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Supporting Information

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A simple unimolecular multiplexer/demultiplexer

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SUPPORTING INFORMATION

REVISED VERSION

1. Materials and methods

Chemicals. Commercially available compounds were reagent grade quality and were used without further purification. Acetonitrile Merck Uvasol™ was employed as the solvent in all the experiments. Triflic acid (CF$_3$SO$_3$H) and tris-*n*-butylamine (*n*-Bu$_3$N) were purchased from Fluka. Polystyrene (M_w 350000) was purchased from Aldrich. Routine monitoring of reactions was carried out using aluminium-supported Merck silica gel 60 TLC plates. Flash column chromatography was performed on Merck silica gel 60 with the indicated solvents. Melting points were taken on a Büchi 510 melting point apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were measured with a Varian Mercury 400 spectrometer. Chemical shifts are expressed in ppm using residual solvent as an internal standard.

Synthesis of 8-methoxyquinolinium hexafluorophosphate [8-MQ-H][PF$_6$]. 8-Hydroxyquinoline (1.45 g. 10.0 mmol), KOH (2.53 g. 45.0 mmol), MeI (2.13 g. 15.0 mmol), and THF (100 mL) were stirred at room temperature for 12 h. After filtration and solvent removal, 8-methoxyquinoline (1.27 g, 80%) was isolated after flash chromatography on silica gel (hexane/EtOAc 3:1) as a red oil. The isolated oil was dissolved in acetone/water and the solution was acidified with 10% aqueous HCl. To the clear solution an excess of NH$_4$PF$_6$ was added in order to precipitate the hexafluorophosphate salt of 8-methoxyquinolinium, that was collected by filtration. The salt was recrystallised from isopropyl alchool to afford [8-MQ-H][PF$_6$] (2.39 g. 98%) as pale green needles. Mp 141-142 °C. ^{1}H NMR (400 MHz, Acetone-d$_6$): δ 9.35 (1H, d, *J* = 5.3 Hz), 9.25 (1H, d, *J* = 8.4 Hz), 8.24 (1H, dd, *J* = 8.4, 5.3 Hz), 7.95-7.96 (2H, m), 7.72 (1H, dd, *J* = 5.8, 3.0 Hz), 4.21 (3H, s); ^{13}C NMR (100.5 MHz, Acetone-d$_6$): δ 149.6, 148.0, 144.5, 131.2, 130.3, 129.5, 123.2, 120.5, 113.7, 56.9.

Preparation of the polystyrene films. A MeCN solution of 8-MQ was added to a CHCl$_3$ solution of polystyrene 1.5% (*w/w*), such that the concentration of the chromophore in the resulting mixture was 2.25×10^{-3} mol L^{-1}. The solution was placed between two microscopy quartz coverslips (previously washed with ethanol and water, and carefully dried). After the solvent had evaporated, one coverslip was removed and the sample was subjected to fluorescence spectroscopic analysis. The thickness of the films was in the order of 0.7 μm.

Photophysical experiments. Absorption spectra were recorded with a Perkin Elmer λ45 spectrophotometer in air equilibrated MeCN solutions at room temperature (*ca.* 298 K), contained in 1-cm spectrofluorimetric quartz cells. The concentration of the compound varied from 7.0×10^{-6} to 1.5×10^{-5} mol L^{-1}. Luminescence spectra were recorded with a Perkin-Elmer LS50B spectrofluorimeter equipped with a Hamamatsu R928 phototube. In the case of the films, a front-face excitation geometry was adopted in order to minimize inner filter and light scattering effects. Luminescence quantum yields were determined with the optically dilute method using naphthalene or anthracene as standards. Luminescence lifetimes were determined with an Edinburgh Instruments FLS920 spectrofluorimeter, exciting the sample at 262 nm with a D_2-filled arc lamp and reading the intensity at either 383 nm or 500 nm in the case of 8-MQ and 8-MQ-H$^+$, respectively. The experimental errors are ±1 nm for the wavelengths and ±10% for the luminescence intensities, quantum yields and lifetimes.

Chemical switching in solution. 8-MQ was obtained in the spectrofluorimetric cell upon addition of 1 equivalent of n-Bu$_3$N to a solution of [8-MQ-H][PF$_6$]. The protonated form, 8-MQ-H$^+$ was regenerated by the subsequent addition of 1 equivalent of CF$_3$SO$_3$H. Small aliquots (typically 5 μL) of a concentrated solution of either n-Bu$_3$N or CF$_3$SO$_3$H were added to a volume of 2.5 mL by using a microsyringe.

