Supramolecular Chemistry

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High-Contrast Red–Green–Blue Tricolor Fluorescence Switching in Bicomponent Molecular Film[**]

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Abstract: *Highly efficient red–green–blue (RGB) tricolor luminescence switching was demonstrated in a bicomponent solid film consisting of (2Z,2′Z)-2,2′-(1,4-phenylene)bis(3-(4-butoxyphenyl)acrylonitrile) (DBDCS) and (2Z,2′Z)-3,3′-(2,5-bis(6-(9H-carbazol-9-yl)hexyloxy)-1,4-phenylene)bis(2-(3,5-bis(trifluoromethyl)phenyl)acrylonitrile) (m-BHCDCS). Reversible RGB luminescence switching with a high ratiometric color contrast ($\lambda_{em} = 594, 527, 458$ nm for red, green, and blue, respectively) was realized by different external stimuli such as heat, solvent vapor exposure, and mechanical force. It was shown that Förster resonance energy transfer in the bicomponent mixture could be efficiently switched on and off through supramolecular control.*

The development of external stimuli-responsive multicolor fluorescence switches, especially of a tricolor red–green–blue (RGB) switching system for the full color reproduction, remains a grand challenge for fundamental science and also for their practical applications. An ideal multicolor fluorescence switching system requires high sensitivity, contrast, and reversibility in switching, high luminescence quantum yield, and independent switching of RGB emitting elements without crosstalk between them. As for the reversible luminescence switching,[1] one of the most successful strategies is to control the molecular stacking and/or supramolecular structure of emitting elements by physical means, which can be distinguished from the irreversible chemical alternation of their molecular structures.[2] Although there have already been a few examples of external stimuli-responsive multicolor reversible fluorescence switches,[3–7] a practical RGB switching system for the full color reproduction with high luminescence quantum yield and high switching contrast in the solid state has not been accomplished yet. Sagara and Kato reported a single chromophore-based tricolor switching system, which is implemented by supramolecular structural changes of the liquid crystalline chromophore by mechanical forces to give luminescence color switching in green, yellow, and red.[4] The Tian group has also demonstrated a multicolor mechanochromic system, which is triggered by modulating the degree of molecular π–π overlap through varying external pressure.[3] However, it was noted in these works that achieving color change in the full RGB range with such single chromophoric systems is inherently limited, because the supramolecular stacking control of the molecular units to give excitonic and/or excimeric coupling are rather limited to the narrow-range color modulation. In fact, the switching color ranges in the Kato and Tian systems were limited within green to red. Therefore, a bicomponent approach is more realistic for RGB switching as was recently demonstrated to achieve a broader color range RGB multicolor switching by mixing a mechanochromic blue-to-green switchable fluorophore and mechanochromic off-to-on switchable red fluorophore (Wei group, 2012).[7] Although broader range RGB luminescent switching was partly demonstrated in the system, high color contrast and independent switching could not be established due to the intrinsic switching crosstalk between the green and red emitting phases; luminescence of both phases were commonly switched by applying shear force although associated with different threshold values.

In this work, we propose a new strategy of supramolecular Förster resonance energy transfer (FRET) control to achieve complete RGB color switching with a bicomponent mixture system consisting of a B-to-G luminescence switching molecule with self-assembly capability (molecule **1**) and an off-to-on red (R) luminescence switching molecule operating under different switching stimuli (molecule **2**). Switching of FRET between the molecule **1** and **2** is a key idea of this strategy to suppress the crosstalk and to achieve high contrast RGB switching. Once molecule **1** forms a self-assembled structure larger than the Förster radius and molecule **2** remains in the off-state, independent and switchable B/G states of molecule **1** can be secured (Scheme 1 a). In contrast, once the molecule **1** is disassembled and the red-luminescent molecule **2** concurrently forms the on-state in the homogeneous mixture of molecule **1** and **2**, FRET from molecule **1** to molecule **2** becomes efficient to completely quench the blue or green luminescence of molecule **1** and to enhance the red luminescence of molecule **2**, which can achieve a clear and bright R state (Scheme 1 b). In this work, we demonstrate a real material system of such reversible and crosstalk-free tricolor

