Indole-azadiene conjugate as a colorimetric and fluorometric probe for selective fluoride ion sensing

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Electronic Supplementary Information (ESI†)

Contents

Evidence for no FHF^- dimer formation

Removal of the indolic NH protons of **1** by F^- does not occur. This is explained by ^1H NMR titration with F^-, as follows:

Fig. S1, A and B, are the ^1H NMR titration data with F^- in the presence and absence of **1** (3.8 mM, in DMSO-d_6). In the presence of **1** (Fig. S1A), as described in the manuscript, F^- addition leads to disappearance of the indolic NH protons of **1** (δ = 11.7 ppm) and upfield shift of the other protons. In this case, new signals assigned to FHF^- dimer appear at ca. 15–17 ppm. However, as shown in Fig. S1B, even in the absence of **1**, FHF^- dimer signals also appear. As reported,[1,2] *n*-tetrabutylammonium fluoride (*n*-$Bu_4N^+F^-$) used as the F^- source is a hydrous salt and decomposed to form FHF^- dimer. The FHF^- dimer signals observed in the absence of **1** is the impurity contained in *n*-$Bu_4N^+F^-$. The amount of FHF^- in the absence and presence of **1** was determined by ^1H NMR analysis using CH_2Cl_2 (7.6 mM) as an internal standard. The concentration of FHF^- obtained in the absence and presence of **1** is plotted in Fig. S1C. The data clearly show that the FHF^- concentration in the presence of **1** is almost the same as that obtained in the absence of **1**. As shown in Fig. S1A, up-field shift of the other protons of **1** almost stops upon addition of 15 equiv of F^-, indicating that almost all of **1** interacts with F^- at this F^- concentration. **If the NH protons of 1 is completely removed by reaction with F^- in a 1:2 stoichiometry, the FHF^- concentration increases 3.8 mM. However, the FHF^- concentration in the presence of 15 equiv of F^- is almost the same as that in the absence of F^-. The data clearly indicate that removal of NH protons of 1 does not occur in the present system.**

[1] R. K. Sharma, J. L. Fry, *J. Org. Chem.,* 1983, **48**, 2112.
[2] J. L. Sessler, H. Maeda, T. Mizuno, V. M. Lynch, H. Furuta, *J. Am. Chem. Soc.,* 2002, **124**, 13474.

