Rapid, selective, sensitive fluorometric detection of cyanide anion in aqueous media by cyanine dyes with indolium–coumarin linkage

Yasuhiro Shiraishi,* Masaya Nakamura, Kohei Yamamoto and Takayuki Hirai

Research Center for Solar Energy Chemistry, and Division of Chemical Engineering, Graduate School of Engineering Science, Osaka University, Toyonaka 560-8531, Japan
shiraish@cheng.es.osaka-u.ac.jp

Electronic Supplementary Information (ESI†)

CONTENTS

Experimental methods

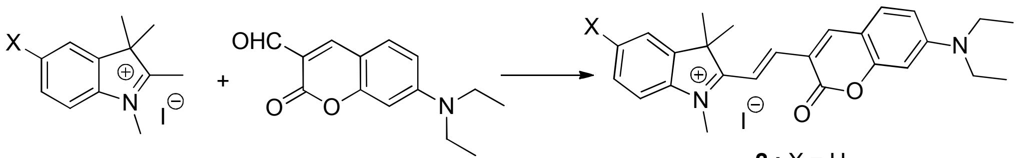
General

Absorption spectra were measured on an UV-visible photodiode-array spectrophotometer (Shimadzu; Multispec-1500) equipped with a temperature controller (S-1700). Fluorescence spectra were measured on a JASCO FP-6500 fluorescence spectrophotometer. Light irradiations were carried out with Xe lamp (300 W; Asahi Spectra Co. Ltd.; MAX-302) equipped with 334 nm (light intensity: 69.1 mW m^{-2}) band-pass filter. ^{1}H and ^{13}C NMR spectra were obtained by a JEOL JNM-ECS400 spectrometer. FAB-MS analysis was performed by a JEOL JMS 700 Mass Spectrometer. The fluorescence quantum yield (Φ_F) was determined according to literature method using Rhodamine B (in ethanol) as a reference.[1]

Calculation details

Calculations were carried out with tight convergence criteria at the DFT level with the Gaussian 03 package,[2] using the B3LYP/6-31G* basis set for all atoms. The excitation energies and the oscillator strength of each structure were calculated by time-dependent density-functional theory (TD-DFT)[3] at the same level of optimization using the polarizable continuum model (PCM)[4] with water as a solvent. Cartesian coordinates for the merocyanine form of **2** and **3** are summarized in the end of this Supporting Information.

Synthesis



Compound 2 **2′** (1,2,3,3-tetramethyl-3*H*-indolium iodide) and **4** (7-diethylaminocoumarine -3-aldehyde) were prepared according to literature procedure, respectively.[5,6] **2′** (123 mg, 0.41 mmol) and **4** (143 mg, 0.58 mmol) were stirred in EtOH (20 mL) for 20 h at 60 °C. The resultant was concentrated by evaporation, and purified by recrystallization with MeOH (3 mL), affording **2** as a green solid (101.6 mg, 47 %).^{1}H-NMR (400 MHz, DMSO-d_6, TMS) δ (ppm): 8.81 (1H, s), 8.24 (1H, d, J = 15.6 Hz), 7.83 (3H, dq, J = 9.3, 2.1 Hz), 7.58 (3H, dq, J = 9.3, 2.5 Hz), 6.92 (1H, dd, J = 9.2, 2.3 Hz), 6.72 (1H, d, J = 2.3 Hz), 3.97 (3H, s), 3.57 (4H, q, J = 7.0 Hz), 1.76 (6H, s), 1.19 (6H, t, J = 7.1 Hz). ^{13}C NMR (100 MHz, DMSO-d_6, TMS) δ (ppm): 180.7, 159.2, 157.4, 153.8, 150.0, 149.1, 142.9, 141.8, 132.1, 128.7, 128.4, 122.6, 114.3, 112.1, 111.2, 110.0, 109.3, 96.4, 51.2, 44.7, 33.6, 25.8, 12.3. FAB-MS: *m/z*: calcd for $C_{26}H_{29}N_2O_2^+$ ([**2** − I^-]$^+$) 401.2; found: 401.2; HRMS (FAB$^+$): *m/z*: calcd for $C_{26}H_{29}N_2O_2^+$ ([**2** − I^-]$^+$): 401.2224; found: 401.2227.