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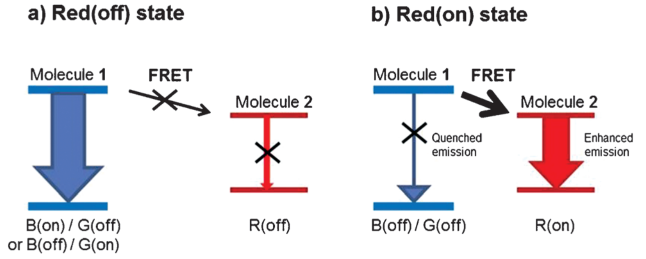
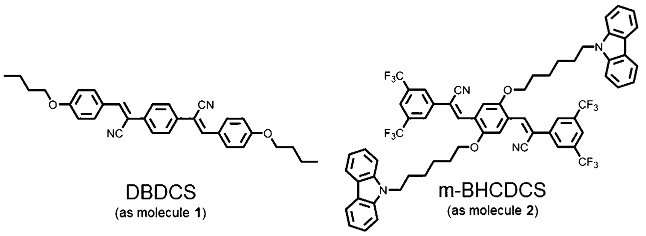


Scheme 1. Strategy of RGB fluorescence switching. a) B or G emitting state and b) R emitting state.

RGB switching system operating through the mechanism proposed in Scheme 1.

To meet the requirements for an optimized RGB switching system proposed in Scheme 1, we selected (2*Z*,2′*Z*)-2,2′-(1,4-phenylene)bis(3-(4-butoxyphenyl)acrylonitrile) (DBDCS), and (2*Z*,2′*Z*)-3,3′-(2,5-bis(6-(9*H*-carbazol-9-yl)-hexyloxy)-1,4-phenylene)bis(2-(3,5-bis(trifluoromethyl)phenyl)acrylonitrile) (*m*-BHCDCS), (see Scheme 2 for the chemical structures), as the viable candidates for molecule **1** and **2**, respectively. As was reported, DBDCS exhibits two distinguishable and reversibly switchable luminescent phases (B and G) in the solid state: 1) the green luminescent phase ($\lambda_{em} = 533$ nm, fluorescence quantum yield $\Phi_F = 0.45$) was generated by solvent vapor annealing (SVA) or mechanical force, and 2) the blue emitting phase ($\lambda_{em} = 458$ nm, $\Phi_F = 0.31$) was generated by thermal annealing (TA).[13] *m*-BHCDCS is a mechanochromic off-to-on switchable red fluorescent material based on a donor–acceptor–donor triad. The red emission is turned on in the amorphous solid state ($\lambda_{em} = 600$ nm, $\Phi_F = 0.10$) triggered by smearing (SM), whereas it is completely quenched upon crystallization with TA or SVA due to the fast intramolecular and intermolecular photoinduced electron transfer (PeT) in the crystalline state.[14] By combining these unique and interlocking self-assembly properties and stimuli-responsive characteristics of two different molecules of DBDCS and *m*-BHCDCS in one single device, we could devise a reversible and multistimuli-responsive tricolor luminescence switching from B to G to R. According to our scenario, the TA- and SVA-treated DBDCS/*m*-BHCDCS mixture would generate a segregated phase structure because of the strong self-assembly tendency of both compounds, which are based on the cyanostilbene skeleton.[11,12] Therefore, in the TA- and SVA-treated mixture, selectively self-assembled DBDCS particles would independently emit their colors, that is, B or G, whereas under these conditions, regions of aggregated *m*-BHDCDS would not fluoresce due to its crystallization-induced off-fluorescence characteristics. Due to the segregated phase structure of DBDCS/*m*-BHDCDS in this case, FRET will be almost completely suppressed from DBDCS (B or G phases) to *m*-BHCDCS, which thus remains in the R(off) state. In the SM-treated mixture, however, red fluorescence would be switched on by *m*-BHCDCS through the crystalline-to-amorphous phase transition, whereas G or B emission of DBDCS would be concurrently quenched due to the efficient FRET from DBDCS to *m*-BHCDCS, which are structurally disassembled by the shear force. Furthermore, we expected a high Φ_F for both segregated (B and G) and amorphous (R) states due to aggregation-induced enhanced emission (AIEE) behavior[8–10] and efficient FRET, respectively.



Scheme 2. Chemical structure of fluorescence-switching molecules.

