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Synthesis, spectral and photochemical properties of the styrylquinoline–naphthol dyad with a dioxytetramethylene bridge

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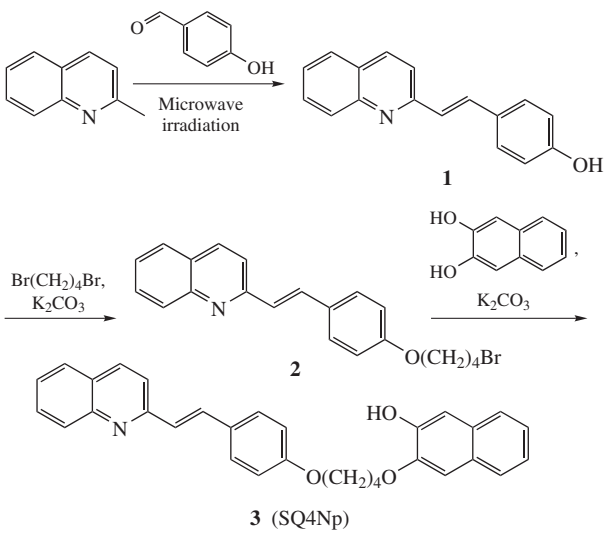
The luminescence of 2-naphthol and 2-styrylquinoline fragments, intramolecular energy transfer from the former to the latter, and photoisomerization of the latter are observed in the newly synthesized bichromophoric dyad.

Supramolecular bichromophoric molecular systems are of interest from the viewpoint of investigating photophysical and photochemical properties such as exciplex and excimer formation[1,2] and electron and energy transfer[3–7] with possible applications in light harvesting and artificial photosynthesis,[8–10] molecular devices,[11] switches[12] and logic gates.[13]

The molecular device is a molecular system that can be switched from one state to another by an external stimulus. For example, 2-styrylquinoline (2SQ) undergoes reversible *trans–cis* photoisomerization under UV irradiation,[14,15] which has been used for designing molecular logic gates.[16] Additionally, the pK_a of 2SQ increases from 4.8 to pK_a^* 12.0 upon excitation from the ground (S_0) to the lowest excited singlet (S_1) state; therefore, 2SQ is a photobase.[14] It was interesting to bind 2SQ in one supramolecular system with a photoacid, namely, 2-naphthol; it is known that the acidity of the latter increases from pK_a 9.5 to pK_a^* 2.8 on going from the S_0 to S_1 state.[17] For this purpose, we synthesized the styrylquinoline–naphthol dyad 2-(*E*)-{4-[4-(3-hydroxynaphthalen-2-yloxy)butoxy]styryl}quinoline (SQ4Np).

The dyad SQ4Np was synthesized in three steps in an overall yield of 67%.† The synthesis started with reaction between quinaldine and 4-hydroxybenzaldehyde followed by alkylation with 1,4-dibromobutane and final treatment with 2,3-dihydroxynaphthalene (Scheme 1).



Scheme 1

The absorption spectrum of the dyad SQ4Np (Figure 1, spectrum *1*) is a superposition of the spectra of model compounds, 2-(4-ethoxystyryl)quinoline EtOSQ (spectrum *2*) and 3-methoxy-2-naphthol MeONp (spectrum *3*). This implies an absence of considerable interaction between two constituting chromophoric groups of SQ4Np in the ground state.

† *2-(*E*)-(4-Hydroxystyryl)quinoline* **1**. An open glass test-tube containing quinaldine (2 mmol) and 4-hydroxybenzaldehyde (4 mmol) was put in a bulb (V = 100 ml) containing 15–20 ml of water and subjected to microwave irradiation (P = 600 W) in a three step mode 3×3 min with 30 s intervals. After cooling, the reaction mixture was treated with aqueous ethanol. The precipitate was filtered off and washed with hot ethanol (2×20 ml). Pale yellow solid of compound **1** was obtained (0.44 g, 90%); mp 268 °C (EtOH).[17]

