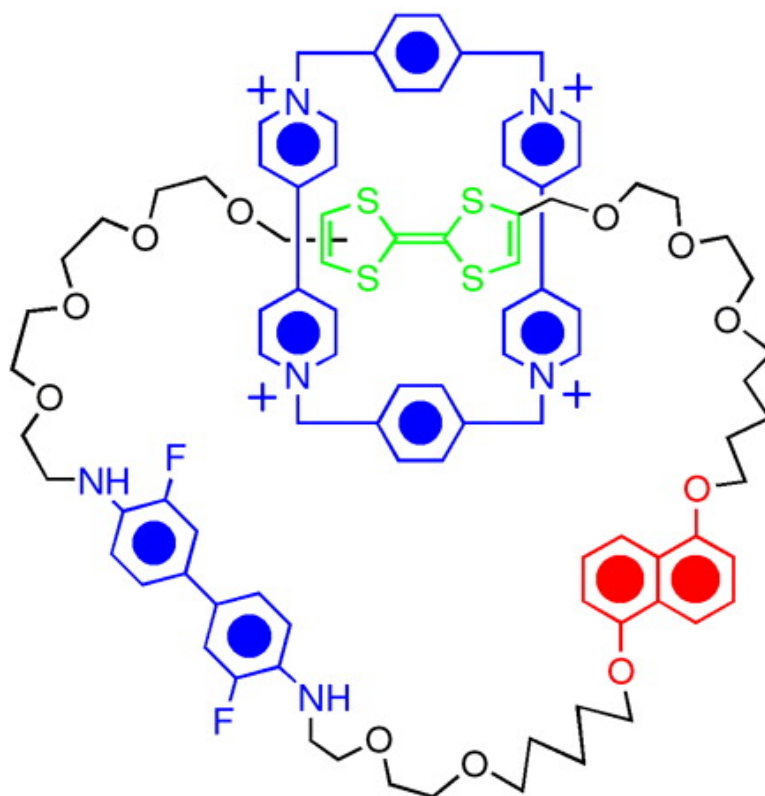## Communication

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An Electrochemical Color-Switchable RGB Dye: Tristable [2]Catenane

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The concept of an electronic paper display (E-PAD), a low-cost and reflective display that feels like a document printed on conventional paper, emerged[1−8] in the late 1990s. Several prototypes of pixel components in the E-PADs have been demonstrated. For example, the Bell Labs/E Ink[7] utilizes microencapsulated suspensions of charged white particles in a black fluid. Another demonstration of the pixel components is based on the phenomenon of electrowetting to manipulate[8] microscale liquid droplets. Although these black/white prototypes have been demonstrated, it is color displays that are the final target. The pixels in color designs must include Red, Green, and Blue units, which make the pixel component both expensive and complex to manufacture.

Here, we propose a new concept for the pixel component in such an E-PAD that consists of a film of a single "RGB" dye compound, which can display all three colors depending on the applied voltage. Compared with other prototypes, the advantages in using RGB dyes are as follows. (1) Each pixel unit needs only a single basic cell instead of three to generate red, green, and blue colors! This feature would reduce dramatically the complexity and, hence, the cost. (2) Molecular compounds are easily embedded in polymer matrixes[9] and even on paper materials. Thus, simple package processing, such as ink-jet printing technology, could be used to make the displays.

To realize such RGB dyes, we consider that the color should be voltage controllable. Examples of such color-changeable dyes are donor/acceptor[9−12] catenanes, composed of a ring incorporating tetrathiafulvalene (TTF) and 1,5-dioxynaphthalene (DNP) donor units, interlocked with the cyclobis(paraquat-p-phenylene) (CB-PQT^{4+}) acceptor ring. These bistable catenanes can be switched electrochemically between two colored states, green (λ_{max} = 854 nm) and red (λ_{max} = 473 nm).

We intend to transform the bistable [2]catenane into a tristable [2]catenane (Figure 1a) containing three donor units that are each responsible for one of the three primary colors. In this communication, we validate using first principle calculations, which were successfully applied to rotaxane systems,[13] that a tristable [2]-catenane with TTF and DNP units for green and red colors, respectively, as well as a third donor unit, namely a substituted benzidine (R-BZD) suitable for generating a blue color, could be the pixel-layer component for the implementation of an E-PAD.

