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Photochromic and fluorescent 5-coumarinyl-4-pyrrolylthiazoles

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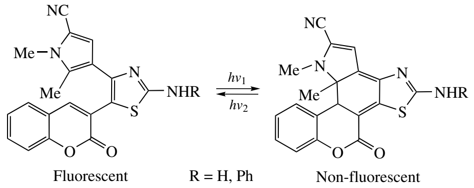
New dihetarylethenes of 5-coumarinyl-4-pyrrolylthiazole chemotype depending on the nature of the substituent at the bridging fragment are capable of either photochromic modulation of the fluorescent properties or emission with anomalous Stokes shift due to the ESIPT-effect.

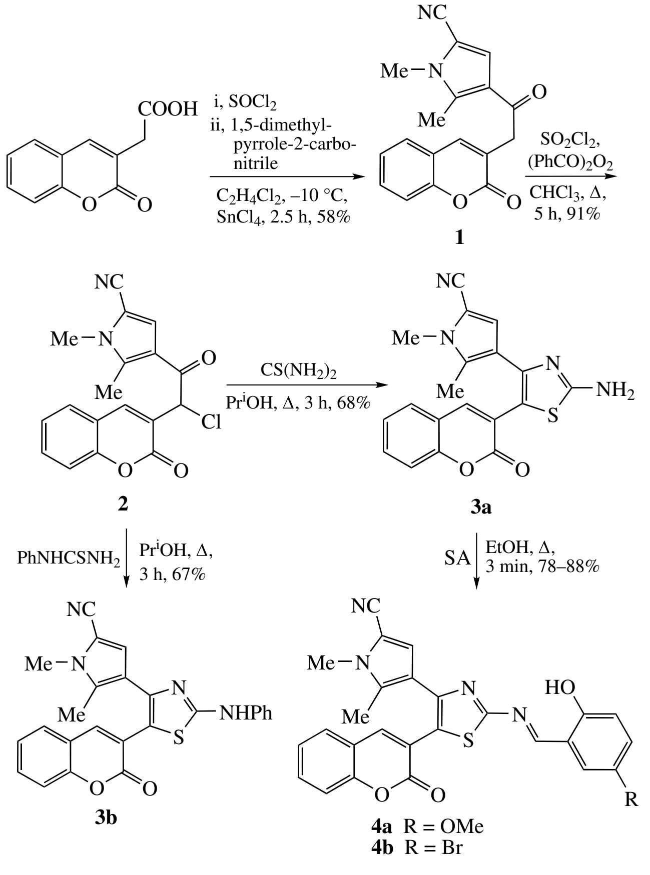


Photochromic dihetarylethenes are of considerable interest as the optical information recording media and the efficient fatigue resistant molecular switches with high thermal stability of the initial and cyclic isomers.[1–8] The mechanism of their photoinduced rearrangements involves the hexatriene–cyclohexadiene rearrangement of the ring-opened isomer into the ring-closed form. Hitherto reported dihetarylethenes usually contain thiophene or benzothiophene moieties. As far as we are aware, there are only a few examples of photochromic pyrrole derivatives,[9–12] although at least one of them was considered for polarization holographic optical recording.[13] In addition to the above, the use of thiazole as a bridging fragment in dihetarylethenes allows one to vary the substituents in this part of the molecule in order to obtain molecular switches with predetermined properties.[14,15]

Herein, we report on a synthesis of 1,3-thiazole-bridged hybrid dihetarylethenes containing pyrrole and coumarin substituents and investigation of their photochromic and fluorescent properties.[†]

The treatment of coumarin-3-acetic acid with thionyl chloride gave its chloride, which upon interaction with 1,5-dimethylpyrrole-2-carbonitrile formed ketone **1**[‡] (Scheme 1). Reaction of **1** with sulfuryl chloride leads to chloro ketone **2**, whose interaction with thiocarbamide or *N*-phenylthiocarbamide yields diarylethenes **3a** and **3b**, respectively.[§] Dihetarylethenes **4a**,**b**[¶] were obtained by condensation of **3a** with substituted salicylic aldehydes (SA) (see Scheme 1).

