DOI: 10.1002/asia.201301071

COMMUNICATION

# Photocontrolled Intramolecular Charge/Energy Transfer and Fluorescence Switching of Tetraphenylethene-Dithienylethene-Perylenemonoimide Triad with Donor-Bridge-Acceptor Structure

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Abstract: Photochromic 1,2-dithienylethene (DTE) derivatives with a high thermal stability and fatigue resistance are appealing for optical switching of fluorescence. Here, we introduce a donor-photochromic bridge-acceptor tetraphenylethene-dithienylethene-perylenemonoimide (TPE-DTE-PMI) triad, in which TPE acts as the electron donor, PMI as the electron acceptor, and DTE as the photochromic bridge. In this system, the localized and intramolecular charge transfer emission of TPE-DTE-PMI with various Stokes shifts have been observed due to the photoinduced intramolecular charge transfer in different solvents. Upon UV irradiation, the fluorescence quenching resulting from photochromic fluorescence resonance energy transfer in TPE-DTE-PMI has been demonstrated in solution and in solid films. The fluorescence on/off switching ratio in polymethylacrylate film exceeds 100, a value much higher than in polymethylmethacrylate film, thus indicating that the fluorescence switching is dependent on matrices.

As representative of molecular photoswitches, 1,2-dithienylethene (DTE) derivatives that can undergo reversible photocyclization reactions, which are thermally irreversible and fatigue resistant, are appealing for molecular optical memory and optical switching in photonic devices.<sup>[1-3]</sup> Compared with absorbance measurements, which are usually used for tracking changes in color by monitoring the absorbance at the maximum absorption wavelength, fluorescent

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under http://dx.doi.org/10.1002/asia.201301071.

spectroscopy provides an alternative to UV/Vis absorption measurements to characterize the properties of molecular photoswitches. This requires that molecular photoswitches display both photochromism and fluorescent switching. Fluorescent on-off switching enables fluorescent imaging<sup>[4]</sup> and sensing<sup>[5]</sup> using molecular photoswitches as probes. A great deal of efforts have been made to develop novel photoswitchable fluorophores with high fluorescent quantum yields, on/off ratios, and switching speeds.<sup>[6-8]</sup> In recent years perylenediimides (PDI) have been extensively investigated because of their excellent photostability, high fluorescence quantum yields in organic solvents, and electron-accepting abilities.<sup>[9]</sup> In addition, PDI and/or photochromic triads have also gained much attention because of extended  $\pi$ -conjugation and enhanced electronic communication between fluorophores.<sup>[10]</sup> However, in most cases, PDIs exhibit strong fluorescent quenching in polar solvents, in aggregates, or in the solid state, as it is common for most planar organic molecules.<sup>[11]</sup> Compared with PDIs, pervlenemonoimides (PMIs) are highly luminescent both in solution and in the solid state, and thus they are more promising for many optical devices and sensing applications.<sup>[12]</sup> Taking advantage of stable photoswitching of DTE and the high fluorescence of PMI, it would be desirable to design DTE-PMI conjugates that possess fluorescence photoswitching behavior both in solution and in the solid state. In addition, tetraphenylethene (TPE) is attracting attention as a typical aggregation-induced emission (AIE) activator;<sup>[13]</sup> the AIE mechanism of TPE has already been well-studied since Tang et al. first found the AIE phenomenon.<sup>[14]</sup> It was found in previous studies that TPE integrates the donating properties and the AIE effect.<sup>[15]</sup> To the best of our knowledge, there are few reports that TPE can act as a moderate donor when linked to strong acceptors.<sup>[15]</sup> Here, we report the synthesis and optical properties of a donor-photochromic bridge-acceptor (D-bridge-A) tetraphenylethene-dithienylethene-perylenemonoimide

