Effects of substituents on fluorometric detection of cyanide anion by indolium–coumarin dyads

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Electronic Supplementary Information (ESI†)

CONTENTS

Methods

Nonlinear fitting of the fluorescence and absorption titration data[1]

When assuming a 1:1 stoichiometry for interaction between the receptor (**X**) and CN^-, the equilibrium is given by the following equation:

$$\mathbf{X} + \mathbf{CN}^- \xleftrightarrow{K_{\text{assoc}}} \mathbf{X}\cdot\mathbf{CN}^- \qquad (1)$$

The association constant, K_{assoc}, is expressed as:

$$K_{\text{assoc}} = \frac{[\mathbf{X}\cdot\mathbf{CN}^-]}{[\mathbf{X}][\mathbf{CN}^-]} = \frac{[\mathbf{X}\cdot\mathbf{CN}^-]}{([\mathbf{X}]_0 - [\mathbf{X}\cdot\mathbf{CN}^-])([\mathbf{CN}^-]_0 - [\mathbf{X}\cdot\mathbf{CN}^-])} \qquad (2)$$

[**X·CN**$^-$], [**X**], and [**CN**$^-$] are the equilibrium concentrations of the **X**–**CN**$^-$ species, free **X**, and free CN^-, respectively. $[\mathbf{X}]_0$ and $[\mathbf{CN}^-]_0$ are the initial concentrations of **X** and CN^-, respectively. The eq. 2 is transformed to:

$$[\mathbf{X}\cdot\mathbf{CN}^-] = \frac{([\mathbf{X}]_0 + [\mathbf{CN}^-]_0 + 1/K_{\text{assoc}}) - \sqrt{([\mathbf{X}]_0 + [\mathbf{CN}^-]_0 + 1/K_{\text{assoc}})^2 - 4[\mathbf{X}]_0[\mathbf{CN}^-]_0}}{2} \qquad (3)$$

Fluorescence intensity is given as follows:[2]

$$I_0 = \Phi^{\lambda}_{\mathbf{X}}[\mathbf{X}]_0 \qquad (4)$$

$$I = \Phi^{\lambda}_{\mathbf{X}}[\mathbf{X}] + \Phi^{\lambda}_{\mathbf{X}\cdot\mathbf{CN}^-}[\mathbf{X}\cdot\mathbf{CN}^-] \qquad (5)$$

$$I_{\max} = \Phi^{\lambda}_{\mathbf{X}}[\mathbf{X}]_{\max} + \Phi^{\lambda}_{\mathbf{X}\cdot\mathbf{CN}^-}[\mathbf{X}\cdot\mathbf{CN}^-]_{\max} \qquad (6)$$

I_0 is the intensity of **X** without anion, I is the intensity of **X** obtained with CN^-, and $I_{\max}$ is the intensity of **X** in the presence of excess amount of CN^-. $\Phi^{\lambda}_{\mathbf{X}}$ and $\Phi^{\lambda}_{\mathbf{X}\cdot\mathbf{CN}^-}$ are the fluorescence quantum yields for **X** and **X**–**CN**$^-$. By means of eqs 4, 5 and 6, the following equation is obtained:

$$\frac{I_{\max} - I_0}{I - I_0} = \frac{[\mathbf{X}\cdot\mathbf{CN}^-]_{\max}}{[\mathbf{X}\cdot\mathbf{CN}^-]} \qquad (7)$$

With excess amount of CN^-, $[\mathbf{X}\cdot\mathbf{CN}^-]_{\max}$ is almost equal to $[\mathbf{X}]_0$. The eq 7 can therefore be replaced as follows:

$$\frac{I_{\max} - I_0}{I - I_0} = \frac{[\mathbf{X}]_0}{[\mathbf{X}\cdot\mathbf{CN}^-]} \qquad (8)$$

From eq. 3 and 8, the following equation is obtained:

$$I = I_0 + \frac{I_{\max} - I_0}{2[\mathbf{X}]_0}\{([\mathbf{X}]_0 + [\mathbf{CN}^-]_0 + 1/K_{\text{assoc}}) - \sqrt{([\mathbf{X}]_0 + [\mathbf{CN}^-]_0 + 1/K_{\text{assoc}})^2 - 4[\mathbf{X}]_0[\mathbf{CN}^-]_0}\} \qquad (9)$$

The eq. 9 was used for fitting of the fluorescence titration data with CN^-.

Absorbance is given by the Beer-Lambert law as follows:

$$A_0 = \varepsilon_0[\mathbf{X}]_0 l \qquad (10)$$

$$A = \varepsilon_0[\mathbf{X}]l + \varepsilon_\infty[\mathbf{X}\cdot\mathbf{CN}^-]l \qquad (11)$$

$$A_{\max} = \varepsilon_0[\mathbf{X}]l + \varepsilon_\infty[\mathbf{X}\cdot\mathbf{CN}^-]_{\max} l \qquad (12)$$

A_0 is the absorbance of **X** without anions, A is the absorbance of **X** obtained with CN^-, and $A_{\max}$ is the absorbance of **X** in the presence of excess amount of CN^-. The eq. 2 can therefore be replaced as follows:

$$\frac{A_{\max} - A_0}{A - A_0} = K_{\text{assoc}}[\mathbf{X}\cdot\mathbf{CN}^-] \qquad (13)$$

From eqs. 3 and 13, the following equation is obtained:

$$A = A_0 + \frac{A_{\max} - A_0}{2[\mathbf{X}]_0}\{([\mathbf{X}]_0 + [\mathbf{CN}^-]_0 + 1/K_{\text{assoc}}) - \sqrt{([\mathbf{X}]_0 + [\mathbf{CN}^-]_0 + 1/K_{\text{assoc}})^2 - 4[\mathbf{X}]_0[\mathbf{CN}^-]_0}\} \qquad (14)$$

The eq. 14 was used for fitting of the absorption titration data with CN^-.

[1] J. Bourson, J. Pouget, B. Valeur, *J. Phys. Chem.* **1993**, *97*, 4552–4557.

[2] R. Yang, K. Li, K. Wang, F. Zhao, N. Li, F. Liu, *Anal. Chem.* **2003**, *75*, 612–621.

Table S1 Calculated excitation energy (E), wavelength (λ), and oscillator strength (f) for low-laying singlet state (S_n) of **4**, **4**–CN^-, and **4**–OH^- species.

species		Main orbital transition (CIC[a])	E (eV) [λ (nm)]	f
4	$S_0 \rightarrow S_1$	HOMO → LUMO (0.62468)	2.272 [545.7]	1.8572
	$S_0 \rightarrow S_2$	HOMO–1 → LUMO (–0.24236) HOMO → LUMO+1 (0.64459)	2.980 [416.1]	0.1782
4–CN^-	$S_0 \rightarrow S_2$	HOMO–1 → LUMO (0.15721) HOMO → LUMO+1 (0.62172)	3.166 [391.7]	1.4472
	$S_0 \rightarrow S_3$	HOMO–1 → LUMO (0.61699) HOMO → LUMO+1 (–0.14169)	3.446 [359.8]	0.2236
4–OH^-	$S_0 \rightarrow S_2$	HOMO-1 → LUMO (0.22718) HOMO → LUMO+1 (0.60097)	3.182 [389.7]	1.4779
	$S_0 \rightarrow S_3$	HOMO–1 → LUMO (0.58629) HOMO → LUMO+1 (–0.21385)	3.392 [365.6]	0.1420

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

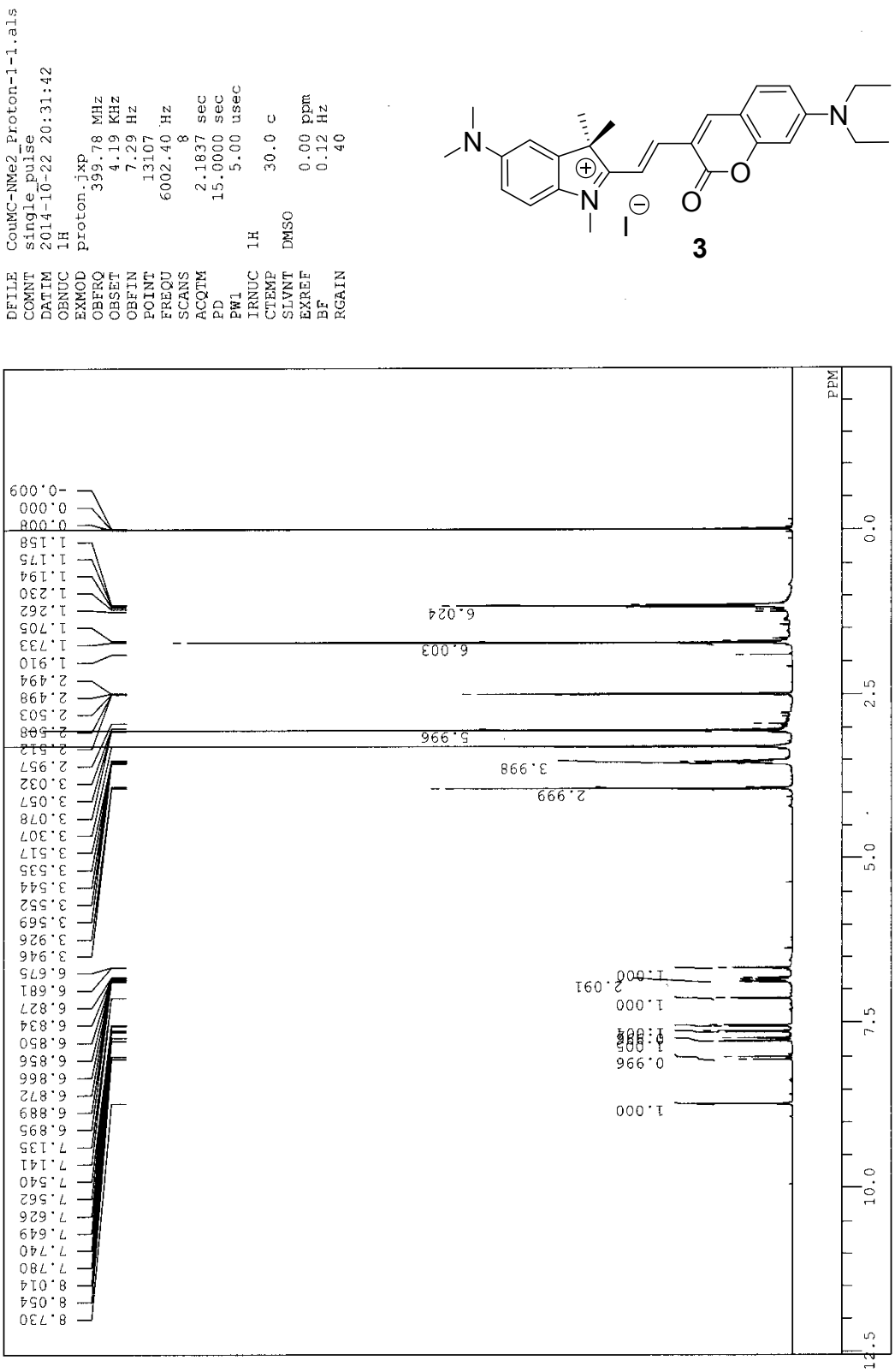


Fig. S1 ^{1}H NMR chart of **3** (DMSO-d_6, 400 MHz).

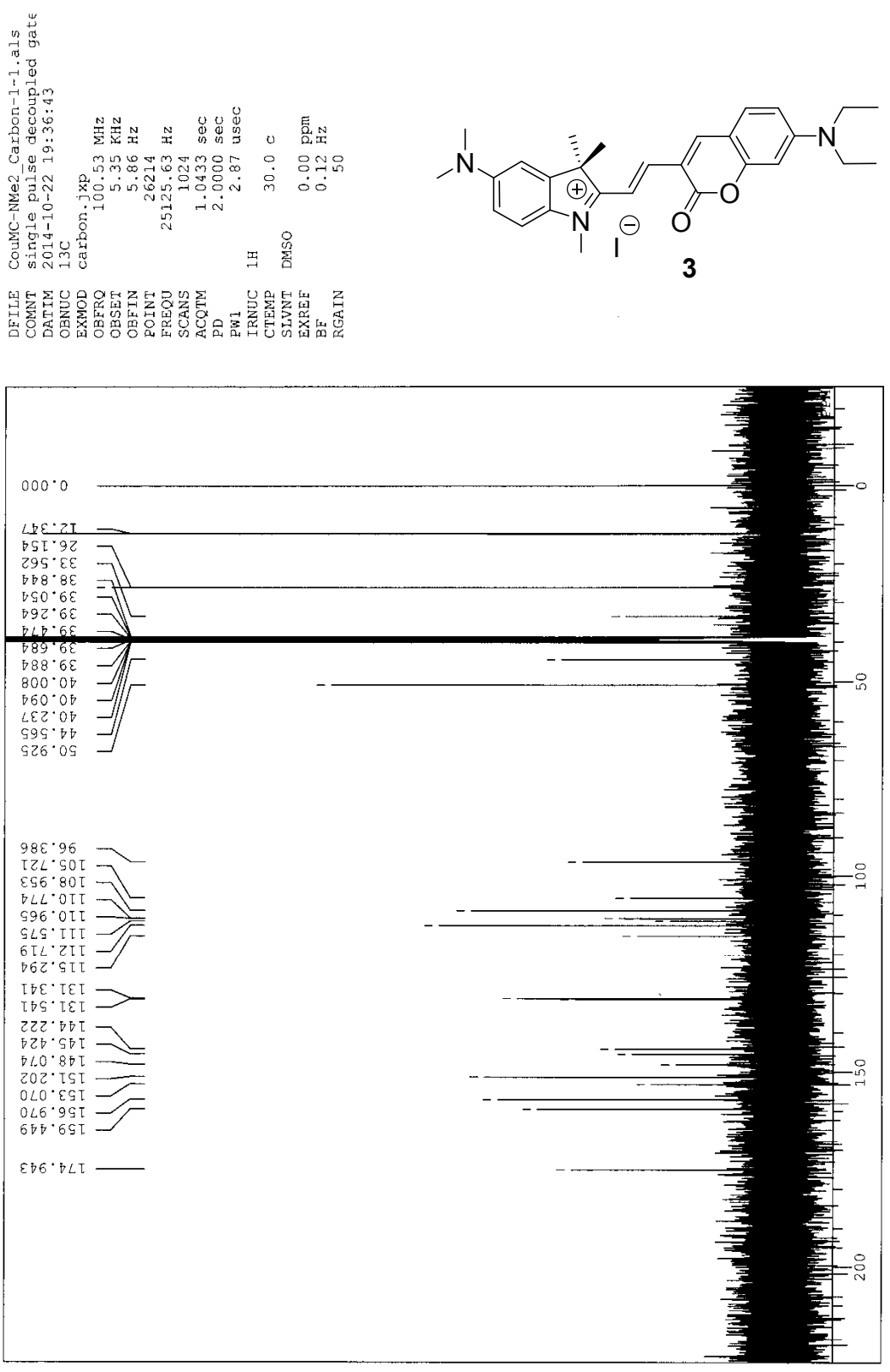


Fig. S2 ^{13}C NMR chart of **3** (DMSO-d_6, 100 MHz).

