Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Electronic Supplementary Information

Evidence for excited state intramolecular charge transfer in benzazole-based pseudo-stilbenes

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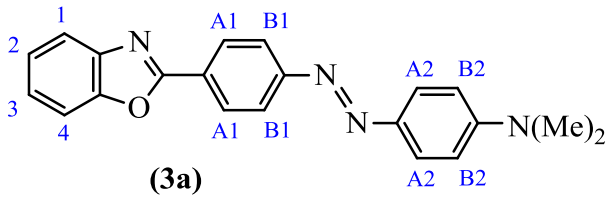
Spectroscopic characterization of the dyes



(3a)

Figure SI 1. Signal attribution to ^{1}H NMR of the dyes **3a**.

(E)-4-((4-(benzo[d]oxazol-2-yl)phenyl)diazenyl)-N,N-dimethylaniline (3a)

Yield: 80%. Melting Point: up to 250ºC.

Elemental analysis (Found: C, 73.96; H, 5.99; N, 15.69. Calc. For $C_{21}H_{20}N_4O$: C, 73.23; H, 5.85; N, 16.27%). IR absorptions - ν_{max}/cm^{-1}: 3058w (arom. CH), 2898w (aliphatic CH), 1602m (arom. C=C), 1138m (C-N), 1052m (C-O), 1422m (N=N). NMR data - δ_H (300 MHz; $CDCl_3$; Me_4Si) 3.10 (6 H, s, CH_3), 6.76 (2 H, d, J_o = 9.1 Hz, H_{B2}), 7.27-7.40 (2 H, m, H_2 and H_3), 7.57-7.62 (1 H, m, H_4), 7.78-7.82 (1 H, m, H_1), 7.91 (2 H, d, J_o = 9.1 Hz, H_{A2}), 7.97 (2 H, d, J_o = 8.6 Hz, H_{B1}), 8.36 (2 H, d, J_o = 8.6 Hz, H_{A1}). δ_C (75.4 MHz; $CDCl_3$; Me_4Si) 40.3, 110.6, 111.5, 120.0, 122.6, 126.6, 125.2, 125.4, 127.3, 128.4, 142.2, 143.7, 150.8, 152.8, 154.9.

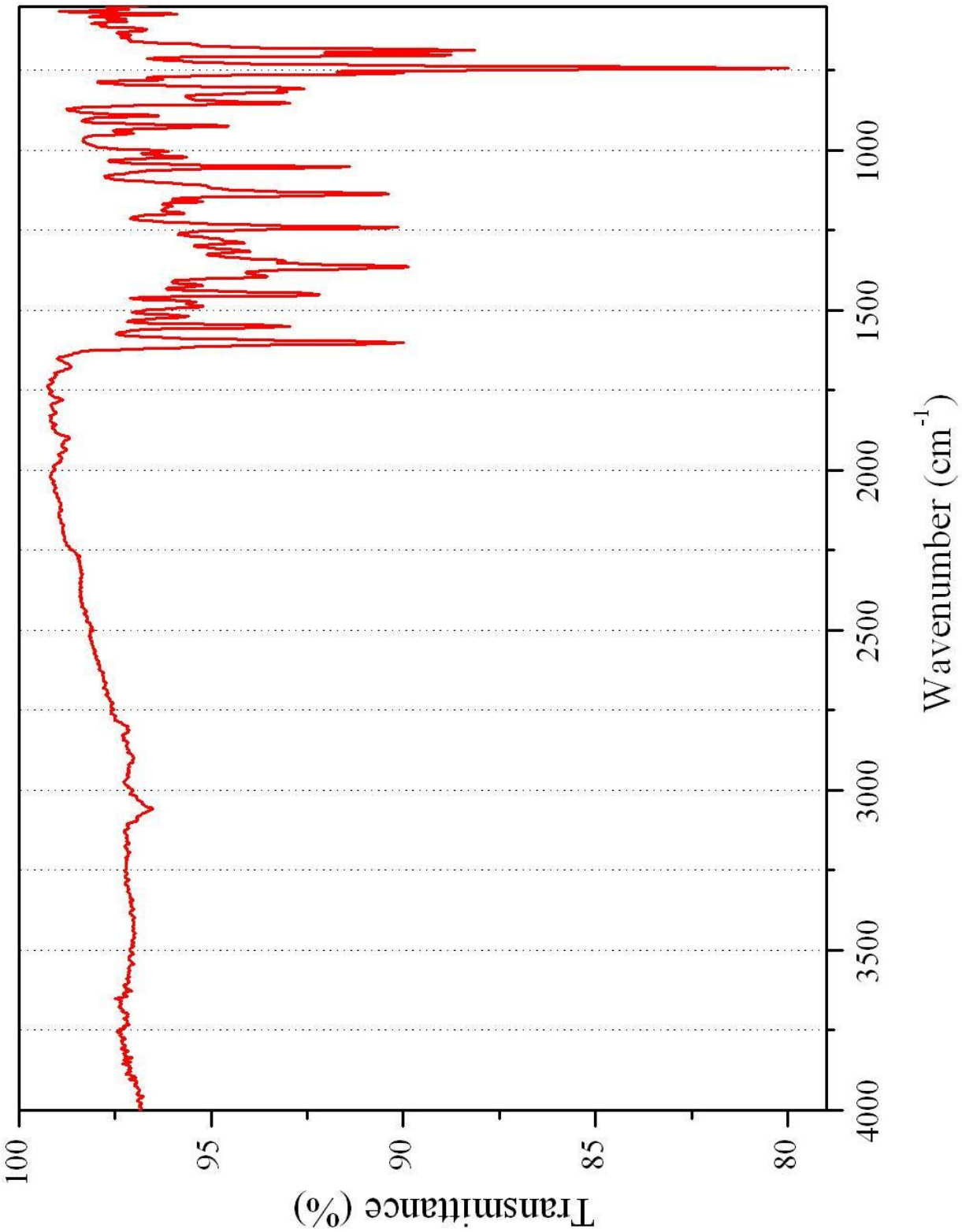


Figure SI 2. FTIR spectrum (ATR) of the dye **3a**.