IR spectra of dihetarylethenes **3**, **4** contain characteristic bands of the coumarin carbonyl groups at 1705–1715 cm^{-1} and pyrrole cyano groups at 2201–2218 cm^{-1}. ^{1}H NMR spectra of **3**, **4**



Scheme 1

[†] The ^{1}H NMR spectra were obtained on a Varian Unity 300 spectrometer (300 MHz), the signals were referred with respect to the signal of residual protons of CHCl$_3$ or DMSO, δ values were measured with precision 0.01 ppm. The IR spectra were recorded on a Varian Excalibur 3100 FT-IR instrument using the attenuated total internal reflection technique (ZnSe crystal). Mass spectra were measured on a Shimadzu GCMS-QP2010SE instrument with direct sample entry into the ion source (EI, 70 eV). The electronic absorption spectra were recorded on a Varian Cary 100 spectrophotometer. The irradiation of solutions with filtered light of a high pressure Hg lamp was performed on a Newport 66941 equipment supplied with a set of interferential light filters. Electronic emission spectra were recorded on a Varian Cary Eclipse spectrofluorimeter. Acetonitrile of the spectroscopic grade (Aldrich) was used to prepare solutions. Melting points were determined on a PTP (M) instrument and were not corrected.

[‡] *1,5-Dimethyl-4-[2-(2-oxo-2*H*-chromen-3-yl)acetyl]-1*H*-pyrrole-2-carbonitrile* **1**. Thionyl chloride (30 mmol, 3.60 g) and 2 drops of DMF were added to a suspension of coumarin-3-acetic acid (10 mmol, 2.24 g) in dry CH$_2$Cl$_2$ (10 ml). After 12 h the resulting clear solution was concentrated on a rotary evaporator to give coumarin-3-acetic acid chloride as yellow-brown crystals, which was further used without additional purification. The obtained acid chloride (10 mmol, 2.54 g) was then

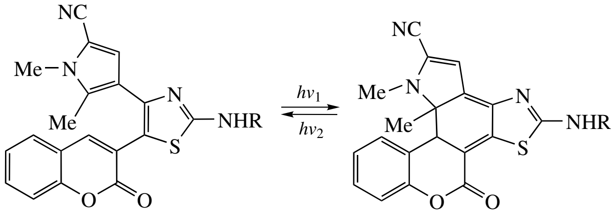
Table 1 Electronic absorption and fluorescence spectra of isomeric forms of **3**, **4** in acetonitrile at 293 K.[a]

Compound	Ring-opened form **O**: Absorption λ_{max}^{abs}/nm	Ring-opened form **O**: Absorption ε_{max}/dm^3 mol^{-1} cm^{-1}	Ring-opened form **O**: Fluorescence λ_{max}^{fl}/nm (I_{fl})	Ring-closed form **C**: Absorption λ_{max}^{abs}/nm	Ring-closed form **C**: Absorption ε_{max}/dm^3 mol^{-1} cm^{-1}
3a	404	15800	495 (452)	580	7800
3b	410	23100	498 (625)	581	8100
4a	424	16200	483 (132), 603 (236)	not formed	
4b	419	28300	489 (113), 572 (164)	not formed	

[a] λ_{max}^{abs}, λ_{max}^{fl} are the maxima of absorption and fluorescence bands, respectively; I_{fl} is the fluorescence intensity (arbitrary units).

demonstrate singlet signals of protons of pyrrole *C*- and *N*-methyl groups at 2.19–2.31 and 3.60–3.65 ppm, respectively. Singlet signals of OH protons of **4a**,**b** appear in the downfield spectral region at 10.96–11.56 ppm. These data together with the absence of aliphatic proton signals of the *sp*^{3}-hybridized carbon atoms (except for Me groups) in ^{1}H NMR spectra clearly point to the ring-opened isomeric form **O** of the prepared dihetarylethenes. Their electronic absorption spectra measured in acetonitrile are characterized by the long wavelength bands with maxima in the range of 404–410 (**3a**,**b**) and 419–424 nm (**4a**,**b**). Compounds **3a**,**b** possess low-intense fluorescence emission in the region of 495–498 nm with quantum yields of 0.006 and 0.009, respectively. The emission spectra of **4a**,**b** contain two peaks at 483–489 and 572–603 nm (Table 1). The fluorescence excitation spectra measured for observation of wavelength corresponding to both emission maxima well match the above mentioned long wavelength absorption bands.