(TPE-DTE-PMI) triad. By covalently coupling TPE and PMI using DTE, we investigate the absorption, emission, photochromism, and fluorescent photoswitching behavior of the donor-photochromic bridge-acceptor structure in solution, in aggregates, and in the solid state. Remarkably, the conjugate emits strongly both in solution and in the solid state, and thus it seems that the AIE effect of TPE has been

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group on the other terminus does not communicate well with PMI when the DTE is

present in the open form  $(DTE_0)$ . After irradiation of

**10** with UV light for 1–3 min, a new peak around 612 nm ap-

peared that is assigned to DTE in its closed (DTE<sub>c</sub>). Similarly, **20** and **30** underwent obvious

photochromic reactions in organic solvents upon irradiation

at 302 nm. The absorption

peaks of DTE in the closed form in **2C** and **3C** are located at 606 nm and 600 nm, respectively. TPE itself is a large con-

jugated structure and here, as a donating group, it increases

throughout the whole molecule of **1C**. Thus, the absorption of

1C is more red-shifted than that of 2C containing the

slightly

conjugation

trinsic absorption of TPE and the peak at about 514 nm is

ascribed to the absorption of PMI. The open forms (10-

**30**) did not show any noticeable absorption in the visible

region above 400 nm except for the intrinsic absorption of

PMI. Only small differences in the absorption of PMI in

10, 20, and 30 could be observed. It is possible that the

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inhibited. Therefore, TPE mostly exhibits the electron-donating property so that the fluorescence photoswitching could be investigated both in solution and in the solid state.

The photochromic switching behavior of TPE-DTE<sub>O</sub>-PMI (**10**) and two control compounds,  $C_8H_{17}OPh-DTE_O-PMI$  (**20**) and PMI-DTE<sub>O</sub>-PMI (**30**), is shown in Scheme 1. The



Scheme 1. Photochromism and molecular structures of DTE-PMI derivatives used in this study.

detailed synthesis and characterization data are provided in the Supporting Information. The absorption spectra of **10– 30** are analyzed successively in order to follow the maintenance of the photochromic bridge and the interaction between intramolecular subunits. Figure 1 a and Figure S2 in the Supporting Information show the absorption spectra of **10**, **20**, and **30** upon irradiation with 302 nm light (0.85 mW cm<sup>-2</sup>) in toluene, THF, and DMF. The electronic spectra of **10–30** display an intense absorption band at about 510 nm with a considerable extinction coefficient (Table S1, Supporting Information), which is assigned to the PMI subunit that the three molecules have in common. Table 1 shows the spectroscopic properties of **10**. In the absorption spectra, the peak at 340 nm corresponds to the in-



that in THF, thus indicating that its AIE effect is inhibited (see Figure S3, Supporting Information). This means that TPE-DTE-PMI does not exhibit the typical AIE properties. Instead, TPE only exhibits the electron-donating property; this conclusion contributes to a better understanding of the

the

 $C_8H_{17}$ OPh- moiety. Comparably, **30** showed a much poorer

photochromic behavior with a small absorption band at

effect of the TPE group on the fluorescence properties and photoswitching process in solution.<sup>[15]</sup> The fluorescence emission spectrum of **10** (Figure 1b) is structured in toluene, and the maximum appears at 560 nm, which can be assigned to the locally excited (LE) state emission of PMI. However, with increasing solvent polarity, the emission peak exhibits a significant red shift and becomes



Figure 1. Absorption and photoluminescence spectra of 10 and 1C (1 µM) in solvents of different polarity.

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Table 1. Optical properties of TPE-DTE-PMI (10) in different matrices.

