TOPICAL REVIEW

Electrochromic materials using mechanically interlocked molecules*

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Abstract

Recent investigations on the design and synthesis of electrochromic materials based on switchable three-station [2]catenanes are summarized. The reasoning and preliminary experiments behind the design of electrochemically controllable red–green–blue (RGB), donor–acceptor [2]catenanes are presented. A basis for color generation is discussed in which the tetracationic cyclophane, cyclobis(paraquat-p-phenylene), serves as the π-electron deficient ring which circumrotates between three π-electron rich recognition sites within a macrocyclic polyether, generating the three different colors (RGB) based on the different charge transfer interactions between the tetracationic cyclophane and recognition sites based on 1,5-dioxynaphthalene (R), tetrathiafulvalene (G) and benzidine (B). Issues relating to the realization of an RGB [2]catenane are raised and discussed: they include (i) color tuning, (ii) thermodynamic considerations, (iii) electrochemistry on model compounds, (iv) molecular design, (v) the electrochemical behavior of three-station [2]catenanes and (vi) electrochromism in polymer gel matrices. Finally, the challenges that need to be met in the future if the ideal RGB catenane is to be prepared, are outlined.

Keywords: interlocked molecules, [2]catenanes, electrochromism, charge-transfer complex, electronic paper display

(Some figures in this article are in colour only in the electronic version.)

1. Introduction

Advances in information technology are accelerating the development of novel organic materials [1, 2]. These organic materials have been proposed as alternatives to inorganic materials. They could lead to thin, flexible and lightweight portable devices, capable of accessing information anywhere, so-called ‘ubiquitous computing’ [3]. Electronic paper displays (E-PADs) are devices which promise to change our life style. The concept of an E-PAD, a low-cost and reflective display that feels like a document printed on conventional paper, emerged as an idea in the late 1990s [4]. Several prototypes of pixel components in the E-PADs have been demonstrated, e.g. electrophoresis of the colored particle in the capsules [5, 6], liquid crystals [7, 8], and electrochromism [9, 10]. Recently, we have proposed mechanically interlocked molecules as a different and unique kind of the electrochromic materials [11]. Mechanically interlocked compounds [12] which consist of a pair of mutually interlocked ring components are referred to as [2] catenanes. The interlocked donor–acceptor compounds

* Invited paper.
Figure 1. The proposed design for electronic paper display (E-PAD) based on the electrochromism of electrochemically-controllable three-station [2]catenanes. The control voltage is applied between the transparent electrode and the soft active matrix to manipulate the three-station [2]catenanes which are capable of exhibiting RGB colors in response to the applied voltage. The RGB colors originate from the CT absorption bands between the tetracationic cyclophane and the three stations on the macrocyclic polyethers.

[13–15] we have been developing in recent years in the shape of two-station [2]catenanes [16–19] are usually composed of the π-electron deficient tetracationic cyclophane, cyclobis(parquat-p-phenylene) (CBPQT4+) [20–23], and another π-electron rich ring, encompassing multiple binding sites (stations) for the CBPQT4+ ring—for instance, tetra(thiafulvalene (TTF) [24–26], 1,5-dioxynaphthalene (DNP) [27–29] and benzidine (BZ) [30, 31], etc. When the π-electron deficient CBPQT4+ ring resides on a π-electron rich binding site, the compound exhibits the color on account of charge-transfer (CT) between the CBPQT4+ ring and the binding site [20–31]. In the case of the two-station [2]catenanes, we have designed an electrochemically controllable one, where the CBPQT4+ ring resides preferentially at one or another binding sites in the ground and electrochemically oxidized states, respectively. We can observe the electrochromism in response to the circumrotation of the CBPQT4+ ring from one binding site to another [32–34]. Based on these findings, we have suggested that electrochemically controllable red–green–blue (RGB) [2]catenanes could be the basis (figure 1) for constructing different kinds of electrochromic devices [11]. In such a system, we might expect that a change in the location of the CBPQT4+ ring between the three π-electron rich stations might generate three different colors (RGB) based on the different CT interactions between the CBPQT4+ ring and the three distinct, carefully chosen stations. Compared to the other prototypes of E-PADs, the advantages in using RGB [2]catenane are as follows: (i) Each pixel unit needs only a single basic cell instead of three to generate the red, green, and blue colors. This feature would reduce dramatically the complexity and, hence, the cost of electrochromic devices. (ii) Molecular compounds are easily embedded in polymer matrices [34] and even on paper as well. Thus, simple package processing, such as ink-jet printing technology, could be used to manufacture the display.