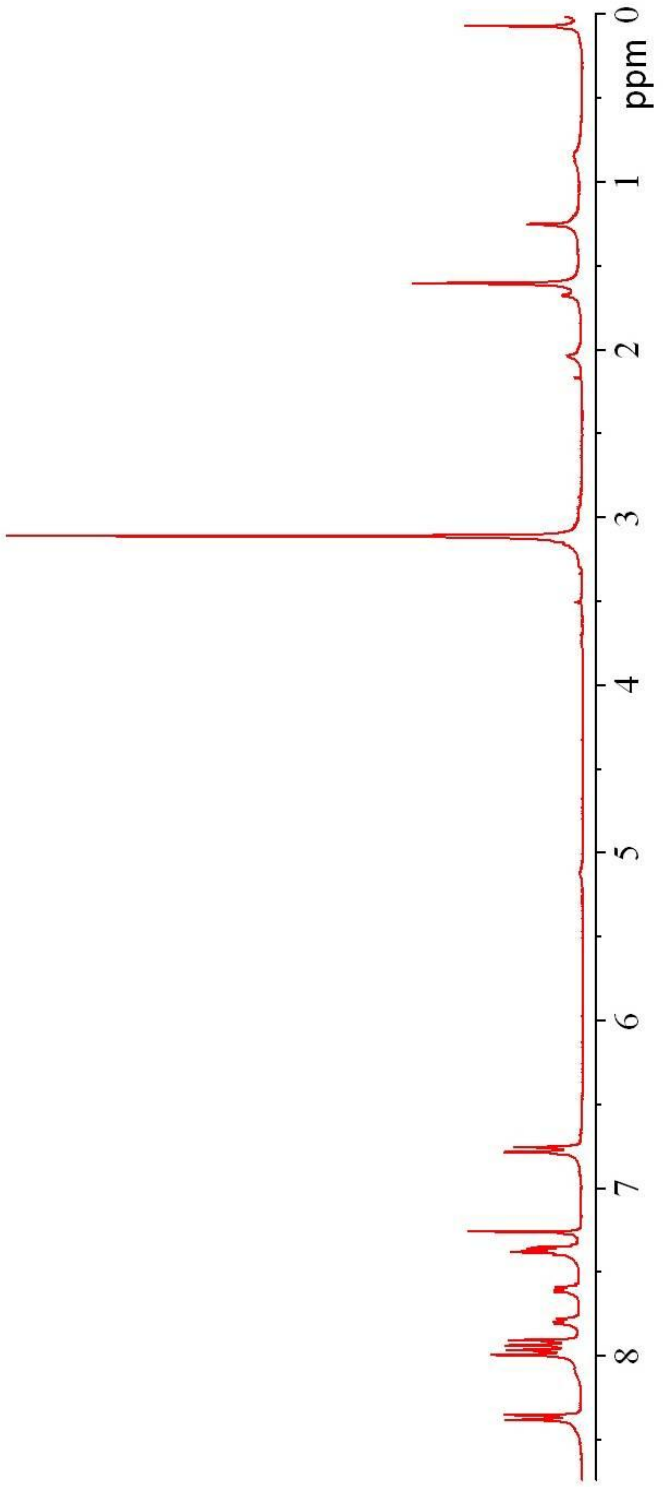


Figure SI 3. ^{1}H NMR spectrum (300 MHz) of the dye **3a** in $CDCl_3$.

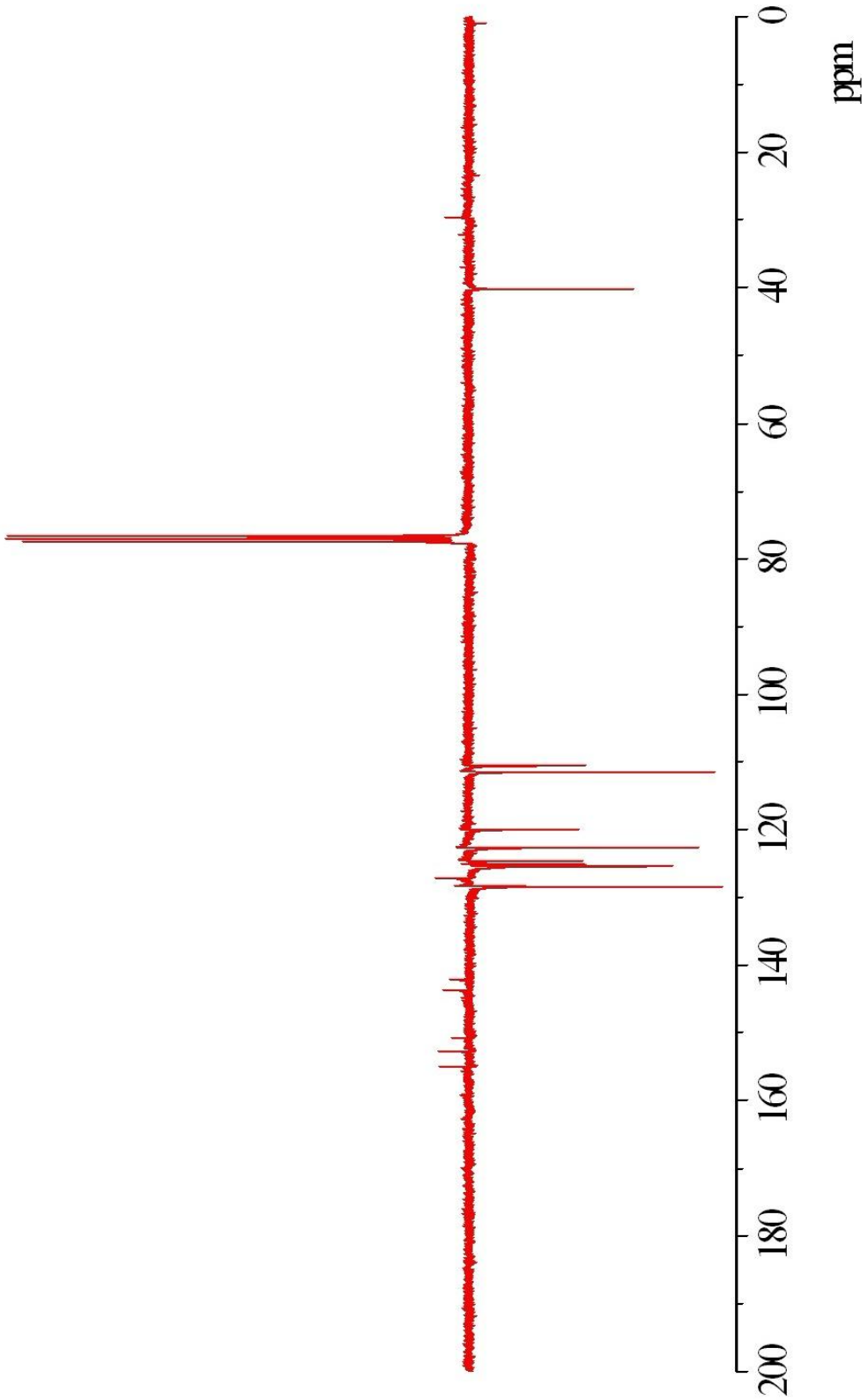
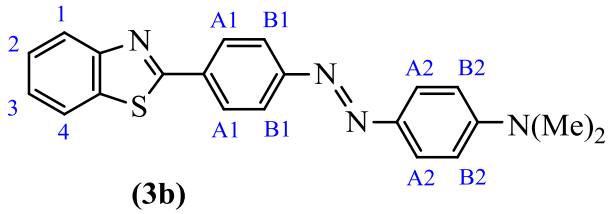


Figure SI 4. ATP spectrum (75.4 MHz) of the dye **3a** in $CDCl_3$.