*2-(*E*)-[4-(4-Bromobut-1-oxy)styryl]quinoline* **2**. A mixture of **1** (1 mmol), 1,4-dibromobutane (10 mmol) and K_2CO_3 (1 mmol) in 20 ml of acetone was refluxed for 6 h. NaOH solution was added to the mixture and the organic layer was separated and acidified with HCl. The resulting orange precipitate was filtered off, washed with hexane (5×3 ml) and neutralized with $NaHCO_3$ in acetone–water solution. The precipitate formed was filtered off, dried and recrystallized from hot hexane to afford white crystals of compound **2** (0.35 g, 91%); mp 92–93 °C (hexane). ^{1}H NMR ($CDCl_3$) δ: 1.94–2.01 (m, 2H, CH_2), 2.05–2.13 (m, 2H, CH_2), 3.51 (t, 2H, CH_2, J 6.6 Hz), 4.04 (t, 2H, CH_2, J 6.0 Hz), 6.92 (d, 2H, *o*-C_6H_4, J 8.6 Hz), 7.28 (d, 1H, =CH, J 16.4 Hz), 7.48 (t, 1H, quinoline, J 7.6 Hz), 7.57 (d, 2H, *m*-C_6H_4, J 8.6 Hz), 7.60–7.66 (m, 2H, quinoline, =CH), 7.69 (t, 1H, quinoline, J 7.6 Hz), 7.77 (d, 1H, quinoline, J 8.0 Hz), 8.06 (d, 1H, quinoline, J 8.4 Hz), 8.10 (d, 1H, quinoline, J 8.6 Hz). IR (ν/cm^{-1}): 3033, 2953, 2871 (ν_{CH_2}), 1633 ($\nu_{C=C}$), 1598, 1515, 1249 (δ_{COC}), 1231, 1184, 958 ($\delta_{CH=CH}$), 826, 757, 511 ($\nu_{C–Br}$). Found (%): C, 65.62; H, 5.23; N, 3.47. Calc. for $C_{21}H_{20}NOBr$ (%): C, 65.98; H, 5.27; N, 3.66.

*2-(*E*)-{4-[4-(3-hydroxynaphthalen-2-yloxy)butoxy]styryl}quinoline SQ4Np* **3**. A mixture of **2** (0.5 mmol), 2,3-dihydroxynaphthalene (2.5 mmol) and K_2CO_3 (1.3 mmol) in 40 ml of butan-2-one was refluxed for 6 h. The solvent was partially removed on a rotary evaporator. The resulting mixture was acidified to pH 6 with dilute HCl. The precipitate formed was filtered off, washed with Et_2O, then repeatedly washed with acetone–water solution to afford white precipitate of product **3** (0.19 g, 82%); mp 191–192 °C. ^{1}H NMR ([$^2H_6$]DMSO) δ: 1.94–2.04 (m, 4H, CH_2), 4.09–4.23 (m, 4H, CH_2), 7.03 (d, 2H, *o*-C_6H_4, J 8.4 Hz), 7.15 (s, 1H, naphthalene), 7.20–7.26 (m, 2H, naphthalene), 7.28 (s, 1H, naphthalene), 7.34 (d, 1H, =CH, J 16.3 Hz), 7.54 (t, 1H, quinoline, J 7.6 Hz), 7.61 (d, 1H, naphthalene, J 6.7 Hz), 7.65–7.71 (m, 3H, *o*-C_6H_4, naphthalene); 7.74 (t, 1H, quinoline, J 7.6 Hz), 7.79 (d, 1H, =CH, J 16.3 Hz), 7.84 (d, 1H, quinoline, J 8.6 Hz), 7.93 (d, 1H, quinoline, J 8.1 Hz), 7.97 (d, 1H, quinoline, J 8.3 Hz), 8.32 (d, 1H, quinoline, J 8.6 Hz), 9.42 (s, 1H, OH). IR (ν/cm^{-1}) δ: 3600–2400 (ν_{OH}), 3057, 3040, 2940, 2857 (ν_{CH_2}), 1635 ($\nu_{C=C}$), 1597, 1511, 1262, 1236 (ν_{COC}), 1176, 976 ($\nu_{CH=CH}$). Found (%): C, 80.44; H, 5.66; N, 2.84. Calc. for $C_{31}H_{27}NO_3$ (%): C, 80.73; H, 5.90; N, 3.03.

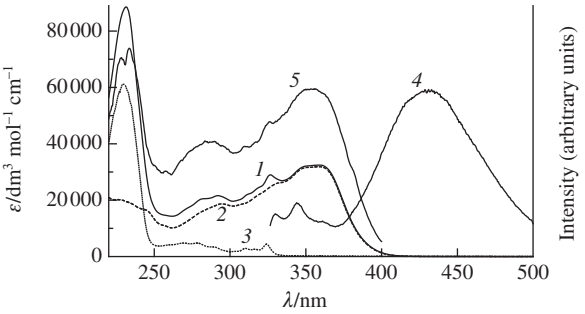


Figure 1 Absorption spectra in ethanol: (*1*) *trans*-SQ4Np, (*2*) *trans*-2-(4-ethoxystyryl)quinoline, (*3*) 3-methoxy-2-naphthol; normalized (*4*) luminescence (excited at 280 nm) and (*5*) excitation (monitored at 430 nm) spectra of *trans*-SQ4Np.

