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Modulation of diarylethene fluorescence by photochromic switching and solvent polarity

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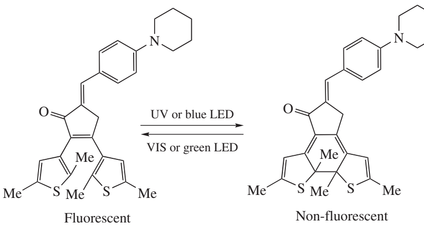
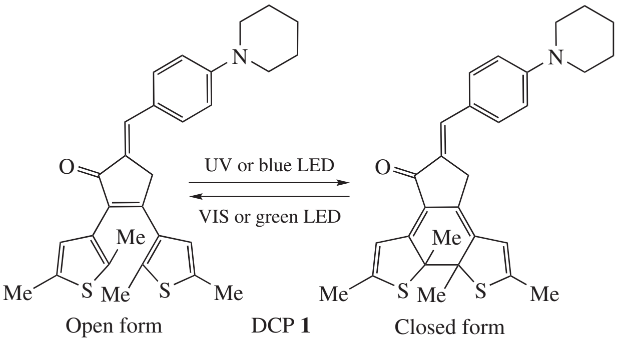
A mechanistic examination of the photochemical properties of a dithienylethene-containing push-pull system with the cyclopentenone bridge has been performed using time-resolved methods. The molecule studied possesses a notable combination of photochromic and fluorescent properties. Visible light only switching was accomplished using blue and green LED sources.



Photochromic materials are of interest due to their potential applications in many areas from sunglasses to optoelectronic systems and photopharmacology.[1–6] In photochromic luminescence switching systems, the emission of a fluorophore can be modulated between ‘on’ and ‘off’ states *via* reversible isomerization under irradiation, while a back reaction can be induced by light (P-type photochromism) or thermally (T-type photochromism). In most cases, fluorescence is quenched due to intramolecular energy transfer and/or electron transfer.[7,8] An alternative approach is based on intermolecular energy transfer.[9–11]

A proper design of the photochromic fluorescent switch is strictly required, and the requirements are the following: high fatigue resistance, rapid response, solid state reactivity and switching by visible light.[12] Probably, the most promising organic P-type photochromes are diarylethenes.[13]

A series of fluorescent 2,3-diarylcyclopent-2-en-1-ones (DCPs) containing conjugated electron-donating 4-(dialkylamino)benzylidene groups in the cyclopentenone bridge were synthesized recently.[14] These compounds exhibit photo- and pH-switchable emission. No mechanistic studies of the photochromic and emissive properties of the fluorescent DCPs have been performed so far. Here, we consider the properties of DCP **1**[15] (Scheme 1), fluorescence switching and solvent polarity effects.



Scheme 1

Figure 1 shows the absorption and emission spectra of DCP **1** and the colors of emitting solutions. The light corresponding to the isosbestic points of the A ⇔ B transitions (see Scheme 1) was used to excite luminescence. Absorption and emission parameters of DCP **1** in different solvents are summarized in Table S1 (see Online Supplementary Materials). The positions of absorption band maxima depend on the dielectric constants of solvents. An increase in solvent polarity leads to the red shift of both long-wavelength absorption and emission band maxima. Moreover, the emission quantum yield dramatically changed from 0.18 in DMSO to 0.002 in *n*-hexane (Table S2, see Online Supplementary Materials).

In principle, an increase of the fluorescence quantum yield in polar solvents can be due to the occurrence of an efficient nonradiative channel in nonpolar solvents, *e.g.*, intersystem crossing, which is blocked due to the stabilization of S1 state in polar solvents. However, an abnormal Stokes shift (a difference between the absorption and emission bands maxima) in polar solvents (see Table S1) cannot be justified by that assumption.

The nature of both luminescence red shift and abnormal Stokes shifts could be explained by the intramolecular charge transfer (ICT) fluorescence theory.[16] The excited state with a high dipole moment (ICT state) was introduced[17] to account for the anomalous fluorescence shift of 4-(dimethylamino)benzonitrile observed[18] in polar solvents. The ICT theory implies the existence of two emissive states after excitation (Figure S1, see Online Supplementary Materials). The former is initial S_1 or so-called locally excited