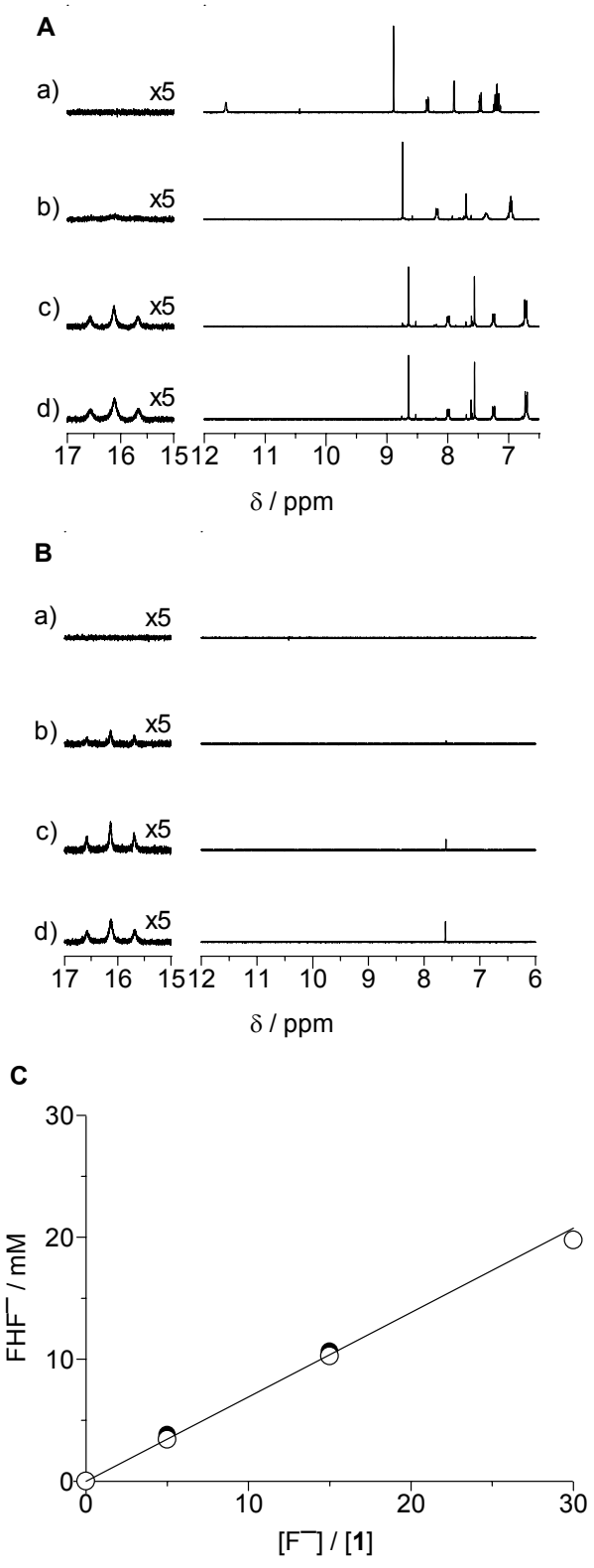


Fig. S1 ^{1}H NMR spectra upon addition of F^- in the (A) presence and (B) absence of **1** (3.8 mM) in DMSO-d_6. The equivalents of F^- added are (a) 0, (b) 5, (c) 15, and (d) 30, respectively. (C) Concentration of FHF^- dimer in solutions in the (black) presence and (white) absence of **1**, measured with CH_2Cl_2 (7.6 mM) as an internal standard.