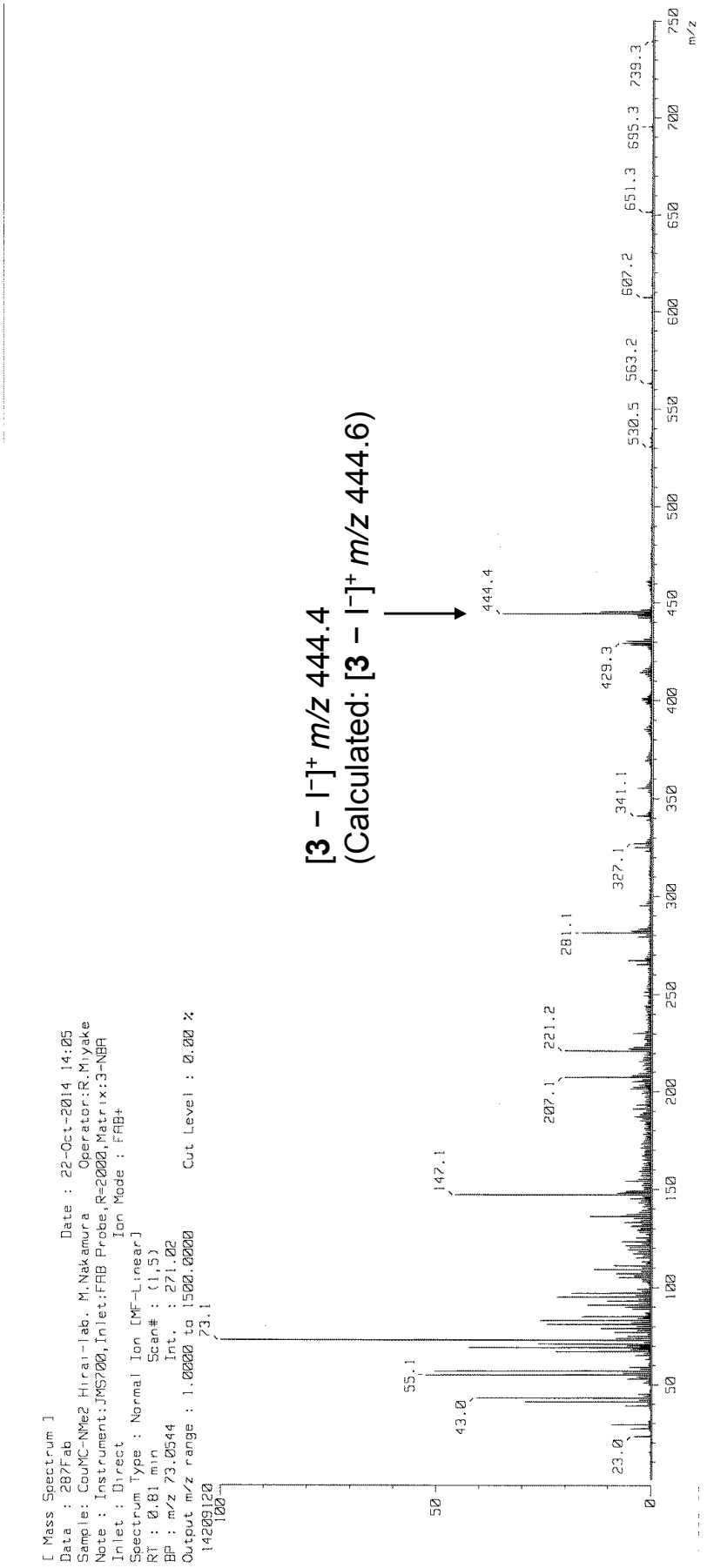


Fig. S3 FAB-MS chart of **3**.

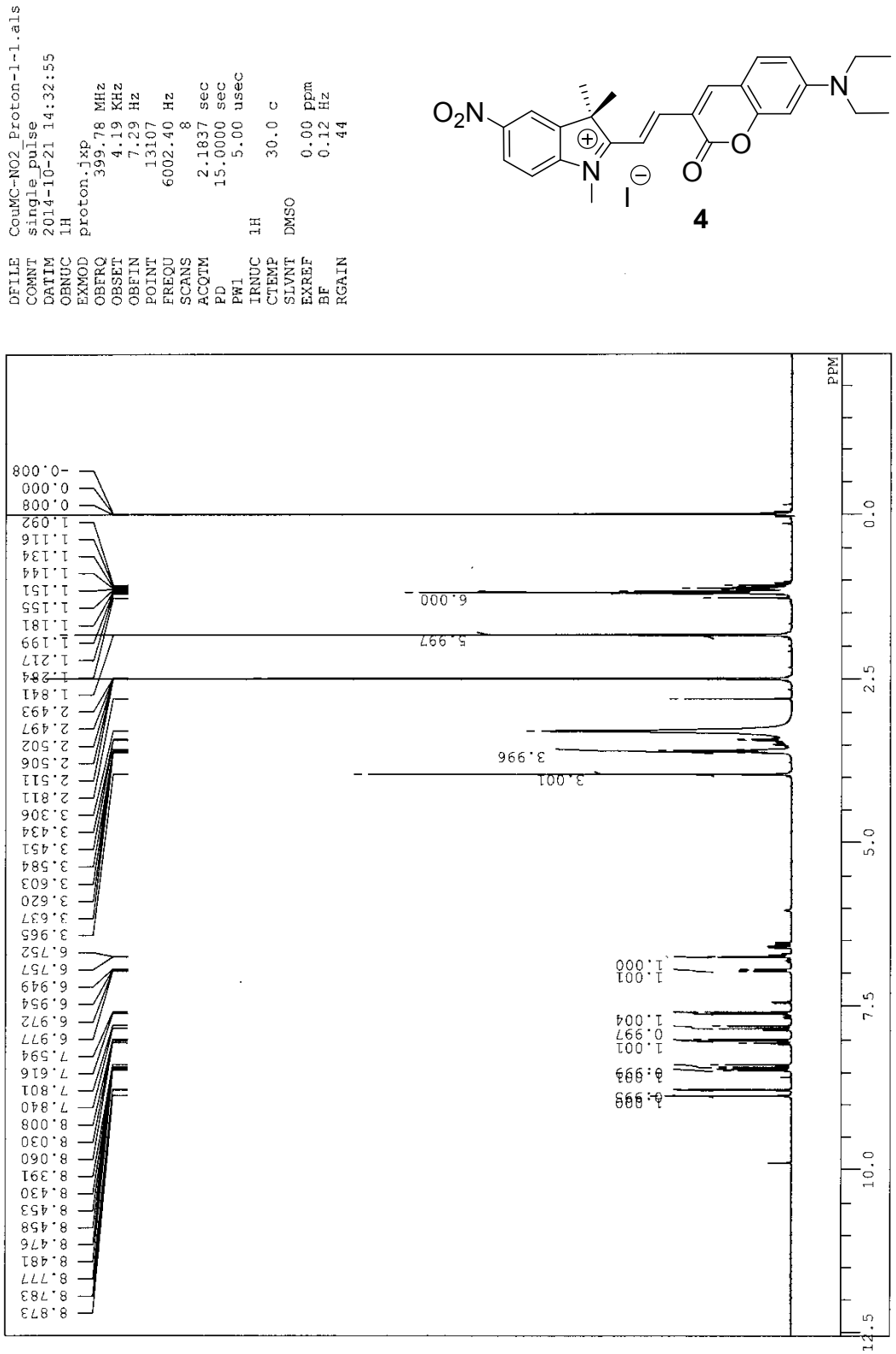


Fig. S4 ^{1}H NMR chart of **4** (DMSO-d_6, 400 MHz).

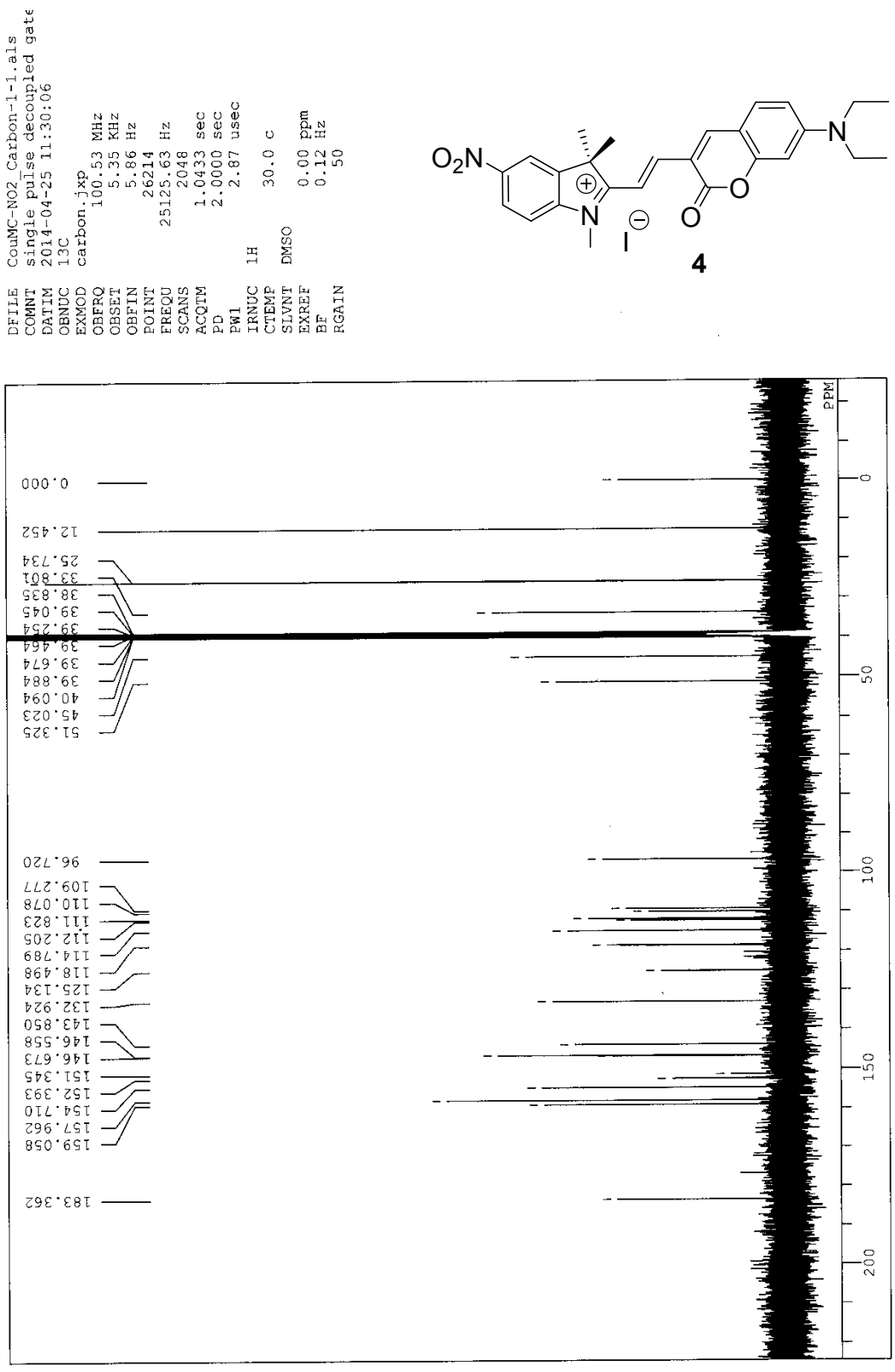


Fig. S5 ^{13}C NMR chart of **4** (DMSO-d_6, 100 MHz).