Irradiation of the solutions of **3a**,**b** in acetonitrile with filtered light of mercury lamp 365 nm leads to the photocoloration caused by the appearance of a new absorption band at 580–581 nm. Its intensity increases upon irradiation while the intensity of the initial absorption bands decreases; during this process three distinct isosbestic points are found (Figure 1). The observed spectral changes are indicative of the occurrence of the photoinduced rearrangement of the ring-opened isomer **O** into the 1,3-cyclohexadiene ring-closed form **C** until the establishment of the photostationary state (Scheme 2). The quantum yields of cyclization



3O

a R = H
b R = Ph

3C

Scheme 2

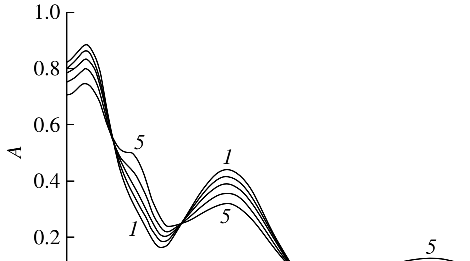


Figure 1 Electronic absorption spectra of **3a** in acetonitrile (2.5×10^{-5} mol dm^{-3}) (*1*) before and after (*2*) 15, (*3*) 25, (*4*) 40 and (*5*) 80 s of irradiation by 365 nm light.

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dissolved in dry $C_2H_4Cl_2$ (50 ml) together with 1,5-dimethylpyrrole-2-carbonitrile (9.75 mmol, 1.12 g). The resulting solution was cooled in water–salt bath (–10 °C), then $SnCl_4$ (15 mmol, 2.05 g) was added with stirring in small portions over 15 min. The mixture was stirred for another 2.5 h and then poured into a mixture of conc. HCl and ice. The organic layer was separated, dried with anhydrous Na_2SO_4, the solvent was removed on a rotary evaporator, the residue was recrystallized from ethanol. Yield 1.95 g (58%), white crystals, mp 162–164 °C. IR (ν_{max}/cm^{-1}): 2218 (C≡N), 1715 (C=O), 1669 (C=O). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.58 (s, 3H, CMe), 3.68 (s, 3H, NMe), 4.00 (s, 2H, CH_2), 7.25–7.66 (m, 6H, H_{arom}). MS (EI), *m/z*: 306 [M]$^+$. Found (%): C, 70.60; H, 4.70; N, 9.05. Calc. for $C_{18}H_{14}N_2O_3$ (%): C, 70.58; H, 4.61; N, 9.15.

§ *4-[2-Chloro-2-(2-oxo-2*H*-chromen-3-yl)acetyl]-1,5-dimethyl-1*H*-pyrrole-2-carbonitrile* **2**. A mixture of compound **1** (4 mmol, 1.20 g), sulfuryl chloride (3.2 mmol, 0.72 g) and benzoyl peroxide (0.2 g) in 25 ml of $CHCl_3$ was refluxed for 5 h, the solvent was then evaporated and the residue was recrystallized from propan-2-ol. Yield 1.22 g (91%), mp 139–142 °C. IR (ν_{max}/cm^{-1}): 2218 (C≡N), 1719 (C=O), 1619 (C=O). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.44 (s, 3H, CMe), 3.81 (s, 3H, NMe), 6.23 (s, 1H, CHCl), 7.33–7.68 (m, 6H, H_{arom}). MS (EI), *m/z*: 340 [M]$^+$. Found (%): C, 63.60; H, 3.70; N, 8.05. Calc. for $C_{18}H_{13}ClN_2O_3$ (%): C, 63.44; H, 3.85; N, 8.22.