2. Color tuning

DFT calculations help in choosing the host–guest pairs for RGB colors. The color of donor–acceptor [2]catenanes arises from the CT band between the HOMO of aromatic crown ethers and the LUMO of CBPQT4+. We have calculated the CT band gap energy between the tetracationic cyclophane, CBPQT4+, and the model guest compounds 1–6 (figure 2) [11]. The results of the calculations are summarized in table 1. The DFT calculations predicted that DNP–DEG, TTF–DEG and DFBZ should be ideal guest molecules to obtain the RGB colors. Based on this prediction, we synthesized some model compounds 7–11 (figure 3) [35, 36]. Figure 4 shows the UV-Vis spectra of the CBPQT4+ inclusion complex in MeCN. The absorption maxima of the CBPQT4+ complexes with DNP–TEG, DFBZ–TEG and TTF–TEG are 525, 610 and 835 nm, respectively. The inset in figure 4 reveals that we obtained RGB colors from these three combinations.

3. Thermodynamics

The binding strengths of the model guests 7–11 with the CBPQT4+ [35, 36] were obtained from measurements...
Table 1. The CT band gap energy (ΔE<sub>CT</sub>) between the HOMO of the guest and the LUMO of CBPQT<sup>4+</sup> •+PF<sub>6</sub> and absorption maxima (λ<sub>max</sub>) of the CT band obtained from DFT calculations<sup>a</sup> and the experiments.

|     | 1  | 2  | 3  | 4  | 5  | 6  |
|-----|----|----|----|----|----|----|
| calc. ΔE<sub>CT</sub> (eV)<sup>b</sup> | 2.68 | 2.60 | 1.82 | 2.06 | 1.46 | 1.64 |
| calc. λ<sub>max</sub> (nm)<sup>c</sup> | 462 | 476 | 677 | 601 | 853 | 756 |
| obs. λ<sub>max</sub> (nm)<sup>d</sup> | 473 | 525 | 670 | − | 854 | 835 |

<sup>a</sup>B3LYP/6-31G<sup>++</sup> + + level based on the structure optimized using B3LYP/6-331G<sup>++</sup>. <br><sup>b</sup>The band gap energy of CT band calculated by DFT. <br><sup>c</sup>The absorption maxima of the CT band calculated from ΔE<sub>CT</sub>. <br><sup>d</sup>The absorption maxima of the CT band obtained from the experiment.

![Structural formulae of the series of model guests 7–11](image)

Figure 3. Structural formulae of the series of model guests 7–11 DNP–TEG, DNP–C5DEG, BZ–TEG, DFBZ–TEG, TTF–TEG.