As depicted in Figure 1 a, a freshly spin-coated DBDCS/*m*-BHCDCS (10:3 w/w, optimized mixing ratio) film shows reversible changes in its luminescence color to distinctive RGB under various treatments. After SVA of the B(on) or the R(on) film, the film shows green emission ($\lambda_{em} = 527$ nm: G(on) state) which coincides well with the green luminescent phase of DBDCS (Figure S1).[13] The green emission color of the film switches to blue ($\lambda_{em} = 458$ nm: B(on) state) upon TA treatment, coinciding with the blue luminescent phase of DBDCS (Figure S1).[13] The differential scanning calorimetry

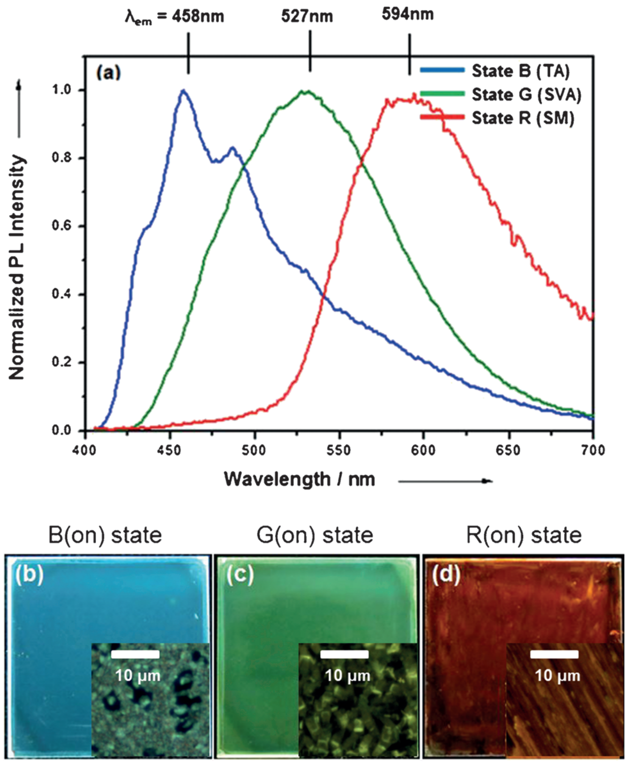


Figure 1. Photoluminescent properties of the bicomponent mixture film (DBDCS/*m*-BHCDCS = 10:3 w/w, $\lambda_{ex} = 275$ nm) comparing the thermally annealed (140 °C, 3 min; B(on) state), solvent-vapor annealed (using dichloromethane; G(on) state), and smeared (R(on) state) films. Photoluminescence spectra (a) and photographic images under UVA light (b–d). Insets in (b–d) show optical microscope images under UVA light.

(DSC) thermograms show that the temperature-induced phase transition of DBDCS and the crystallization of *m*-BHCDCS are independent in the mixture system (see Figure S6). Furthermore, the green emission changes to red emission ($\lambda_{em} = 594$ nm : R(on) state) by applying mechanical force, such as smearing, corresponding to the red luminescent phase of *m*-BHCDCS (Figure S1).[14] We evaluated the RGB color switching behavior of the mixtures by reproducing colors in the Commission Internationale de l'Eclairage (CIE) 1931 chromaticity diagram (Figure S2). Reversibility of the tricolor switching was confirmed by repeating SVA–TA–SVA–SM processes (Figures 2 and S3). The characteristic RGB emission spectra were repeatedly reproduced for each treatment, indicating that the structural changes of the components indeed induce good reversibility of the tricolor switching system.

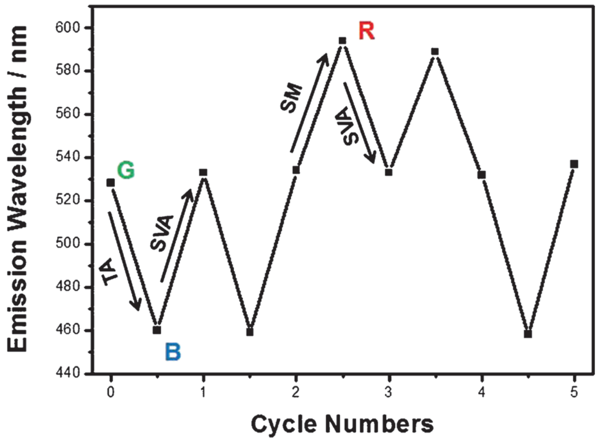


Figure 2. Reversible multistimuli tricolor fluorescence switching of the DBDCS/*m*-BHCDCS bicomponent system by exposing it to organic vapor (SVA: G(on) around 530 nm), heating (TA : B(on) around 460 nm), and smearing (SM: R(on) around 590 nm) treatments (excited at 275 nm).