Solvent	$\Delta f^{[a]}$	$\lambda_{\max}$ (abs.) [nm]	$\lambda_{\max}$ (PL) [nm]	Stokes Shift [nm]	$oldsymbol{\Phi}_{ ext{F-O}}{}^{[b]} \ [\%]$	$\Phi_{ ext{F-PSS}}^{[c]}$ [%]
Toluene	0.014	516.5	564.0	47.5	80	18
THF	0.21	511.5	583.0	71.5	65	19
DMF	0.27	516.0	623.0	107	22	11
PMMA	_	510.5	589.0	78.5	_	
PMA	-	508.5	596.0	87.5	-	

[a]  $\Delta f$ = the orientational polarisability.  $\lambda_{max}$  (abs) is the lowest energy absorption peak at 1  $\mu$ M of **10**;  $\lambda_{max}$  (PL) was measured at  $\lambda_{ex}$ =514 nm and 1  $\mu$ M of **10**. [b] Quantum yield of the open form. [c] Quantum yield of the photostationary state (302 nm, PSS).  $\Phi_{\rm F}$  values were estimated against rhodamine B (quantum yield of 70% in ethanol),  $\lambda_{ex}$ =514 nm ( $\lambda_{em}$ =520–800 nm). PMMA=polymethyl methacrylate. PMA=polymethacrylate.

structureless (Table 1). The large solvatochromic shift of the fluorescence (620 nm in DMF compared to 560 nm in toluene) in polar solvents indicates a strong photo-induced intramolecular charge transfer (ICT) character of the fluorescent state. As predicted, upon irradiation with UV light (302 nm), there is a significant energy overlap between the emission band of PMI and the absorption band of 1C. Thus, the resulting fluorescence of 10 decreases upon UV irradiation, thereby indicating a photochromic fluorescence resonance energy transfer from PMI to the ring-closed isomer of DTE as an efficient quencher, which originates from photoisomerization of 10 to 1C (Figure 1b). The FRET quenching efficiency in TPE-DTE-PMI after UV irradiation was calculated from the observed quenching of the donor intensity. For the open form of DTE ( $DTE_0$ ) the conjugation is markedly restricted, and thus only charge transfer is allowed within the TPE-DTE-PMI triad. On the contrary, for the closed form of DTE ( $DTE_{c}$ ) for which the conjugation is obviously improved, the emission of PMI overlaps well with the absorbance of DTE<sub>c</sub>. Therefore, energy transfer dominates in the closed form of TPE-DTE-PMI triad.<sup>[10a]</sup>

Compounds 10, 20, and 30 possess the same DTE-PMI subunits. The difference in their molecular structure is that the three fluorophores contain different substituted groups at the other terminus of the triads. Therefore, the comparison of 10 with 20 and 30 could lead to insights into the optical properties influenced by structural differences. The absorbance and fluorescence of the three fluorophores change similarly with an increasing polarity of the solvent. The quantum yields of 10, 20, and 30 are very close in toluene ( $\sim 80\%$ ) and THF (65%). The three compounds also have the similar emission spectra in DMF. It is worth noting that **10** has the highest quantum yield in DMF (22%), while it is 14% for 20 and 11% for 30 (Table S2, Supporting Information). The ICT properties in the open-form triads are the same, while an electron-donating group such as TPE and C<sub>8</sub>H<sub>17</sub>OPh could improve the quantum yields of the triads in polar solvents. The fact that TPE-DTE-PMI has the strongest emission in a good solvent argues against the AIE effect, as TPE usually quenches emission in a good solvent. It seems that here the AIE effect of TPE is too weak to be observed. The photochromism of **30** is the poorest among the three compounds owing to the electron-withdrawing PMI group, while both **10** and **20** contain electron-donating groups. After irradiation with UV light, the conjugation is extended by the closed-form DTE. Therefore, photochromic fluorescence resonance energy transfer from PMI to the ring-closed isomer of DTE as an efficient quencher is induced by the photoisomerization.

