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Mendeleev Commun., 2014, **24**, 140–142

Mendeleev Communications

Self-quenching and self-sensitization in the photochemistry of a styrylquinoline–merocyanine dyad

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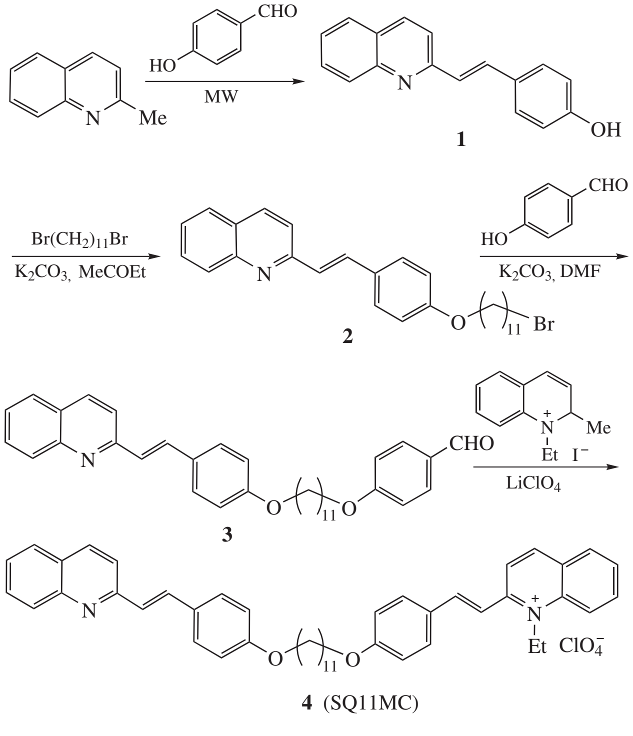
DOI: 10.1016/j.mencom.2014.04.003

Forster resonance energy transfer from a styrylquinoline moiety to merocyanine results in the quenching of the former and the sensitization of the latter in a novel styrylquinoline–merocyanine dyad and appears in the photoluminescence and photoisomerization of the dyad.

Dyads with photoactive chromophores (photochromes) can be reversibly switched between different states upon light excitation and used as the models of molecular devices, switches and logic gates.[1–7] In a recently investigated bis-styrylquinoline dyad, both of the styrylquinoline chromophores underwent photoisomerization so that the dyad could be photochemically switched from one state to another.[8] However, due to symmetry, both chromophores of the dyad had the same absorption spectra that made impossible the selective excitation of a particular chromophore; it was also impossible to distinguish spectrally some dyad isomers.

To correct these drawbacks, we synthesized a novel non-symmetric styrylquinoline–merocyanine dyad SQ11MC [(*E*)-1-ethyl-2-[2-(4-{11-[4-(2-quinolin-2-ylvinyl)phenoxy]undecyloxy}-phenyl)vinyl]quinolinium perchlorate], where two chromophores have different absorption spectra. The dyad SQ11MC was prepared in four steps in an overall yield of 38%.[†] The synthetic route to the SQ11MC dyad includes the condensation of quinaldine with



Scheme 1

[†] (*E*)-*2-[2-(4-Hydroxyphenyl)vinyl]quinoline* **1** and (*E*)-*2-{2-[4-(11-bromoundecyloxy)phenyl]vinyl}quinoline* **2** were prepared using known procedures.[9]

For **1**: yield 90%, mp 268 °C (EtOH).