(3b)

Figure SI 5. Signal attribution to ^{1}H NMR of the dyes **3b**.

(E)-4-((4-(benzo[d]thiazol-2-yl)phenyl)diazenyl)-N,N-dimethylaniline (3b)

Yield: 72%. Melting Point: up to 250ºC (according the literature).[1] Elemental analysis (Found: C, 69.20; H, 5.42; N, 14.00. Calc. For $C_{21}H_{20}N_4O$: C, 69.97; H, 5.59; N, 15.54%). IR absorptions - ν_{max}/cm^{-1}: 3050w, 3024w and 3018w (arom. CH), 2882w, 2920w and 2901w (aliphatic CH), 1602m (arom. C=C), 1135m (C-N), 1415m (N=N). NMR data - δ_H (300 MHz; $CDCl_3$; Me_4Si) 1.62 (6 H, t, CH_3), 6.80 (2 H, d, J_o = 8.9 Hz, H_{B2}), 7.42 (1 H, t, J_o = 8.1 Hz, J_m = 1.0 Hz, H_2 or H_3), 7.54 (1 H, t, J_o = 8.2 Hz, J_m = 1.0 Hz, H_2 or H_3), 7.94-8.00 (5 H, m, H_{A2}, H_1 or H_4, H_{B1}), 8.12 (1 H, d, J_o = 8.5 Hz, H_1 or H_4), 8.24 (2 H, d, J_o = 8.3 Hz, H_{A1}). δ_C (75.4 MHz; $CDCl_3$; Me_4Si) 40.3, 111.5, 121.6l, 122.8, 123.3, 125.3, 125.4, 126.4, 128.3, 133.9, 135.0, 144.8, 152.7, 154.7.

[1] V. F. Bystrov, Zh. N. Belaya, B. E. Gruz, G. P. Syrova, A. I. Tolmachev, L. M. Shulezhko, L. M. Yagupol'skii, Zhurnal Obshchei Kimii **1968**, 38, 1001.

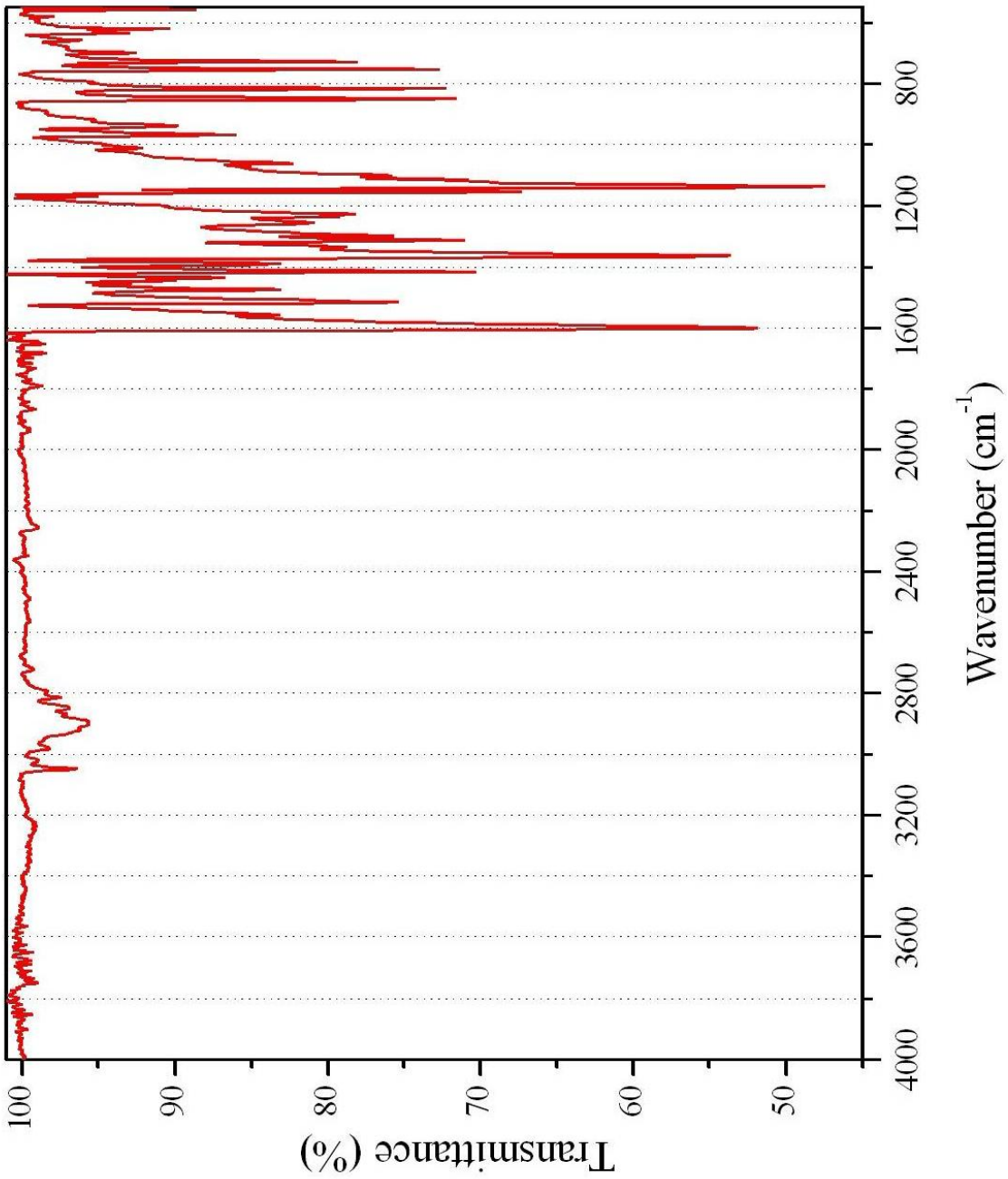


Figure SI 6. FTIR spectrum (KBr) of the dye **3b**.