*4-[2-Amino-5-(2-oxo-2*H*-chromen-3-yl)thiazol-4-yl]-1,5-dimethyl-1*H*-pyrrole-2-carbonitrile* **3a**. A solution of chloro ketone **2** (2.5 mmol, 0.85 g) and thiocarbamide (3.0 mmol, 0.23 g) in propan-2-ol (25 ml) was refluxed for 3 h, cooled and poured into the water solution of K_2CO_3 (2 g in 150 ml of water). The precipitated crystals were filtered. Yield 0.62 g (68%), yellow crystals, mp 193–195 °C (decomp.). IR (ν_{max}/cm^{-1}): 3478 (NH), 3255 (NH), 3061 (NH), 2218 (C≡N), 1705 (C=O), 1622 (C=N). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.19 (s, 3H, CMe), 3.64 (s, 3H, NMe), 5.09 (br. s, 2H, NH_2), 6.85 (s, 1H, H_{arom}), 7.25–7.55 (m, 5H, H_{arom}). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 168.1, 159.5, 152.1, 144.4, 139.0, 134.5, 130.9, 127.8, 124.4, 120.7, 119.0, 118.9, 117.0, 115.6, 113.8, 111.1, 102.0, 32.3, 11.0. MS (EI), *m/z*: 362 [M]$^+$. Found (%): C, 62.52; H, 3.95, N, 15.16. Calc. for $C_{19}H_{14}N_4O_2S$ (%): C, 62.97; H, 3.89; N, 15.46.

*4-[2-Phenylamino-5-(2-oxo-2*H*-chromen-3-yl)thiazol-4-yl]-1,5-dimethyl-1*H*-pyrrole-2-carbonitrile* **3b**. The above procedure was applied using *N*-phenylthiocarbamide (3.0 mmol, 0.46 g). Yield 0.73 g (67%), yellow crystals, mp 176–177.5 °C. IR (ν_{max}/cm^{-1}): 3479 (NH), 3255 (NH), 3061 (NH), 2201 (C≡N), 1705 (C=O), 1622 (C=N). ^{1}H NMR (300 MHz, DMSO-d_6) δ: 2.19 (s, 3H, CMe), 3.60 (s, 3H, NMe), 6.86 (s, 1H, H_{arom}), 7.15–7.75 (m, 5H, H_{arom}). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 163.0, 159.7, 152.4, 144.3, 140.8, 140.2, 135.1, 131.5, 128.9, 128.7, 128.2, 124.7, 121.4, 121.2, 120.1, 119.1, 119.0, 117.2, 116.6, 115.9, 114.0, 112.5, 102.3, 32.5, 11.3. MS (EI), *m/z*: 438 [M]$^+$. Found (%): C, 68.52; H, 4.25; N, 12.56. Calc. for $C_{25}H_{18}N_4O_2S$ (%): C, 68.48; H, 4. 14; N, 12.78.

¶ *4-[2-(2-Hydroxy-5-methoxybenzylidenamino)-5-(2-oxo-2*H*-chromen-3-yl)thiazol-4-yl]-1,5-dimethyl-1*H*-pyrrole-2-carbonitrile* **4a**. 2-Hydroxy-5-methylbenzaldehyde (2.6 mmol, 0.9 g) was added to the solution of amine **3a** (2.5 mmol, 0.4 g) in ethanol (15 ml), the mixture was refluxed for 15 min, *p*-toluensulfonic acid (10 mg) was then added and the reflux was continued for another 15 min. The solution was cooled, the residue was recrystallized from ethanol. Yield 0.97 g (78%), mp 115–116 °C. IR (ν_{max}/cm^{-1}): 2209 (C≡N), 1714 (C=O), 1492 (arom.). ^{1}H NMR (300 MHz, DMSO-d_6) δ: 2.31 (s, 3H, CMe), 3.65 (s, 3H, NMe), 3.75 (s, 3H, OMe), 6.94–7.66 (m, 5H, H_{arom}), 7.98 (s, 1H, H_{arom}), 9.33 (s, 1H, CH=N), 10.96 (s, 1H, OH). MS (EI), *m/z*: 496 [M]$^+$. Found (%): C, 65.37; H, 4.10; N, 11.52. Calc. for $C_{27}H_{20}N_4O_4S$ (%): C, 65.31; H, 4.06; N, 11.28.

