A Light-Induced Photochromic Nanoswitch Capable of Non-Destructive Readout via Fluorescence Emission: Cluster vs. Single-Molecule Excitation of Dihydroindolizines

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Supplementary Information

Synthesis

Dimethyl-1',10'a-dihydro-9'(trans-2-[4''N,N-dimethylphenyl)-ethenyl]-spiro[9-H-fluorene-9,1'-pyrrolo-[1,2-a]quinoline]-2',3-dicarboxylate ((DHI (1)).
Dimethyl-cyclopropeno-fluorene-dicarboxylate (0.306g, 1.0 mmol)[1] was dissolved in 50 mL of anhydrous diethyl ether. To this mixture, dimethyl-styryl-quinoline (CAS: Benzenamine, N,N-dimethyl-4-[(1E)-2-(4-quinolinyl)ethenyl]-)[2] (0.274g, 1.0 mmol) was added as a quickly dissolving solid. The mixture was stirred in the dark and under Ar for 48h at RT. Reaction progress was monitored by thin layer chromatography (SiO_2/CH_2Cl_2, R_f ((DHI (1)) = 0.21). After the completion of the addition reaction, the solvent was removed in vacuum at RT. The yellowish reaction mixture was separated by descending column chromatography in the dark (50 x 2.5 cm, eluent: CH_2Cl_2, stationary phase: silica gel). The reaction product was further purified by recrystallization from diethyl ether.
Yield: 0.240 g (41.5%) of yellow crystals, mp: 167°C

UV/Vis:

DHI (1) c=1.65 x 10^{-4} M, T=283K
PMMA: λ_{max} (log ε): 262 nm (4.72), 354 nm (4.12)
CH_2Cl_2: λ_{max} (log ε): 265 nm (4.87), 355 nm (4.22)
EtOH: λ_{max} (log ε): 269 nm (4.94), 354 nm (4.18)
Note that the solvent effects on the UV-absorption of the DHI (1) are minimal.

Betaine (2) $c_{(DHI + Betaine)}$ = c=1.65 x 10^{-4} M, photostationary state at 283K: approx. 45 %
PMMA: λ_{max} (log ε): 620 nm (4.32)
CH_2Cl_2: λ_{max} (log ε): 473 nm (4.21), 540 nm (4.22), 745 (3.97)
EtOH: λ_{max} (log ε): 465 nm (4.16), 527 nm (4.32), 730 (3.94)
The absorption coefficients (M^{-1} cm^{-1}) were calculated based on the conversion efficiency when reaching the photostationary state. The DHI (1) does not show any absorption beyond 460nm.

[1] T. Shrestha, J. Melin, J. Liu, O. Dolgounitcheva, V. G. Zakrzewski, M. R. Pokhrel, E. Gogritchiani, J. V. Ortiz, C. Turró, S. H. Bossmann, New Insights in the Photochromic Spirodihydroindolizine/Betaine-System, *Photochem. Photobiol. Sci.*, 2008, **7**, 1449-1456.
[2] S.-L. Wang, T.-I. Ho, Substituent effects on intramolecular charge-transfer behavior of styrylheterocycles., *J. Photochem. Photobiol. A: Chem*, 2000, **135**, 119-126.
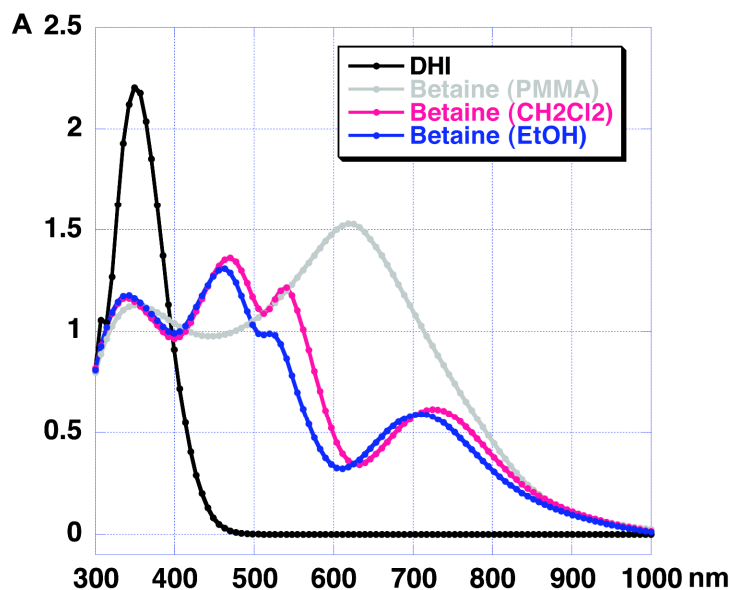
Figure SI_1: UV/Vis-Absorption Spectra of DHI (1, black line) in CH_2Cl_2 c=1.65 x 10^{-4} M, T=283K and mixtures of DHI (1) and Betaine (2) in PMMA, CH_2Cl_2 and EtOH. The photostationary state at T=283K consists of approx. 55±3% DHI and 45±3% Betaine.