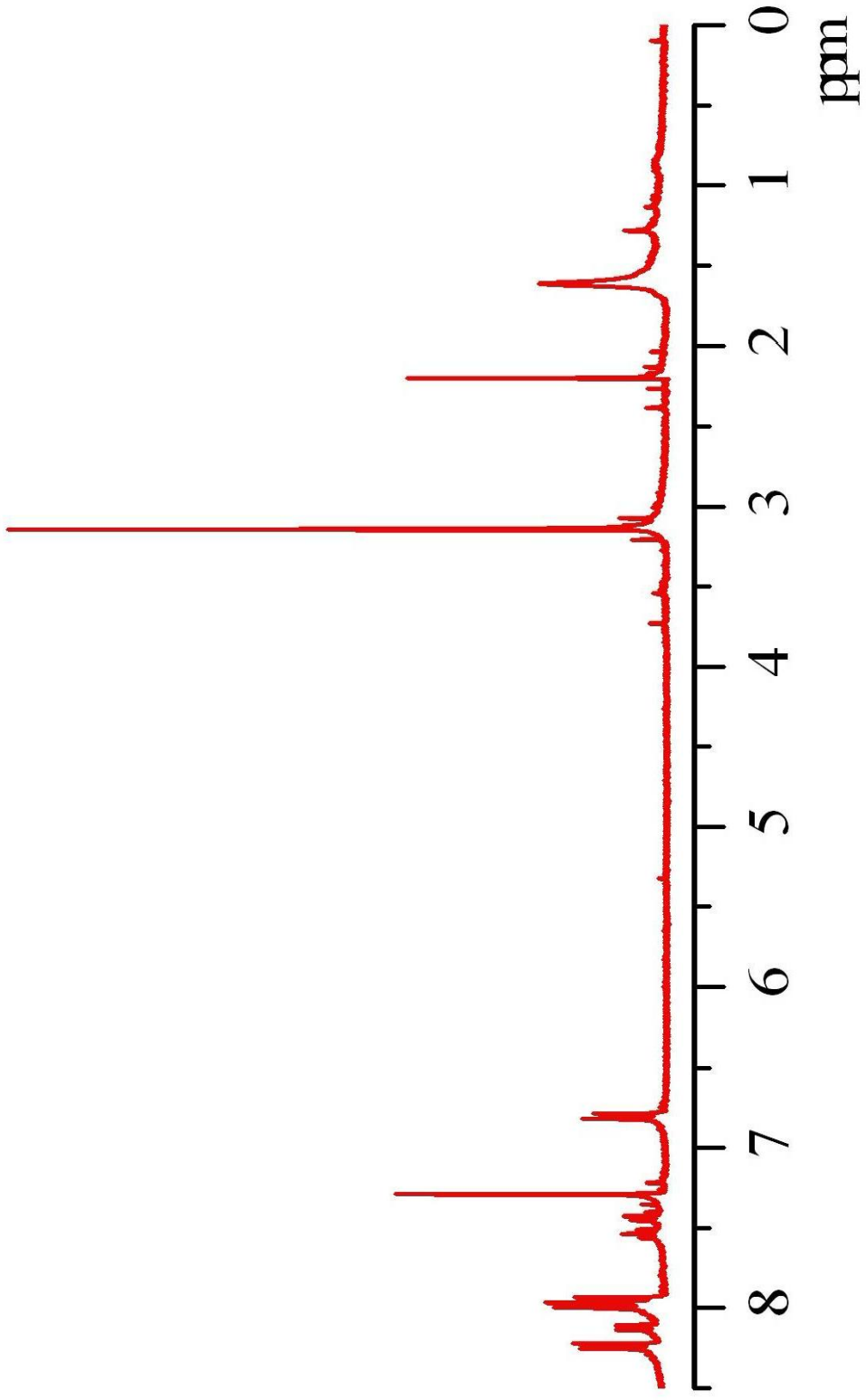


Figure SI 7. ^{1}H NMR spectrum (300 MHz) of the dye **3b** in $CDCl_3$.