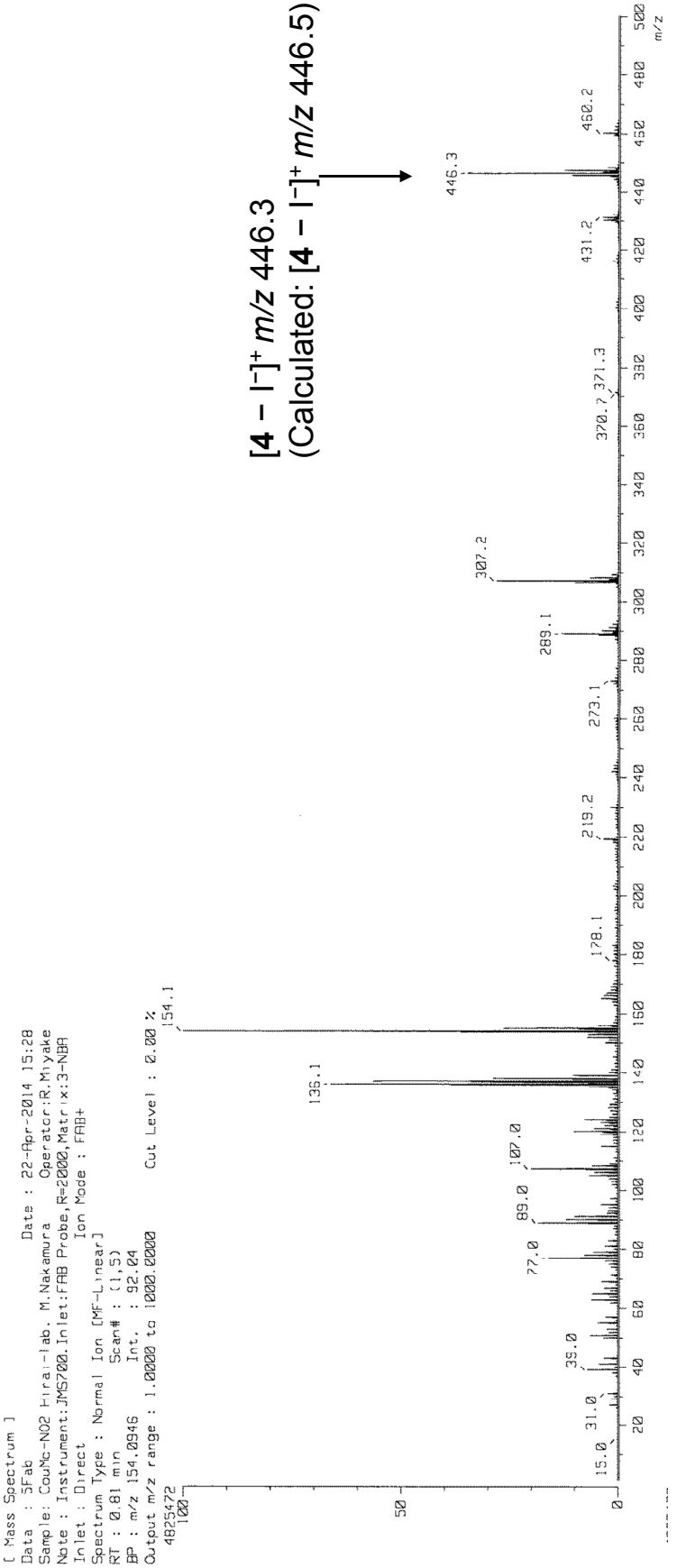


Fig. S6 FAB-MS chart of **4**.

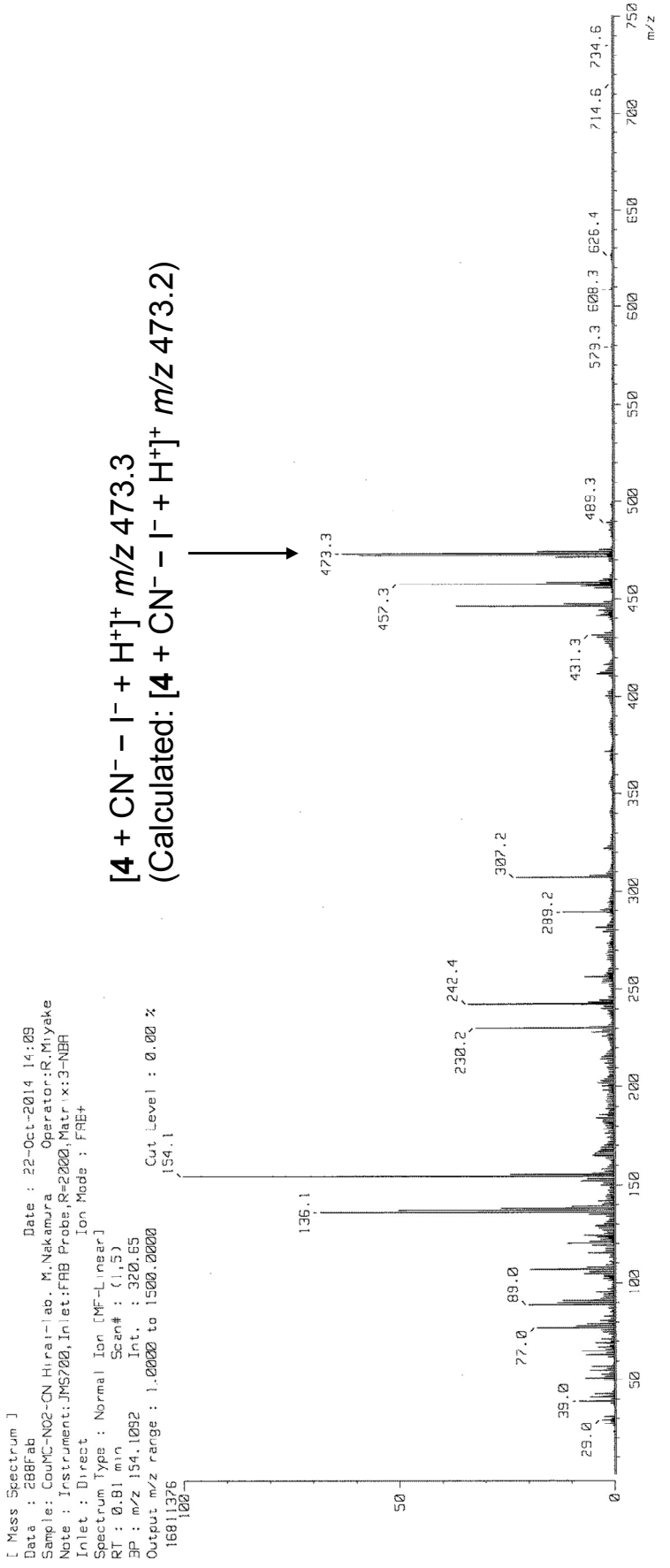


Fig. S7 FAB-MS chart of **4**-CN^- species.

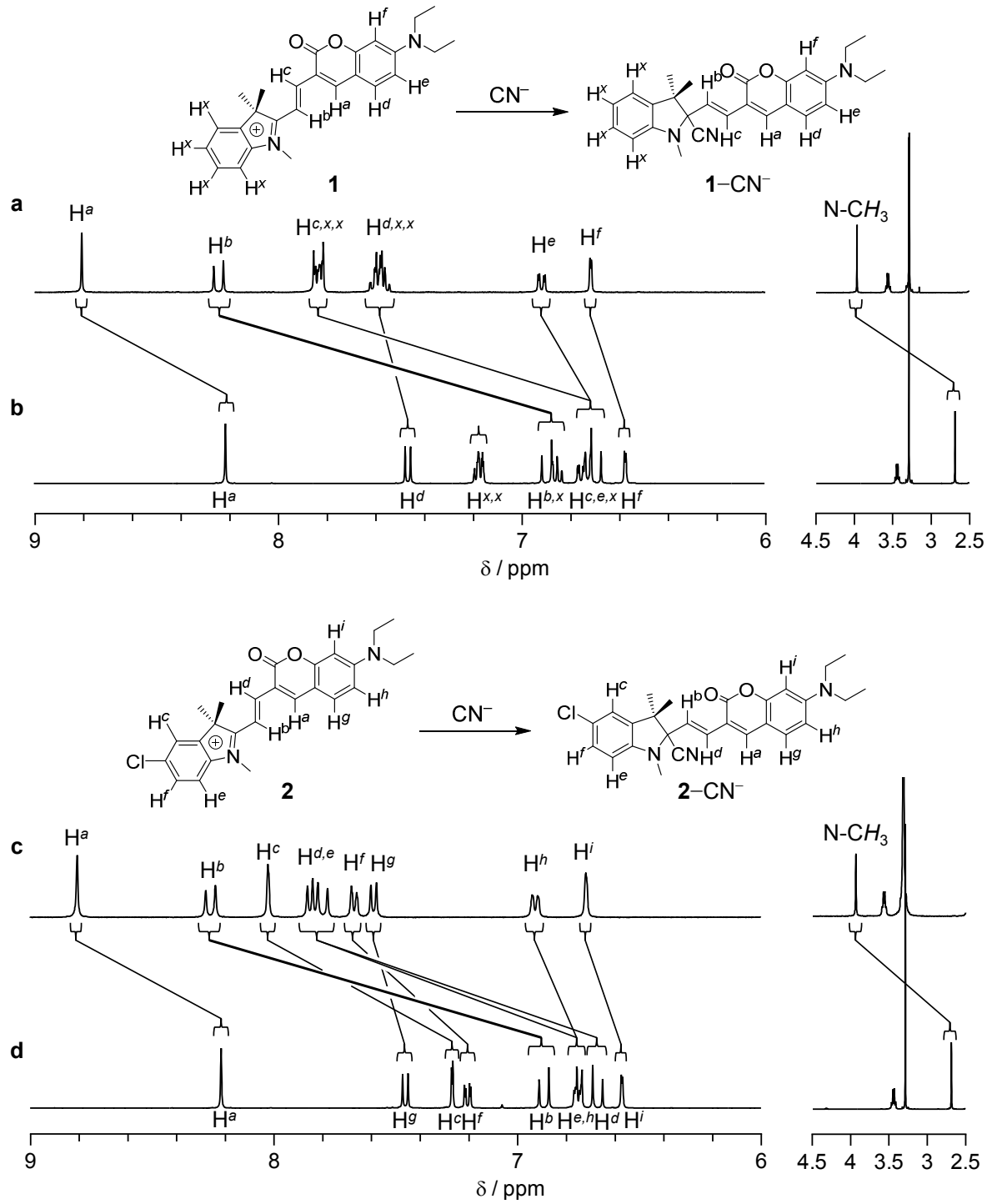


Fig. S8 ^{1}H NMR charts (400 MHz, 30 °C, DMSO-d_6) of (a) **1** (30 mM), (b) **1**−CN^- (30 mM), (c) **2** (30 mM), and (d) **2**−CN^- (30 mM). The intensity in the region of 2.5–4.5 ppm is scaled down to 1/3.

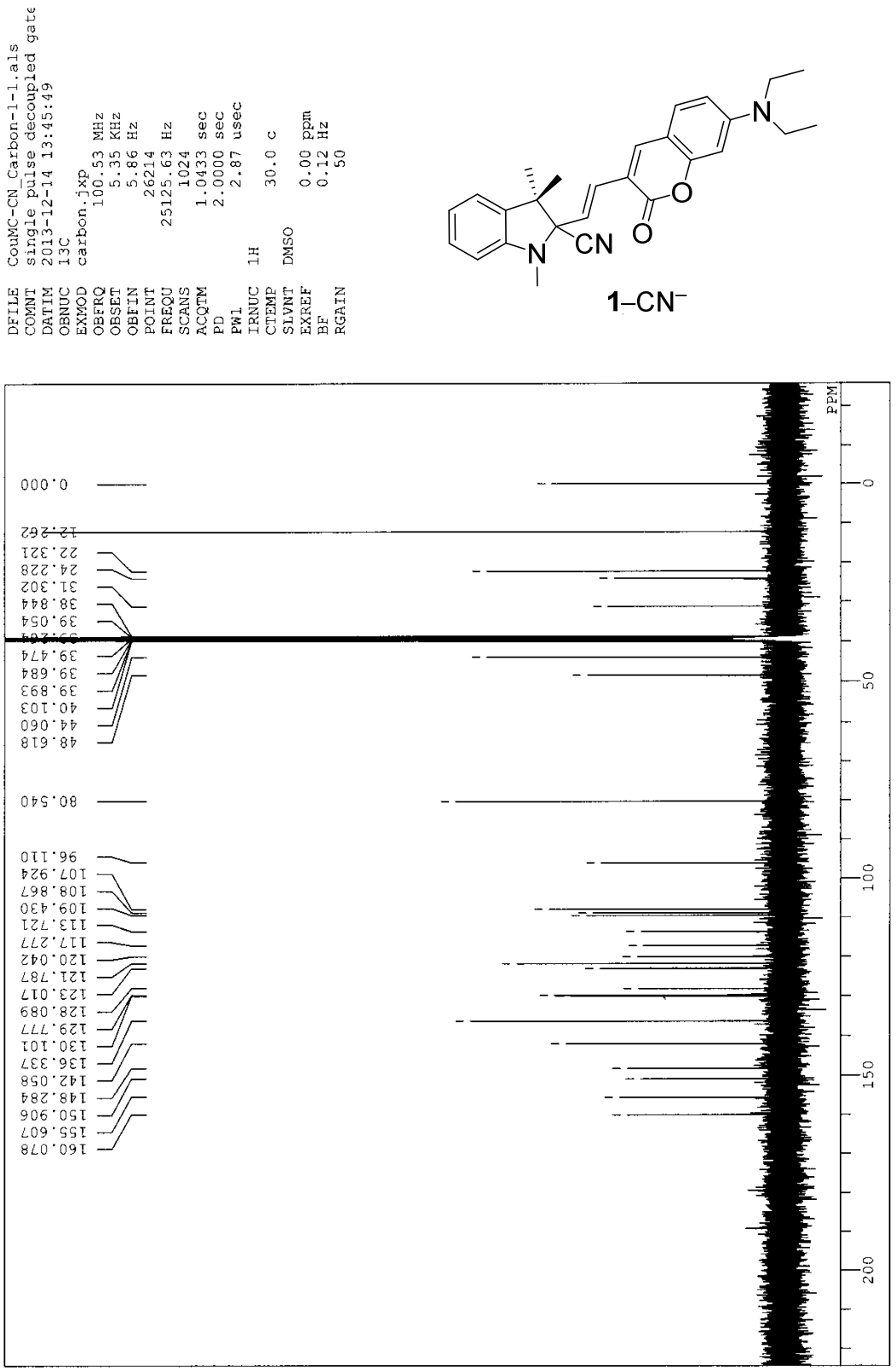


Fig. S9 ^{13}C NMR chart of **1**-CN$^-$ species (DMSO-d_6, 100 MHz)