Compound 3 **3′** (5-chloro-1,2,3,3-tetramethyl-3*H*-indolium iodide) was prepared according to literature procedure.[5] **3′** (130 mg, 0.39 mmol) and **4** (77 mg, 0.31 mmol) were stirred in EtOH (10 mL) for 3 h at 80 °C. The resultant was concentrated by evaporation, and purified by recrystallization with a mixture of EtOH and ethyl acetate (1/1, 6 mL), affording **3** as a green solid (68.7 mg, 39 %). ^{1}H-NMR (400 MHz, DMSO-d_6, TMS) δ (ppm): 8.81 (1H, s), 8.26 (1H, d, J = 16.0 Hz), 8.03 (1H, d, J = 1.8 Hz), 7.82 (2H, dd, J = 22.2, 12.1 Hz), 7.67 (1H, dd, J = 8.7, 2.3 Hz), 7.59 (1H, d, J = 9.2 Hz), 6.93 (1H, dd, J = 9.2, 2.3 Hz), 6.72 (1H, d, J =

1.8 Hz), 3.94 (3H, s), 3.58 (4H, q, J = 6.9 Hz), 1.77 (6H, s), 1.19 (6H, t, J = 7.1 Hz). ^{13}C NMR (100 MHz, DMSO-d_6, TMS) δ (ppm): 180.8, 159.2, 157.6, 154.0, 150.4, 149.8, 144.8, 140.8, 133.0, 132.3, 128.8, 123.2, 115.9, 112.1, 111.3, 109.8, 109.4, 96.5, 51.4, 44.8, 33.7, 25.6, 12.4. FAB-MS: *m/z*: calcd for $C_{26}H_{28}N_2O_2Cl^+$ ([**3** − I^-]$^+$); 435.2; found: 435.2; HRMS (FAB$^+$): *m/z*: calcd for $C_{26}H_{28}N_2O_2Cl^+$ ([**3** − I^-]$^+$): 435.1834; found: 435.1836.

[1] a) B. Bag, P. K. Bharadwaj, *J. Phys. Chem. B,* 2005, **109***,* 4377–4390. b) A. Proutiere, E. Megnassan, H. Hucteau, *J. Phys. Chem*. 1992**, 96**, 3485–3489.

[2] a) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, Jr., J. A. Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03 (Revision B.05)*, Gaussian, Inc., Wallingford CT, 2004. b) R. Dennington II, T. Keith, J. Millam, K. Eppinnett, W. L. Hovell, R. Gilliland, *GaussView, (Version 3.09)*, Semichem, Inc., Shawnee Mission, KS, 2003.

[3] R. E. Stratmann, G. E. Scuseria, M. J. Frisch, *J. Chem. Phys.* 1998, **109**, 8218–8224.

[4] M. Cossi, V. Barone, R. Cammi, J. Tomasi, *Chem. Phys. Lett.* 1996, **255**, 327–335.

[5] Q. Li, J. Tan, B. Peng, *Molecules* 1997, **2**, 91–98.

[6] W. Xuan, C. Chen, Y. Cao, W. He, W. Jiang, K. Liu, W. Wang, *Chem. Commun*., 2012, **48**, 7292–7294.

Table S1 Calculated excitation energy (*E*), wavelength (λ), and oscillator strength (*f*) for low-laying singlet state (S_n) of **3** and **3**–CN^- species.