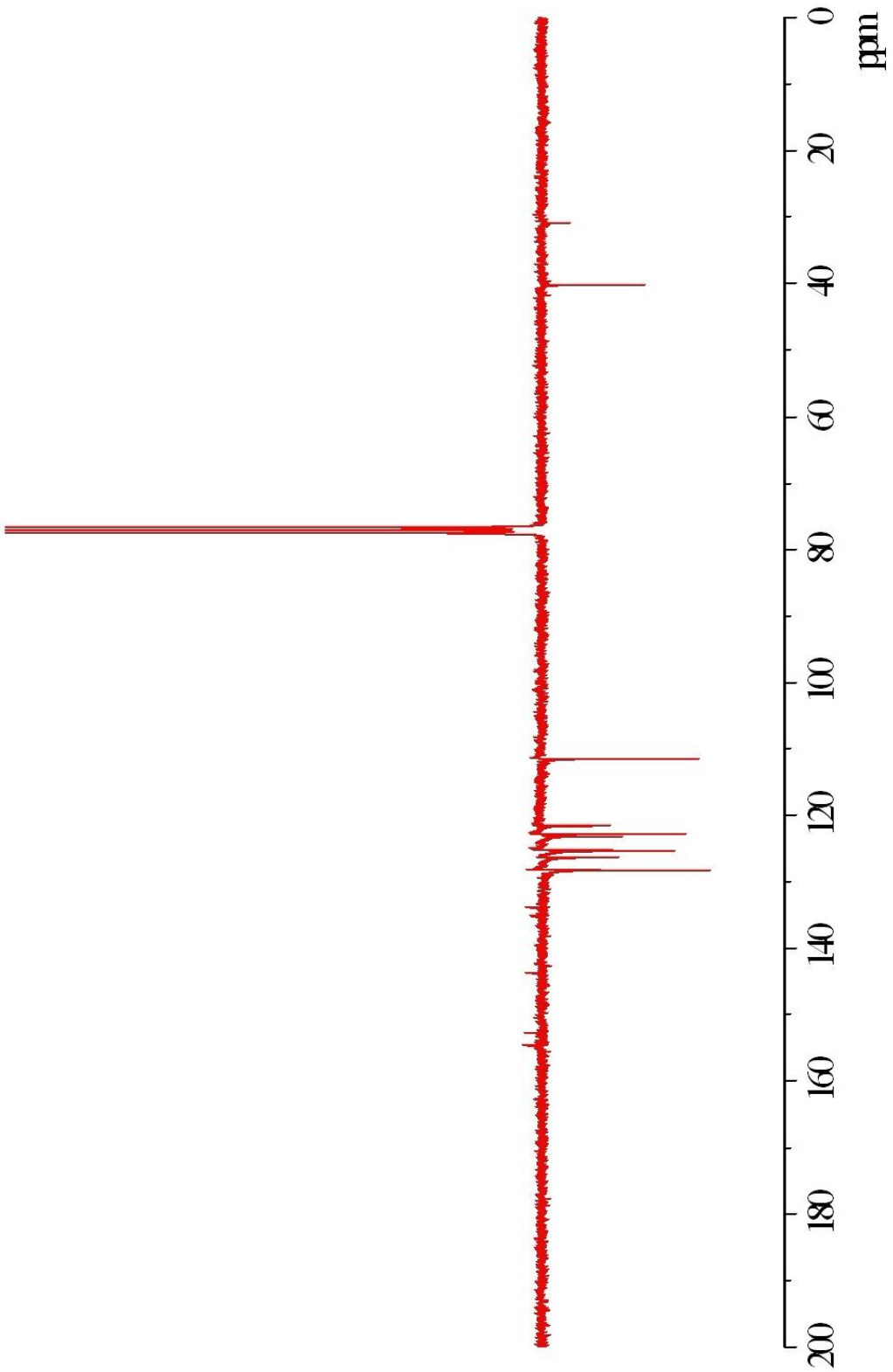


Figure SI 8. ATP spectrum (75.4 MHz) of the dye **3b** in $CDCl_3$.

Photophysical data

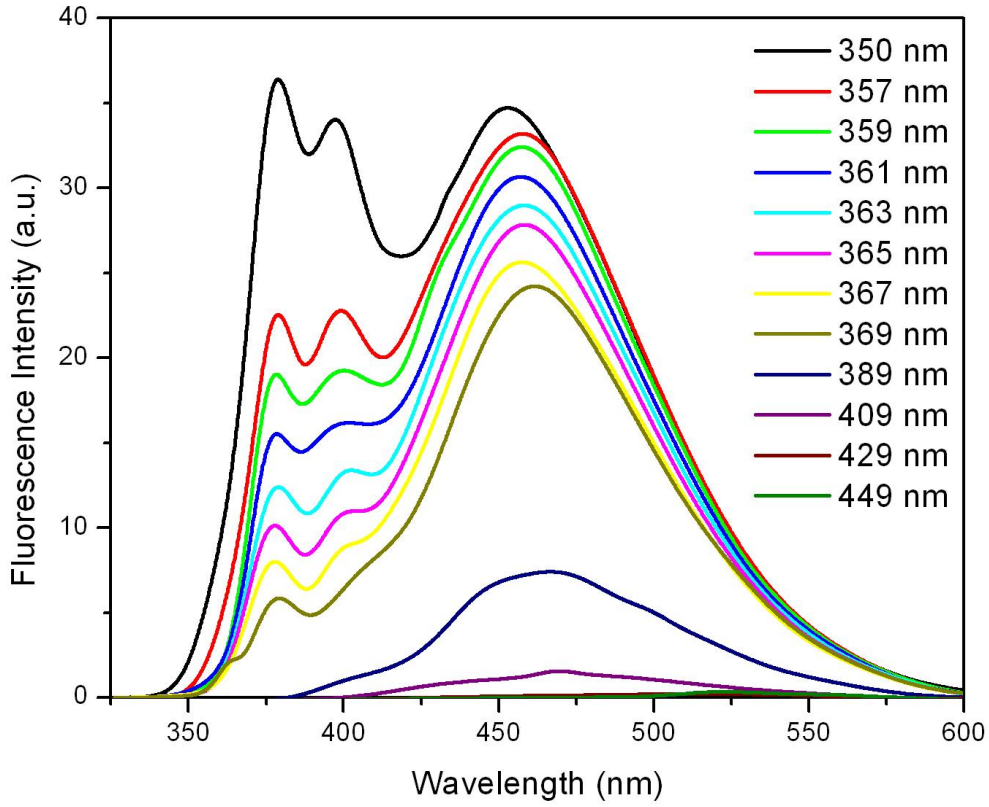


Figure SI 9. Scanning in the excitation wavelength of the dye **3a** in dichloromethane.

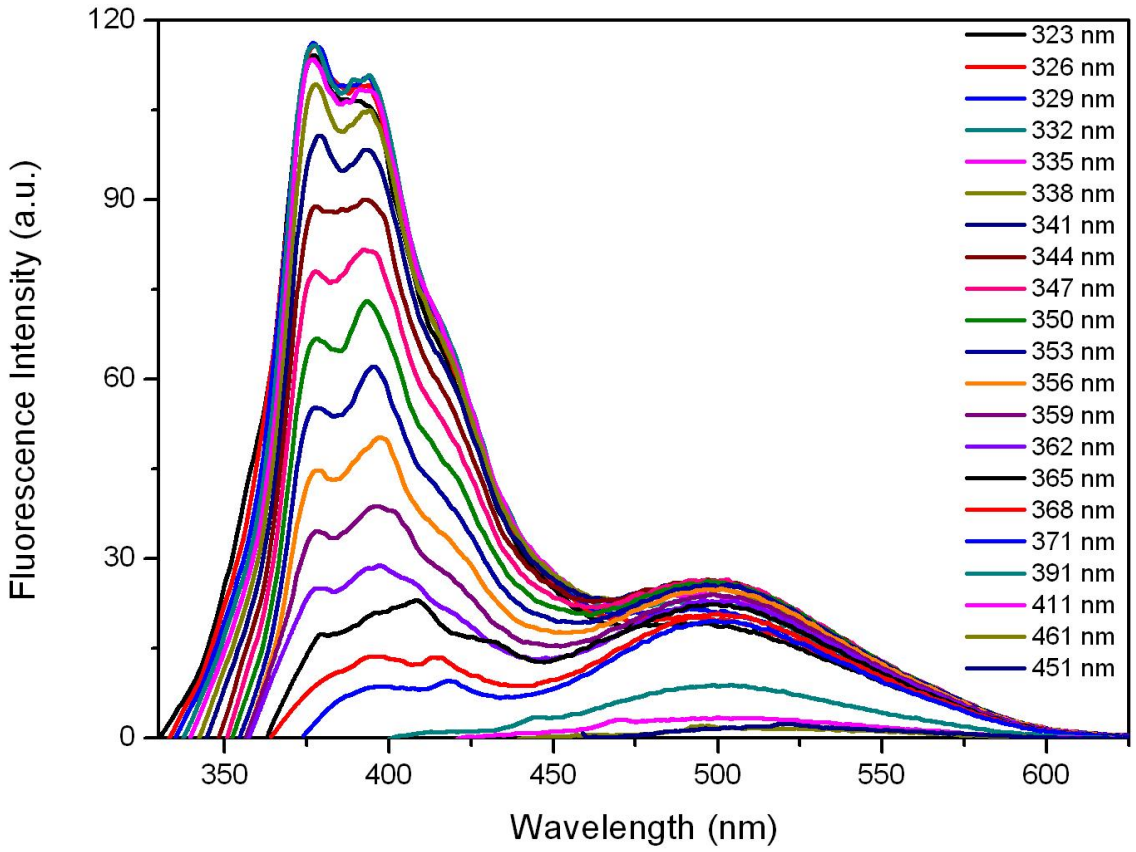


Figure SI 10. Scanning in the excitation wavelength of the dye **3a** in ethanol.