Optimized structures of both 10 and 1C obtained by density functional theory (DFT) calculations are shown in Figure S1 in the Supporting Information. In the open form, 10, the HOMO is localized around TPE and the adjacent thiophene subunits with significant orbital density, while the LUMO in **10** is restricted to the strong electron-withdrawing PMI subunit. By comparison, the HOMO in 1C is delocalized with orbital density transfer from TPE through the thiophene subunit due to the extended conjugation. The LUMOs in 1C are localized around PMI and the pentafluorocyclopentene. The HOMOs and LUMOs of 10 and 1C indicated that photoswitchable intramolecular charge and energy transfer occurs in the donor-photochromic bridgeacceptor triad upon alternating irradiation with UV and visible light. Thus, it is demonstrated experimentally that, by a primary externally photoswitching process (photoisomerization of DTE), two secondary externally initiated processes (photoinduced intramolecular charge transfer in the ringopened isomer and fluorescence resonance energy transfer in the ring-closed isomer) can be switched reversibly by UV/ visible light.

The initial ring-opened isomer **10** exhibits one absorption peak at around 510 nm, which was observed in solution and in solid film. Upon irradiation with UV light (302 nm), the resulting UV/Vis absorption spectra (Figure 2a) shows the evolution of two peaks around 510 nm and 620 nm, in which the former peak is attributed to the PMI moiety and the latter one to the closed form in DTE. Upon UV irradiation for 120 s at around  $0.85 \text{ mW cm}^{-2}$ , TPE-DTE-PMI in toluene attained 95% of the absorbance at the photostationary state (PSS) under 302 nm irradiation. The photoisomerization attains the stationary state at about 3 min. The absorbance of **10** and **1C** at 620 nm increased and decreased reversibly in solution with alternating irradiation with UV and visible light, thus demonstrating the highly reversible and bistable photochromism between **10** and **1C** (Figure 2b).

The initial open-form compound **10** exhibits a strong emission from PMI at around 560–620 nm in solution and in the solid film, depending on the polarity of the solvent or polymer matrices. The resulting fluorescence spectra (Figure 3a and Figure S4, Supporting Information) of TPE-DTE-PMI in solution upon UV irradiation (302 nm) show a gradual decrease in the emission intensity at 560–600 nm because of the photochromic fluorescence resonance energy transfer of PMI to the ring-closed isomer of DTE in **1C**. The reversibility of this process can be demonstrated by cycling forward and backward between the open and closed form. When a solution of **10** in toluene was excited at 514 nm, a strong emission at 567 nm was observed and, after UV irradiation, fluorescence quenching >80% was detect-

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Figure 2. (a) Absorption spectra of 10 (1  $\mu$ M) in toluene upon irradiation with UV light (302 nm). The photostationary state was determined by irradiating a solution of 10 with UV light until no changes were observed in the spectrum. Inset: Photos of 10 in toluene taken at daylight after irradiation with visible light and UV light, respectively. (b) Reversible absorption switching for 10 (1  $\mu$ M) in toluene measured at 620 nm upon alternating irradiation with UV light (302 nm, 3 min) and visible light (>495 nm, 20 min).



Figure 3. (a) Emission spectra change of 10 (1  $\mu$ M) in toluene upon irradiation with UV light (302 nm). Inset: Photos of 10 in toluene taken at 365 nm UV light after irradiation with visible light and UV light, respectively. (b) Reversible fluorescence switching for 10 (1  $\mu$ M) in toluene measured at 567 nm ( $\lambda_{ex}$ =514 nm) upon alternating irradiation with UV light (302 nm, 3 min) and visible light (>495 nm, 20 min).

ed. The cycling behavior at alternating UV and visible-light irradiation shows decent reversibility and good fatigue resistance (Figure 3b).