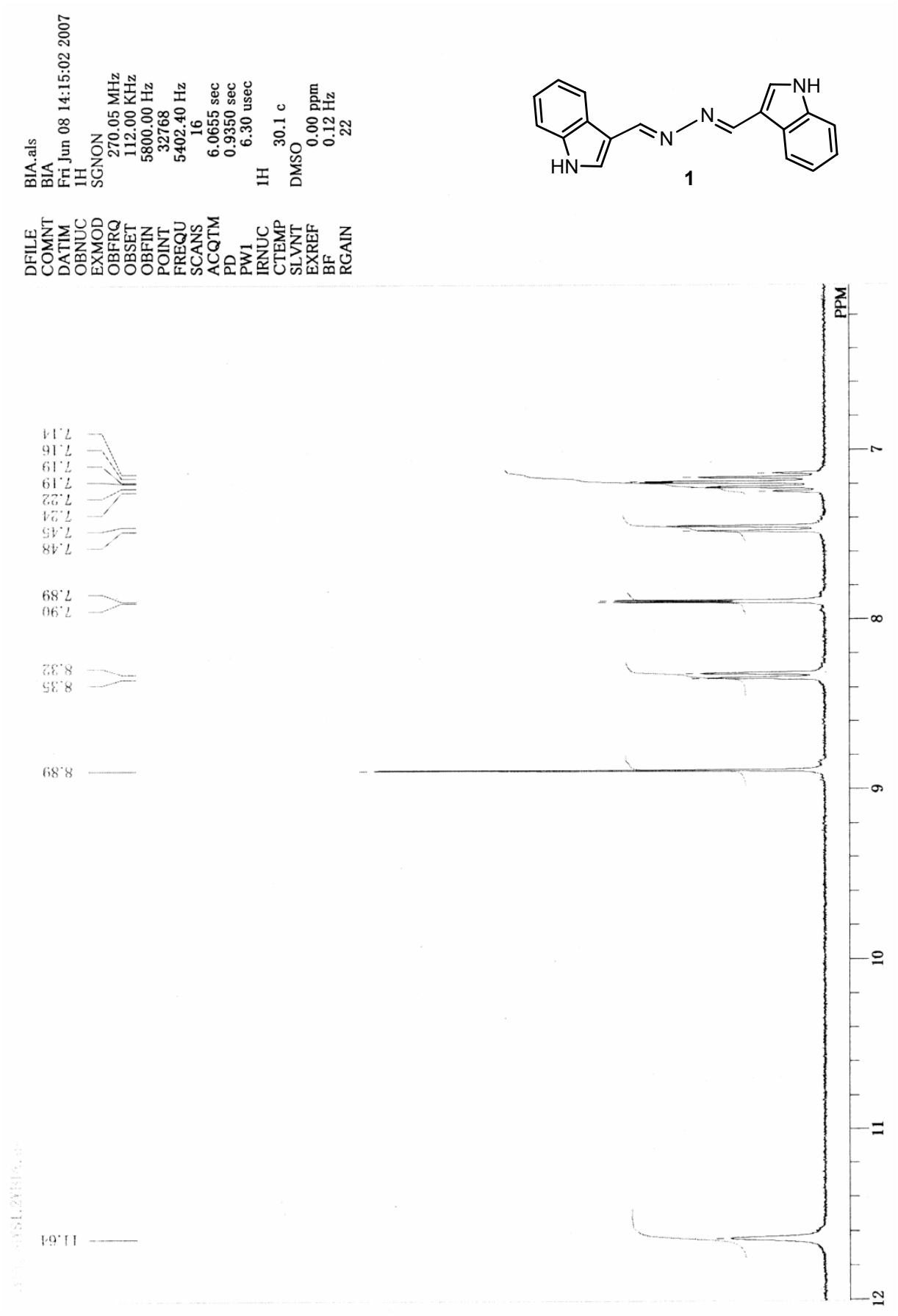


Fig. S2 ^{1}H NMR chart of **1** (DMSO-d_6, 270 MHz)

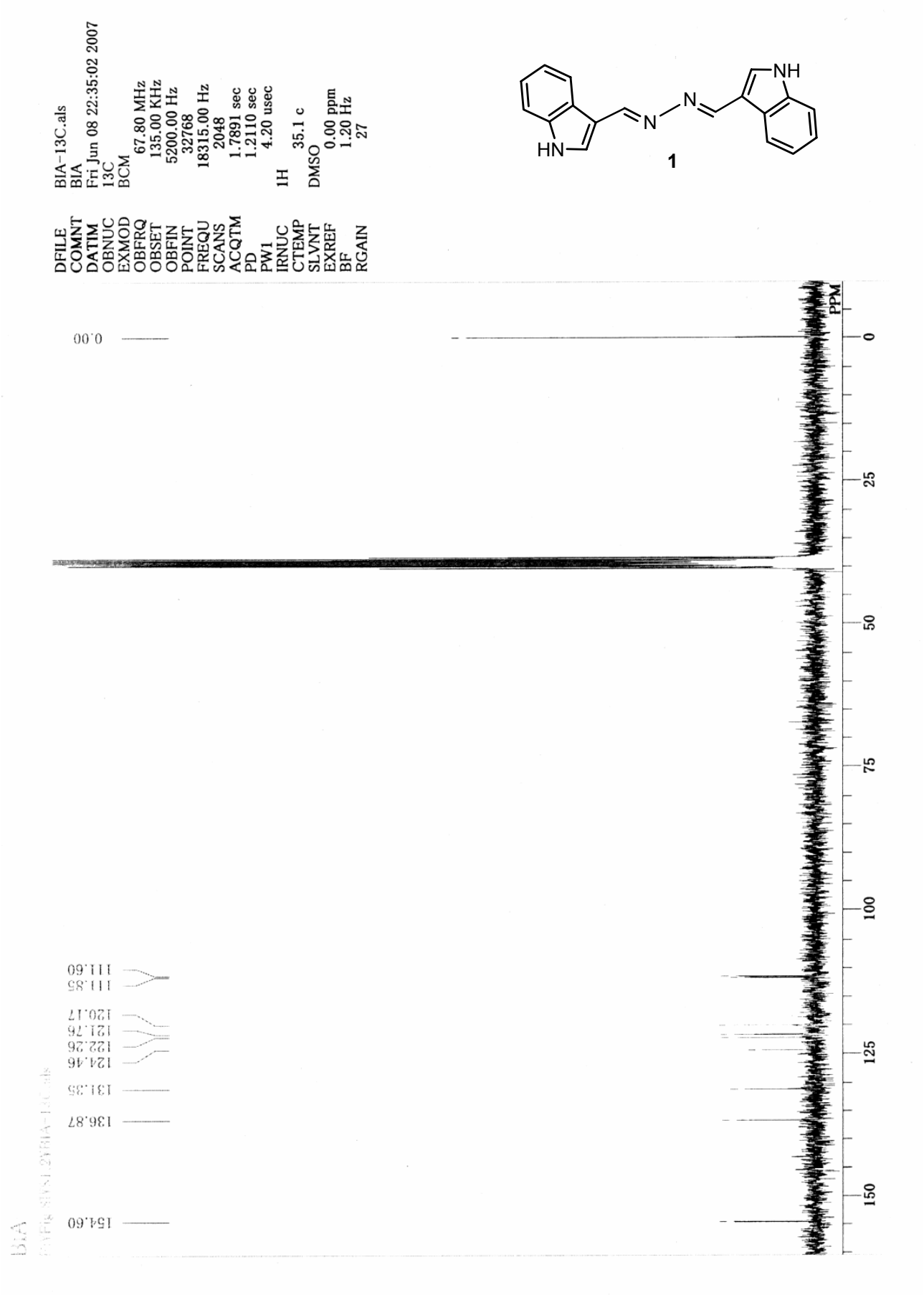


Fig. S3 ^{13}C NMR chart of **1** (DMSO-d_6, 68 MHz)