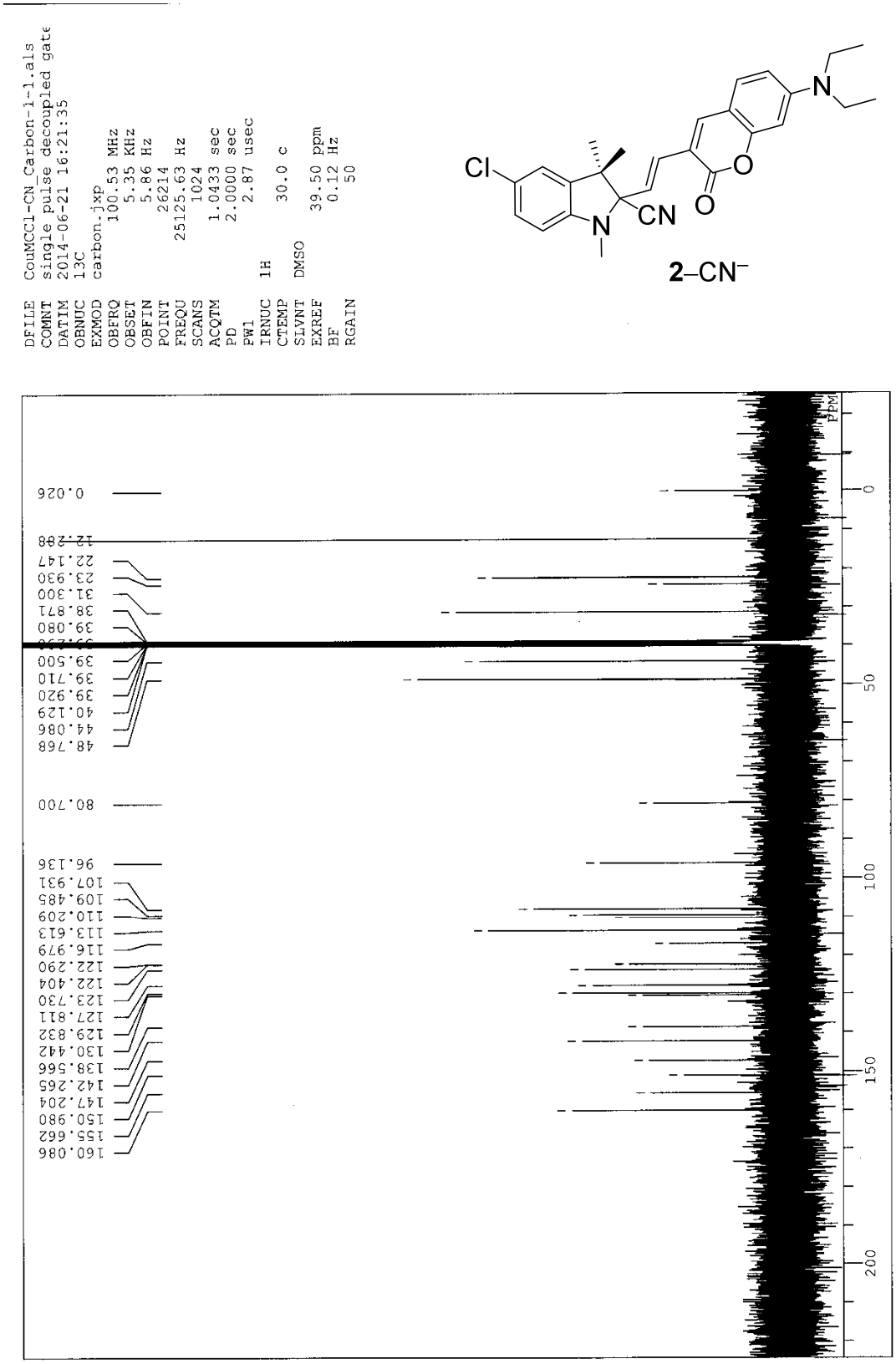


Fig. S10 ^{13}C NMR chart of **2**-CN$^-$ species (DMSO-d$_6$, 100 MHz)

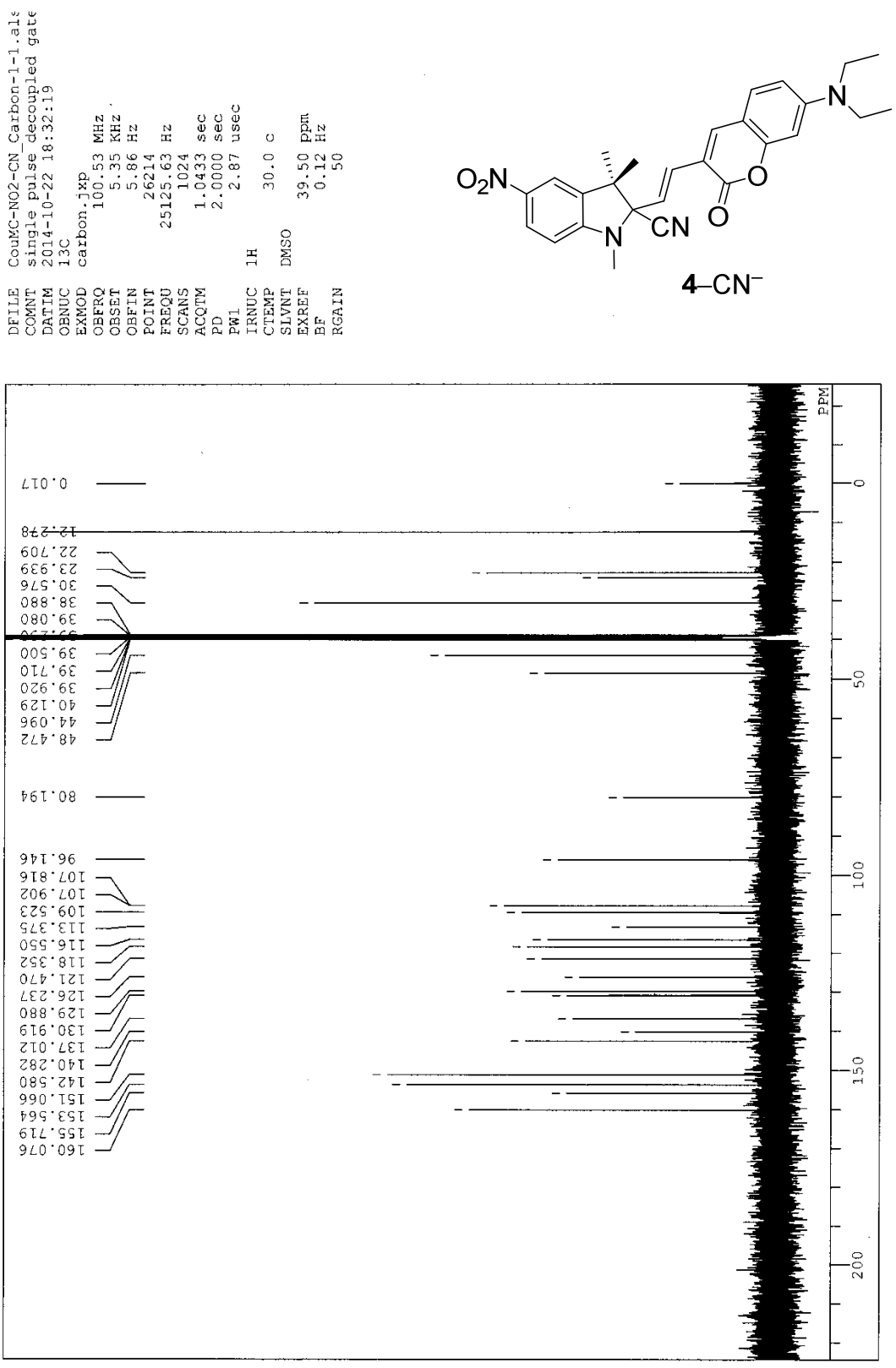


Fig. S11 ^{13}C NMR chart of **4**-CN$^-$ species (DMSO-d_6, 100 MHz)

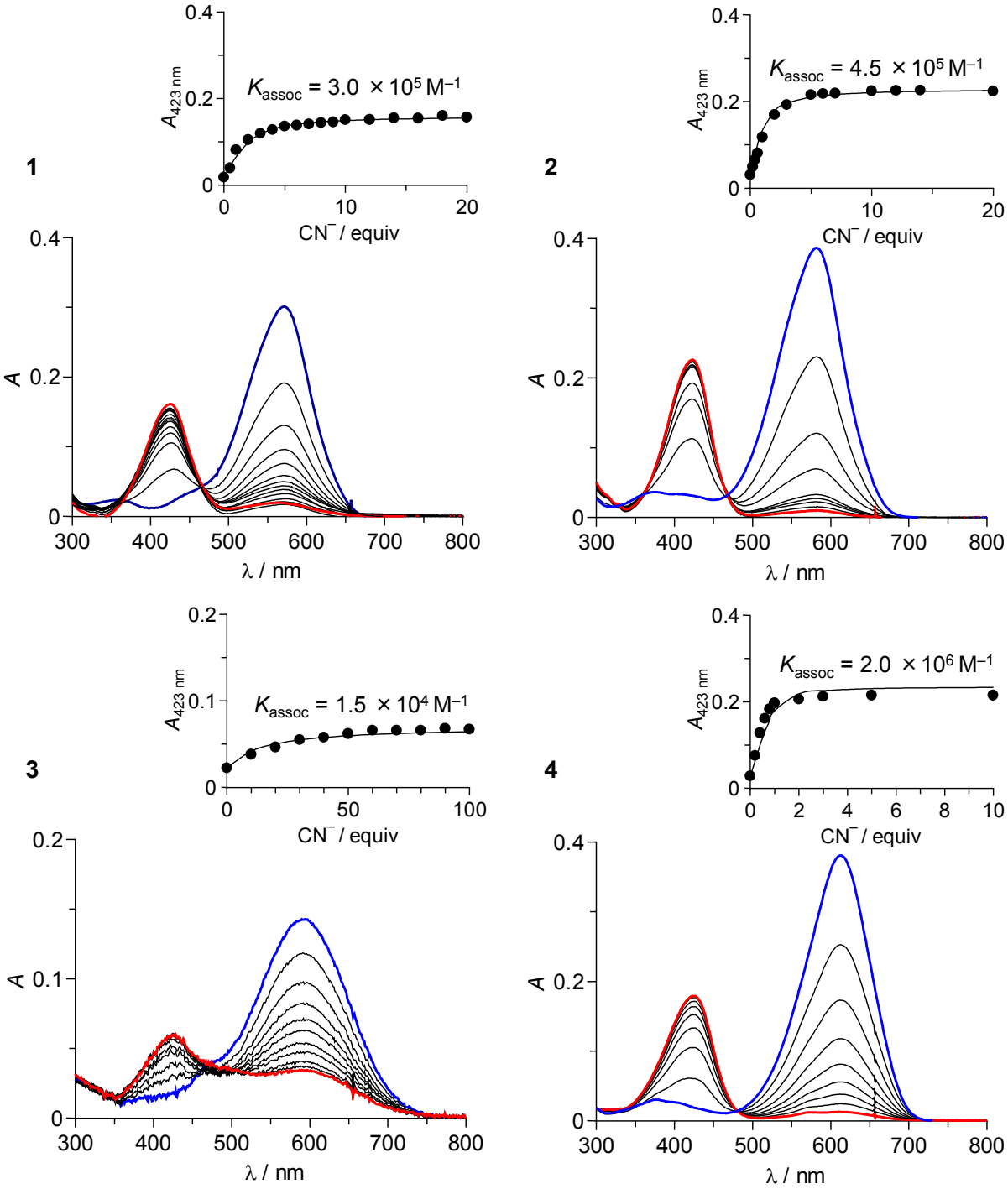


Fig. S12 Absorption titration of **1**, **2**, **3**, and **4** (5 μM) with CN^- in a water/MeCN mixture (7/3 v/v; CHES, 100 mM; pH 9.0) at 25 °C. The blue and red lines show the data obtained without CN^- and with 50 equiv of CN^-, respectively. (inset) Change in the absorption intensity at the maximum wavelengths, where the lines show the nonlinear fitting curves obtained based on 1:1 association.

