Electronic Supplementary Information

A Fluorescent and Halochromic Indolizine Switch

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Synthesis. Chemicals were purchased from commercial sources and used as received. ESIMS were recorded with a Bruker micrOTO-Q II spectrometer. NMR spectra were recorded with a Bruker Avance 400 spectrometer.

1. A solution of 2,3,3-trimethyl-3*H*-indole (1.59 g, 10 mmol) and TCNE (1.28 g, 10 mmol) in DMF (30 mL) was stirred at 80 °C for 1 hour under Ar. After cooling down to ambient temperature, the mixture was diluted with H_2O (100 mL) and stirred for a further 10 min. The resulting precipitate was filtered off and recrystallized from AcOEt to give **1** (1.61 g, 62%) as an orange solid. ESIMS: m/z = 261.1152 [M + H]$^+$ (m/z calcd. for $C_{16}H_{13}N_4$ = 261.1140); ^{1}H NMR ($CDCl_3$): δ = 1.55 (6H, s), 6.07 (1H, s), 7.35–7.55 (3H, m), 7.67 (1H, s), 9.01 (1H, d, 8.0 Hz); ^{13}C NMR ($CDCl_3$): δ = 27.4, 46.4, 96.7, 106.5, 113.7, 114.2, 119.8, 121.8, 125.4, 127.3, 128.7, 139.0, 140.1, 153.3, 166.0.

Crystallographic Analysis. The data crystal of **1** was glued onto the end of a thin glass fiber, while that of **2** was mounted onto the end of a thin glass fiber using Paratone-N for data collection at 100 K under N_2. X-ray intensity data were measured with a Bruker SMART APEX2 CCD-based diffractometer, using Mo Kα radiation (λ = 0.71073 Å).[S1] The raw data frames were integrated with the SAINT+ program by using a narrow-frame integration algorithm. Corrections for Lorentz and polarization effects were also applied with SAINT+. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied using the program SADABS. The structure was solved with a combination of direct methods and difference Fourier syntheses and refined by full-matrix least-squares on F^2 with the SHELXTL software package.[S2] Crystal data, data collection parameters and results of the analyses are listed in Table S1. Crystallographic data were deposited with the Cambridge Crystallographic Data Centre (CCDC No. 1426007 and 1430926). Copies of this information may be obtained free of charge from: The

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S1 Apex2 Version 2.2-0 and SAINT+ Version 7.46A, Bruker Analytical X-Ray System, Inc., Madison, WI, USA, 2007.

S2 (a) G. M. Sheldrick, SHELXTL Version 6.1, Bruker Analytical X-Ray Systems, Inc., Madison, WI, USA, 2000. (b) G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112–122.

Director, CCDC12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(1223) 336−033; e−mail: deposit@ccdc.cam.ac.uk; www.http://www.ccdc.cam.ac.uk].

Orange single crystals of **1**, suitable for X-ray diffraction analysis, were obtained after the slow evaporation of the solvent from an AcOEt solution of the compound. The molecule crystallized in the orthorhombic crystal system and the systematic absences in the intensity data suggested space groups *Pnma* and *Pna*2$_1$. The former space group was chosen and confirmed by the successful solution of the structure. The molecule has crystallographic mirror symmetry. All non-hydrogen atoms were refined with anisotropic displacement parameters. Even though most of the hydrogen atoms could be located from the difference Fourier map, they were placed in geometrically idealized positions and included as standard riding atoms, during the least-squares refinements, except for atom H4.