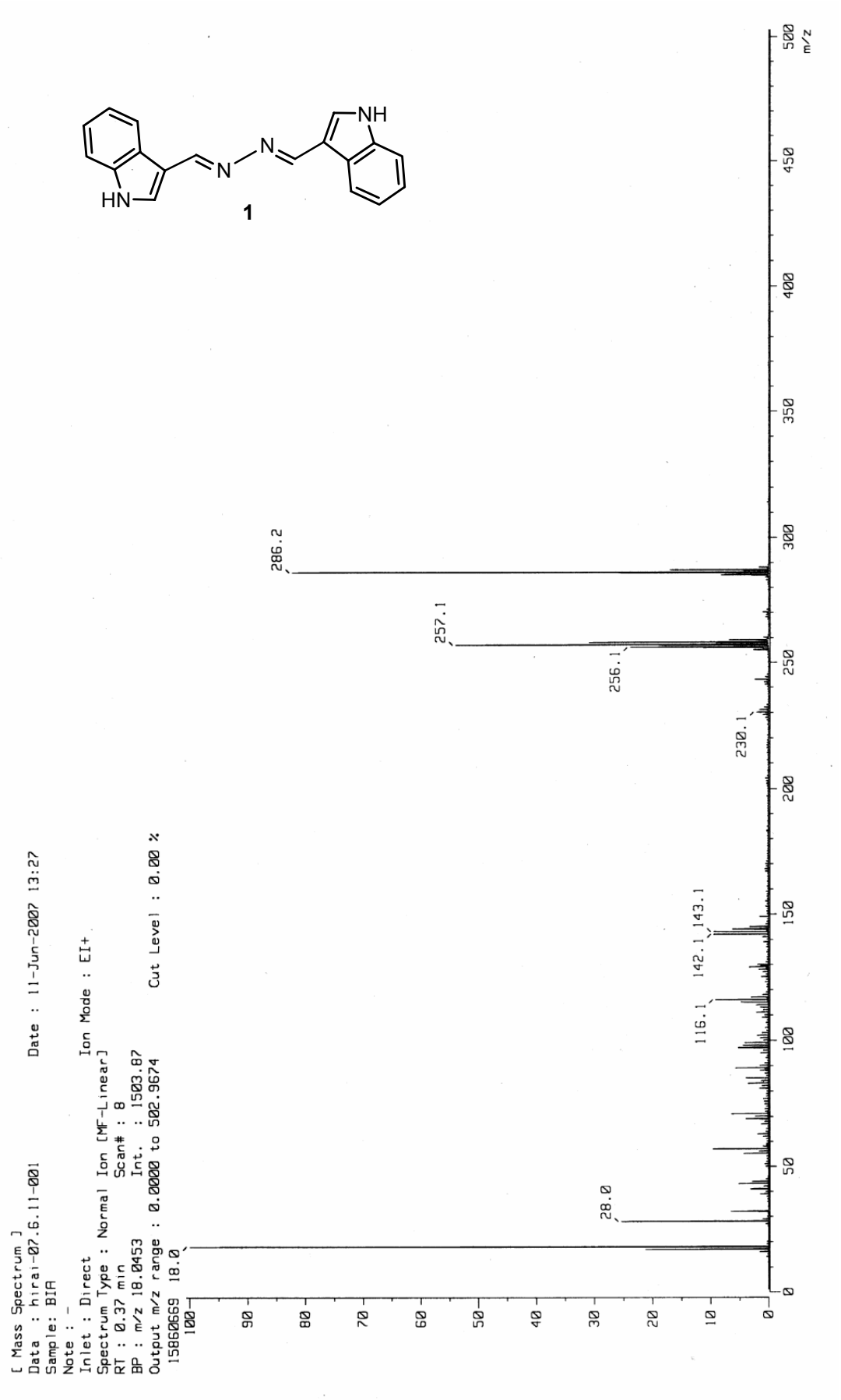


Fig. S4 EI-MS chart of **1**.