To better understand the mechanistic origin of the R(on), G(on), and B(on) emissions in DBDCS/*m*-BHCDCS mixture, photophysical properties of them including Φ_F and fluorescence lifetime τ_F were explored (Table 1). Interestingly, the R(on) state shows a significantly higher Φ_F of 0.17 compared to that of the pure *m*-BHCDCS film ($\Phi_F = 0.10$), which evidences efficient FRET from DBDCS to *m*-BHCDCS. The B(on) and G(on) states exhibit smaller Φ_F compared to the pure samples, which contributes to the shared absorbance of non-emissive *m*-BHCDCS which provides an additional nonradiative decay route. We quantified the FRET efficiency η through

$$\eta = 1 - \tau_{F,D}(\mathrm{mix})/\tau_{F,D}(\mathrm{pure}) \qquad (1)$$

in which $\tau_{F,D}$(mix) and $\tau_{F,D}$(pure) are the amplitude-averaged fluorescent lifetimes of DBDCS in the mixture and the pure DBDCS sample, respectively. In the B(on) and G(on) states $\tau_{F,D}$ is barely shortened, with FRET efficiency η of only 0.06 and 0.03, respectively. On the other hand, in the SM state generating R(on), $\tau_{F,D}$ is remarkably reduced from 6.1 ns to 1.6 ns, indicating that FRET is significantly enhanced in the amorphous mixture of R(on) SM state ($\eta = 0.75$).

Table 1: Photoluminescence quantum yield, lifetime, and FRET efficiency of the pure DBDCS and DBDCS/*m*-BHCDCS mixtures ($\lambda_{ex} = 377$ nm, $\lambda_{em}^{TA} = 470$ nm and λ_{em}^{SVA} and $\lambda_{em}^{SM} = 500$ nm) in different emitting states of B(on), G(on), and R(on).

State	pure		mixture		
	Φ_F	τ_F [ns]	Φ_F	τ_F [ns]	η
B(on) state	0.31	2.5	0.23	2.4	0.06
G(on) state	0.45	11.5	0.26	11.1	0.03
R(on) state	0.10	6.1	0.17	1.6	0.75

[a] TA = thermal annealing, SVA = solvent-vapor annealing, SM = smearing. [b] Original data are shown in Figure S4 in the SI. [c] $\eta = 1 - \tau_{F,D}$ (mix)/$\tau_{F,D}$ (pure).

The mechanism of shear-induced FRET efficiency control can be rationalized by optical microscopy (OM) studies under UV irradiation. The optical micrograph of the B(on) and G(on) states (see inset in Figure 1 b,c) show segregated microcrystallites of DBDCS and *m*-BHCDCS. Such macroscopic aggregation in the TA- and SVA-treated films is induced by selective self-assembly driven by the crystalline nature of both, DBDCS and *m*-BHCDCS, under those conditions. Thus, FRET between the two chromophores can be well suppressed, because it can only take place close to the contacts between the macroscopically separated crystallites, and thus either B(on) or G(on) emission of DBDCS is efficiently observed, which is concurrent with the R(off) state due to the crystalline nature of *m*-BHCDCS. However, upon smearing, the *m*-BHCDCS crystals collapse to form an amorphous morphology, and no more microcrystalline structures are observed (inset in Figure 1 d). The close contact between the two chromophores in the SM sample thus greatly enhances FRET efficiency to 0.75 which rationalizes the efficiency-enhanced red luminescence ($\Phi_F = 0.17$) of the SM R(on) state. To ensure the morphological characteristics, X-ray diffraction (XRD) patterns were recorded for the three mixture film samples. It clearly shows the crystalline nature of the B(on) and G(on) state, in contrast to the amorphous R(on) state (Figure S5).

Using the multistimuli-responsive characteristics of the DBDCS/*m*-BHCDCS mixture, RGB fluorescence patterning was demonstrated (Figure 3). Under 254 nm UV irradiation, green photoluminescence, G(on), was observed for the SVA film (Figure 3, top). Thermal annealing (140 °C for 3 min on hot plate) triggered a change in the fluorescent color from G(on) to B(on) (Figure 3, bottom left). Similarly, G(on) was changed to R(on) by shearing on the SVA film using a plastic stick, and B(on) of the TA film was switched to R(on) by shearing (Figure 3, bottom right). We could restore the changed colors (B, R) to the initial G(on) state by exposing a patterned sample again to solvent-vapor annealing (CH_2Cl_2 for 5 min). Because of the high contrast crosstalk-free switching characteristic, three luminescent colors could be inscribed into a single film with well-defined RGB color patterning (Figure 3, center).