It is found that **10** not only does not show evident fluorescent quenching in the solid state due to aggregationcaused quenching but also no strong fluorescent quenching in solution due to the AIE effect induced by TPE groups. In the solid state, **10** shows a different behavior with regard to the photoswitching speed, fluorescent intensity, and the on/ off ratio, depending on the surrounding matrices. In polymethyl methacrylate (PMMA) with a glass transition temperature of 104°C, the absorption band of 10 at 620 nm increases slowly upon 302 nm irradiation, thus indicating the slow photochromic transformation of **10** to **1C** (Figure 4a). In comparison, the absorption band of 10 increases much faster in polymethacrylate (PMA), which has a much lower glass transition temperature of 0°C as compared to PMMA film (Figure 4b). This is attributed to the different capability of molecular motion in sticky or soft matrices. In soft PMA with a lower glass transition temperature, the photochromic speed is much faster than that in sticky PMMA. The highly reversible and bistable photochromism between 10 and 1C in PMMA and PMA films was verified by using alternating UV and visible-light irradiation (Figure S5, Supporting Information). The fluorescence quenching is efficient with a higher fluorescence on/off switching ratio in PMMA film than in solution (Figure 4c). However, in PMA film, 10 even shows a much faster photochromic fluorescent quenching with an on/ off ratio that is higher than 100 (Figure 4d). The reversible photoswitchable fluorescence of 10 in PMMA and PMA films was demonstrated by cycling forward and backward, from the open to the closed form and reverse (Figure 4e and 4f). When TPE-DTE-PMI was excited at 514 nm in PMA film, a strong emissions at 600 nm was observed after visible-light illumination for 1C, and the emission of 10 after UV irradiation was nearly completely quenched.

Optical switches usually work in solid-state devices despite many reports on fluorescent molecular switches in solution. Therefore, the effects of solid matrices on the photoswitchable absorption and emission properties of fluorophores are

indispensable. Here we found that both electron-withdrawing and electron-donating substituted groups determine the photoswitching properties. The fluorescent switching is dependent on the matrices such as solvents with different polarities or polymer matrices with different glass transition temperatures. The design of new molecules combined with their optical characterization in different matrices will be helpful for the development of novel photoswitchable fluorophores.

In conclusion, we have demonstrated a simple design of a donor-photochromic bridge-acceptor triad TPE-DTE-PMI, in which TPE is used as the electron donor and PMI as the electron acceptor with DTE as the photochromic bridge. In this system, the LE state and ICT emission of **10** with various Stokes shifts have been observed due to the photoinduced intramolecular charge transfer in different solvents. Upon UV irradiation, the fluorescence quenching resulting from photochromic fluorescence resonance energy transfer of **1C** has been demonstrated in solution and solid films. Both secondary photoinduced processes at 514 nm excitation are reversibly controlled by primary externally photoswitching stimuli with UV/visible-light irradiation. Thus, we conclude that DTE acts as a reversible adjustor for intra-

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Figure 4. Photochromism and fluorescence switching of **10** in solid film. (a,c) Absorption and emission spectra of **10** in PMMA film upon irradiation with UV light (**10**/PMMA = 1:100, w/w). (b,d) Absorption and emission spectra of **10** in PMA film upon irradiation with UV light (**10**/PMA = 1:100, w/w). (e,f) Reversible fluorescence switching for **10** in PMMA and PMA film measured at 600 nm ( $\lambda_{ex}$ =514 nm) upon alternating irradiation with UV light (302 nm, 5 min) and visible light (>495 nm, 10 min).

molecular charge transfer in the ring-opened isomer **10** and for photochromic energy transfer in ring-closed isomer **1C** upon irradiation with UV light and visible light, respectively.

#### Acknowledgements

This work was supported by the NSFC (20874025, 21174045), National Basic Research Program of China (Grant No. 2013CB922104). M.P.A. acknowledges the NSFC Research Fellowship for International Young Scientists (21150110141, 212111128) and the Special Fellowship of China Post-doctoral Science Foundation (2012T50642). We also thank the Analytical and Testing Center of Huazhong University of Science and Technology.