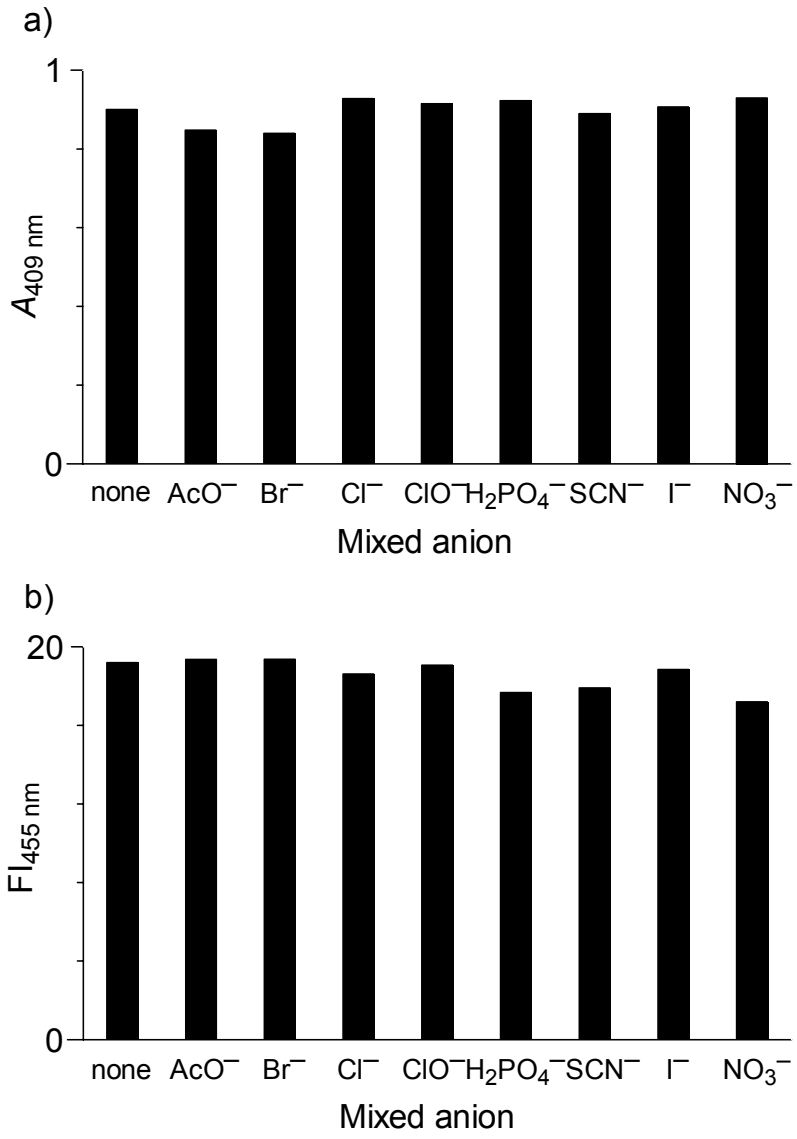


Fig. S5 (a) Absorbance at 409 nm and (b) fluorescence (λ_{ex} = 420 nm) intensity at 455 nm of **1** (25 μM), when measured with 50 equiv of F^- in the presence of 50 equiv of other anions (as a *n*-bu_4N^+ salt).

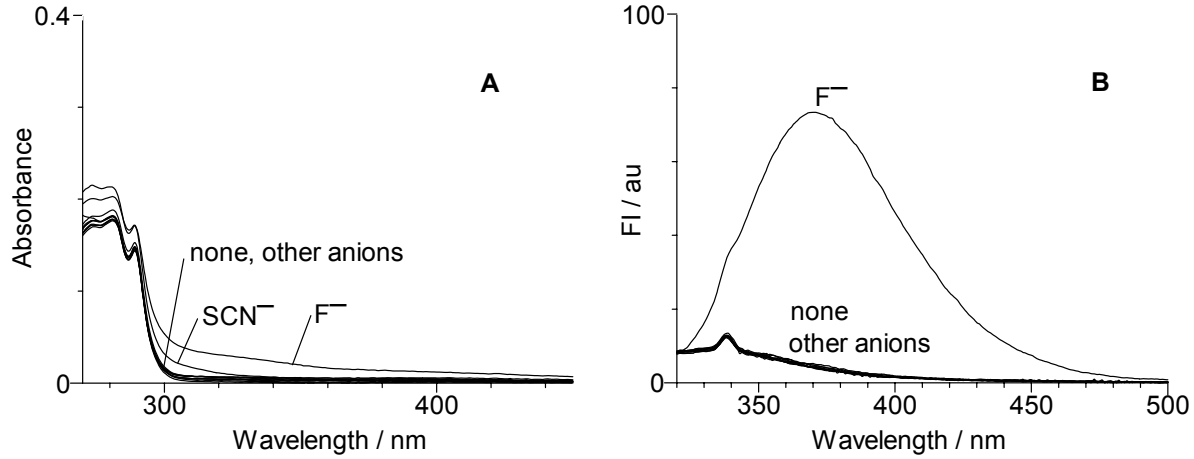


Fig. S6 Change in (A) absorption and (B) fluorescence (λ_{ex} = 310 nm) spectra of indole (25 μM) dissolved in DMSO upon addition of 50 equiv of respective anions (as a *n*-bu_4N^+ salt).