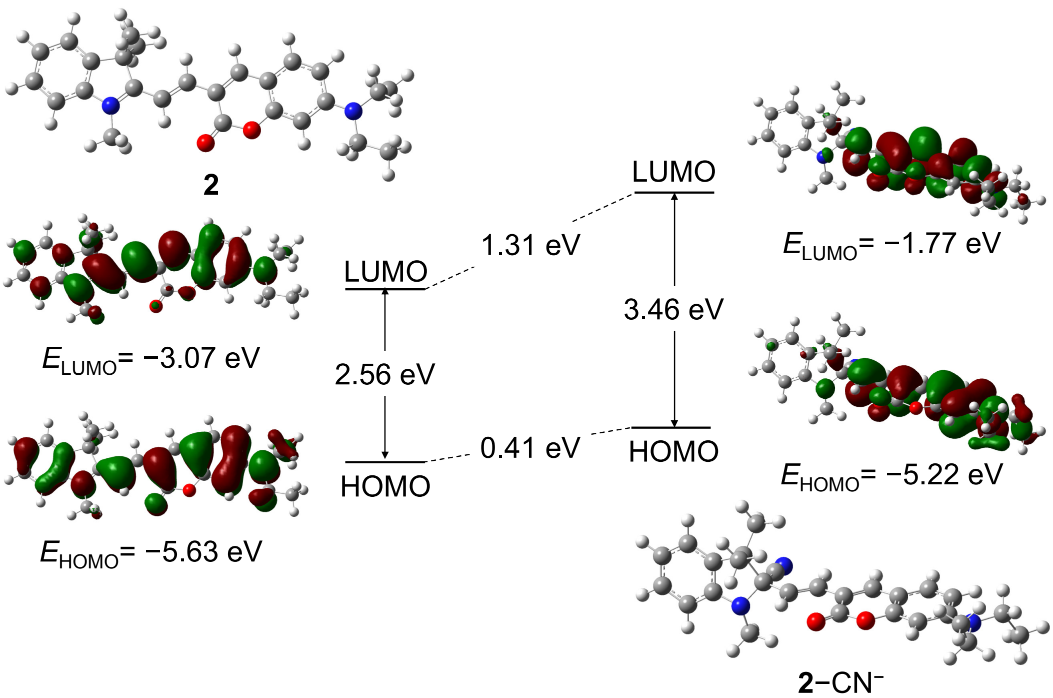
species		Main orbital transition (CIC^a)	*E* (eV) [λ (nm)]	*f*
3	$S_0 \rightarrow S_1$	HOMO → LUMO (0.62264)	2.3706 [523.01]	1.8812
3–CN^-	$S_0 \rightarrow S_1$	HOMO → LUMO (0.63542)	3.1818 [389.67]	1.1388
	$S_0 \rightarrow S_4$	HOMO–1 → LUMO+2 (–0.10646) HOMO → LUMO+1 (0.55446) HOMO–1 → LUMO+1 (0.14735) HOMO–2 → LUMO (0.30346)	4.3376 [285.84]	0.2380

^{a} CI expansion coefficients for the main orbital transitions.

Table S2 Calculated excitation energy (E), wavelength (λ), and oscillator strength (f) for low-laying singlet state (S_n) of **2** and **2**–CN^- species.

species		Main orbital transition (CIC[a])	E (eV) [λ (nm)]	f
2	$S_0 \rightarrow S_1$	HOMO → LUMO (0.62391)	2.4001 [516.58]	1.800
2–CN^-	$S_0 \rightarrow S_1$	HOMO–1 → LUMO (0.20711) HOMO → LUMO (0.61624)	3.1746 [390.56]	0.9701
	$S_0 \rightarrow S_2$	HOMO–1 → LUMO (0.67061) HOMO → LUMO (–0.17037)	3.2855 [377.36]	0.1752
	$S_0 \rightarrow S_4$	HOMO–3 → LUMO (0.11621) HOMO–2 → LUMO (0.33682) HOMO → LUMO+1 (0.5512)	4.3667 [283.93]	0.2789