Yellow single crystals of **2**, suitable for X-ray diffraction analysis, were obtained after the addition of CF_3CO_2H (5 eq.) to a PhMe solution of **1** and the slow evaporation of the solvent. The molecule crystallized in the monoclinic crystal system and the systematic absences in the intensity data were consistent with the space group $P2_1/n$. There is one counter $CF_3CO_2^-$ anion, as well as one molecule of CF_3CO_2H present in the asymmetric crystal unit. All non-hydrogen atoms were refined with anisotropic displacement parameters. Even though most of the hydrogen atoms could be located from the difference Fourier map, they were placed in geometrically idealized positions and included as standard riding atoms, during the least-squares refinements, except for atoms H4a and H4b for the NH_2 group. A NH_2 group, instead of a NH_3^+ group, is proposed because there was no evidence of a third peak in the difference map for an additional H atom.

Spectroscopy. UV/VIS absorption spectra were recorded with a Varian Cary 100 Bio spectrometer, using quartz cells with a path length of 1.0 cm. IR absorption spectra were recorded with a Perkin Elmer Frontier FT-IR spectrometer on neat samples. Emission spectra were recorded with a Varian Cary Eclipse spectrometer in aerated solutions. Fluorescence quantum yields were determined with a 9,10-diphenylanthracene standard, following a literature protocol.[S3]

Cyclic Voltammetry. Voltammograms were recorded with a CH Instruments 610A electrochemical analyzer in a MeCN solution of Bu_4NPF_6 (0.1 M) at a scan rate of 100 mV s^{-1} under Ar, using a three-electrode cell, The reference was a Ag/Ag$^+$ electrode (1 mM $AgNO_3$ in MeCN). The counter and working were a platinum wire and a glassy-carbon electrode respectively.

Fluorescence Imaging. A solution of PBMA (10 mg mL^{-1}, $M_W = 337 \times 10^3$), **1** (5% w/w relative to PBMA) and **3** (5% w/w relative to PBMA) in CH_2Cl_2 (0.1 mL) was deposited dropwise on a glass slide. The substrate was spun at 1200 rpm for 1 min with a Chemat Technologies KW-4A spin coater. The coated slide was stored under reduced pressure for 1 hour and then imaged with a Leica SP5 confocal laser-scanning microscope.

S3   J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, Springer, New York, 2006.

Table S1. Crystallographic Data for **1** and **2**.

Empirical Formula	$C_{16}H_{12}N_4$	$C_{16}H_{13}N_4 \cdot F_3C_2O_2 \cdot F_3C_2O_2H$
Formula Weight	260.30	188.35
Crystal System	Orthorhombic	Monoclinic
Lattice Parameters:		
a (Å)	13.0779(6)	8.6010(4)
b (Å)	6.7374(3)	21.0213(10)
c (Å)	14.8646(7)	11.9369(6)
β (°)	90	104.717(1)
V (Å³)	1309.74(10)	2087.43(17)
Space Group	$Pnma$ (# 62)	$P2_1/n$ (# 14)
Z Value	4	4
ρ_{calc} (g cm⁻³)	1.320	1.554
μ (Mo Kα) (mm⁻¹)	0.082	0.145
T (K)	296	100
$2\Theta_{max}$ (°)	54.0	56.0
No. Obs. ($I > 2\sigma(I)$)	1368	4118
No. Parameters	123	318
Goodness of Fit	1.052	1.020
Max. Shift in Cycle	0.001	0.000
Residuals*: R1; wR2	0.0377; 0.1014	0.0381; 0.0951
Absorption Correction, Max/min	Multi-Scan 0.9678/0.9918	Multi-Scan 0.9914/0.9363
Largest Peak in Final Diff. Map (e⁻ Å⁻³)	0.293	0.367

* $R = \Sigma_{hkl}(||F_{obs}| - |F_{calc}||)/\Sigma_{hkl}|F_{obs}|$; $R_w = [\Sigma_{hkl}w(|F_{obs}| - |F_{calc}|)^2/\Sigma_{hkl}wF_{obs}^2]^{1/2}$;
  $w = 1/\sigma^2(F_{obs})$; $GOF = [\Sigma_{hkl}w(|F_{obs}| - |F_{calc}|)^2/(n_{data} - n_{vari})]^{1/2}$.