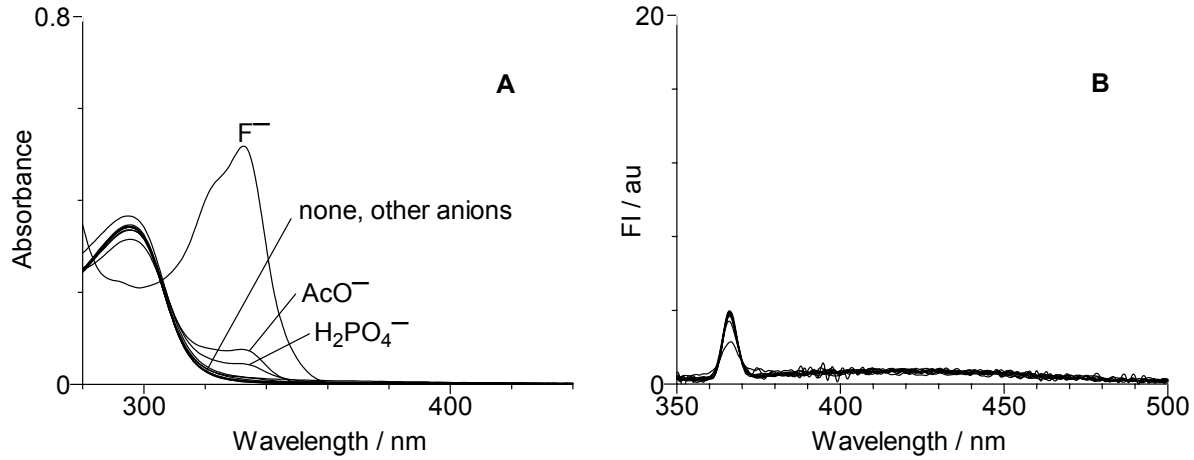


Fig. S7 Change in (A) absorption and (B) fluorescence (λ_{ex} = 333 nm) spectra of indole-3-carbaldehyde (25 μM) dissolved in DMSO upon addition of 50 equiv of respective anions (as a *n*-bu_4N^+ salt).

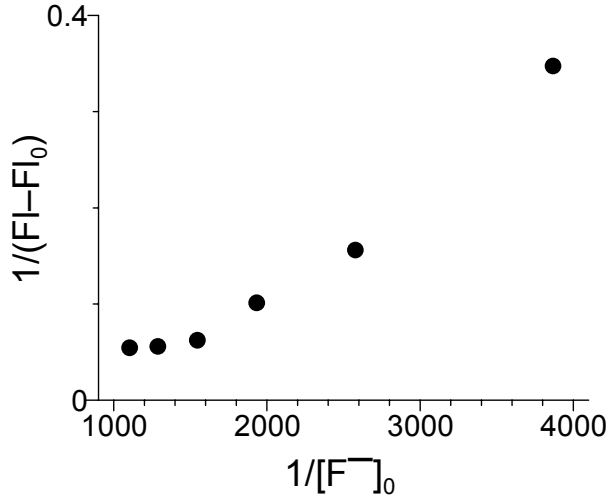


Fig. S8 Benesi-Hildebrand plots (λ_{em} = 455 nm) of **1**, assuming 1:1 stoichiometry for association between **1** and F^-.

