF<sup>2+</sup>][ClO<sub>4</sub><sup>-</sup>]<sub>2</sub>, along with part of one of the polyether arms in 1/5DN38C10, were found to be disordered. In each case, this disorder was resolved into two partial occupancy orientations, with only the non-hydrogen atoms of the major occupancy orientation being refined anisotropically. The remaining non-hydrogen atoms in all three structures were refined anisotropically. In each structure, the C–H hydrogen atoms were placed in calculated positions, assigned isotropic thermal parameters, *U*(H) = 1.2*U*<sub>eq</sub>(C), and allowed to ride on their parent atoms. The O–H hydrogen atoms of the included H<sub>2</sub>O molecules in [1/5DN38C10·TTF<sup>2+</sup>][ClO<sub>4</sub><sup>-</sup>]<sub>2</sub> could not be located. Computations were carried out using the SHELXTL PC program system.<sup>30</sup>

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**Table 2.** Crystal Data, Data Collection and Refinement Parameters<sup>a</sup>

	TTF <sup>2+</sup> ·2ClO <sub>4</sub> <sup>-</sup>	[1/5DN38C10·TTF <sup>2+</sup> ][ClO <sub>4</sub> <sup>-</sup> ] <sub>2</sub>	1/5DN38C10
formula	C <sub>6</sub> H <sub>4</sub> S <sub>4</sub> ·2ClO <sub>4</sub>	C <sub>42</sub> H <sub>48</sub> O <sub>10</sub> S <sub>4</sub> ·2ClO <sub>4</sub>	C <sub>36</sub> H <sub>44</sub> O <sub>10</sub>
solvent		PhH·2H <sub>2</sub> O	
formula weight	403.2	1154.1	636.7
color, habit	pale yellow rhombs	orange rhombs	clear blocks
crystal size (mm)	0.27 × 0.27 × 0.08	0.83 × 0.60 × 0.60	0.50 × 0.47 × 0.43
crystal system	monoclinic	triclinic	monoclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i> (no. 14)	<i>P</i> 1 (no. 2)	<i>P</i> 2 <sub>1</sub> / <i>c</i> (no. 14)
cell dimensions			
<i>a</i> (Å)	9.694(2)	10.565(3)	8.197(1)
<i>b</i> (Å)	13.753(2)	11.245(3)	17.451(1)
<i>c</i> (Å)	10.581(1)	12.669(3)	11.980(1)
α (deg)		102.14(2)	
β (deg)	104.64(1)	90.75(2)	108.30(1)
γ (deg)		113.33(2)	
<i>V</i> (Å <sup>3</sup> )	1364.9(3)	1343.5(6)	1627.1(3)
<i>Z</i>	4	1 <sup>b</sup>	2 <sup>b</sup>
<i>D</i> <sub>c</sub> (g cm <sup>-3</sup> )	1.962	1.426	1.300
<i>F</i> (000)	808	604	680
radiation used	Mo Kα	Mo Kα	Cu Kα
μ (mm <sup>-1</sup> )	1.12	0.35	0.78
θ range (deg)	2.2–25.0	1.7–25.0	4.6–63.0
scan type	ω	ω	2θ – θ
no. of unique reflections			
measured	2408	4611	2635
observed,   <i>F</i> <sub>o</sub>   > 4σ(  <i>F</i> <sub>o</sub>  )	1898	3200	2301
absorption correction	semiempirical		
max, min transmission	0.97, 0.86		
no. of variables	194	370	213
<i>R</i> <sub>1</sub> <sup>c</sup>	0.043	0.067	0.046
<i>wR</i> <sub>2</sub> <sup>d</sup>	0.103	0.179	0.122
weighting factors <i>a</i> , <i>b</i> <sup>e</sup>	0.054, 1.274	0.113, 0.602	0.058, 0.439
largest diff peak, hole (e Å <sup>-3</sup> )	0.48, –0.34	0.84, –0.36	0.22, –0.15

<sup>a</sup> Details in common: graphite-monochromated radiation, Siemens P4/PC diffractometer, 293 K, refinement based on *F*<sup>2</sup>. <sup>b</sup> The (super)molecule has crystallographic *C*<sub>i</sub> symmetry. <sup>c</sup>  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ . <sup>d</sup>  $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}$ . <sup>e</sup>  $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$ .

**Molecular Modeling.** Single-point calculations (MP2/6-31+G\*) and geometry optimizations (HF/6-31+G\*) for TTF<sup>2+</sup> were performed using Gaussian 94.<sup>31</sup> A model complex, derived from the solid-state geometry of 1/5DN38C10 by replacing the two polyether chains with MeO substituents, was employed to calculate the electrostatic potential surface using Spartan 4.1.<sup>32</sup>

**Photophysical and Electrochemical Experiments.** The equipment and procedures used for absorption, luminescence, and electrochemical measurements have been reported previously.<sup>33</sup> The standards used for luminescence quantum yield measurements were quinine sulfate in 1 N H<sub>2</sub>SO<sub>4</sub> ( $\Phi = 0.546$ )<sup>34</sup> and anthracene in degassed EtOH ( $\Phi = 0.27$ ).<sup>35</sup> For the electrochemical experiments described here, it is worth noting that the concentration of the electroactive species was in the order of 10<sup>-4</sup> M; Et<sub>4</sub>N·PF<sub>6</sub> (0.05 M) was added as supporting electrolyte, ferrocene and phenothiazine being used as internal references.<sup>36</sup> Cyclic voltammograms (CV) were obtained at sweep rates of 10, 20, 50, 100,

200, 500, and 1000 mV s<sup>-1</sup>, while differential pulse voltammograms (DPV) were performed with scan rates of 20 or 4 mV s<sup>-1</sup>, a pulse height of 75 or 10 mV, and a duration of 40 ms. For reversible processes, the same half-wave potential values were obtained from the DPV peaks and from an average of the cathodic and anodic CV peaks. The potential values for not fully reversible processes were estimated from the DPV peaks. The experimental errors on the potential values for reversible and not fully reversible processes were estimated to be ±2 and ±5 mV, respectively.

**Acknowledgment.** This research was sponsored by The Deutsche Forschungsgemeinschaft, The Royal Society, The Engineering and Physical Sciences Research Council, The Wolfson Foundation, The EU (Contract FMRX-CT96-0076), MURST (Supramolecular Devices Project), The University of Bologna (Funds for Selected Topics), Odense University, and The University of California, Los Angeles.

**Supporting Information Available:** Crystallographic data for TTF<sup>2+</sup>·2ClO<sub>4</sub><sup>-</sup>, [1/5DN38C10·TTF<sup>2+</sup>][ClO<sub>4</sub><sup>-</sup>]<sub>2</sub>, and 1/5DN38C10 (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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