*4-[2-(5-Bromo-2-hydroxybenzylidenamino)-5-(2-oxo-2*H*-chromen-3-yl)thiazol-4-yl]-1,5-dimethyl-1*H*-pyrrole-2-carbonitrile* **4b**. The above procedure was applied using 5-bromo-2-hydroxybenzaldehyde (2.6 mmol, 0.53 g). Yield 1.2 g (88%), yellow crystals, mp 210–212 °C. IR (ν_{max}/cm^{-1}): 2209 (C≡N), 1715 (C=O), 1492 (arom.). ^{1}H NMR (300 MHz, DMSO-d_6), δ: 2.31 (s, 3H, Me), 3.65 (s, 3H, Me), 6.96–7.66 (m, 7H, H_{arom}), 8.04–8.06 (m, 2H, H_{arom}), 9.31 (s, 1H, CH=N), 11.56 (s, 1H, OH). MS (EI), *m/z*: 545 [M]$^+$. Found (%): C, 57.92; H, 3.09; N, 10.13. Calc. for $C_{26}H_{17}BrN_4O_3S$ (%): C, 57.26; H, 3.14; N, 10.27.

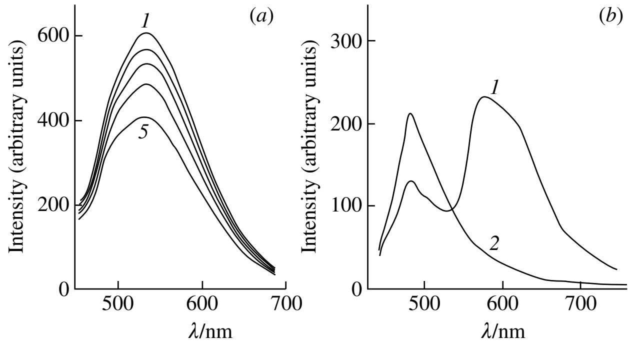

Figure 2 Fluorescence spectra in acetonitrile: (*a*) **3a** (2.5×10^{-5} mol dm^{-3}) (*1*) before and after (*2*) 15, (*3*) 25, (*4*) 40 and (*5*) 80 s of irradiation with 365 nm light; (*b*) **4a** (*1*) before and (*2*) after addition of CF_3COOH.

reaction of diarylethenes **3a**,**b** in acetonitrile at room temperature were 0.24 and 0.21, respectively.

The existence of the photostationary state is associated with considerable overlapping of the absorption bands corresponding to the transition $S_0 \rightarrow S_1$ of the initial form **O** and the transition $S_0 \rightarrow S_2$ of the photoinduced isomer **C**.[1,3,16] The fluorescence intensity of the open forms **3O** decreases symbate with the rise of a new long-wave band at 580–581 nm without changes in the position of maximum of the emission band (Figure 2). The ring-closed isomers of **3C** do not fluoresce at ambient temperature.

The ring-closed isomers **3C** demonstrate high thermal stability, the intensities of their longest wavelength absorption bands remain sustained within 48 h at 293 K. Irradiation of their colored solutions in acetonitrile with the light $\lambda_{\text{irr}} > 500$ nm results in the complete bleaching due to the reopening into the initial forms **3O** and is accompanied by the full recovery of the initial absorption and fluorescence spectra. Dihetarylethenes **3a**,**b** are sufficiently fatigue resistant with respect to photodegradation and survive at least 10 cycles of photocoloration–photobleaching without notable decrease in the optical density at the absorption maxima.

Dihetarylethenes **4a**,**b** do not reveal photochromic properties that may be explained by the ESIPT-effect due to the O→N proton transfer in the excited state.[17,18] Previously, the analogous inhibition of the photochromic properties was observed for pyrroledione-bridged dithienylethenes.[19,20] One of the characteristic features of this process is the dual composition of emission band. Indeed, the fluorescence spectra of **4a**,**b** contain the short wavelength component at 483–489 nm (with the usual Stokes shift, as in ethenes **3a**,**b**) and the long wavelength component at 572–603 nm with the anomalous Stokes shift (ASS) (Table 1). The protonation of these compounds in solutions with trifluoroacetic acid (‘blocking’ of the nitrogen center of proton transfer) leads to an increase in the intensity of the short wavelength fluorescence band and the complete disappearance of the long wavelength emission maximum [Figure 2(*b*)].

In conclusion, the synthesized coumarinyl(pyrrolyl)thiazoles depending on the nature of the substituent in the bridging fragment are capable of either photomodulation of fluorescent properties or ASS-emission due to the ESIPT-effect.

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