For **2**: yield 75%, white crystals, mp 84–86 °C (MeOH). ^{1}H NMR (CDCl$_3$) δ: 1.24–1.38 (m, 10H, CH$_2$), 1.40–1.50 (m, 4H, CH$_2$), 1.76–1.89 (m, 4H, CH$_2$), 3.41 (t, 2H, BrCH$_2$, *J* 6.8 Hz), 3.99 (t, 2H, OCH$_2$, *J* 6.6 Hz), 6.91 (d, 2H, *o*-H$_{C_6H_4}$, *J* 8.7 Hz), 7.26 (d, 1H, =CH, *J* 16.4 Hz), 7.48 (t, 1H, quinoline, *J* 7.6 Hz), 7.56 (d, 2H, *m*-H$_{C_6H_4}$, *J* 8.7 Hz), 7.62 (d, 1H, =CH, *J* 16.4 Hz), 7.64 (d, 1H, quinoline, *J* 8.6 Hz), 7.68 (t, 1H, quinoline, *J* 7.6 Hz), 7.76 (d, 1H, quinoline, *J* 8.4 Hz), 8.04 (d, 1H, quinoline, *J* 8.6 Hz), 8.09 (d, 1H, quinoline, *J* 8.7 Hz). IR (ν/cm^{-1}): 3057, 3037, 2937, 2851 (ν_{CH_2}), 1632 ($\nu_{C=C}$), 1607, 1596, 1513, 1262 (ν_{COC}), 1234, 1174, 974 ($\delta_{CH=CH}$), 822, 749, 513 (δ_{CBr}). Found (%): C, 69.80; H, 7.24; N, 2.87. Calc. for C$_{28}$H$_{34}$NOBr (%): C, 69.99; H, 7.13; N, 2.92.

(*E*)-*4-{11-[4-(2-Quinolin-2-ylvinyl)phenoxy]undecyloxy}benzaldehyde* **3**. A mixture of **2** (0.4 mmol), 4-hydroxybenzaldehyde (0.4 mmol) and K$_2$CO$_3$ (1.2 mmol) in 5 ml of DMF was heated with stirring at 90–100 °C for 12 h. After cooling, the mixture was diluted with 20 ml of water, and the precipitate was filtered off and recrystallized from methanol to afford white crystals of product **3** (0.163 g, 78%); mp 116–118 °C. ^{1}H NMR (CDCl$_3$) δ: 1.29–1.41 (m, 10H, CH$_2$), 1.43–1.51 (m, 4H, CH$_2$), 1.77–1.86 (m, 4H, CH$_2$), 4.00 (t, 2H, OCH$_2$, *J* 6.5 Hz), 4.04 (t, 2H, OCH$_2$, *J* 6.5 Hz), 6.92 (d, 2H, C$_6$H$_4$, *J* 8.7 Hz), 6.98 (d, 2H, C$_6$H$_4$, *J* 8.7 Hz), 7.28 (d, 1H, =CH, *J* 16.2 Hz), 7.47 (t, 1H, quinoline, *J* 7.6 Hz), 7.57 (d, 2H, C$_6$H$_4$, *J* 8.7 Hz), 7.63 (d, 1H, =CH, *J* 16.2 Hz), 7.65 (d, 1H, quinoline, *J* 8.5 Hz), 7.69 (t, 1H, quinoline, *J* 7.7 Hz), 7.77 (d, 1H, quinoline, *J* 8.2 Hz), 7.82 (d, 2H, C$_6$H$_4$, *J* 8.7 Hz), 8.07 (d, 1H, quinoline, *J* 8.6 Hz), 8.10 (d, 1H, quinoline, *J* 8.6 Hz), 9.87 (s, 1H, CHO). IR (ν/cm^{-1}): 3061, 3036, 2924, 2853 (ν_{CH_2}), 1689 ($\nu_{C=O}$), 1632 ($\nu_{C=C}$), 1604, 1578, 1513, 1256 (ν_{COC}), 1233, 1164, 972 ($\delta_{CH=CH}$), 829, 758. Found (%): C, 80.75; H, 7.46; N, 2.53. Calc. for C$_{35}$H$_{39}$NO$_3$ (%): C, 80.58; H, 7.54; N, 2.68.