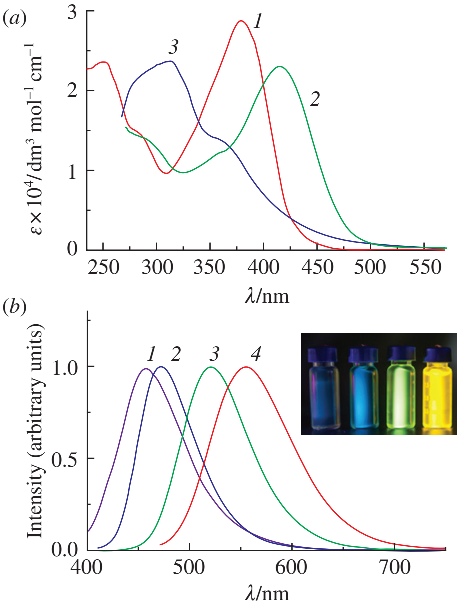


Figure 1 (*a*) Electronic absorption spectra of DCP **1** in (*1*) hexane, (*2*) DMSO, and (*3*) DMSO + 0.083 M HCl. (*b*) Normalized emission spectra of DCP **1** in (*1*) hexane (λ_{ex} = 393 nm), (*2*) toluene (λ_{ex} = 411 nm), (*3*) 1,2-dichloroethane (λ_{ex} = 423 nm), and (*4*) DMSO (λ_{ex} = 426 nm). λ_{ex} – excitation wavelength. Insert: DCP **1** solutions in different solvents under UV irradiation.

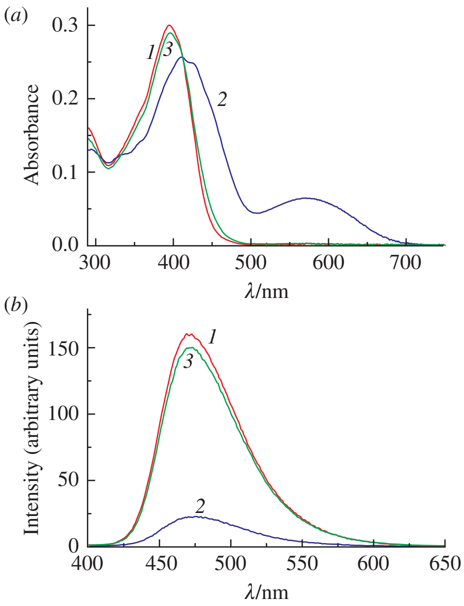


Figure 2 Spectral evolution of DCP **1** in toluene (1.16×10^{-5} M, 1 cm cell) caused by photochromic reactions: (*a*) absorption and (*b*) luminescence spectra (λ_{ex} = 320 nm). Curves *1*–*3* correspond to the initial spectrum and the spectra after irradiation at 360 nm and consequent irradiation at 360 and 530 nm, respectively.

(LE) state. The latter is the ICT state formed from the LE state due to charge separation. Solvent polarity strongly affects the ICT state energy. In polar solvents, it is lower than that in nonpolar ones to result in a red shift of the fluorescence band.

The assumption that the DCP **1** fluorescence is emitted from the ICT state was supported by the Lippert–Mataga plot (Figure S1, see Online Supplementary Materials) of the dependence of the Stokes shift on solvent polarity.[19] It allows one to estimate an increase in the dipole moment in the excited state. The dipole moment change upon excitation (μ_e–μ_g) was 13.6 ± 1.3 D. Thus, the excited state causing the emission has a high dipole moment, as evidenced by the ICT state formation.

The acidification of DCP **1** solutions changes both absorption and fluorescent properties to vanish the long-wavelength band [Figure 1(*a*), curve *3*] because the dimethylamino group protonation destroys electron-donating ability. Consequently, charge transfer is blocked, and ICT is not formed. As a result, the emission band disappears completely after the addition of acid. This effect supports the assumption of DCP **1** emission due to the ICT process.

The dual fluorescence is typically observed in the ICT systems (F_A and F_B in Figure S2, see Online Supplementary Materials). Fluorescence from the LE and ICT states dominates in nonpolar and polar solvents, respectively. Nevertheless, DCP **1** does not exhibit emission from the LE state. It can be explained by competition with the photochromic reaction (see Scheme 1) occurring from the LE state. Photocyclization is an extremely rapid process; therefore, it can decrease dramatically the lifetime and quantum yield of the LE state. On the other hand, the ICT state has too low energy to undergo a ring-closure reaction. For this reason, the photochromic reaction does not cause a significant effect on the ICT emission quantum yield.

Figure 2 shows changes in the absorption and luminescence spectra of DCP **1** in toluene caused by photochemical reactions. UV irradiation results in a ring-closure reaction (see Scheme 1), whereas visible irradiation of a solution rich in the B-form results in the backward reaction.