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



Calculated energy diagrams for **2** and **2**–CN^-

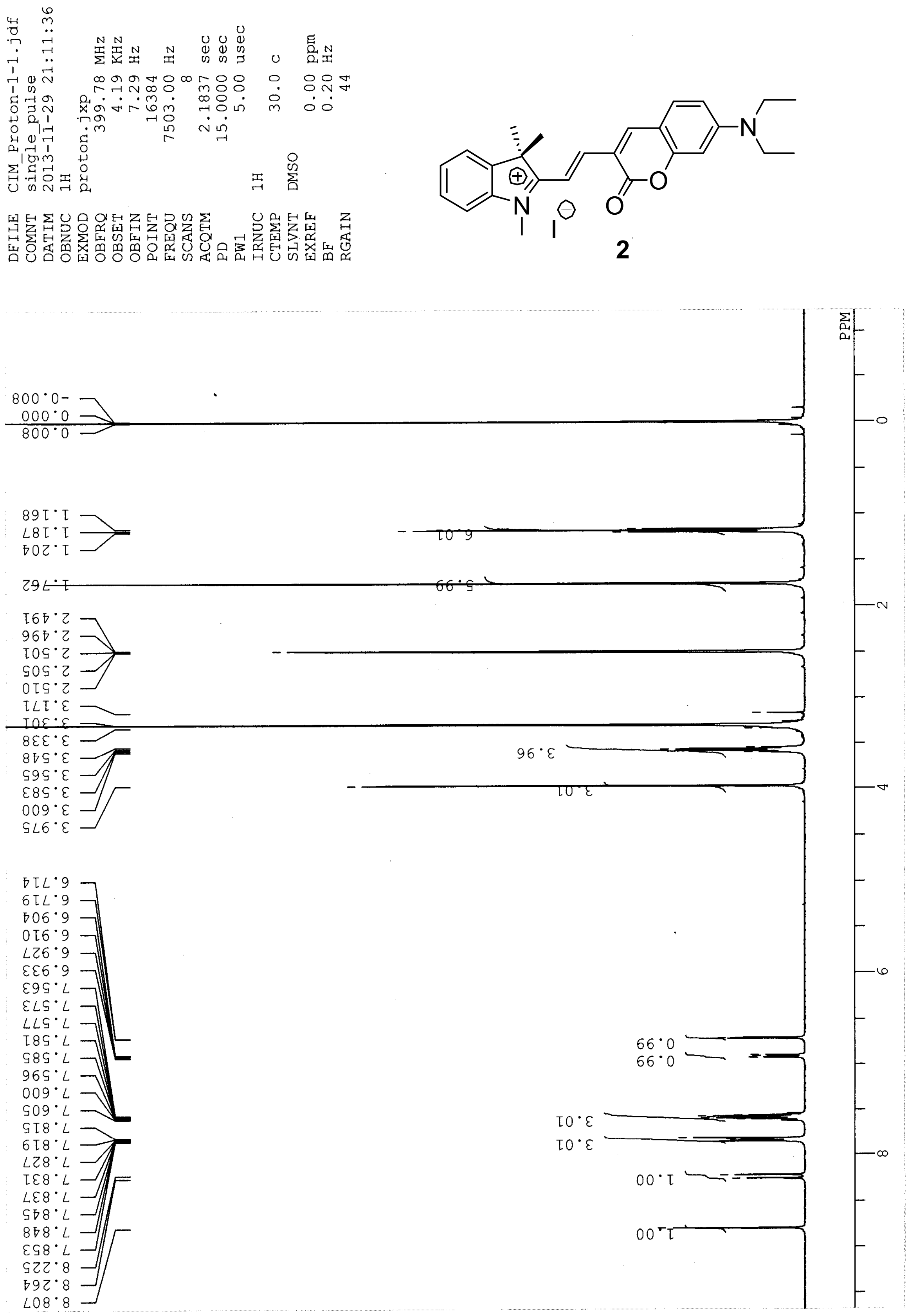


Fig. S1 [1]H NMR chart of **2** (DMSO-d_6, 400 MHz).

