Supporting Information.

Analytical characterization of BSP-3

¹H NMR (400 MHz, CDCl₃) δ 7.98 (dd, 1H, J = 8.9 and 2.8 Hz, 7-H of benzopyran); 7.90 (d, 1H, J = 2.8 Hz, 5-H of benzopyran); 7.17 (m, 1H, 6-H of indoline); 7.06 (dd, 1H, J = 1.3 and 7.3 Hz, 4-H of indoline) 6.93 (s, 1H, H4); 6.88 (dt, 1H, J = 7.3 and 0.8 Hz, 5-H of indoline); 6.83 (d, 1H, J = 1.7 Hz, H3); 6.81 (d, 1H, J = 1.7 Hz, H3"); 6.75 (d, 1H, J = 10 Hz, 4-H of benzopyran); 6.71 (d, 1H, J = 8.9 Hz, 8-H of benzopyran); 6.61 (d, 1H, J = 7.7 Hz, 7-H of indoline); 6.21 (d, 1H, J = 1.7 Hz, H5); 6.14 (d,1H, J = 1.7 Hz, H5"); 5.67 (d, 1H, J = 10 Hz, 3-H of benzopyran); 4.29 (m, 2H, NCH₂); 3.94 (m, 4H, 20CH₂); 3.71 (2H, CH₂COO); 1.81-0.86 (16CH₂, 4CH₃). ¹³C NMR (100.6 MHz) δ 170.5, 159.5, 157.6, 146.6, 141.0, 136.3, 135.8, 134.7, 133.1, 132.6, 130.3, 128.8, 128.2, 127.8, 126.2, 125.8, 122.7, 121.8, 121.7, 119.9, 118.9, 118.5, 116.3, 115.4, 106.5, 98.0, 96.6, 70.2, 68.1, 63.1, 52.7, 34.8, 31.9, 30.3, 29.7, 29.5, 29.4, 29.3, 29.2, 28.9, 26.0, 25.7, 22.7, 19.7, 14.1, 14.0. HRMS calculated for C₅₃H₆₆N₂O₇S₃, m/z: 938.4257. Found m/z: 938.3226. Spectrum (CH₃CN) λ_{max}nm: 362, 252, 572.



Figure S1: Exposure effects to 375 nm UV LEDs: (a) Baseline corrected conversion of **BSP-1** $(10^{-4}$

M in ACN) to the isomer MC-1.





Figure S2: (a) Thermal relaxation profiles for MC-2 in six organic solvents; (b) thermal relaxation profile for MC-3 in the same solvents. Prior to acquisition of the spectra, the solutions were irradiated with UV-LED device ($\lambda_{max} = 375$ nm) for 180 s at 293 K. [BSP-2] and [BSP-3] = 10⁻⁴ M in all cases.





Figure S3: Thermal relaxation rate of MC-2 over the temperature range 283-308 K. Arrhenius and Eyring parameters derived from this analysis are reported in Table 2. Prior to acquisition of the spectra, the solutions were irradiated with the UV-LED device ($\lambda_{max} = 375$ nm) for 180 s in the spectrophotometer chamber. [BSP-2] = 10⁻⁴ M in all cases.





Figure S4: Thermal relaxation profiles for MC-1 over the temperature range 283-308 K. Prior to acquisition of the spectra, the solutions were irradiated with UV-LED device ($\lambda_{max} = 375$ nm) for 180 s in the spectrophotometer chamber. [BSP-1] = 10⁻⁴ M in all cases in acetonitrile.





Figure S5: Solvatochromic effect of **MC-2** in 5 different solvents. All the solutions were 10^{-4} M. Spectra were measured after exposure to the 375 nm UV LED light source for 180 seconds.