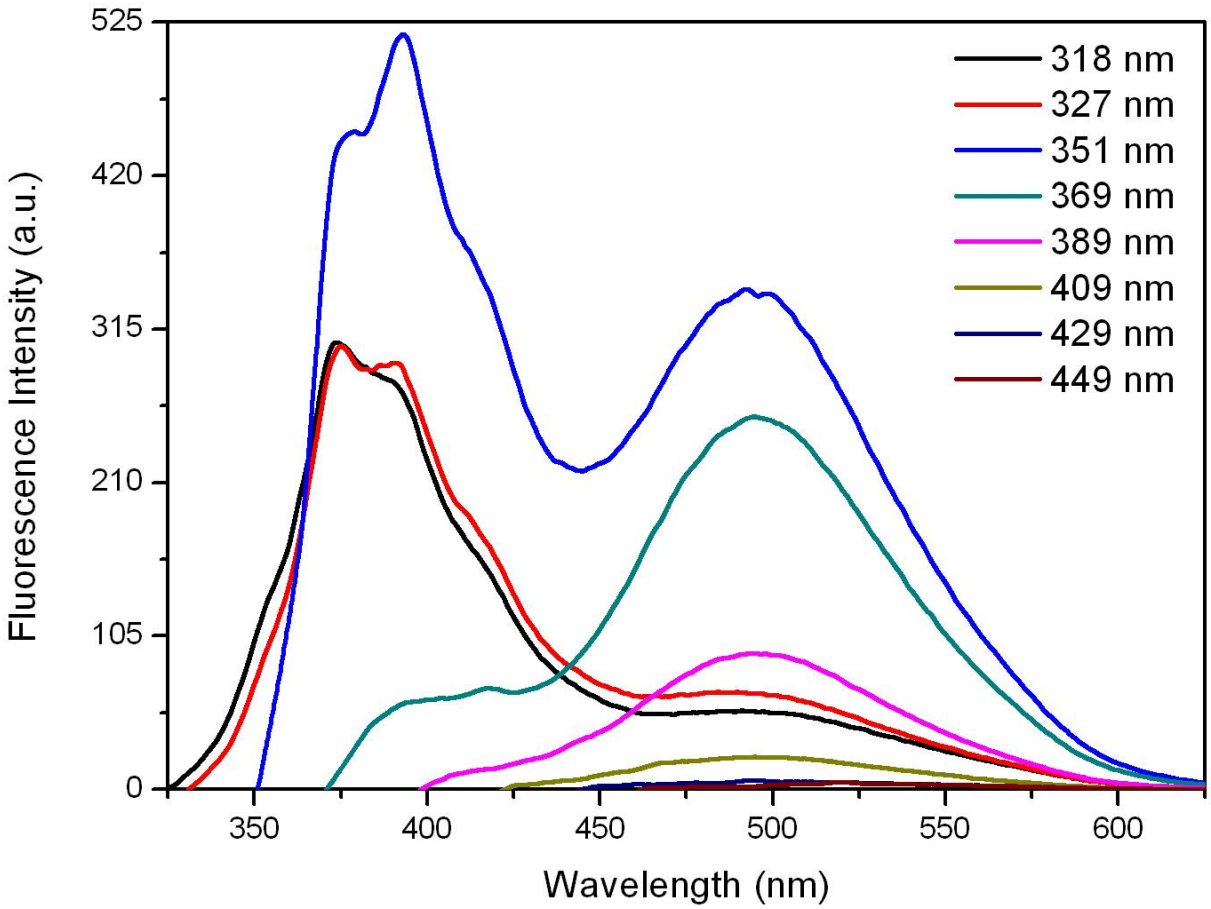


Figure SI 11. Scanning in the excitation wavelength of the dye **3a** in acetonitrile.