Chemical switching in polymer films. A few drops of a 10^{-2} mol L^{-1} MeCN solution of CF$_3$COOH were deposited on the film containing 8-MQ so as to cover the whole surface with a thin layer of liquid. The solvent was let to evaporate in air, and the dry film was subjected to fluorescence spectroscopic analysis. Subsequently, a few drops of a 10^{-2} mol L^{-1} MeCN solution of n-Bu$_3$N were deposited on the same film (now containing 8-MQ-H$^+$) so as to cover the whole surface with a thin layer of liquid. The solvent was let to evaporate in air, and the dry film was subjected to fluorescence spectroscopic analysis.

2. Photophysical data for 8-MQ and 8-MQ-H$^+$

Table S1. Absorption and photoluminescence data for the examined compounds in MeCN.

Compound	Absorption (RT)		Fluorescence (RT)				Fluor. 77K[a]
	λ_{max} (nm)	ε (L mol^{-1} cm^{-1})	λ_{max} (nm)	Φ_F	τ_F (ns)	k_F (s^{-1})[b]	λ_{max} (nm)
8-MQ	301	2200	388	0.079	6.7	1.2×10^7	386
8-MQ-H$^+$	317	1400	500	0.036	11	3.3×10^6	445
	358	1400					

[a] MeCN rigid matrix. [b] Radiative rate constant, calculated as $k_F = \Phi_F/\tau_F$.