Based on the general design (Figure 1b) a number of requirements need to be addressed. The nature of the spacer units (S), and the substituents (R) on the BZD unit, will be selected computationally. Several candidate donors (Figure 1c) were considered. In this design, we use three different voltages, V_0 = 0, V_1, and V_2 to control the color, where at V_0 all three donor units are neutral and the CBPQT^{4+} ring encircles the TTF unit (green). At an applied voltage V_1, the TTF unit is oxidized and becomes doubly charged, repelling the CBPQT^{4+} ring and driving its movement to
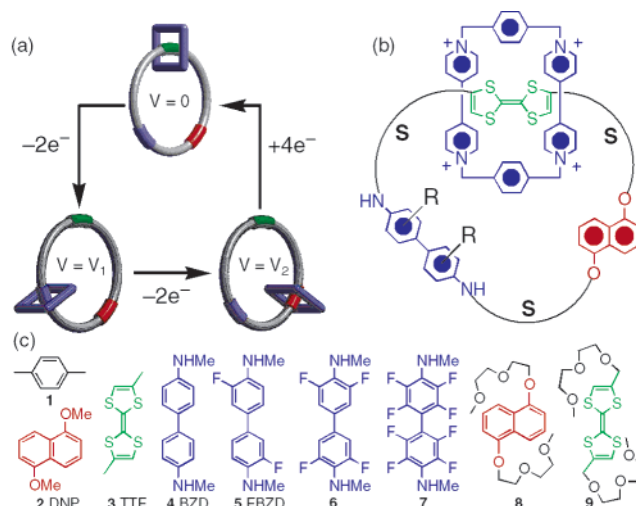

Figure 1. (a) Proposed mechanism of switching in a tristable [2]catenane working under different voltages. The ring has to switch locations over green (V = 0), blue (V = V_1), and red (V = V_2) sites, respectively. (b) A proposed general design of the RGB tristable [2]catenane. The colored units refer to the TTF (green), R-BZD (blue), and DNP (red) donors. (c) Candidate donor units that were screened.

the second donor R-BZD. This geometry of the [2]catenane corresponds to the second state, leading to a blue color. As the voltage is changed to V_2, the R-BZD component is oxidized, driving the CBPQT^{4+} ring to the DNP unit (red). When the voltage is reset back to V_0, the CBPQT^{4+} ring will move back to the original TTF unit. Each of the three colored states are accessed at different voltages even although the mobile ring may move clockwise or counterclockwise. Following this proposed mechanism, the tristable [2]catenane represents three colors depending on the applied voltage.

To ensure the ideal performance for this RGB tristable [2]-catenane, we must arrange the correct sequence of display colors, binding energies, and oxidation potentials. When the CBPQT^{4+} ring encircles the unsubstituted BZD unit, a green-blue color is obtained[14] with an absorption maximum at 670 nm. The absorption spectrum of this system arises from a charge-transfer transition from the HOMO of the donor unit [e.g., TTF, R-BZD, or DNP] to the LUMO of the CBPQT^{4+} ring.[10] Introducing substituent groups (R) onto the BZD unit will shift its HOMO energy, thus modifying the color it generates.

Several candidates were screened (Table 1) to find the ideal donor units to generate a blue color. We used the B3LYP/6-31G**++// B3LYP/6-31G* flavors of density functional theory (DFT), including the Poison−Boltzmann continuum solvent model, to determine[15] the HOMO of each group. Such DFT calculations usually underestimate[16] the band gaps of conjugated organic molecules by ~40% compared with experiment. Consequently, we determined an empirical scaling factor to correct the band gap calculated from

Table 1. Frontier Molecular Orbital Energies and UV−vis Absorption Maxima for the Donor−Acceptor Pairs[a]

	1	DNP	TTF	BZD	FBZD	6	7
HOMO[b]	−6.40	−5.72	−4.91	−5.15	−5.31	−5.60	−5.96
LUMO[c]	−3.95	−3.95	−3.95	−3.95	−3.95	−3.95	−3.95
ΔE_g[d]	3.72	2.68	1.45	1.83	2.06	2.51	3.06
calcd (nm)	333	462	853	677	601	494	405
exptl (nm)	330[e]	473[e]	854[f]	670[g]			

[a] See more details in Support Information. [b] eV. [c] eV, the LUMO is for CBPQT^{4+} surrounded by four PF$_6^-$ counterions. [d] Band gap has been corrected by an empirical factor, 0.6645. [e] Reference 17. [f] Reference 18. [g] Reference 14. [h] Reference 10.
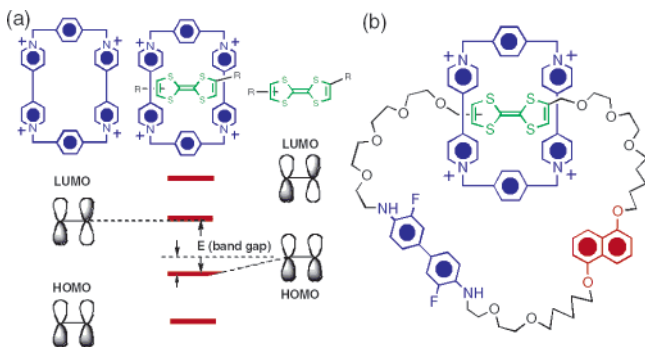
Figure 2. (a) MO shift during the process of constructing the complex between the CBPQT^{4+} ring and donor groups. (b) Molecular structure of the proposed tristable [2]catenane.