(*E*)-*1-Ethyl-2-[2-(4-{11-[4-(2-quinolin-2-ylvinyl)phenoxy]undecyloxy}phenyl)vinyl]quinolinium perchlorate* SQ11MC **4**. A mixture of **3** (0.23 mmol), *N*-ethylquinaldinium iodide (0.23 mmol) and 0.3 ml of piperidine in 6 ml of methanol was refluxed for 6 h. After cooling, the yellow precipitate was filtered off, washed twice with 5 ml of acetone and dissolved in boiling ethanol. Then, 100 mg (0.94 mmol) of lithium perchlorate was added and the perchlorate was filtered off after cooling, washed twice with 5 ml of chloroform–hexane (1 : 1) to afford yellow crystalline powder of **4** (0.128 g, 72%); mp 241–243 °C. ^{1}H NMR (DMSO-*d*$_6$) δ: 1.26–1.38 (m, 10H, CH$_2$), 1.39–1.47 (m, 4H, CH$_2$), 1.55 (t, 3H, Me, *J* 7.2 Hz), 1.68–1.78 (m, 4H, CH$_2$), 4.00 (t, 2H, OCH$_2$, *J* 6.2 Hz), 4.08 (t, 2H, OCH$_2$, *J* 6.3 Hz), 5.12 (q, 2H, CH$_2$, *J* 7.2 Hz), 6.96 (d, 2H, C$_6$H$_4$, *J* 8.8 Hz), 7.10 (d, 2H, C$_6$H$_4$, *J* 8.6 Hz), 7.29 (d, 1H, =CH, *J* 16.2 Hz), 7.51 (t, 1H, quinoline, *J* 7.6 Hz), 7.62–7.72 (m, 4H, quinoline, C$_6$H$_4$), 7.74 (d, 1H, =CH, *J* 16.2 Hz), 7.80 (d, 1H, quinoline, *J* 8.6 Hz), 7.88–7.98 (m, 5H, quinoline, C$_6$H$_4$), 8.15 (t, 1H, quinoline, *J* 8.0 Hz), 8.25 (d, 1H, =CH, *J* 15.6 Hz), 8.28–8.33 (m, 2H, quinoline), 8.52 (d, 1H, quinoline, *J* 8.8 Hz), 8.55 (d, 1H, quinoline, *J* 9.1 Hz), 8.98 (d, 1H, quinoline, *J* 9.0 Hz). IR (ν/cm^{-1}): 3037, 2937, 2854 (ν_{CH_2}), 1591, 1573, 1513, 1256 (ν_{COC}), 1234, 1167, 1087, 967 ($\delta_{CH=CH}$), 833, 764. Found (%): C, 72.53; H, 6.79; N, 3.53. Calc. for C$_{47}$H$_{51}$N$_2$O$_6$Cl (%): C, 72.80; H, 6.63; N, 3.61.

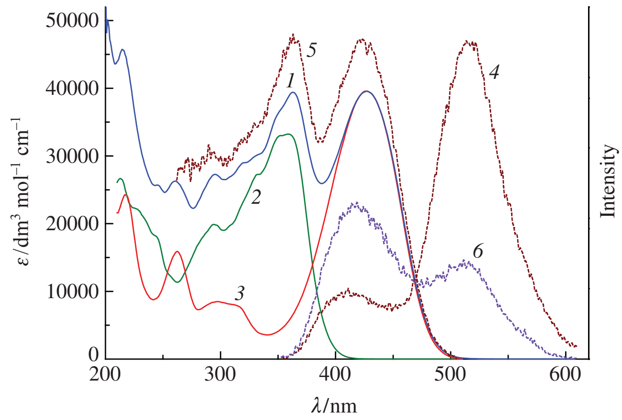


Figure 1 Absorption spectra in ethanol: (*1*) *EE*-SQ11MC, (*2*) (*E*)-2-(4-methoxystyryl)quinoline MeSQ, (*3*) (*E*)-*N*-ethyl-2-(4-methoxystyryl)quinolinium perchlorate MeMC, (*4*) normalized luminescence spectrum of *EE*-SQ11MC (excited at 310 nm), (*5*) luminescence excitation spectrum of *EE*-SQ11MC (monitored at 515 nm) and (*6*) luminescence spectrum of photostationary state PS_{470} (excited at 310 nm). Absorption spectra of the model compounds are red-shifted by 160 cm^{-1}.

4-hydroxybenzaldehyde, the alkylation of (*E*)-2-[2-(4-hydroxyphenyl)vinyl]quinoline **1** with 1,11-dibromoundecane, the reaction of (*E*)-2-{2-[4-(11-bromoundecyloxy)phenyl]vinyl}quinoline **2** with 4-hydroxybenzaldehyde and the condensation of aldehyde **3** with *N*-ethylquinaldinium iodide followed by ion exchange (Scheme 1).

Figure 1 shows the absorption spectra of the dyad SQ11MC: spectrum *1* is a superposition of the spectra of the model compounds, (*E*)-2-(4-methoxystyryl)quinoline MeSQ, spectrum *2*, and (*E*)-1-ethyl-2-(4-methoxystyryl)quinolinium perchlorate–O-methylated merocyanine MeMC, spectrum *3* (to take into account a bathochromic effect of the long polymethylene chain in the dyad in comparison with that of the methoxy group, the spectra of the model compounds are red-shifted by 160 cm^{-1}).