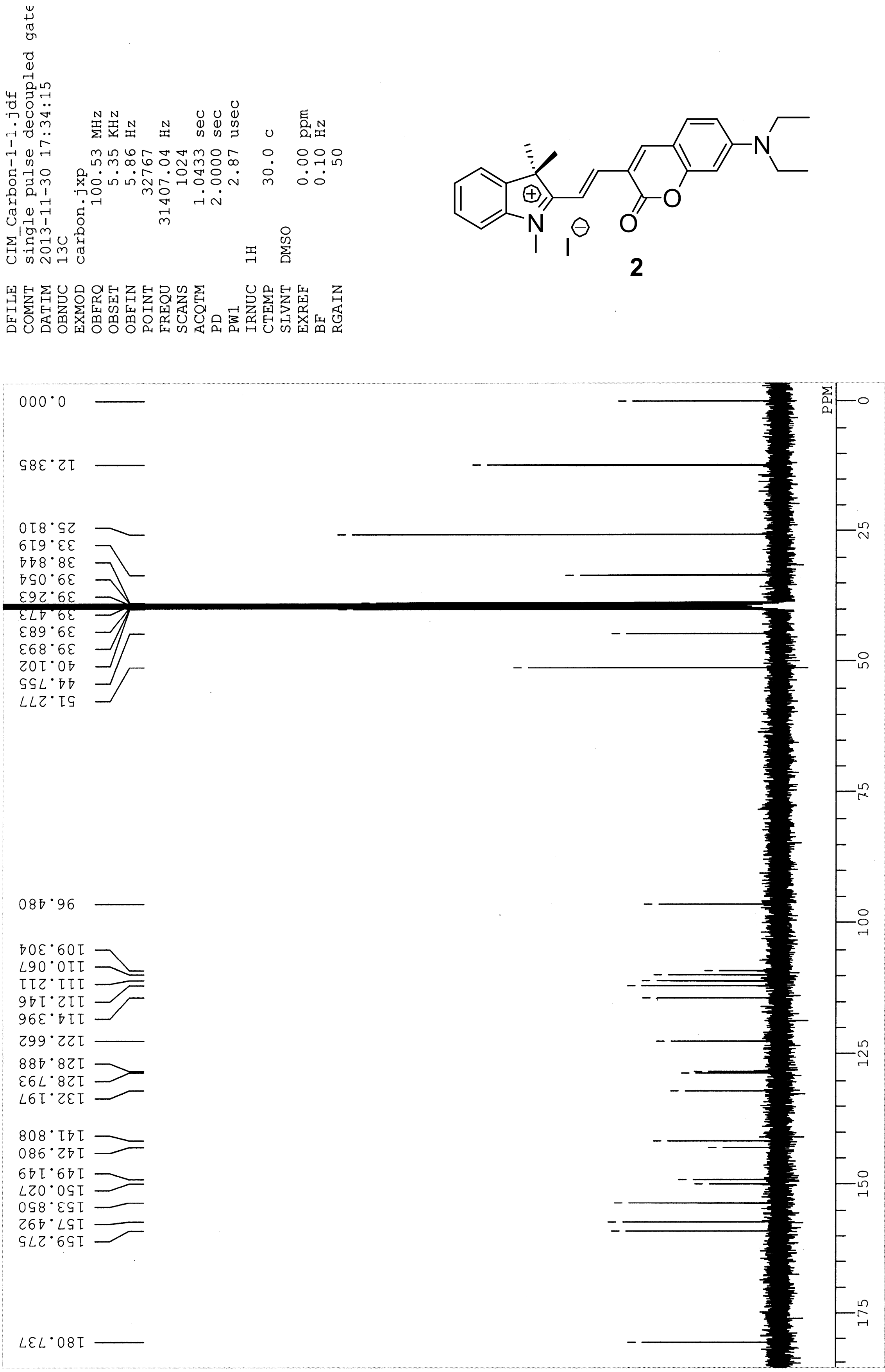


Fig. S2 ^{13}C NMR chart of **2** (DMSO-d_6, 100 MHz).