DFT by comparing calculated with available experimental values and then used this factor to predict the unknown absorption maxima.

As shown in Figure 2a, the maximum adsorption (ΔE_g) of rotaxane is contributed from the charge transfer from the HOMO of donor groups to the LUMO of the CBPQT^{4+} ring. During the formation of the model complexes, the electrostatic charge on the CBPQT^{4+} ring shifts the HOMOs of the donor groups. Thus, the band gap can be written as

$$\Delta E_g = \frac{1}{\alpha}(E_{LUMO} - E_{HOMO} + \lambda)$$

where α is the correction factor for the DFT results, which should be around 0.6, and λ is the shift of the HOMO for the donor group affected by the charges on the CBPQT^{4+} ring molecule. Table 1 shows the fitting results. We found that $\lambda = 0.011$ eV and $\alpha = 0.6645$ gives the closest fitting results to experiments. The largest error is 9 nm. Thus we believe these unknown components follow a similar rule. We find that the complex with the ring locating over difluorinated BZD (FBZD) has an adsorption (Table 1) at ∼600 nm leading to the desired blue color.

Next we must consider the sequence of oxidation steps such that each color is generated in a stepwise manner in response to an applied voltage. We addressed this requirement by considering the oxidation potentials and the binding energies of the donors and the impact of the spacers that link them together.

The energies of the HOMOs for different donor units depend (Table 2) on their complexation with the CBPQT^{4+} ring. The HOMO energy is proportional to the oxidation potential (V_{ox}). From these data, we determine that the three donor units, TTF-**9**, FBZD, and DNP, produce the correct ordering of the donor-unit oxidation potentials (V_{ox}) and of binding strengths (E_b[donor unit⊂CBPQT^{4+}]):

$$V_{ox}[\text{DNP}] > V_{ox}[\text{FBZD}] > V_{ox}[\text{TTF-}\mathbf{9}]$$

$$E_b[\text{TTF-}\mathbf{9}{\subset}\text{CBPQT}^{4+}] > E_b[\text{FBZD}{\subset}\text{CBPQT}^{4+}] >$$
$$E_b[\text{DNP}{\subset}\text{CBPQT}^{4+}]$$

Table 2. Binding Energy (ΔE_b) between the Donors DNP, TTF, FBZD, DNP-**8**, and TTF-**9**, and the CBPQT^{4+} Ring at the B3LYP/6-31G**++ Level Based on the Structure Optimized Using B3LYP/6-31G*

	DNP[a]	TTF	BZD	FBZD[a]	DNP-**8**	TTF-**9**[a]
HOMO[b]	−5.72	−4.91	−5.15	−5.31	−5.67	−5.03
ΔE_b[c]	−5.28	−14.71	−23.25	−17.25	−48.18	−70.79
exptl $\Delta G°$[d]	−3.9[e]	−5.5[f]	−4.1[e]		−6.0[e]	−7.8[g]

[a] Ideal donors. [b] eV. [c] Binding energy (kcal/mol) with BSSE correction at B3LYP/6-31G**++//B3LYP/6-31G*. [d] Binding energies (kcal/mol) calculated from the dissociation constants using $\Delta G° = RT \ln K_a$. [e] Reference 17. [f] Reference 18. [g] Reference 10.

Thus, we propose the molecular structure shown in Figure 2b for the desired RGB tristable [2]catenane. In addition, we demonstrated that a bistable catenane can switch between red and green colors in a polymer matrix;[9] thus we expect this tristable catenane can also switch colors in a polymer matrix.

In summary, to extend voltage-controllable red−green bistable catanenes, we used quantum mechanics to assist the design of a Red−Green−Blue dye that can switch colors under three different applied voltages. Computationally guided methods could also be used for the design of other display regimes such as CMYK. This dye can be potentially used for the pixel component in low cost paper-like electronic displays.

Supporting Information Available: Computational methods and detailed results. This material is available free of charge at http://pubs.acs.org.

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