Carried out in MeCN solutions by isothermal titration calorimetry (ITC). The thermodynamic data are summarized in Table 2. Of all these model guests, TTF–TEG has the largest association constant (K<sub>a</sub> = 416 ± 10<sup>3</sup> M<sup>−1</sup>) with the CBPQT<sup>4+</sup>. DNP–TEG is the second largest (K<sub>a</sub> = 43.9 ± 10<sup>3</sup> M<sup>−1</sup>). In the case of DNP–C5DEG, it is evident that the simple modification, where the second closest oxygen atoms from the naphthalene ring were replaced by methylene groups, drastically reduces the binding affinity to CBPQT<sup>4+</sup> [35]. X-Ray crystallographic data for the 1:1 complex formed between DNP–TEG and CBPQT<sup>4+</sup> indicates that the second closest oxygen atoms from the naphthalene ring are involved in [CH ⋅⋅⋅ O] interactions with the CBPQT<sup>4+</sup> ring [27–29]. In the case of the DNP–C5DEG, the absence of oxygen atoms to form [CH ⋅⋅⋅ O] interactions results in a much reduced binding affinity. The K<sub>a</sub> value (1.91 ± 10<sup>3</sup> M<sup>−1</sup>) for DFBZ–TEG is much smaller than that (0.312 ± 10<sup>3</sup> M<sup>−1</sup>) of BZ–TEG, presumably because of the detrimental effect that the fluorine atoms have, both electronically and sterically, on the binding of a BZ unit inside the CBPQT<sup>4+</sup> cavity [36].

4. Electrochemistry

Electrochemistry on the model compounds 7 and 9–11 was performed using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) [35, 36]. The half-wave potentials (E<sub>1/2</sub>) were determined from the DPV peaks. The E<sub>1/2</sub> values are summarized in Table 3. DNP–TEG shows a quasi-reversible redox process and it has the largest E<sub>1/2</sub> value [33, 35]. TTF–TEG shows a reversible redox process and it has the smallest E<sub>1/2</sub> value [25, 33, 35]. Both BZ–TEG [30, 31] and DFBZ–TEG–TEG [36] exhibit reversible redox processes and their E<sub>1/2</sub> values lie between those of TTF–TEG and DNP–TEG.
Table 3. Electrochemical data for the model compounds *.

| Compound  | Oxidation (V) | Reduction (V) |
|-----------|---------------|---------------|
| 7, DNP–TEG | +1.16         |               |
| 9, BZ–TEG  | +0.46, +0.65  |               |
| 10, DBBZ–TEG | +0.65, +0.83 |               |
| 11, TTF–TEG | +0.36, +0.71  |               |
| CBPQT•4PF6  |               | –0.29, –0.72  |

*Argon-purged MeCN, room temperature, 0.1 M TBA • PF6 as supporting electrolyte. Working electrode: glassy carbon. Counter electrode: Pt wire. Reference electrode: saturated calomel electrode.

Table 4. DPV peak potentials versus SCE (V) for RGB1•4PF6 and RGB2•4PF6.

| Compound          | Scan direction | DPV peak top potential b |
|-------------------|----------------|-------------------------|
| RGB1•4PF6         | Anodic         | +0.39, +0.49, +0.71     |
|                   | Cathodic       | +0.38, +0.49, +0.71     |
| RGB2•4PF6         | Anodic         | +0.48, +0.58, +0.70     |
|                   | Cathodic       | +0.53, +0.70            |

*Argon-purged MeCN, room temperature, 0.1 M TBA•PF6 as supporting electrolyte. Working electrode: glassy carbon. Counter electrode: Pt wire. Reference electrode: saturated calomel electrode.

bThe relation between the peak potential in the DPV measurement (E_{max}), half-wave potential (E_{1/2}), and pulse height (E = 25 mV) is (E_{1/2} = E_{max} + E/2).