**Keywords:** dithienylethene • donor-acceptor systems • fluorescence • photochromism • perylene monoimide • tetraphenylethene

- [1] C. C. Warford, V. Lemieux, N. R. Branda in *Molecular Switches*, 2nd ed. (Eds.: B. L. Feringa, W. R. Browne), Wiley-VCH, Weinheim, **2011**, pp. 1–35.
- [2] M. Irie, Chem. Rev. 2000, 100, 1685–1716.
- [3] a) H. Tian, S. Yang, Chem. Soc. Rev. 2004, 33, 85–97; b) X. Guo,
   D. Zhang, Y. Gui, M. Wan, J. Li,
   Y. Liu, D. Zhu, Adv. Mater. 2004, 16, 636–640.
- [4] W. Tan, J. Zhou, F. Li, T. Yi, H. Tian, *Chem. Asian J.* 2011, 6, 1263–1268.
- [5] S. Pu, Z. Tong, G. Liu, R. Wang, J. Mater. Chem. C 2013, 1, 4726– 4739.
- [6] a) M. Irie, T. Fukaminato, T. Sasaki, N. Tamai, T. Kawai, *Nature* 2002, 420, 759–760; b) Z. Zhou, H. Hu, H. Yang, T. Yi, K. Huang, M. Yu, F. Li, C. Huang, *Chem. Commun.* 2008, 4786–4788; c) Y. He, Y. Zhu, Z. Chen, W. He, X. Wang, *Chem. Commun.* 2013, 49, 5556–5558.
- [7] a) M.-Q. Zhu, G.-F. Zhang, C. Li, M. P. Aldred, E. Chang, R. A. Drezek, A. D. Q. Li, J. Am. Chem. Soc. 2011, 133, 365–372; b) M.-Q. Zhu, G.-F. Zhang, C. Li, M. P. Aldred, A. D. Q. Li, J. Innovative Opt. Health Sci. 2011, 4, 395–408; c) M.-Q. Zhu, L. Zhu, J. J. Han, W. Wu, J. K. Hurst, A. D. Q. Li, J. Am. Chem. Soc. 2006, 128, 4303–4309.
- [8] a) C. Li, W.-L. Gong, Z. Hu, M. P. Aldred, G.-F. Zhang, Z.-L. Huang, M.-Q. Zhu, *RSC Adv.* **2013**, *3*, 8967–8972; b) W.-L. Gong, G.-F. Zhang, C. Li, M. P. Aldred, M.-Q. Zhu, *RSC Adv.* **2013**, *3*, 9167–9170.
- [9] a) T. Fukaminato, T. Sasaki, T. Kawai, N. Tamai, M. Irie, J. Am. Chem. Soc. 2004, 126, 14843–14849; b) T. Fukaminato, T. Doi, N. Tamaoki, K. Okuno, Y. Ishibashi, H. Miyasaka, M. Irie, J. Am. Chem. Soc. 2011, 133, 4984–4990; c) T. Fukaminato, T. Umemoto, Y. Iwata, S. Yokojima, S. Nakamura, J. Am. Chem. Soc. 2007, 129, 5932–5938.
- [10] a) J. M. Endtner, F. Effenberger, A. Hartschuh, H. Port, J. Am. Chem. Soc. 2000, 122, 3037-3046; b) J. Zhang, Q. Zou, H. Tian, Adv. Mater. 2013, 25, 378-399; c) J. Jin, J. Zhang, L. Zou, H. Tian, Analyst 2013, 138, 1641-1644; d) W. Tan, X. Li, J. Zhang, H. Tian, Dyes Pigm. 2011, 89, 260-265; e) S. D. Straight, P. A. Liddell, Y. Terazono, T. A. Moore, A. L. Moore, D. Gust, Adv. Funct. Mater. 2007, 17, 777-785; f) J. E. Bullock, R. Carmieli, S. M. Mickley, J. Vura-Weis, M. R. Wasielewski, J. Am. Chem. Soc. 2009, 131, 11919-11929.
- [11] a) F. Würthner, Chem. Commun. 2004, 1564–1579; b) Q. Zhao, X. A. Zhang, Q. Wei, J. Wang, X. Y. Shen, A. Qin, J. Z. Sun, B. Z. Tang, Chem. Commun. 2012, 48, 11671–11673; c) Y. Yu, Q. Shi, Y. Li, T. Liu, L. Zhang, Z. Shuai, Y. Li, Chem. Asian J. 2012, 7, 2904– 2911.
- [12] a) L. Huang, S.-W. Tam-Chang, *Chem. Commun.* 2011, 47, 2291–2293; b) S.-W. Tam-Chang, L. Huang, *Chem. Commun.* 2008, 1957–1967; c) N. Tasios, C. Grigoriadis, M. R. Hansen, H. Wonneberger,