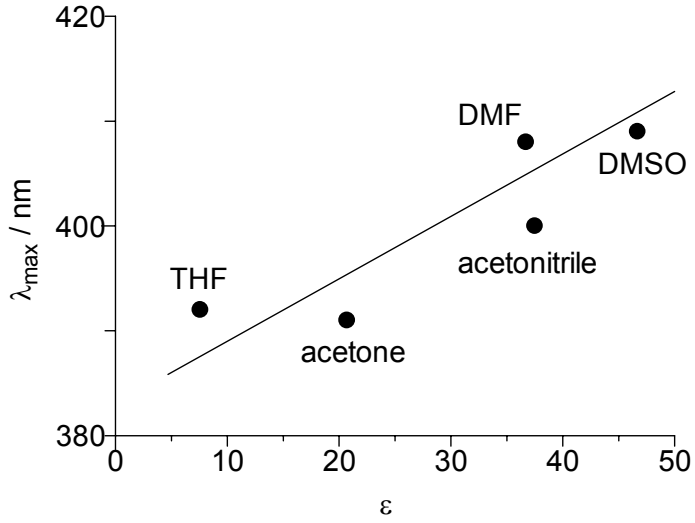
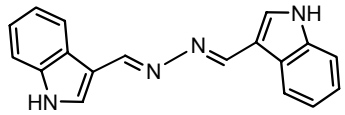
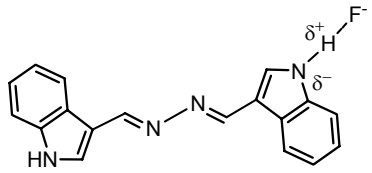
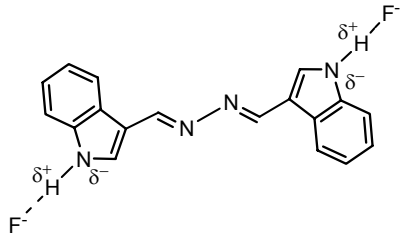


Fig. S9 Relationship between λ_{max} of the absorption band of **1**-2F^- complex and the dielectric constants for the medium, ε, where the respective ε values are cited from literature (B. R. Knauer and J. J. Napier, *J. Am. Chem. Soc.*, 1976, **98**, 4395). The measurements were carried out with **1** (25 μM) and 500 equiv (THF), 200 equiv (acetone), 100 equiv (DMF), and 50 equiv (MeCN and DMSO) of F^-.

Table S1. Calculated excitation energy (*E*), wavelength (λ), and oscillator strength (*f*) for low-laying singlet states (S_n) of free **1** and **1**-F^- and **1**-$2F^-$ complexes.

	orbital transition (CIC[a])	*E* (eV)	λ (nm)	*f*
				
1				
$\Delta H_f° = -4082.93$ kJ mol^{-1}				
$S_0 \rightarrow S_1$	HOMO → LUMO (0.65)	3.3157	373.93	1.2927
$S_0 \rightarrow S_2$	HOMO–4 → LUMO (0.69)	3.7258	332.78	0.0010
$S_0 \rightarrow S_3$	HOMO–1 → LUMO (0.56) HOMO → LUMO+1 (–0.40) HOMO–3 → LUMO (0.12)	4.0162	308.71	0.0000
				
1–F^-				
$\Delta H_f° = -5066.16$ kJ mol^{-1}				
$S_0 \rightarrow S_1$	HOMO → LUMO (0.65)	3.0712	403.70	1.3846
$S_0 \rightarrow S_2$	HOMO–2 → LUMO (0.69)	3.7247	332.87	0.0008
$S_0 \rightarrow S_3$	HOMO → LUMO (0.65) HOMO–2→LUMO+1 (0.17) HOMO–1→LUMO+1 (0.12)	3.7969	326.54	0.1416
				
1–$2F^-$				
$\Delta H_f° = -5633.54$ kJ mol^{-1}				
$S_0 \rightarrow S_1$	HOMO → LUMO (0.65)	2.9939	414.12	1.5771
$S_0 \rightarrow S_2$	HOMO–5 → LUMO (0.69)	3.5888	345.47	0.0008
$S_0 \rightarrow S_3$	HOMO → LUMO+1 (0.64) HOMO–1 → LUMO (–0.20) HOMO–3 → LUMO (–0.12)	3.7464	330.94	0.0000

[a] CI expansion coefficients for the main orbital transitions.