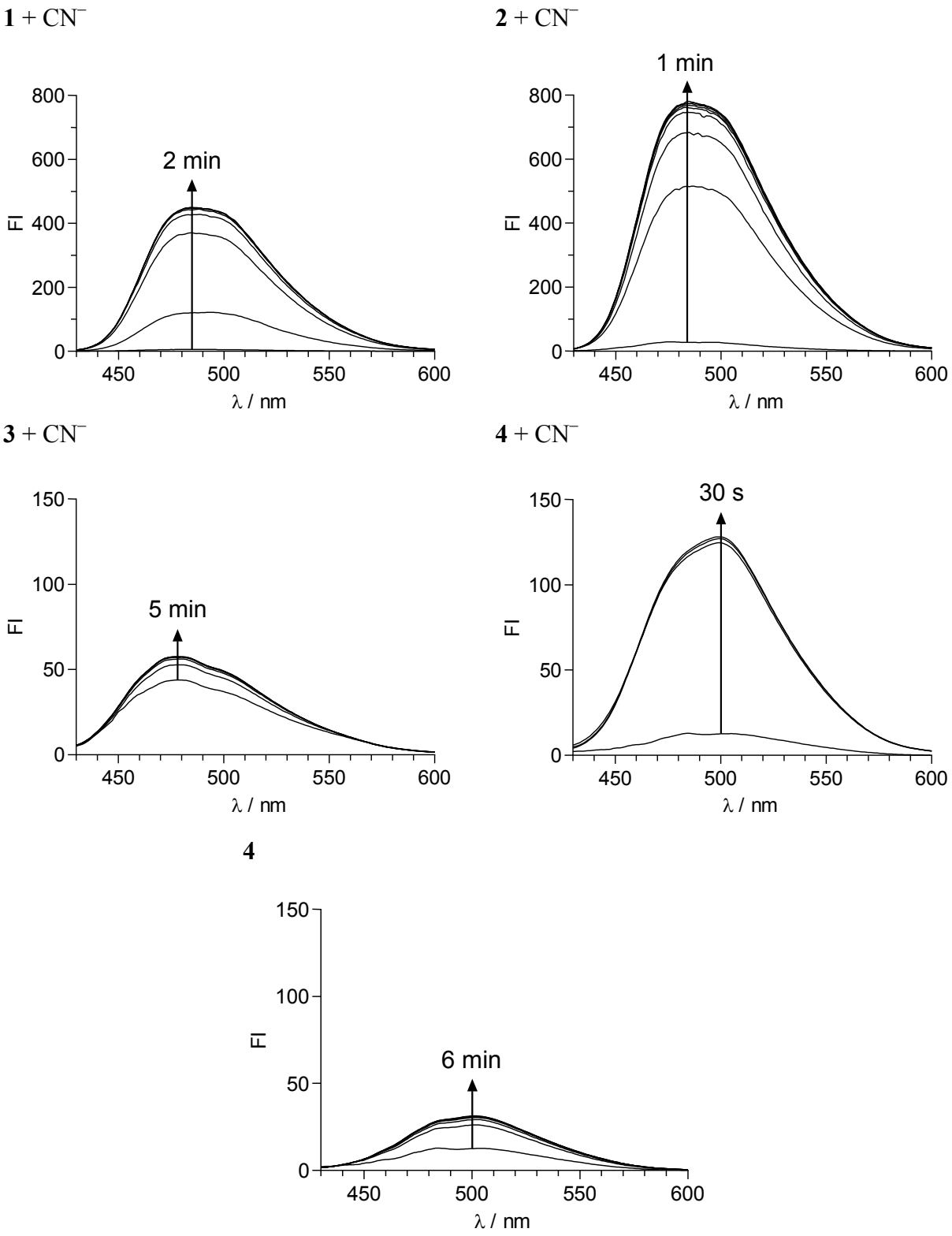


Fig. S13 Time-dependent change in fluorescence spectra (λ_{ex} = 415 nm) of **1** (5 μM), **2** (5 μM), **3** (5 μM), and **4** (5 μM) with 50 equiv of CN^-. The data for **4** (5 μM) obtained without CN^- are also shown in this figure.

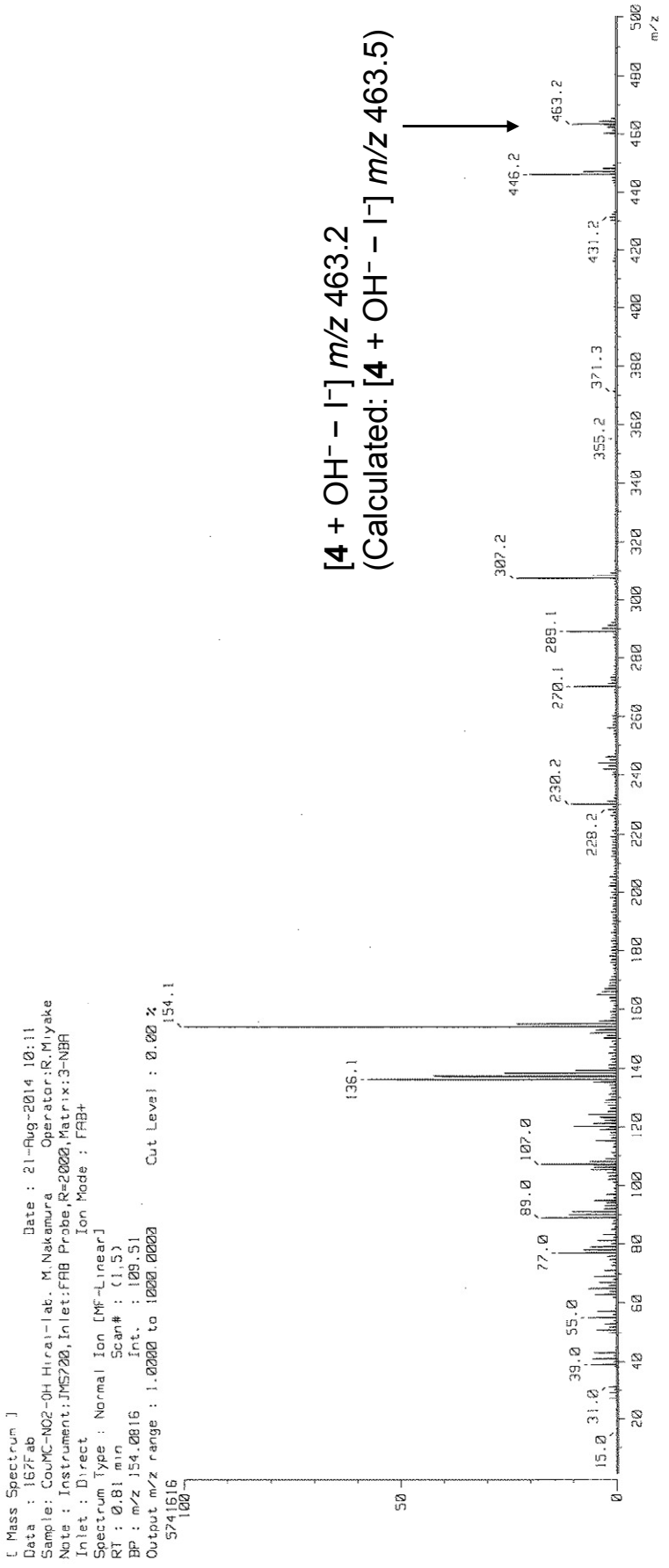


Fig. S14 FAB-MS chart of **4**-OH^- species.

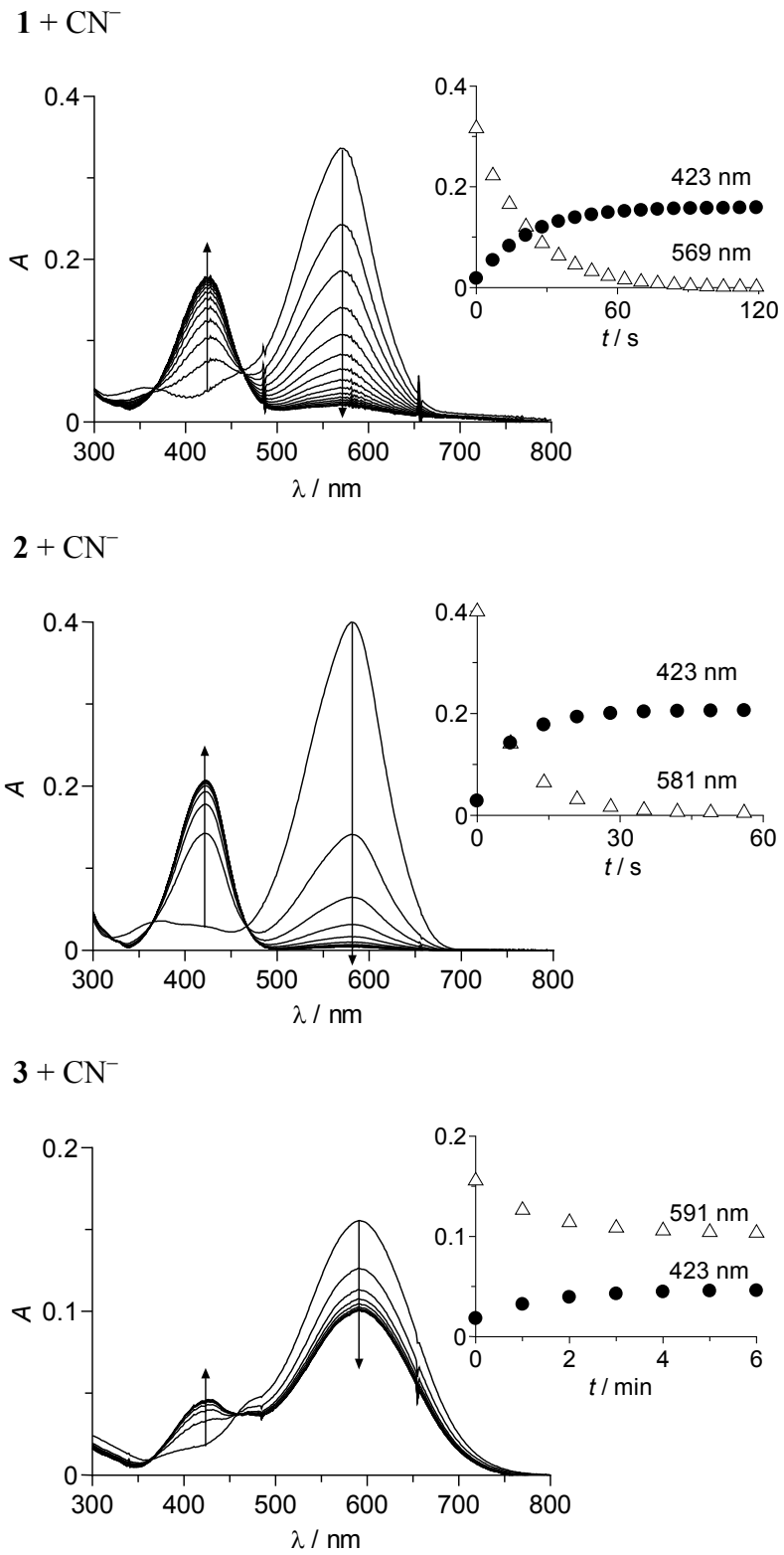


Fig. S15 Time-dependent change in the absorption spectra of **1**, **2**, and **3** measured with 50 equiv of CN^- in a buffered water/MeCN mixture (7/3 v/v; pH 9.0) at 25 °C. The data were obtained immediately after addition of the receptors and CN^-. (inset) Change in absorbance.