The electrochemical properties of the RGB [2] catenanes RGB1◦+ and RGB2◦+ were investigated by CV and DPV [17]. Interestingly, CV and DPV peaks were different in the anodic and cathodic scans, an observation which is attributable to the electromechanical movement of the interlocked CBPQT◦+ ring on the polyether macrocycle [33]. Table 4 summarizes the DPV peak potentials of the three-station RGB2 catenanes RGB1◦+ and RGB2◦+. Each peak was assignable using the spectroelectrochemistry [35]. Based on the results of thermodynamics, electrochemistry and spectroelectrochemistry, we established the electromechanical behavior of the three-station RGB catenanes RGB1◦+ (scheme 1) and RGB2◦+ (scheme 2) [35]. In the anodic scan of the RGB1◦+, a small DPV peak was observed at +0.39 V. This oxidation has been assigned to the oxidation of the unoccupied TTF [state (i’) → (iii)] [25, 33]. In the case of the RGB1◦+, there is an equilibrium between the states (i’) and (i). The oxidations of the occupied TTF and the BZ units take place at almost the same potential (E = +0.50 V)[state (i) → (ii) → (iii)]. The TTF radical cation repels the CBPQT◦+ ring by Coulombic repulsion [32, 33]. This translocation of the CBPQT◦+ ring was confirmed by means of spectroelectrochemistry. The association constants for complexation of DNP–TEG and BZ–TEG (K_{a} = 43.9 × 10^{4} M^{-1}, 1.91 × 10^{3} M^{-1}, respectively) with CBPQT•4PF6 suggest the CBPQT◦+ ring resides on the DNP station preferentially [state (ii)]. Further oxidations from the radical cations to the dications occurs at +0.72 V[state (iii) → (iv)]. This process is reversible. After the reduction of the BZ radical cation at +0.50 V[state (iii) → (ii)], the reduction of the TTF radical cation takes place at +0.39 V. This potential is almost the same one as that for the oxidation of an unoccupied TTF, an observation which implies that the CBPQT◦+ ring does not reside on the TTF radical

6. Electromechanical behavior of RGB1◦+ and RGB2◦+

Based on our preliminary investigations, we were led to propose the design of the RGB catenanes illustrated in figure 5 [11, 35]. In the first generation RGB catenane (12◦+, RGB1◦+), the three stations—TTF diol, BZ and DNP—were simply linked by oligoethyleneglycol chains. In the second generation RGB catenane (13◦+, RGB2◦+), the second closest oxygen atoms from the naphthalene ring were substituted by methylene groups. In other words, the three stations—TTF diol, BZ and DNPC5DEG—were linked by oligoethyleneglycol chains. In the third generation RGB catenane (14◦+, RGB3◦+), the three stations—TTF diol, DFBZ and DNPC5DEG—were also linked by the oligoethyleneglycol chains. We have already synthesized the RGB1◦+ and RGB2◦+[17].
Scheme 1. Expected electromechanical behavior of the three-station [2]catenane RGB1 • 4PF6. In the ground state, RGB1 • 4PF6 is in equilibrium between states (i) and (i'). The red and blue arrows represent the oxidation and reduction processes, respectively.

Scheme 2. Expected electromechanical behavior of RGB2 • 4PF6. The red and blue arrows represent the oxidation and reduction processes, respectively. As the reduction potentials of the TTF+ and BZ+ radical cations are almost the same, two reduction processes can be proposed: (iii) → (ii) → (i) and (iii) → (ii') → (i). In the latter case, the CBPQT4+ ring visits all of the three stations.

cation [state (ii)]. Overall, we have not been able to determine a state in which the CBPQT4+ ring resides preferentially on the BZ unit. As a consequence, we conclude that the three-station [2]catenane RGB14+ is, in reality, a bistable entity.

In the anodic scan of the RGB24+, the first oxidation takes place at the BZ unit at +0.49 V[state (i) → (ii)]. As could be predicted from the association constant (K_a = 122 M⁻¹) between CBPQT4+ • 4PF6 and DNP–C5DEG, the association of the CBPQT4+ ring with the DNP unit is quite weak in this [2]catenane. Thus, the CBPQT4+ ring resides almost exclusively on the TTF unit and inhibits the first oxidation of the TTF unit. The occupied TTF unit is oxidized at +0.54 V[state (ii) → (iii)]. This step is accompanied by the translocation of the CBPQT4+ ring to the neutral DNP unit. Then, the TTF and BZ radical cations are oxidized to the dications at +0.71 V[state (iii) → (iv)]. This process is reversible. In the cathodic scan, the reductions of the TTF and BZ radical cations take place at similar potentials (E = +0.54 V). In some molecules, the reduction of the BZ radical cation occurs before that of the TTF radical cation. In such a case, the CBPQT4+ ring resides preferentially on the neutral BZ unit [state (iii) → (ii') → (i)]. In other molecules, another route might well be followed [state (iii) → (ii) → (i)]. In the former route, the CBPQT4+...
Figure 6. Structural formulae of the first, second and third generation RG [2]catenanes 15\(^{4+}\) and 16\(^{4+}\)