A closed form of DCP **1** absorbs in the whole region of its fluorescence allowing fluorescence resonance energy transfer (FRET) from the excited fluorophore to the conjugated photochromic moiety resulting in a significant decrease of the emission intensity (the observed decrease of fluorescence intensity can be partially explained by the closed form absorption). The ‘off’ effect is not complete because of the residual amount of the A-form in a photostationary state. Green light irradiation (530 nm) completely restores the fluorescence intensity.

The quantum yield of the ring-closure reaction strongly depends on the solvent polarity (see Table S2). This effect is probably a consequence of the competition between ring closure and charge transfer (see Figure 3). Both processes occur from the excited open isomer of DCP **1** within the same time domain. The formation of the closed form of diarylethenes completes typically within 1–10 ps,[20–22] which is similar to the reported lifetimes of ICT state formation.[23–25] As a result, hardly detectable fluorescence observed in hexane was accompanied by an effective photochromic reaction. On the contrary, DCP **1** emitting strongly in DMSO demonstrates weak photochromism.

Fluorescence single photon counting and fluorescence up-conversion methods were used to observe the dynamics of excited states in 0.05–20 ns and 0.1–100 ps time domains, respectively. Typical kinetic curves obtained in the single photon counting experiments (Figures S3–S5, see Online Supplementary Materials) were fitted by a monoexponential model (Table 1). The signals in hexane were too low to obtain quantitative results. The decay rate of an emissive excited state was solvent-dependent; thus, the lifetime in DMSO is almost 10 times longer than that in toluene.

The lifetimes of LE states were measured using fluorescence up-conversion (excitation at 400 nm, Figure S6, see Online Supple-

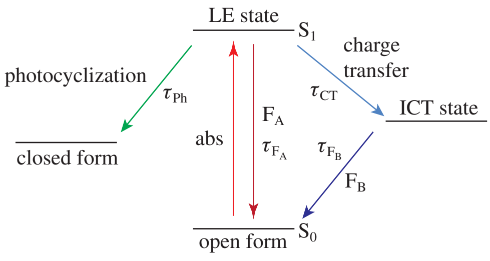


Figure 3 Tentative scheme of processes occurring after DCP **1** photoexcitation.

Table 1 Lifetimes of DCP **1** ICT excited states determined from the single photon data.

Solvent	τ_i/ns
toluene	0.27
1,2-dichloroethane	1.4
DMSO	2.3

mentary Materials). Kinetic curves were well-fitted by an exponential function with characteristic times of 6 and 1.3 ps in *n*-hexane and acetonitrile, respectively. In hexane, only weak residual fluorescence remained after the fast decay completion. In acetonitrile, on the contrary, strong residual fluorescence remained due to a significant concentration of emissive species in solution. In both solutions, the residual fluorescence was attributed to the ICT emission (F_B, see Figure 3). The low concentration of the ICT state in hexane was confirmed by both stationary experiments and fluorescence single photon counting.

Since the LE state is being consumed simultaneously in photocyclization and charge transfer, its observed decay lifetime is determined from Scheme 2 as

$$\tau_{obs} = \frac{\tau_{\mathrm{CT}}\tau_{\mathrm{Fl}}\tau_{\mathrm{Ph}}}{\tau_{\mathrm{CT}}\tau_{\mathrm{Fl}} + \tau_{\mathrm{CT}}\tau_{\mathrm{Ph}} + \tau_{\mathrm{Fl}}\tau_{\mathrm{Ph}}}, \qquad (1)$$

where τ_{CT}, τ_{Fl} and τ_{Ph} are the characteristic lifetimes of charge transfer, fluorescence from the LE state, and photocyclization, respectively.

The order of observed LE state lifetimes is consistent with the characteristic lifetimes of photocyclization and LE → ICT transition reported previously.[20–25]

Finally, we probed visible light switching[26] of DCP **1** in both directions. The open isomer exhibited intense absorbance up to 500 nm in DMSO [see Figure 1(*a*)], and irradiation with blue LED resulted in cyclization with the formation of a new band in the visible region (Figure S7, see Online Supplementary Materials). Green LED light induced cycloreversion, and five cycles of photochromic performance were demonstrated (Figure S8, see Online Supplementary Materials). Moreover, visible light irradiation allowed us to perform fluorescence switching (Figure S8, see Online Supplementary Materials), which is a rare property of diarylethenes.[27]

In conclusion, the consolidation of photochromic and ICT state forming moieties within a single molecule skeleton opens new opportunities for an accurate control over the emission of the entire structure. Experiments with the fluorescent DCPs incorporated into polymeric films can be more appropriate for practical applications.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2019.09.029.

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