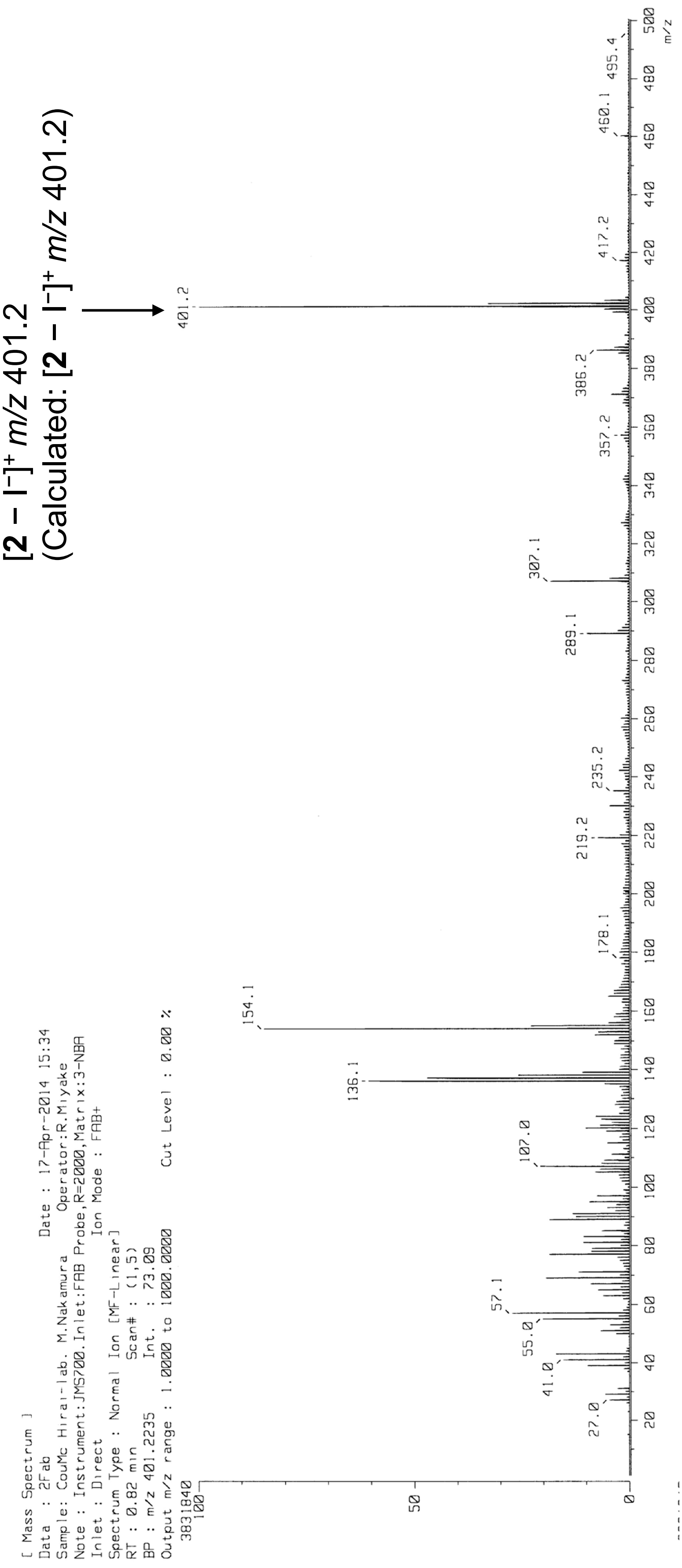
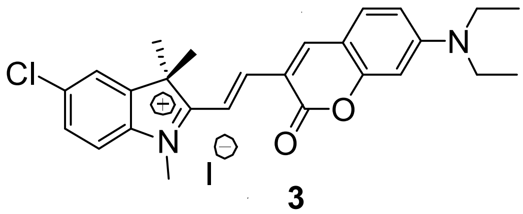


Fig. S3 FAB-MS chart of **2**.