*Chem. Asian J.* **2013**, *00*, 0–0

These are not the final page numbers! 77

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### **AN ASIAN JOURNAL**

C. Li, H. W. Spiess, K. Müllen, G. Floudas, J. Am. Chem. Soc. 2010, 132, 7478-7487.

- [13] a) J. Huang, X. Yang, X. Li, P. Chen, R. Tang, F. Li, P. Lu, Y. Ma, L. Wang, J. Qin, Q. Li, Z. Li, *Chem. Commun.* 2012, 48, 9586–9588;
  b) J. Huang, X. Yang, J. Wang, C. Zhong, L. Wang, J. Qin, Z. Li, *J. Mater. Chem.* 2012, 22, 2478–2484;
  c) M. P. Aldred, C. Li, G.-F. Zhang, W.-L. Gong, A. D. Q. Li, Y. Dai, D. Ma, M.-Q. Zhu, *J. Mater. Chem.* 2012, 22, 7515–7528;
  d) M. P. Aldred, C. Li, M.-Q. Zhu, *Chem. Eur. J.* 2012, 18, 16037–16045;
  e) W.-L. Gong, G. F. Zhang, M. P. Aldred, Q. Fu, D.-K. Huang, Y. Shen, X.-F. Qiao, D. Ma, M.-Q. Zhu, *RSC Adv.* 2012, 2, 10821–10828.
- [14] a) J. Luo, Z. Xie, J. W. Y. Lam, L. Cheng, H. Chen, C. Qiu, H. S. Kwok, X. Zhan, Y. Liu, D. Zhu, B. Z. Tang, *Chem. Commun.* 2001,

1740-1741; b) Y. Hong, J. W. Y. Lam, B. Z. Tang, Chem. Soc. Rev. 2011, 40, 5361-5388.

[15] a) R. Hu, C. F. A. Gómez-Durán, J. W. Y. Lam, J. L. Belmonte-Vázquez, C. Deng, S. Chen, R. Ye, E. Peña-Cabrera, Y. Zhong, K. S. Wong, B. Z. Tang, *Chem. Commun.* **2012**, *48*, 10099–10101; b) Q. Zhao, S. Zhang, Y. Liu, J. Mei, S. Chen, P. Lu, A. Qin, Y. Ma, J. Z. Sun, B. Z. Tang, *J. Mater. Chem.* **2012**, *22*, 7387–7394; c) G.-F. Zhang, M. P. Aldred, W.-L. Gong, C. Li, M.-Q. Zhu, *Chem. Commun.* **2012**, *48*, 7711–7713.

> Received: August 10, 2013 Published online: ■ ■ ↓, 0000

# COMMUNICATION

The matrix reloaded: We report the synthesis and photophysical characterization of a donor-photochromic bridge-acceptor tetraphenylethene-dithienylethene-perylenemonoimide (TPE-DTE-PMI) triad that simultane-ously exhibits photocontrolled intra-molecular charge/energy transfer and enhanced reversible fluorescence switching, depending on the surround-ing matrices.



# Photochromism

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Photocontrolled Intramolecular Charge/Energy Transfer and Fluorescence Switching of Tetraphenylethene-Dithienylethene-Perylenemonoimide Triad with Donor-Bridge-Acceptor Structure