ring visits all of the three stations. Taking the half-wave potentials \([E_{1/2}(\text{TTF} - \text{TEG}) < E_{1/2}(\text{BZ} - \text{TEG})]\) of TTF–TEG and BZ–TEG into account, the former route may be the major one. We are, therefore, led to the conclusion that the three-station [2]catenane RGB\(^{2+}\) is a quasi-tristable [2]catenane [35].

7. Electrochromism in polymer gel matrix

The electrochromism of the two-station [2]catenanes RG\(^{1+}\) and RG\(^{2+}\) (figure 6) in a polymer gel matrix (polymethylmethacrylate gel) has been observed [34]. The kinetics of the electrochromism were obtained from CV measurements. Scheme 3 illustrates the switching cycle mechanism for the bistable [2]catenanes [32–34]. In the neutral state, the CBPQT\(^{4+}\) ring resides preferentially on the TTF site (ground state). The oxidation of the TTF unit is accompanied by a rapidly driven shuttling of the CBPQT\(^{4+}\) ring to the DNP site. Upon reduction of the TTF site back to its charge-neutral state, the [2]catenane passes through a metastable state. The relaxation rate from this metastable state to the ground state (\(k\) in scheme 3) is typically too fast to be observed at room temperature in the solution phase. In the polymer environment, however, this relaxation is slowed down significantly [34], indicating that the mechanical movement of the CBPQT\(^{4+}\) ring is affected strongly by the viscosity of the medium [37, 38]. The 1/e decay time (\(\tau = 1/k\)) at room temperature of the two-station [2]catenanes RG\(^{1+}\) and RG\(^{2+}\) are 0.6 and 800 s, respectively [34]. This result means that we can control the colorimetric retention time by varying the molecular structure of the [2]catenanes.

8. Conclusions

Recent studies on electrochromic materials using inclusion complexes and mechanically interlocked molecules are summarized. We have already obtained the RGB colors from the inclusion complexes formed between CBPQT\(^{4+}\) • 4PF\(_6\) and DNP–TEG, TTF–TEG and DFBZ–TEG, respectively [35, 36]. The consistency between the association constants of the 1:1 complexes and the oxidation potentials for the \(\pi\)-electron donor units in a [2]catenane, incorporating DNP–C5DEG, TTF–TEG and DFBZ–TEG units in a macrocyclic polymer interlocked by a CBPQT\(^{4+}\) ring, has lead to the realization of an electrochemically controllable three-station [2]catenane [36]. With the combination of DNP–C5DEG, TTF–TEG, DFBZ–TEG, the station having the stronger affinity to CBPQT\(^{4+}\) • 4PF\(_6\) is oxidized at lower potential. In addition, we have already demonstrated electrochromic devices using the two-station [2]catenanes in polymer gel matrices [34].

In the case of the three-station [2]catenanes, we have not been able to confirm the RGB colors in the solution state, because the absorption bands of the oxidized TTF and BZ units screen the CT band between the CBPQT\(^{4+}\) and the recognition sites. This problem is one that we
believe can be solved in the fullness of time. In the case of the electrochromism in polymer gel matrices, the relaxation of the metastable state to the ground state is much slower (about 2000 times) than that observed in the solution phase. Thus, the [2]catenane can exhibit the color of the CT band as long as it is in the metastable state. An investigation of an incremental nature will lead ultimately to the development of the mechanically interlocked molecules in the field of the electrochromic devices.

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