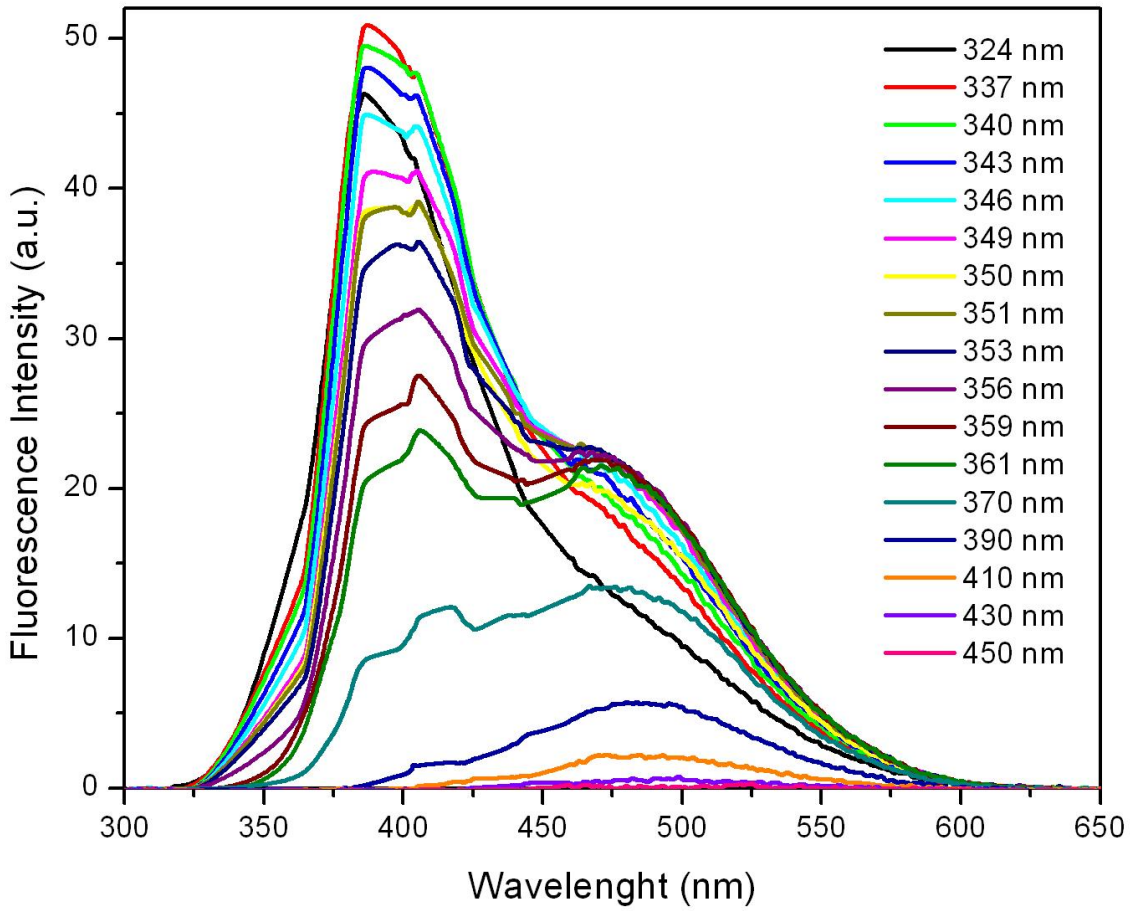


Figure SI 12. Scanning in the excitation wavelength of the dye **3b** in dichloromethane.

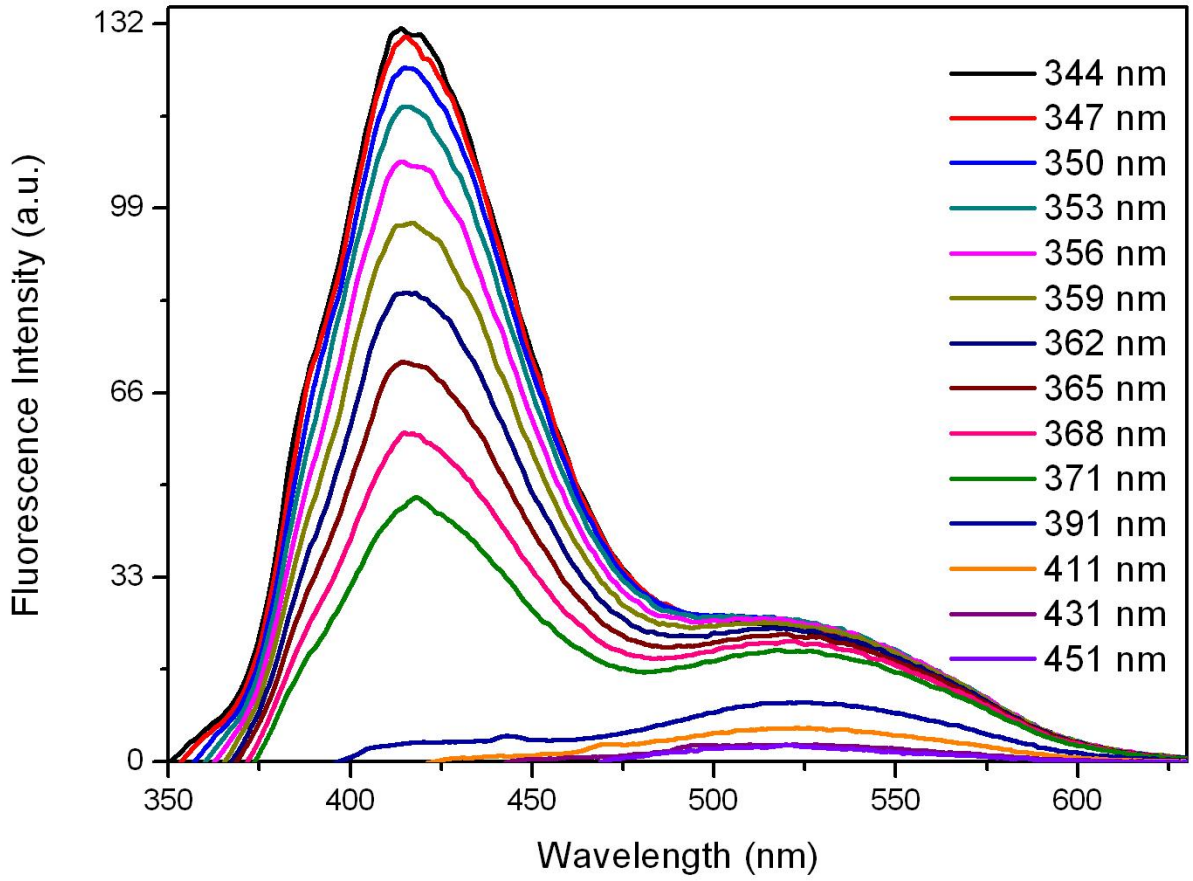


Figure SI 13. Scanning in the excitation wavelength of the dye **3b** in ethanol.

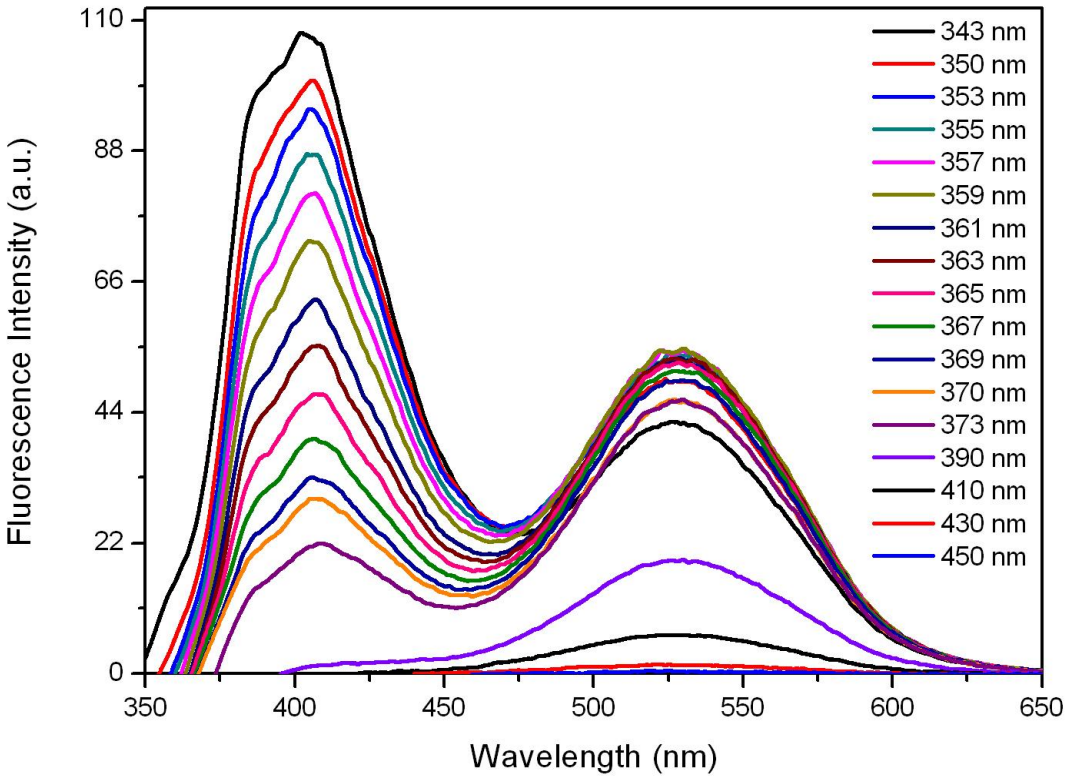


Figure SI 14. Scanning in the excitation wavelength of the dye **3b** in acetonitrile.