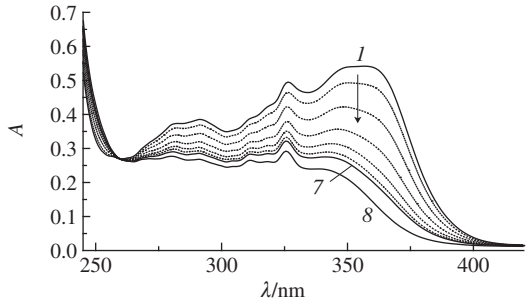


Figure 2 Spectral variations during the irradiation of air-saturated solution of *trans*-SQ4Np (1.66×10^{-5} M) in ethanol with light at 365 nm, intensity, 1.25×10^{-9} Einstein cm^{-2} s^{-1}, irradiation time, (*1*) 0, (*2*) 5, (*3*) 15, (*4*) 30, (*5*) 50, (6) 80 and (*7*) 580 s, the last spectrum corresponds to photostationary state PS_{365}; (*8*) spectrum of *cis*-SQ4Np calculated by Fischer's method.

From a comparison with the model spectra, it follows that, at wavelengths $\lambda < 330$ nm, both the naphthol (Np) and styrylquinoline (SQ) fragments of SQ4Np absorb light, whereas the long-wavelength absorption band (LWAB) in the region of 340–390 nm belongs to the SQ fragment only.

In accordance with this fact, upon excitation of SQ4Np in the region of $\lambda < 330$ nm, emission from both chromophores was observed: from the Np fragment at 350 nm, and from the SQ fragment at 430 nm (Figure 1, spectrum *4*). Irradiation of SQ4Np within LWAB resulted in excitation and subsequent emission of the SQ fragment only. Based on absorption maxima, the energies of the lowest excited (Franck–Condon) singlet states localized on Np (S_{1_Np}) and SQ (S_{1_SQ}) fragments were calculated to be 3.80 and 3.46 eV.

The important feature of the excitation spectrum of SQ4Np (Figure 1, spectrum *5*) is maxima at ~230 and 320 nm, which correspond to the absorption of the Np fragment, whereas monitoring the luminescence of the SQ fragment at 430 nm. Naphthol contribution to the styrylquinoline fluorescence suggests the Forster resonance energy transfer from the excited Np fragment to the SQ fragment with the subsequent emission of the latter.

According to quantum-chemical calculations,[19] the most elongated conformer of SQ4Np with the *trans*-configuration of all single C–C and C–O bonds is 2.94 nm in length, with a center-to-center distance of 1.67 nm between two fragments. This is less than the value of the Forster radius $R_0 = 3.6$ nm, as calculated for the naphthol–styrylquinoline donor–acceptor pair according to ref. 20 and explains effective energy transfer in the covalently bound dyad.

The acidity of the two fragments of SQ4Np changes in the opposite direction upon excitation. The measured ground state pK_a of SQ4Np are 5.0 (quinoline ring) and 10.4 (hydroxyl group), and its acidities in the excited state (pK_a^*) calculated by the Forster cycle[21] are 12.9 (quinoline ring) and 6.6 (hydroxyl group), respectively. Compared to unsubstituted 2-naphthol, the acidity of hydroxyl group in the Np fragment decreased, especially in the excited state (pK_a^* changed from 2.8 to 6.6).

Obviously, this is the effect of the oxygen atom in the neighbouring alkoxy group. According to B3LYP/6-31G* calculation, there is an intramolecular hydrogen bond between hydroxyl and alkoxy groups. The conformer with hydroxyl hydrogen turned to the neighbouring oxygen is 4.3 kcal mol^{-1} more stable than the conformer with the opposite disposition of hydroxyl hydrogen. In the former conformer, the calculated distance between hydroxyl hydrogen and alkoxy oxygen is 2.05 Å, which is less than the sum of van der Waals radii (1.2 Å for H and 1.52 Å for O).[22]

Irradiation of SQ4Np solution with UV light resulted in spectral changes characteristic of photoisomerization: reduction and hypsochromic shift of LWAB (Figure 2). The system achieved a photostationary state (PS_λ), whose composition depended on irradiation wavelength (λ). The observation of an isosbestic point at 259 nm indicated the absence of secondary reactions. Based on the spectra of *trans*-isomer and two photostationary states, PS_{313} and PS_{365}, the spectrum of *cis*-isomer was calculated by Fischer's method[23] (Figure 2, spectrum *8*). The quantum yields of *trans–cis* (φ_{tc}) and *cis–trans* (φ_{ct}) photoisomerization found by the numerical solution of differential kinetic equations are $\varphi_{tc} = 0.58$ and $\varphi_{ct} = 0.52$. These values coincide with the data for EtOSQ[15] and corroborate that the SQ fragment in SQ4Np maintains photochemical activity.

Thus, the bichromophoric dyad SQ4Np was synthesized, and its properties were investigated. Due to a variety of photoprocesses observed in the dyad, it possesses high potential as a controllable molecular photoswitch.

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