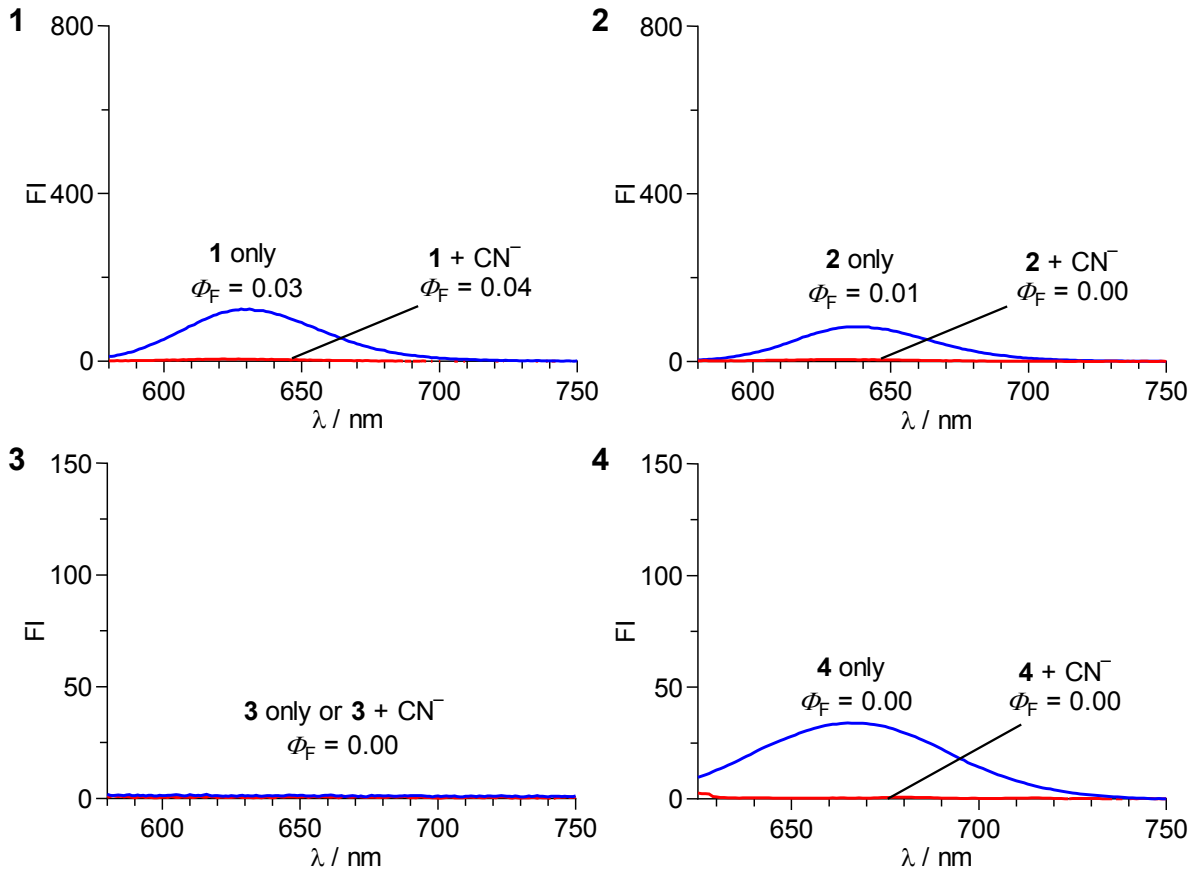
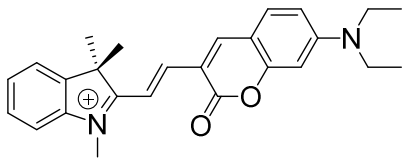
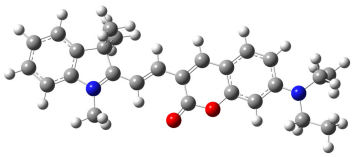


Fig. S16 Fluorescence spectra of **1** (5 μM, λ_{ex} = 570 nm), **2** (5 μM, λ_{ex} = 570 nm), **3** (5 μM, λ_{ex} = 570 nm), and **4** (5 μM, λ_{ex} = 608 nm) in a buffered water/MeCN mixture (7/3 v/v; CHES 100 mM, pH 9.0) at 25 °C. The blue and red lines show the data obtained without CN^- and with 50 equiv of CN^-, respectively. The fluorescence quantum yields for the respective solutions are also shown here.

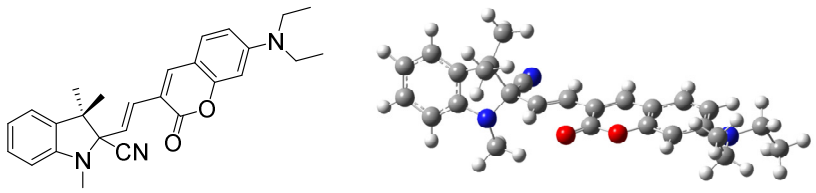
Cartesian Coordinates (in Å) of **1** (PCM: water)





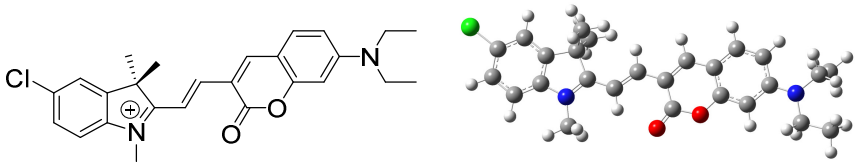
C	-8.154502	-0.848079	0.026544	H	-9.068165	-1.439185	0.005227
C	-8.233218	0.546181	0.117566	H	-9.206834	1.03034	0.166486
C	-7.079527	1.337209	0.147288	H	-7.159492	2.419427	0.217963
C	-5.858171	0.672666	0.08265	H	-6.857707	-2.578153	-0.107617
C	-5.759697	-0.717277	-0.008377	H	-3.698793	2.971211	-0.699274
C	-6.911579	-1.492348	-0.037392	H	-5.199426	3.195541	0.224411
N	-4.545823	1.213517	0.093678	H	-3.681533	2.858662	1.084592
C	-3.609933	0.253807	0.016626	H	-2.9304	-2.131163	-1.460376
C	-4.295723	-1.116085	-0.059865	H	-4.591738	-2.744151	-1.4618
C	-4.260635	2.646656	0.181208	H	-4.218343	-1.200195	-2.252059
C	-3.981705	-1.837755	-1.394472	H	-2.883349	-2.295408	1.152495
C	-3.936738	-2.002374	1.159231	H	-4.145881	-1.482497	2.099415
C	-2.235681	0.581708	0.015026	H	-4.542297	-2.913867	1.129259
C	-1.199315	-0.324029	-0.0608	H	-1.970463	1.628405	0.078538
C	0.199813	-0.038527	-0.065843	H	-1.424715	-1.384902	-0.12624
C	1.111658	-1.093166	-0.148109	H	0.731127	-2.115252	-0.204838
C	2.494592	-0.886818	-0.161139	H	3.134054	-2.953166	-0.28813
C	2.977908	0.443911	-0.087153	H	5.505979	-2.465795	-0.296162
O	2.095564	1.485637	-0.000858	H	4.591666	1.802242	-0.017296
C	0.71767	1.330411	0.014358	H	7.308434	-1.886905	-0.804248
C	3.470394	-1.91819	-0.237423	H	8.548767	-0.687507	-0.601253
C	4.810873	-1.636964	-0.24358	H	6.495293	2.003832	-0.820303
C	5.291831	-0.280727	-0.183793	H	6.748982	1.784063	0.911563
C	4.320313	0.756643	-0.091549	H	8.660185	-2.359809	1.240747
N	6.623139	0.005319	-0.218524	H	8.270179	-0.762075	1.906312
C	7.629056	-1.066939	-0.156843	H	6.994833	-1.980421	1.723653
C	7.050354	1.416676	-0.080082	H	8.694733	2.765102	-0.190123
C	7.900847	-1.570109	1.265345	H	9.168643	1.19518	0.462149
C	8.538267	1.685456	-0.286072	H	8.87761	1.389607	-1.284209
O	0.070005	2.358533	0.093976				

Cartesian Coordinates (in Å) of **1**–CN^- (PCM: water)



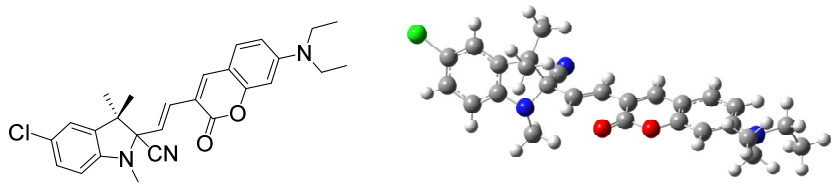
C	3.413382	0.329081	0.05296	N	3.620996	2.975486	-0.020414
C	1.975611	-0.112164	0.192622	H	1.85394	-1.142075	0.503898
C	0.900786	0.657359	-0.058713	H	1.055483	1.694849	-0.360577
C	-0.51156	0.292644	0.016059	H	-1.16085	2.231601	-0.592395
C	-1.47426	1.229445	-0.293954	H	-3.627233	2.871137	-0.854666
C	-2.860816	0.944313	-0.243089	H	-5.970065	2.247222	-0.710385
C	-3.257902	-0.350798	0.147719	H	-4.789168	-1.765106	0.525035
O	-2.307997	-1.28865	0.456899	H	-7.692542	1.308905	-1.284632
C	-0.940597	-1.044747	0.412768	H	-8.84553	0.107402	-0.751751
C	-3.894288	1.858536	-0.553855	H	-6.693376	-1.794546	1.314855
C	-5.221258	1.499867	-0.476011	H	-8.347276	-1.353257	0.954489
C	-5.614387	0.180325	-0.07822	H	-9.313231	2.294648	0.349168
C	-4.583069	-0.742507	0.232022	H	-8.854367	1.089493	1.567541
N	-6.934916	-0.172999	0.000988	H	-7.683877	2.318457	1.054253
C	-8.013407	0.732979	-0.411179	H	-7.769947	-3.510934	-0.154131
C	-7.358311	-1.48491	0.502264	H	-8.125194	-2.27669	-1.377982
C	-8.491349	1.664647	0.708392	H	-6.444793	-2.731785	-1.041978
C	-7.425586	-2.563781	-0.585002	H	6.882826	-0.528675	-2.361364
O	-0.228343	-1.988581	0.716498	H	8.980622	-0.553231	-1.01407
C	4.197492	-0.324251	-1.181602	H	8.875278	-0.352903	1.457984
C	5.616635	-0.305186	-0.62871	H	6.69952	-0.114226	2.623095
C	5.564558	-0.199057	0.771641	H	4.52475	-0.062782	-3.305971
N	4.232185	-0.106018	1.209299	H	2.939828	0.497409	-2.756039
C	3.509229	1.818998	-0.036544	H	4.392684	1.469784	-2.430326
C	6.835743	-0.441861	-1.276284	H	2.719538	-1.846114	-1.742645
C	8.017462	-0.458059	-0.516332	H	4.401596	-2.259447	-2.128924
C	7.955911	-0.346262	0.874059	H	3.830457	-2.365353	-0.454627
C	6.728738	-0.211253	1.540346	H	2.847192	0.372435	2.692205
C	4.002645	0.449593	-2.490515	H	4.41338	-0.19819	3.288559
C	3.752306	-1.790049	-1.382331	H	4.25938	1.464208	2.662543
C	3.926933	0.422151	2.53025				

Cartesian Coordinates (in Å) of **2** (PCM: water)



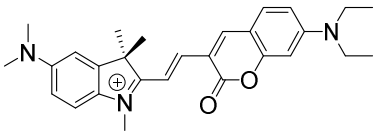
C	-7.491308	-0.422116	0.034142	H	-8.490496	1.485621	0.173079
C	-7.533677	0.971037	0.123812	H	-6.389331	2.791541	0.220522
C	-6.345867	1.707216	0.150697	H	-6.285501	-2.216923	-0.100871
C	-5.150496	0.997357	0.085527	H	-2.905846	3.204115	-0.704239
C	-5.110616	-0.395506	-0.004549	H	-4.388718	3.491673	0.230798
C	-6.286629	-1.130556	-0.031605	H	-2.880651	3.089604	1.079875
N	-3.820219	1.4835	0.094403	H	-2.34652	-1.915933	-1.469467
C	-2.923315	0.484107	0.015813	H	-4.028102	-2.470733	-1.464976
C	-3.665045	-0.85672	-0.060422	H	-3.604203	-0.938291	-2.253442
C	-3.474351	2.903266	0.180398	H	-2.300782	-2.09772	1.141556
C	-3.386496	-1.586186	-1.398681	H	-3.522425	-1.23435	2.097655
C	-3.340691	-1.760518	1.155334	H	-3.983918	-2.645961	1.126207
C	-1.539499	0.755584	0.011094	H	-1.233132	1.791116	0.071082
C	-0.536722	-0.190018	-0.063307	H	-0.801121	-1.242358	-0.12395
C	0.86972	0.045392	-0.070181	H	1.328626	-2.050005	-0.204428
C	1.744796	-1.041834	-0.149863	H	3.698763	-2.972068	-0.28753
C	3.132826	-0.883909	-0.162869	H	6.086391	-2.569171	-0.294338
C	3.66325	0.429683	-0.09067	H	5.324127	1.729767	-0.021958
O	2.818393	1.502127	-0.007943	H	7.906774	-2.049758	-0.814048
C	1.436038	1.395906	0.005953	H	9.188974	-0.896099	-0.603036
C	4.071865	-1.949738	-0.237461	H	7.240395	1.861684	-0.82231
C	5.420965	-1.716253	-0.242764	H	7.466992	1.63707	0.912719
C	5.949679	-0.377382	-0.182536	H	9.245436	-2.583113	1.226066
C	5.015345	0.694457	-0.09378	H	8.906257	-0.979477	1.905197
N	7.289353	-0.138878	-0.21297	H	7.592989	-2.154992	1.712332
C	8.256871	-1.246633	-0.160774	H	9.45922	2.54492	-0.163808
C	7.766204	1.257133	-0.074612	H	9.868143	0.958036	0.491448
C	8.511672	-1.769856	1.257392	H	9.605308	1.165434	-1.257999
C	9.265007	1.47175	-0.263411	Cl	-9.006359	-1.320477	0.002722
O	0.825274	2.44639	0.081129				

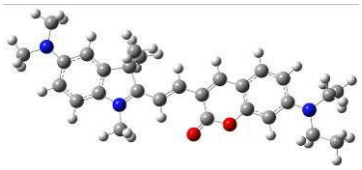
Cartesian Coordinates (in Å) of **2**–CN^- (PCM: water)