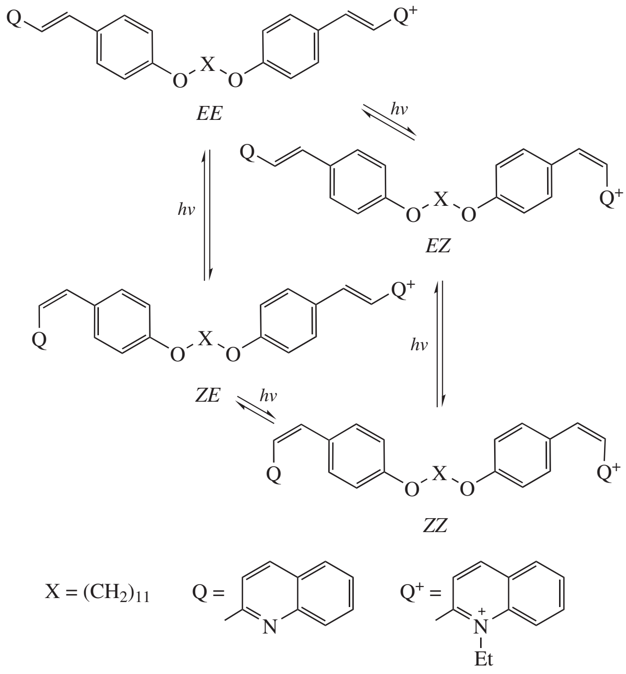
From a comparison with the model spectra, it follows that, at wavelengths $\lambda < 410$ nm, both styrylquinoline (SQ) and merocyanine (MC) fragments of SQ11MC absorb light, whereas the long-wavelength absorption band (LWAB) in the region of 410–490 nm with a maximum at 427 nm belongs to MC only.

In accordance with this fact, upon the excitation of SQ11MC at 310 nm, emission from both chromophores was observed at 414 and 516 nm from SQ and MC, respectively (Figure 1, spectrum *4*). Excitation of SQ11MC within LWAB resulted in the absorption and subsequent emission of MC only (at 516 nm).

Figure 1 also shows the excitation spectrum of SQ11MC luminescence (spectrum *5*). Despite monitoring at 515 nm, where only MC emits, we observed maxima due to both fragments of the dyad in the excitation spectrum: SQ at 365 nm and MC at 425 nm. This means that, after the excitation of SQ, energy transfer (ET) takes place to MC with the subsequent emission of the latter. The absorption band of MC at 427 nm (LWAB in spectra *1* and *3*) overlaps SQ emission band at 414 nm (short-wavelength band in spectrum *4*). This is a necessary condition for the Forster resonance ET (FRET).[10] The FRET results in the quenching of SQ-fragment fluorescence in the dyad. The ET efficiency (φ_{ET}) is defined by the equation

$$\varphi_{ET} = 1 - \varphi'_D/\varphi_D, \qquad (1)$$

where φ_D and φ'_D are donor (SQ) fluorescence quantum yields in the absence of a quencher in MeSQ and in the presence of a quencher (MC) in the dyad SQ11MC, respectively. For the test systems, $\varphi_D = 0.015^{\ddagger}$ and $\varphi'_D = 1.9\times10^{-3}$; therefore, $\varphi_{ET} = 0.87$.



Scheme 2 Phototransformations of the dyad SQ11MC (the perchlorate anion is omitted).

Upon irradiation, both model compounds, MeSQ and MeMC, underwent reversible photoisomerization between *trans*- and *cis*-isomers; spectral changes ceased after achieving a photostationary state (PS_λ) whose composition depended on irradiation wavelength (λ). Kinetics of absorbance (A) change during reversible photochemical reaction is described by the equation

$$dA/dt = -(\varepsilon_t - \varepsilon_c)(\varphi_{tc}A_t - \varphi_{ct}A_c)I_0(1 - 10^{-A})/A, \qquad (2)$$

where A_t, A_c and ε_t, ε_c are the absorbance and molar absorption coefficient of *trans*- and *cis*- isomers at the irradiation wavelength, respectively; I_0 is the light intensity, and φ_{tc} and φ_{ct} are the quantum yields of *trans–cis* and *cis–trans* photoisomerization, respectively. Numerical solution of equation (2) gave quantum yields $\varphi_{tc} = 0.56$ and $\varphi_{ct} = 0.43$ for MeSQ, $\varphi_{tc} = 0.65$ and $\varphi_{ct} = 0.81$ for MeMC.