Table ESI1 UV-Vis data of the precursors **1a-b** and azo dyes **3a-b**, where the concentration is presented in mol·L^{-1}.

Dye	*Solvent*	*Conc.*
1a	Dichloromethane	2.10×10^{-5}
	Ethanol 95%	1.22×10^{-4}
	Acetonitrile	2.30×10^{-5}
1b	Dichloromethane	6.89×10^{-5}
	Ethanol 95%	1.92×10^{-4}
	Acetonitrile	2.62×10^{-5}
3a	Dichloromethane	9.74×10^{-6}
	Ethanol 95%	9.62×10^{-6}
	Acetonitrile	5.26×10^{-5}
3b	Dichloromethane	8.37×10^{-6}
	Ethanol 95%	9.29×10^{-6}
	Acetonitrile	5.02×10^{-5}

Viscosity Experiments

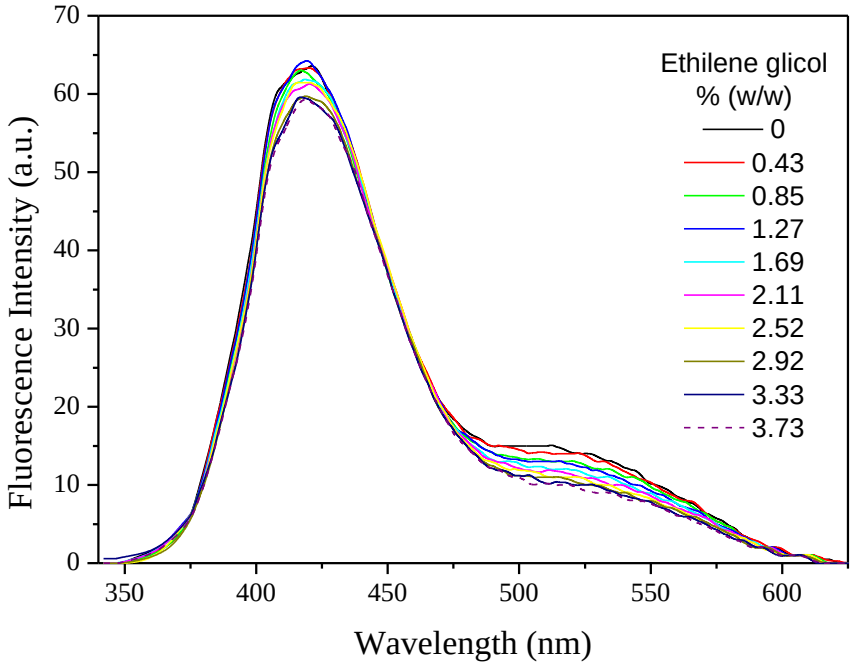


Figure SI 15. Fluorescence spectra of the dye **3b** in ethanol-ethylene glycol mixtures of varying composition, λ_{ex} = 357 nm.

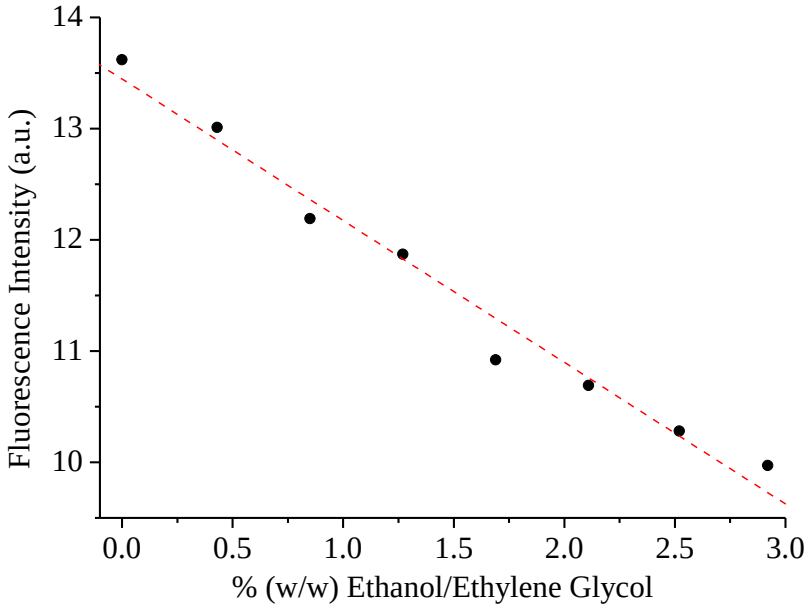


Figure SI 16. Plot of variation of the ICT band intensity of the dye **3b** with the variation of percentage of ethanol/ethylene glycol mixture (w/w).

Table ESI2. Relevant data for the viscosity experiments, where EtOH and EtGly are related to ethanol and ethylene glycol, respectively.

#	V_{EtOH} (ml)	W_{EtOH} (g)	V_{EtGly} (ml)	W_{EtGly} (g)	% EtGly (w/w)	LE Intensity		ICT Intensity	
						3a	3b	3a	3b
1	2.5	1.97	0	0	0	38.39	63.40	22.12	13.62
2			0.075	0.008	0.43	38.80	63.27	21.14	13.01
3			0.150	0.017	0.85	38.29	62.96	20.50	12.19
4			0.225	0.025	1.27	38.64	64.24	20.05	11.87
5			0.300	0.034	1.69	38.49	61.85	19.57	10.92
6			0.375	0.042	2.11	39.47	61.08	18.54	10.69
7			0.450	0.051	2.52	38.20	61.50	18.02	10.28
8			0.525	0.059	2.92	37.80	59.70	17.30	9.97
9			0.600	0.068	3.33	38.40	59.35	17.01	9.88
10			0.675	0.076	3.73	31.20	59.10	15.19	9.29