IR: ν = 3055, 3010, 2980, 2825, 1735, 1685, 1590, 1495, 1445, 1265, 1210, 1155, 1100, 1015, 820, 725 cm^{-1}

^{1}H-NMR (CDCl$_3$) δ [ppm]: 7.74-7.72 (d, J=7.6 Hz, 1H), 7.66-7.64 (d, J=7.5 Hz, 1H), 7.40-7.38 (d, J=7.5 Hz, 2H), 7.32-7.30 (m, 2H), 7.10-7.00 (m. 6H), 6.80-6.78 (m, 4H), 6.78-6.76 (m, 1H), 6.59-6.56 (d, J=15.6 Hz, 1H), 6.38-6.35 (d, J=15.6 Hz, 1H), 5.41-5.40 (d, J=0.9 Hz, 1H), 5.02-5.01 (d, J=0.9 Hz, 1H), 4.04 (s, 3H), 3.23 (s, 3H), 2.93 (s, 6H)

^{13}C-NMR (CDCl$_3$) δ [ppm]: 162.82, 162.61, 148.69, 144.33, 141.42, 140.31, 130.09, 127.75, 127.54, 127.32, 127.10, 126.65, 126.35, 124.97, 124.33, 123.55, 122,28, 121.53, 120.12, 119.06, 118.90, 114.98, 68.37, 62.09, 53.58, 51.04, 40.01

MS: (120 eV, CI, CH$_4$): m/z (%) = 581 (7.4) (M$^+$+1), 580 (52.3) (M$^+$), 273 (3.7)

Elemental Analysis: C$_{38}$H$_{32}$N$_2$O$_4$, calc. C 78.60 H 5.55 N 4.82; found C 78.51 H 5.51 N 4.73

Interpolation of the $E_T(30)$ values of MMA and PMMA

The $E_T(30)$ values for various solvents shown in were obtained from the literature.[3] The data for the determination of the $E_T(30)$ values for MMA and PMMA were obtained from the Ph. D. thesis of Dr. Frahn, who has measured λ_{max} of the solvatochromic dye 1-Naphthalene-car-bonitrile, 4-[[1-[4-(2,5-dihydro-2,5-dioxo-1H-pyrrol-1-yl)phenyl]-4-piperidinylidene] methyl]-in various media.[4] Figure SI_2 shows the linear correlations that were obtained from plots of λ_{max} and the corresponding excited state energies in EV vs. $E_T(30)$ (empirical parameters of solvent polarity).[3]

[3] C. Reichardt, Solvatochromic Dyes as Solvent Polarity Indicators, *Chem. Rev.*, 1994, **94**, 2319-2358.

[4] M. S. Frahn, Radiation-Induced Poly M. S. Frahn, Radiation-Induced Polymerization Monitored with Fluorogenic Molecular Probes, *Ph.D. thesis*, Technische Universiteit Delft, The Netherlands, 2003, page 138.
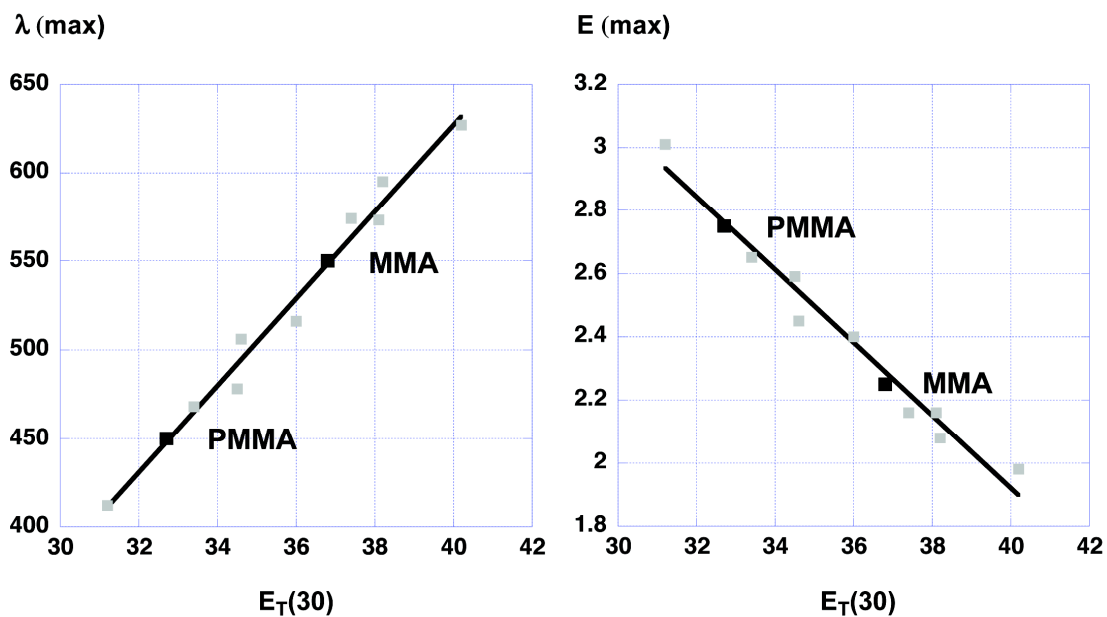
Figure SI_2: Linear correlations that were obtained from plots of λ_{max} and the corresponding excited state energies in EV of the solvatochromic dye MFP in various media[4] vs. $E_T(30)$. The linear fits permit the determination of $E_T(30) = 32.7$ (kcal mol^{-1}l) for PMMA and $E_T(30) = 36.8$ (kcal mol^{-1}l) for MMA.