3. Fluorescence spectra corresponding to the MUX/DEMUX binary logic functions
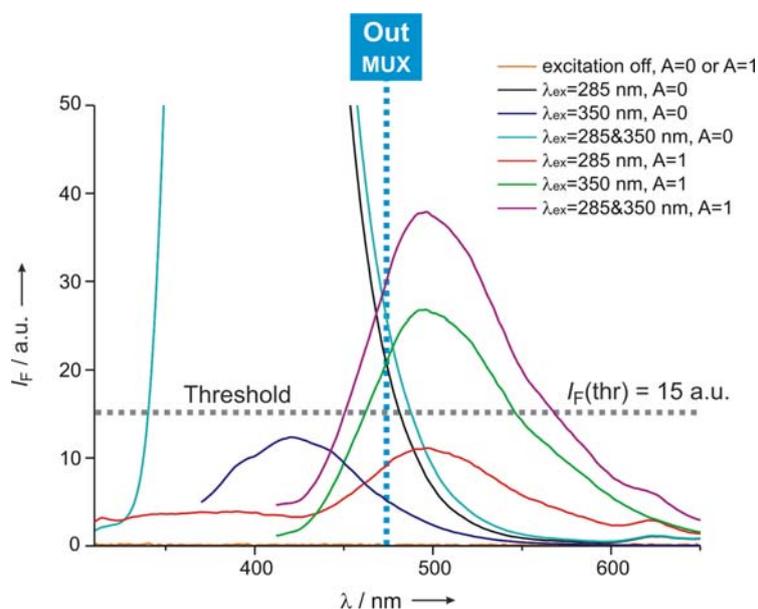

Figure S1. Fluorescence spectra recorded at RT on a 1.5×10^{-5} mol L^{-1} MeCN solution of 8-MQ under various excitation conditions and in the absence (A=0) or in the presence (A=1) of one equivalent of triflic acid. The output wavelength and threshold value relevant for the binary logic operation are indicated. These spectra correspond to the states of the truth table of the 2:1 multiplexer, displayed in Table 1.
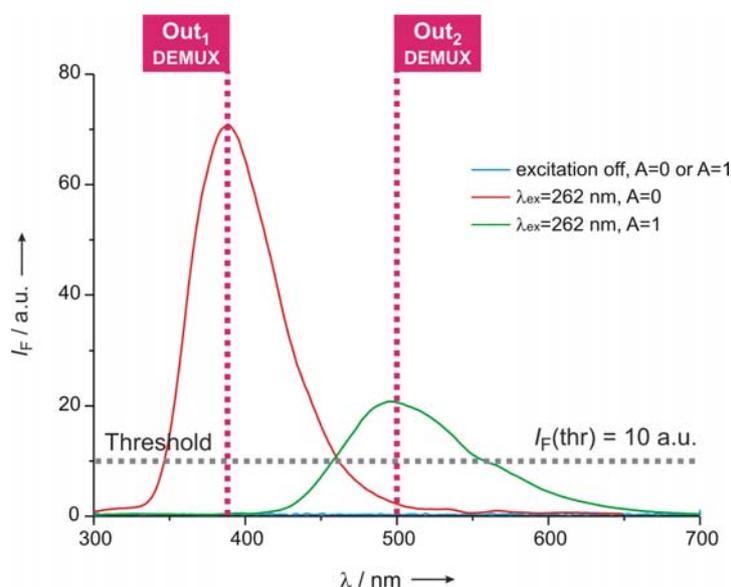
Figure S2. Fluorescence spectra recorded at RT on a 1.5×10^{-5} mol L^{-1} MeCN solution of 8-MQ upon excitation at an isosbestic point at 262 nm in the absence (A=0) or in the presence (A=1) of one equivalent of triflic acid. The output wavelengths and threshold value relevant for the binary logic operation are indicated. These spectra correspond to the states of the truth table of the 1:2 demultiplexer, displayed in Table 2.
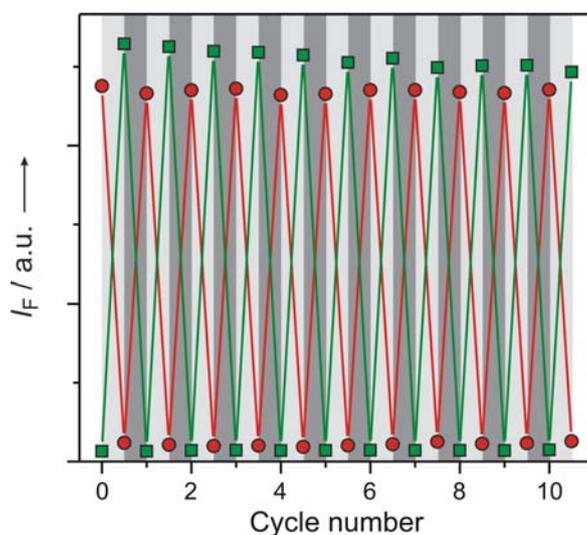
4. Acid-base switching cycles

Figure S3. Emission intensity values) at 388 nm (red circles) and 500 nm (green squares) upon several protonation-deprotonation cycles performed on a MeCN solution containing 7.4×10^{-6} mol L^{-1} 8-MQ. Conditions: λ_{ex} = 262 nm, RT; addition of 1 equivalent of CF_3SO_3H (light grey areas); addition of 1 equivalent of n-Bu_3N (dark grey areas).
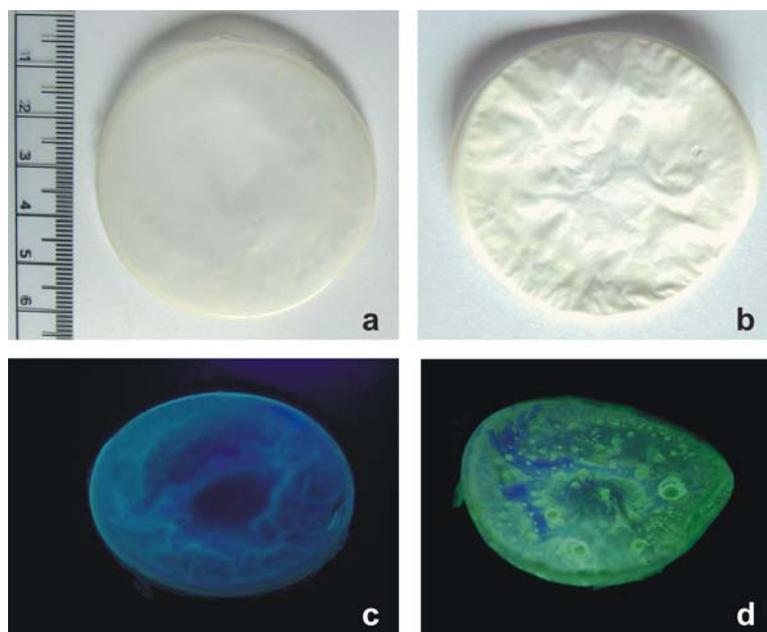
5. Photographs of the polymer films

Figure S4. Photographs of a polystyrene solid film containing 8-MQ under ambient light (top) and under irradiation with a near-UV lamp (bottom; λ_{irr} = 365 nm; a cutoff filter at 395 nm was placed in front of the camera to reduce the effect of scattered excitation light). Conditions: a and c, as-prepared film; b and d, after treatment with a MeCN solution of CF$_3$COOH on both sides followed by drying in air. The film was prepared as described in Materials and methods, except from the fact that the solution was placed in a Petri dish for solvent evaporation.