Cartesian Coordinates (in Å) of 1

C	1.665692	0.241590	-0.000340
N	0.555401	-0.420039	-0.000227
N	-0.555401	0.420039	-0.000442
C	-1.665692	-0.241590	-0.000171
C	2.952324	-0.416489	-0.000281
C	3.180611	-1.780150	-0.000355
N	4.530173	-2.024075	-0.000201
C	5.222952	-0.824298	0.000023
C	6.597931	-0.574076	0.000279
C	7.005752	0.755081	0.000480
C	6.065273	1.804907	0.000461
C	4.699489	1.548277	0.000218
C	4.255697	0.215638	-0.000028
C	-2.952324	0.416489	-0.000157
C	-3.180611	1.780150	-0.000346
N	-4.530173	2.024074	-0.000245
C	-5.222952	0.824298	0.000011
C	-6.597931	0.574076	0.000189
C	-7.005752	-0.755080	0.000406
C	-6.065273	-1.804907	0.000438
C	-4.699490	-1.548277	0.000250
C	-4.255697	-0.215638	0.000039
H	1.646045	1.336337	-0.000352
H	-1.646045	-1.336337	0.000366
H	2.460566	-2.585259	-0.000501
H	4.952126	-2.940102	-0.001058
H	7.321102	-1.385558	0.000287
H	8.067003	0.987595	0.000652
H	6.417417	2.832788	0.000644
H	3.987072	2.368899	0.000232
H	-2.460566	2.585258	-0.000524
H	-4.952126	2.940103	-0.000243
H	-7.321102	1.385558	0.000154
H	-8.067003	-0.987595	0.000553
H	-6.417417	-2.832788	0.000615
H	-3.987072	-2.368899	0.000282

Cartesian Coordinates (in Å) of 1–F^- Complex

C	1.268422	-0.417775	-0.000212
N	0.195267	0.340921	-0.000314
N	-0.954494	-0.418689	-0.000401
C	-2.045064	0.277960	-0.000177
C	2.595659	0.071937	-0.000122
C	3.029756	1.425663	-0.000096
N	4.358634	1.557537	-0.000181
C	4.870157	0.267146	0.000084
C	6.217697	-0.107875	0.000281
C	6.520065	-1.467579	0.000444
C	5.494060	-2.435091	0.000416
C	4.150032	-2.063429	0.000227
C	3.819653	-0.699053	0.000063
C	-3.348234	-0.362245	-0.000198
C	-3.608058	-1.717235	-0.000479
N	-4.974255	-1.938012	-0.000317
C	-5.636117	-0.727903	-0.000061
N	-7.004516	-0.439603	0.000114
C	-7.381503	0.899505	0.000407
C	-6.415399	1.926207	0.000521
C	-5.056005	1.633278	0.000341
C	-4.641148	0.291245	0.000043
H	-5.414120	-2.844322	-0.000413
H	5.510497	2.630216	-0.000268
F	6.392232	3.087413	-0.000316
H	1.127997	-1.506565	-0.000166
H	-2.000621	1.372416	0.000056
H	2.379882	2.294472	-0.000157
H	6.977363	0.668645	0.000279
H	7.559759	-1.790500	0.000584
H	5.756758	-3.491962	0.000542
H	3.373067	-2.826784	0.000217
H	-2.904676	-2.536652	-0.000723
H	-7.748366	-1.233396	0.000039
H	-8.437840	1.157087	0.000560
H	-6.741350	2.963376	0.000756
H	-4.321251	2.434045	0.000431

Cartesian Coordinates (in Å) of 1–2F⁻ Complex

F	-6.841838	2.978717	0.000845	C	-6.879838	-1.611659	-0.000379
C	1.642440	0.413675	0.000208	C	-5.819210	-2.545559	-0.000392
N	0.598749	-0.361120	0.000216	C	-4.489565	-2.127635	-0.000282
N	-0.598782	0.361077	0.000172	C	-4.198670	-0.751259	-0.000154
C	-1.642472	-0.413718	0.000218	H	-5.950187	2.503989	0.000691
C	3.002871	-0.053443	0.000101	H	5.950400	-2.503812	0.000712
C	3.474353	-1.382469	-0.000073	F	6.842177	-2.978303	0.000604
N	4.821095	-1.479835	0.000296	H	1.485578	1.501353	0.000133
C	5.287072	-0.183216	-0.000039	H	-1.485610	-1.501396	0.000234
C	6.621971	0.243396	-0.000168	H	2.852106	-2.271503	-0.000126
C	6.879777	1.611621	-0.000369	H	7.407843	-0.507878	-0.000079
C	5.819149	2.545517	-0.000453	H	7.909262	1.969714	-0.000438
C	4.489512	2.127573	-0.000340	H	6.045639	3.611838	-0.000585
C	4.198646	0.751191	-0.000131	H	3.686910	2.864495	-0.000387
C	-3.002906	0.053398	0.000050	H	-2.852180	2.271471	-0.000414
C	-3.474405	1.382423	-0.000264	H	-7.407852	0.507868	-0.000191
N	-4.821155	1.479747	0.000148	H	-7.909323	-1.969748	-0.000425
C	-5.287100	0.183145	-0.000149	H	-6.045708	-3.611878	-0.000459
C	-6.622007	-0.243438	-0.000261	H	-3.686982	-2.864578	-0.000266