Note that, according to synthetic procedures, the *EE* isomer of the dyad SQ11MC is formed, where both diarylethylene chromophores are in *trans*-configuration. Both of these chromophores are photoactive, so the dyad SQ11MC can exist in four isomeric forms, which can be reversibly transformed from one to another (Scheme 2). However, upon the irradiation of SQ11MC with visible light at 436 nm, within LWAB belonging to MC, only this fragment underwent photoisomerization; *i.e.*, only interconversion between *EE* and *EZ* isomers occurred. The treatment of the reaction kinetics by equation (2) gave the quantum yields of MC photoisomerization $\varphi_{tc} = 0.58$ and $\varphi_{ct} = 0.89$. These values are close to those for the model compound MeMC.

Additionally, irradiation at 436 nm revealed an isosbestic point at 346 nm. At this point, the *trans*- and *cis*- isomers of MC in a dyad have equal absorbance. Therefore, absorbance changes at 346 and 427 nm characterize the transformation of only SQ or MC, respectively. Using these two wavelengths, we can selectively monitor the photoisomerization of one or another fragment in the dyad.

During irradiation of the dyad at 365 nm, both dyad fragments underwent photoisomerization (Figure 2). We observed definitely two reactions: fast transformation of MC (at 427 nm) and slow transformation of SQ (at 346 nm) (Figure 2, insert). According to Scheme 2, upon irradiation at $\lambda < 410$ nm, four dyad isomers

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[‡] Fluorescence quantum yields (error, 15%) were measured using a dilute alcohol solution of anthracene as a standard (fluorescence quantum yield, 0.3).[11]

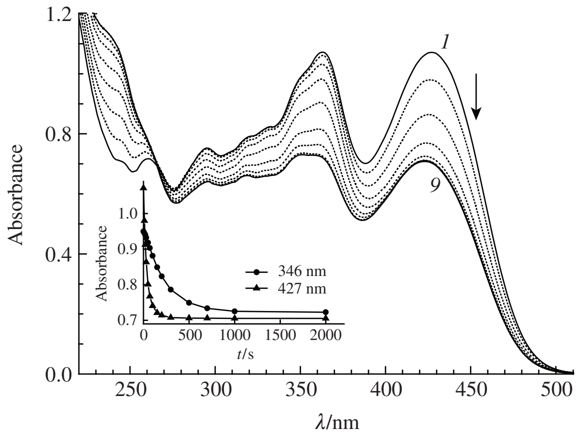

Figure 2 Spectral variations during the irradiation of air-saturated solution of *EE*-SQ11MC (2.7×10^{-5} mol dm^{-3}) in ethanol with light at 365 nm; intensity, 9.5×10^{-10} einstein cm^{-2} s^{-1}, irradiation time (*1*)–(*9*): 0, 10, 30, 70, 150, 300, 500, 1000 and 4000 s, respectively. Spectrum *9* corresponds to photostationary state PS$_{365}$. Insert: kinetics of absorbance at 346 and 427 nm.

can take part in eight reactions simultaneously. To simplify the kinetic scheme, we assumed that all transformations of every photoactive fragment can be characterized by a set of two averaged quantum yields, φ_{tc} and φ_{ct}. With this assumption, the simultaneous numerical solution of two equations (2) describing the kinetics of absorbance changes in SQ and MC gave the quantum yields $\varphi_{tc} = 0.067$ and $\varphi_{ct} = 0.41$ for the SQ fragment and $\varphi_{tc} = 2.0$ and $\varphi_{ct} = 2.9$ for the MC fragment. Note that these values are calculated taking into account light absorbed by a definite fragment.

The quantum yield of the *trans–cis* photoisomerization of the SQ fragment decreased whereas that of the MC fragment increased, as compared to that of the model compounds. Obviously, this is a result of the FRET, which gives rise to the quenching of SQ photoisomerization and the sensitization of MC photoisomerization in the dyad.