C	2.773822	0.434981	0.158908	N	2.948443	3.055731	-0.229505
C	1.339243	-0.010551	0.312131	H	1.222571	-0.999748	0.736838
C	0.262241	0.708898	-0.053393	H	0.412443	1.70784	-0.467788
C	-1.146061	0.331149	0.027854	H	-1.808996	2.187123	-0.789221
C	-2.114861	1.215356	-0.397048	H	-4.277902	2.756209	-1.164692
C	-3.497671	0.913401	-0.346606	H	-6.613456	2.110742	-1.009628
C	-3.884653	-0.342533	0.164267	H	-5.40327	-1.737124	0.649332
O	-2.92859	-1.228372	0.586925	H	-8.31016	1.096049	-1.517619
C	-1.564453	-0.966044	0.54957	H	-9.455284	-0.071102	-0.899384
C	-4.537037	1.774474	-0.769483	H	-7.324235	-1.724457	1.391197
C	-5.859955	1.403261	-0.684358	H	-8.975729	-1.349021	0.953446
C	-6.24295	0.123538	-0.164911	H	-9.991242	2.195975	-0.02001
C	-5.20548	-0.745945	0.258972	H	-9.531501	1.125534	1.318019
N	-7.559381	-0.242641	-0.079601	H	-8.378059	2.326994	0.710135
C	-8.642352	0.5997	-0.600855	H	-8.339796	-3.593585	0.072877
C	-7.974536	-1.506768	0.53803	H	-8.685928	-2.489981	-1.272246
C	-9.163389	1.623647	0.414056	H	-7.006756	-2.880875	-0.858049
C	-8.000193	-2.686684	-0.440457	H	6.324512	-0.664911	-2.040504
O	-0.845472	-1.861731	0.963314	H	8.206371	-0.008694	1.78596
C	3.600794	-0.350677	-0.966115	H	5.996356	0.342758	2.854737
C	5.001701	-0.247096	-0.378036	H	3.988347	-0.340476	-3.096979
C	4.906809	0.02555	0.997845	H	2.383248	0.259676	-2.66091
N	3.565997	0.156132	1.381504	H	3.815812	1.283849	-2.413674
C	2.853083	1.904318	-0.107073	H	2.161283	-1.951169	-1.384207
C	6.234579	-0.447485	-0.97797	H	3.859283	-2.382659	-1.665766
C	7.378103	-0.355634	-0.172932	H	3.234082	-2.297099	-0.00939
C	7.299641	-0.080943	1.189538	H	2.129631	0.773627	2.759713
C	6.049908	0.117613	1.792411	H	3.68351	0.298393	3.462649
C	3.438312	0.258509	-2.36305	H	3.527701	1.878304	2.649084
C	3.180829	-1.837369	-1.001153	Cl	8.969001	-0.587899	-0.918818
C	3.213067	0.823064	2.626073				

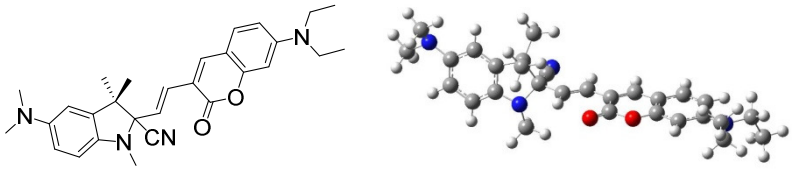
Cartesian Coordinates (in Å) of **3** (PCM: water)





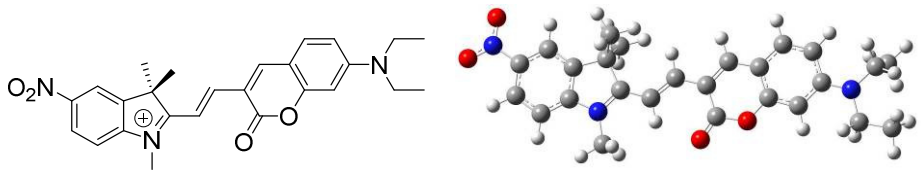
C	-7.223225	-0.292163	0.041458	H	-4.027841	3.610381	0.22121
C	-7.19881	1.128386	0.130193	H	-2.520489	3.198059	1.067852
C	-6.008297	1.846734	0.152501	H	-2.057707	-1.816381	-1.474148
C	-4.813266	1.134518	0.085619	H	-3.747298	-2.348571	-1.463777
C	-4.801368	-0.259228	-0.001798	H	-3.305556	-0.822687	-2.253041
C	-5.97875	-0.981666	-0.024889	H	-2.006307	-1.995589	1.139163
N	-3.477397	1.597524	0.088949	H	-3.211269	-1.110572	2.096085
C	-2.59573	0.591095	0.009891	H	-3.698253	-2.518573	1.133575
C	-3.359127	-0.738888	-0.061345	H	-0.880899	1.873447	0.059181
C	-3.118154	3.014897	0.170572	H	-0.498679	-1.163739	-0.133058
C	-3.093062	-1.472996	-1.398643	H	1.619572	-2.006056	-0.217872
C	-3.041198	-1.642943	1.154923	H	3.976928	-2.970761	-0.298524
C	-1.201381	0.841683	0.000964	H	6.371587	-2.611285	-0.297695
C	-0.21747	-0.115791	-0.073799	H	5.687604	1.69716	-0.022224
C	1.200548	0.093476	-0.082348	H	8.212932	-2.135336	-0.778118
C	2.052883	-1.005341	-0.162285	H	9.513506	-1.004233	-0.561116
C	3.448843	-0.874256	-0.173888	H	7.602756	1.798266	-0.808687
C	4.002155	0.426531	-0.099403	H	7.839964	1.562661	0.922762
C	3.175515	1.514338	-0.017849	H	9.507367	-2.669485	1.289382
C	1.79112	1.431905	-0.005747	H	9.191092	-1.050559	1.942561
C	4.367248	-1.954964	-0.246508	H	7.856967	-2.201382	1.744158
C	5.722412	-1.745804	-0.247193	H	9.838022	2.44014	-0.181298
C	6.275391	-0.419132	-0.184519	H	10.225589	0.85111	0.481501
C	5.361008	0.667617	-0.09761	H	9.950051	1.049825	-1.266643
N	7.623372	-0.205182	-0.213344	N	-8.413535	-0.977747	0.020021
C	8.567128	-1.329791	-0.129749	C	-8.421509	-2.431022	-0.072343
C	8.123587	1.180045	-0.068729	H	-7.938137	-2.781593	-0.994612
C	8.79014	-1.840915	1.298474	H	-7.907438	-2.895037	0.780631
C	9.624222	1.369826	-0.271406	H	-9.453823	-2.782524	-0.076683
O	1.198908	2.494331	0.068848	C	-9.677768	-0.257225	0.085751
H	-8.12608	1.686848	0.182939	H	-9.767814	0.320602	1.015635
H	-6.044678	2.931827	0.220604	H	-9.794715	0.434649	-0.759404
H	-5.948047	-2.06299	-0.093245	H	-10.49846	-0.974616	0.052256
H	-2.548339	3.307958	-0.715605				

Cartesian Coordinates (in Å) of **3**–CN^- (PCM: water)



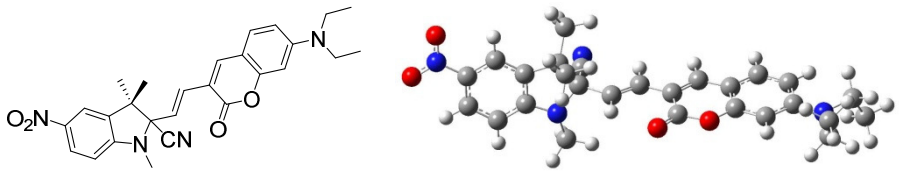
C	-2.455733	-0.510855	0.080707	H	4.623041	-2.517368	-1.603235
C	-1.02282	-0.092151	0.307914	H	6.951862	-1.878653	-1.345963
C	0.060473	-0.727354	-0.175707	H	5.701323	1.627328	0.927162
C	1.466113	-0.357431	-0.026215	H	8.639128	-0.77297	-1.679539
C	2.44356	-1.147936	-0.591998	H	9.772821	0.282585	-0.869743
C	3.823915	-0.844736	-0.490993	H	7.624954	1.521594	1.650313
C	4.198007	0.313982	0.219691	H	9.279041	1.250185	1.150233
O	3.233453	1.106394	0.784339	H	10.317303	-2.101538	-0.381866
C	1.872184	0.838129	0.706147	H	9.858	-1.265552	1.114059
C	4.871988	-1.611664	-1.051083	H	8.70546	-2.353245	0.319003
C	6.191063	-1.243859	-0.907199	H	8.599116	3.597034	0.64738
C	6.560533	-0.062644	-0.184563	H	8.956642	2.7311	-0.859296
C	5.514352	0.712127	0.378208	H	7.273401	3.019618	-0.382554
N	7.872876	0.301709	-0.042253	H	-6.01596	0.936151	-1.810672
C	8.964169	-0.434292	-0.691061	H	-7.860138	-0.589205	1.787355
C	8.272576	1.455917	0.770242	H	-5.664338	-1.13329	2.716691
C	9.489236	-1.609411	0.141167	H	-3.694341	0.992508	-2.89802
C	8.272507	2.778806	-0.004669	H	-2.091978	0.29979	-2.617092
O	1.145312	1.642461	1.267602	H	-3.529312	-0.747351	-2.616321
C	-3.309224	0.498477	-0.824356	H	-1.907131	2.186759	-0.873402
C	-4.702735	0.229673	-0.269145	H	-3.618751	2.63118	-1.020544
C	-4.585592	-0.354213	1.002913	H	-2.960613	2.170306	0.559082
N	-3.227648	-0.526542	1.346222	H	-1.775759	-1.459787	2.516483
C	-2.526329	-1.880182	-0.517373	H	-3.328627	-1.190044	3.323569
C	-5.941968	0.516465	-0.809692	H	-3.167706	-2.513631	2.140202
C	-7.12082	0.227656	-0.076876	N	-8.384808	0.480825	-0.671683
C	-6.982414	-0.356589	1.193309	C	-8.608551	1.841444	-1.164757
C	-5.723755	-0.665725	1.736392	H	-9.478255	1.845296	-1.830811
C	-3.147086	0.235499	-2.325723	H	-8.79855	2.557861	-0.345549
C	-2.916779	1.960454	-0.514102	H	-7.747387	2.195862	-1.733531
C	-2.85989	-1.48254	2.379254	C	-9.555242	-0.037156	0.021107
N	-2.613629	-2.975631	-0.895513	H	-9.773175	0.485245	0.970646
H	-0.911393	0.805449	0.902716	H	-10.42723	0.077267	-0.631189
H	-0.079964	-1.637853	-0.76161	H	-9.426603	-1.102169	0.23569
H	2.147048	-2.043176	-1.141827				

Cartesian Coordinates (in Å) of **4** (PCM: water)



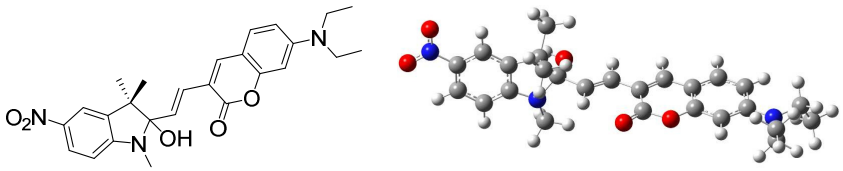
C	-7.24765	-0.303406	0.038931	H	-6.073356	-2.116092	-0.096174
C	-7.277277	1.091421	0.126349	H	-2.63753	3.263596	-0.714829
C	-6.08474	1.811042	0.149221	H	-4.112704	3.572549	0.225675
C	-4.896317	1.083751	0.082789	H	-2.607406	3.15046	1.069759
C	-4.871693	-0.313694	-0.005474	H	-2.128538	-1.865557	-1.473483
C	-6.052216	-1.031659	-0.028808	H	-3.815444	-2.403239	-1.46506
N	-3.570477	1.556071	0.089089	H	-3.377361	-0.876007	-2.256787
C	-2.677271	0.542351	0.010247	H	-2.080969	-2.047261	1.136414
C	-3.432112	-0.790941	-0.063312	H	-3.289812	-1.168841	2.095217
C	-3.206666	2.971708	0.172432	H	-3.770163	-2.5757	1.125238
C	-3.164896	-1.524991	-1.401573	H	-0.981679	1.835277	0.061322
C	-3.116699	-1.697707	1.152824	H	-0.573999	-1.204611	-0.12799
C	-1.298377	0.802865	0.003642	H	1.546018	-2.032898	-0.20617
C	-0.299406	-0.154768	-0.069626	H	3.904369	-2.975539	-0.284138
C	1.102849	0.069213	-0.076556	H	6.295342	-2.594533	-0.286269
C	1.971311	-1.028423	-0.153182	H	5.571175	1.714089	-0.024175
C	3.356926	-0.881153	-0.164147	H	8.118193	-2.090014	-0.807753
C	3.899429	0.429859	-0.093401	H	9.409818	-0.946159	-0.598974
O	3.064444	1.509777	-0.014791	H	7.490275	1.824137	-0.823874
C	1.6815	1.416404	-0.003046	H	7.708361	1.604753	0.913328
C	4.287459	-1.956869	-0.234984	H	9.457295	-2.632513	1.230193
C	5.637202	-1.735851	-0.237594	H	9.129755	-1.02686	1.910267
C	6.177699	-0.40014	-0.178256	H	7.808378	-2.193675	1.71903
C	5.252385	0.681709	-0.094234	H	9.712987	2.489501	-0.157469
N	7.517072	-0.174095	-0.203809	H	10.104569	0.900706	0.503541
C	8.476306	-1.29025	-0.154977	H	9.850486	1.106225	-1.247717
C	8.007962	1.218926	-0.071279	N	-8.512177	-1.031725	0.018058
C	8.729005	-1.814511	1.26303	O	-8.47453	-2.263387	-0.058993
C	9.509359	1.417914	-0.255145	O	-9.562274	-0.385903	0.078287
O	1.079799	2.471355	0.068121	H	-8.230106	1.609199	0.176425
H	-6.112821	2.895711	0.216876				