We have developed an innovative material system of reversible and crosstalk-free tricolor RGB fluorescence

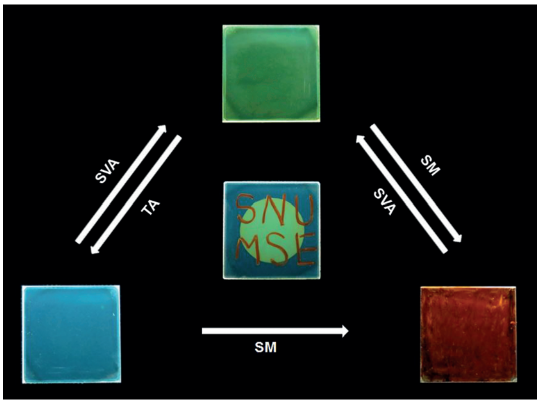


Figure 3. RGB fluorescence switching in DBDCS/*m*-BHCDCS bicomponent film: fluorescence changes by various stimuli of SVA, TA, and SM (2.5 cm×2.5 cm quartz plate, illuminated with handheld UV lamp of 254 nm wavelength).

switching based on the novel strategy of blending two different self-assembling and stimuli-responsive molecules, DBDCS and *m*-BHCDCS. DBDCS is a B-to-G luminescence switching molecule with self-assembly capability, whereas *m*-BHCDCS is an off-to-on red (R) luminescence switching molecule operating under different switching stimuli. Switching of FRET between DBDCS and *m*-BHCDCS by supramolecular structure control was a key idea of this system to suppress the crosstalk and to achieve high-contrast RGB switching. Reversible and independent RGB luminescence switching ($\lambda_{em} = 594$, 527, and 458 nm and $\Phi_F = 0.17$, 0.26, and 0.23 for R, G, and B, respectively) were implemented by different external stimuli such as heat, solvent vapor exposure, and mechanical force.

Keywords: fluorescence switching · Förster resonance energy transfer · mechanochromic luminescence · self-assembly · supramolecular chemistry

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[1] a) Y. Sagara, T. Kato, *Nat. Chem.* **2009**, *1*, 605; b) Z. Chi, X. Zhang, B. Xu, X. Zhou, C. Ma, Y. Zhang, S. Liu, J. Xu, *Chem. Soc. Rev.* **2012**, *41*, 3878.

[2] L. Bu, M. Sun, D. Zhang, W. Liu, Y. Wang, M. Zheng, S. Xue, W. Yang, *J. Mater. Chem. C* **2013**, *1*, 2028.

[3] Y. Dong, B. Xu, J. Zhang, X. Tan, L. Wang, J. Chen, H. Lv, S. Wen, B. Li, L. Ye, B. Zou, W. Tian, *Angew. Chem. Int. Ed.* **2012**, *51*, 10782; *Angew. Chem.* **2012**, *124*, 10940.

[4] Y. Sagara, T. Kato, *Angew. Chem. Int. Ed.* **2011**, *50*, 9128; *Angew. Chem.* **2011**, *123*, 9294.

[5] Y. Gong, Y. Zhang, W. Z. Yuan, J. Z. Sun, Y. Zhang, *J. Phys. Chem. C* **2014**, *118*, 10998.

[6] K. Nagura, S. Saito, H. Yusa, H. Yamawaki, H. Fujihisa, H. Sato, Y. Shimoikeda, S. Yamaguchi, *J. Am. Chem. Soc.* **2013**, *135*, 10322.

[7] M.-J. Teng, X.-R. Jia, X.-F. Chen, Y. Wei, *Angew. Chem. Int. Ed.* **2012**, *51*, 6398; *Angew. Chem.* **2012**, *124*, 6504.

[8] B.-K. An, S.-K. Kwon, S.-D. Jung, S. Y. Park, *J. Am. Chem. Soc.* **2002**, *124*, 14410.

[9] B.-K. An, J. Gierschner, S. Y. Park, *Acc. Chem. Res.* **2012**, *45*, 544.

[10] J. Gierschner, S. Y. Park, *J. Mater. Chem. C* **2013**, *1*, 5818.

[11] S. Kim, S.-J. Yoon, S. Y. Park, *J. Am. Chem. Soc.* **2012**, *134*, 12091.

[12] J. H. Kim, B.-K. An, S.-J. Yoon, S. K. Park, J. E. Kwon, C.-K. Lim, S. Y. Park, *Adv. Funct. Mater.* **2014**, *24*, 2746.

[13] S.-J. Yoon, J. W. Chung, J. Gierschner, K. S. Kim, M.-G. Choi, D. Kim, S. Y. Park, *J. Am. Chem. Soc.* **2010**, *132*, 13675.

[14] M. S. Kwon, J. Gierschner, S.-J. Yoon, S. Y. Park, *Adv. Mater.* **2012**, *24*, 5487.

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