Let us consider data for SQ, which is an energy donor. Since both processes in SQ – emission (fluorescence) and photoisomerization – take place from the same (lowest singlet) excited state of the *trans*-isomer, we should expect the same effect of the FRET on these processes. The calculation of the ET efficiency from the photoisomerization quenching by equation (1), taking φ_{tc} data for SQ in MeSQ instead of φ_D and φ_{tc} data for SQ in the dyad instead of φ'_D, gave $\varphi_\mathrm{ET} = 0.88$, which is close to the above value calculated from the fluorescence quenching (0.87).

The quantum yields of MC photoisomerization in the dyad are more than unity as a result of an additional sensitized reaction of MC as an energy acceptor. The *trans–cis* photoisomerization of MC in the dyad proceeds in two isomers, *EE* and *ZE*, and the observed φ_{tc} is an averaged value for these two reactions. From the ratio of molar extinction coefficients for the models MeSQ and MeMC at 365 nm, we can calculate that, upon irradiation of *EE* isomer of the dyad, MC absorbs only 18% of incident light, but SQ – 82%. After excitation, SQ transfers 87% of energy to MC, so 71% of the latter is excited as a result of the FRET from SQ. This is 3.9 times more than the part of MC excited under direct light absorption. Thus, we should expect a corresponding increase in φ_{tc} for the *trans–cis* photoisomerization of MC in *EE* isomer, and this is an upper limit for the observed φ_{tc} for the dyad as a whole. We can conclude that the photoisomerization of the MC fragment in *EE* isomer is a mainly sensitized reaction (provided irradiation at 365 nm).

The sensitization of MC also appears in its enhanced fluorescence. Upon excitation at 427 nm (MC absorption band maximum where SQ does not absorb), the MC fluorescence quantum yield coincides with that of MeMC (2.7×10^{-3}). Upon excitation at 363 nm (SQ absorption band maximum, where SQ absorbs five times stronger than MC), the MC fluorescence quantum yield increases to 0.01. Generally, provided excitation in a UV region of 280–360 nm, where the absorption of SQ prevails over that of MC (spectra *2* and *3* in Figure 1), both fluorescence and photoisomerization of MC in *EE* isomer of the dyad are mainly sensitized processes.

In *ZE* isomer of the dyad, MC absorbs 54% of incident light (at 365 nm). Additionally, *cis*-SQ in *ZE* is a much worse energy donor than *trans*-SQ in *EE*, so we should expect φ_{tc} for MC in *ZE* to be close to the value for MeMC, and it is a lower limit for observed φ_{tc}. Experimental φ_{tc} is within these limits.

The assumption that *cis*-SQ is a much worse energy donor than *trans*-SQ is based on the fact that fluorescence quantum yields for the *cis*-isomers of diarylethylenes are usually much less than those for *trans*-isomers (see, for example, data for stilbene[12]), that results in low values of the Forster radius and low ET efficiency for *cis*-isomer. Being a worse energy donor, *cis*-SQ is less quenched, and this explains why the observed φ_{ct} for SQ in the dyad is close to the value for MeSQ.

Thus, the novel bichromophoric dyad SQ11MC was synthesized and its properties were studied. SQ11MC is a rare case of a dyad with two reactive photochromes where the FRET results in two observable complementary effects, which are quantitatively characterized, quenching and sensitization: a decrease in fluorescence and photoisomerization quantum yields of the donor (SQ) with a simultaneous increase in fluorescence and photoisomerization quantum yields of the acceptor (MC).

Due to a variety of photoprocesses observed in the dyad, it possesses a high potential as a controllable molecular photoswitch. For example, using the fact that only *trans*-isomers emit, we can switch between preferential emission at 414 or 516 nm by photoswitching between different photostationary states, which have different ratios of *trans*-isomers of the SQ and MC moieties. As an example, Figure 1 shows the luminescence spectrum of the photostationary state PS$_{470}$ (spectrum *6*), where two bands at 414 and 516 nm have a reverse ratio ($I_{414}/I_{516} = 2.4$), as compared to the *EE*-SQ11MC (spectrum *4*, $I_{516}/I_{414} = 3.4$). The fluorescence photoswitching property can be used in the design of novel photonic devices for information processing.

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Received: 28th October 2013; Com. 13/4233