Cartesian Coordinates (in Å) of **4**–CN^- (PCM: water)



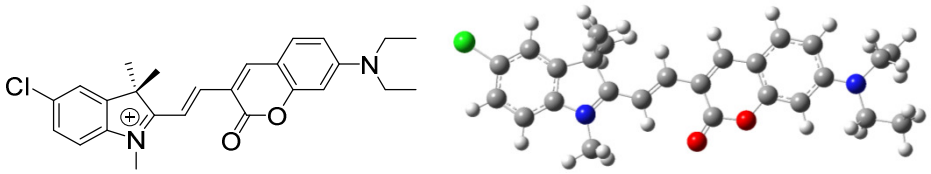
C	2.544996	0.532372	0.084487	H	1.015985	-0.89779	0.734416
C	1.118872	0.07036	0.260808	H	0.164187	1.7323	-0.605709
C	0.030476	0.754559	-0.138292	H	-2.06576	2.168205	-0.925628
C	-1.370681	0.359995	-0.030907	H	-4.545752	2.686365	-1.303012
C	-2.355173	1.211153	-0.487413	H	-6.870275	2.01938	-1.092979
C	-3.732412	0.892988	-0.410417	H	-5.591584	-1.733406	0.726751
C	-4.097246	-0.343926	0.160617	H	-8.568647	0.968481	-1.519211
O	-3.125254	-1.198185	0.611071	H	-9.68853	-0.181047	-0.827184
C	-1.765707	-0.918491	0.551247	H	-7.502402	-1.714837	1.489074
C	-4.787761	1.72074	-0.860137	H	-9.163813	-1.381737	1.054349
C	-6.10448	1.337334	-0.742997	H	-10.22665	2.119478	-0.036463
C	-6.465021	0.078166	-0.160206	H	-9.734335	1.10927	1.336465
C	-5.411301	-0.758802	0.289091	H	-8.601448	2.292034	0.65736
N	-7.774954	-0.299656	-0.040219	H	-8.504829	-3.65182	0.259994
C	-8.876687	0.509662	-0.57495	H	-8.880487	-2.608938	-1.125257
C	-8.164862	-1.542594	0.634938	H	-7.191722	-2.9594	-0.713763
C	-9.38671	1.571533	0.405742	H	6.168391	-0.785352	-1.879393
C	-8.183528	-2.76221	-0.293738	H	7.911564	0.124914	1.958214
O	-1.030112	-1.782727	1.001181	H	5.674385	0.617373	2.909141
C	3.409704	-0.338572	-0.946946	H	3.874292	-0.488569	-3.056077
C	4.790572	-0.207251	-0.320033	H	2.26329	0.160894	-2.725805
C	4.65091	0.182822	1.032219	H	3.700337	1.183952	-2.500836
N	3.325601	0.393471	1.342745	H	1.967857	-1.954718	-1.287852
C	2.598488	1.972274	-0.304764	H	3.668715	-2.412223	-1.50556
C	6.032619	-0.479413	-0.846065	H	3.010582	-2.217834	0.127934
C	7.152637	-0.350461	-0.000162	H	1.815109	1.005428	2.638823
C	7.023513	0.031469	1.340854	H	3.345212	0.579391	3.424581
C	5.768199	0.306376	1.872093	H	3.194132	2.135637	2.563429
C	3.30662	0.16968	-2.389694	N	8.466305	-0.617725	-0.531965
C	2.979972	-1.821961	-0.892108	O	8.569731	-0.932533	-1.727621
C	2.901953	1.075331	2.556728	O	9.447521	-0.5268	0.221404
N	2.671526	3.10787	-0.536855				

Cartesian Coordinates (in Å) of **4**–OH^- (PCM: water)



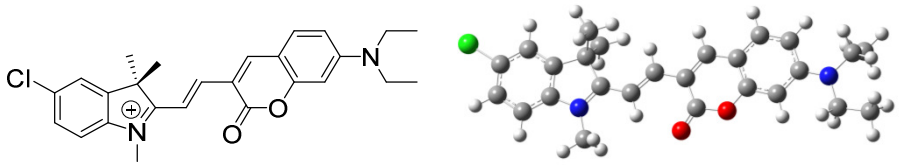
C	-2.581597	-0.622535	-0.087976	H	2.030019	-2.044061	-1.250495
C	-1.176467	-0.144719	0.174602	H	4.516072	-2.506863	-1.671808
C	-0.077038	-0.760721	-0.294799	H	6.839176	-1.875319	-1.348878
C	1.32379	-0.385171	-0.113183	H	5.539649	1.580491	0.971054
C	2.314173	-1.160376	-0.676254	H	8.527769	-0.754299	-1.632597
C	3.692897	-0.858704	-0.541277	H	9.645545	0.282917	-0.777973
C	4.051366	0.283177	0.202867	H	7.450567	1.453933	1.735661
O	3.074404	1.062597	0.764565	H	9.114292	1.19468	1.262031
C	1.714266	0.795	0.652536	H	10.189796	-2.111111	-0.342629
C	4.75267	-1.613175	-1.095157	H	9.70121	-1.317217	1.166903
C	6.068739	-1.249111	-0.914664	H	8.566679	-2.386552	0.322521
C	6.422434	-0.084282	-0.15925	H	8.44475	3.553259	0.803572
C	5.3645	0.677599	0.398279	H	8.830088	2.724597	-0.717146
N	7.732386	0.276059	0.01905	H	7.13835	3.002301	-0.264804
C	8.835923	-0.440111	-0.630647	H	-6.250951	0.977278	-1.740988
C	8.115453	1.409646	0.867095	H	-7.919171	-0.5488	1.93208
C	9.350872	-1.635763	0.178652	H	-5.662577	-1.182211	2.746593
C	8.130178	2.75154	0.12559	H	-4.00136	0.825523	-2.995979
O	0.976251	1.587516	1.216192	H	-2.35367	0.207788	-2.79297
C	-3.469219	0.394822	-0.93843	H	-3.733867	-0.899591	-2.691225
C	-4.841514	0.165323	-0.324073	H	-2.059519	2.069878	-1.062231
C	-4.67373	-0.445279	0.945568	H	-3.768994	2.531368	-1.186567
N	-3.354148	-0.712878	1.180045	H	-3.081972	2.10829	0.390054
C	-6.093966	0.508826	-0.773767	H	-1.815371	-1.586038	2.26866
C	-7.200904	0.239438	0.060572	H	-3.250062	-1.166018	3.225205
C	-7.043049	-0.35576	1.320887	H	-3.276756	-2.59782	2.163179
C	-5.779208	-0.707969	1.775818	N	-8.519336	0.582125	-0.392627
C	-3.386687	0.106587	-2.442589	O	-8.649827	1.100976	-1.514652
C	-3.064086	1.86535	-0.677506	O	-9.490725	0.354536	0.348521
C	-2.906875	-1.568406	2.266686	O	-2.500019	-1.902614	-0.690815
H	-1.08804	0.74966	0.777488	H	-3.408897	-2.256829	-0.830287
H	-0.213272	-1.66182	-0.891666				

Cartesian Coordinates (in Å) of **2** (PCM: MeCN)



C	-7.483692	-0.444223	0.03557	H	-8.499506	1.456214	0.157207
C	-7.538505	0.949141	0.11354	H	-6.411859	2.780015	0.195523
C	-6.357297	1.695867	0.135528	H	-6.262622	-2.22866	-0.083106
C	-5.155723	0.996421	0.077895	H	-2.932853	3.21929	-0.727519
C	-5.102835	-0.396672	-0.000703	H	-4.417795	3.498951	0.206326
C	-6.272346	-1.142039	-0.022913	H	-2.905941	3.117329	1.057508
N	-3.829797	1.495178	0.083572	H	-2.325606	-1.910854	-1.449836
C	-2.923946	0.50376	0.01296	H	-4.00202	-2.478086	-1.438077
C	-3.652962	-0.845528	-0.051026	H	-3.590412	-0.951589	-2.243354
C	-3.497959	2.919002	0.15948	H	-2.283091	-2.072052	1.160291
C	-3.367617	-1.587726	-1.3811	H	-3.496705	-1.193077	2.111063
C	-3.322111	-1.732587	1.174992	H	-3.966504	-2.617561	1.162985
C	-1.542035	0.785064	0.007528	H	-1.239239	1.821892	0.0657
C	-0.538801	-0.159832	-0.066903	H	-0.808862	-1.209775	-0.129869
C	0.867993	0.067236	-0.074223	H	1.317572	-2.030524	-0.228119
C	1.736687	-1.024239	-0.163292	H	3.680847	-2.96287	-0.318776
C	3.125376	-0.872906	-0.175225	H	6.069628	-2.572333	-0.318043
C	3.662339	0.43761	-0.090856	H	5.329886	1.727427	-0.007933
O	2.823519	1.514061	-0.000823	H	7.897577	-2.055132	-0.831748
C	1.440505	1.414862	0.011012	H	9.183164	-0.909773	-0.601236
C	4.058871	-1.942953	-0.258759	H	7.247818	1.857348	-0.801413
C	5.409047	-1.716563	-0.259778	H	7.466733	1.615857	0.932371
C	5.944695	-0.381103	-0.185653	H	9.226068	-2.617329	1.208119
C	5.015827	0.694754	-0.089311	H	8.887633	-1.021418	1.905268
N	7.285368	-0.148826	-0.210401	H	7.572499	-2.190877	1.691763
C	8.247785	-1.261443	-0.167119	H	9.466549	2.525189	-0.129139
C	7.767997	1.243675	-0.057289	H	9.866793	0.931331	0.513779
C	8.494247	-1.802637	1.245774	H	9.61102	1.154804	-1.234773
C	9.26835	1.453753	-0.238768	Cl	-8.989792	-1.356058	0.009639
O	0.833148	2.466018	0.094675				

Cartesian Coordinates (in Å) of **2** (PCM: CH_2Cl_2)



C	-7.488225	-0.432512	0.038521	H	-8.493181	1.47138	0.17229
C	-7.534884	0.960806	0.123495	H	-6.398473	2.785057	0.21192
C	-6.350105	1.701548	0.146053	H	-6.276311	-2.220552	-0.092082
C	-5.151807	0.997159	0.081482	H	-2.918577	3.214064	-0.716028
C	-5.106229	-0.395844	-0.003729	H	-4.401259	3.495834	0.220151
C	-6.279774	-1.134867	-0.026553	H	-2.890461	3.103475	1.067671
N	-3.823657	1.489739	0.087081	H	-2.33872	-1.912614	-1.469147
C	-2.922015	0.494099	0.010743	H	-4.017196	-2.473447	-1.457505
C	-3.658156	-0.851191	-0.06036	H	-3.601469	-0.943966	-2.253683
C	-3.484493	2.9116	0.169643	H	-2.284077	-2.073144	1.151713
C	-3.379322	-1.585979	-1.395736	H	-3.519477	-1.223136	2.099794
C	-3.327835	-1.748327	1.158989	H	-3.959695	-2.641836	1.130623
C	-1.53951	0.77008	0.006727	H	-1.232475	1.805565	0.067681
C	-0.537527	-0.176624	-0.068195	H	-0.809102	-1.226261	-0.130565
C	0.86848	0.051837	-0.07446	H	1.326401	-2.044285	-0.21767
C	1.74152	-1.036832	-0.158671	H	3.694802	-2.968495	-0.303127
C	3.129484	-0.880495	-0.170139	H	6.081487	-2.5676	-0.302881
C	3.661114	0.433062	-0.09126	H	5.323102	1.728906	-0.013849
O	2.819116	1.506375	-0.005247	H	7.903477	-2.046767	-0.825398
C	1.436095	1.402772	0.007585	H	9.186167	-0.897874	-0.597641
C	4.067766	-1.946976	-0.248067	H	7.245696	1.861141	-0.813426
C	5.416712	-1.71519	-0.249866	H	7.46354	1.63161	0.922183
C	5.947024	-0.377165	-0.182556	H	9.232803	-2.601909	1.216069
C	5.013565	0.695033	-0.090909	H	8.893855	-1.004384	1.908373
N	7.286686	-0.140927	-0.208521	H	7.579542	-2.175261	1.700485
C	8.251982	-1.251024	-0.16237	H	9.463017	2.537728	-0.141766
C	7.766465	1.253755	-0.064688	H	9.865148	0.94828	0.510112
C	8.500279	-1.787847	1.251807	H	9.610932	1.162272	-1.239925
C	9.266574	1.465503	-0.245877	Cl	-8.997222	-1.336219	0.012083
O	0.823259	2.450119	0.084078				