3

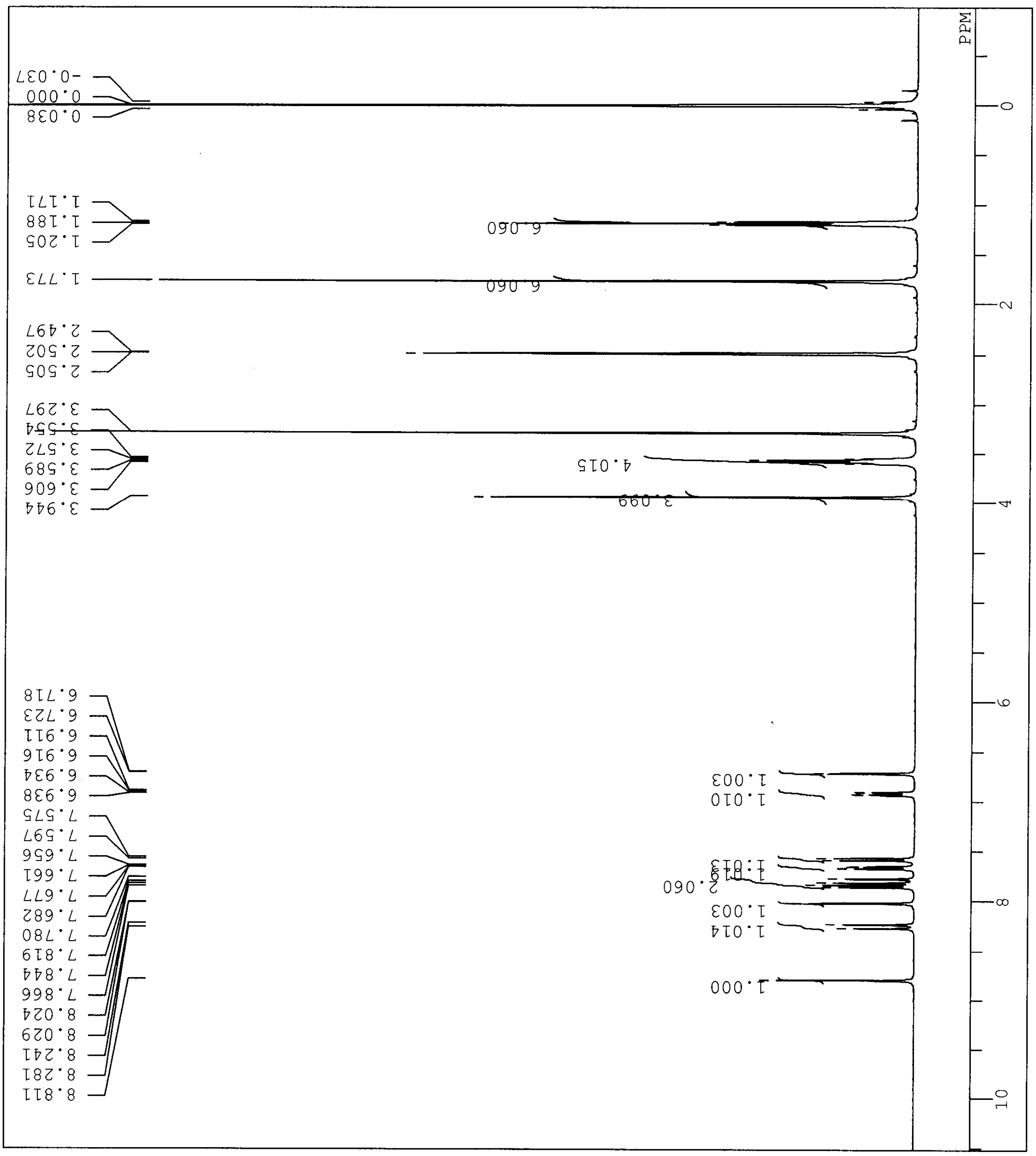
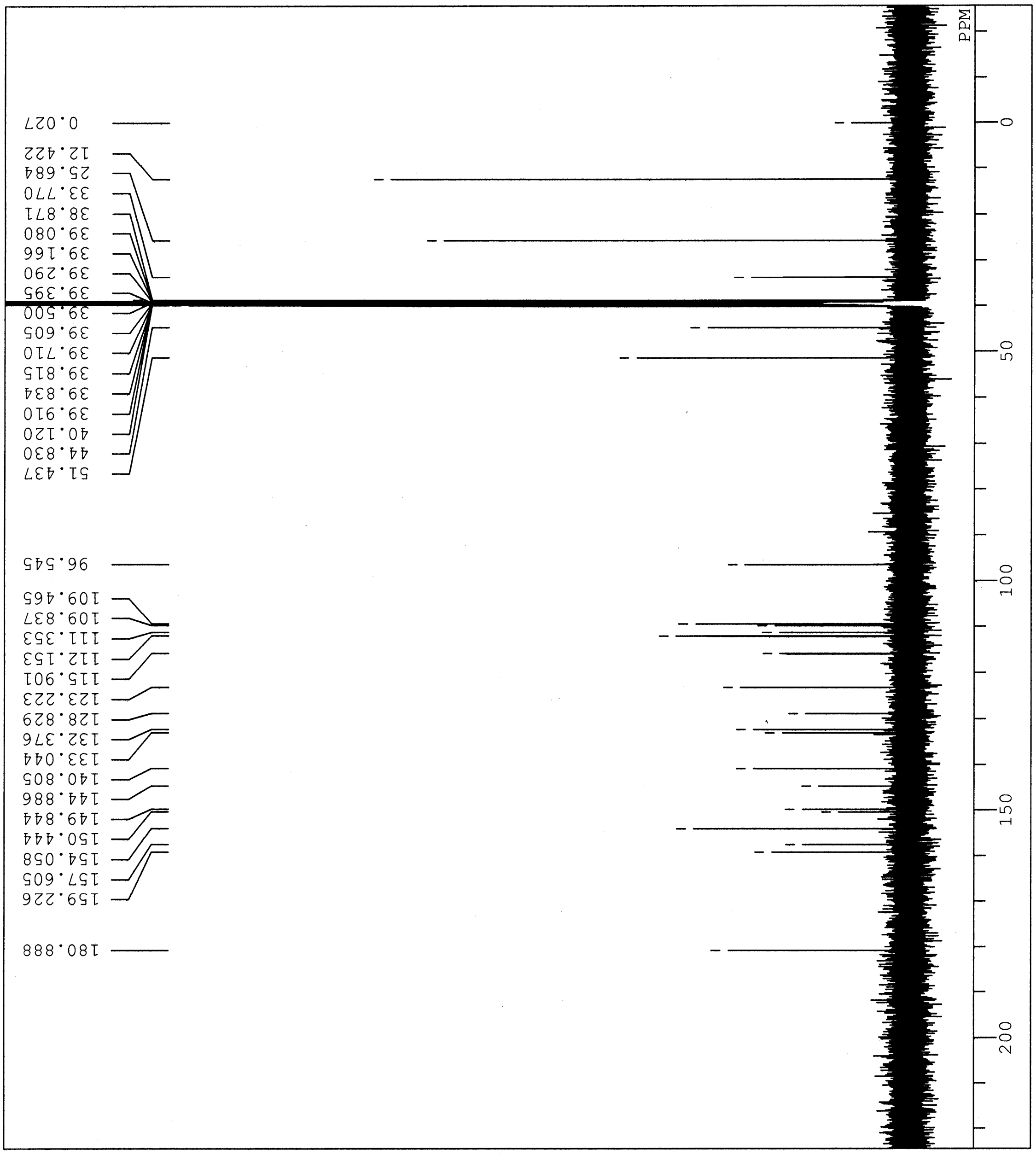
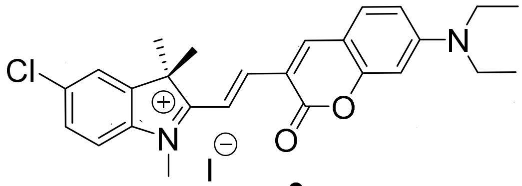


Fig. S4 ^{1}H NMR chart of **3** (DMSO-d_6, 400 MHz).





3

Fig. S5 ^{13}C NMR chart of **3** (DMSO-d_6, 100 MHz).

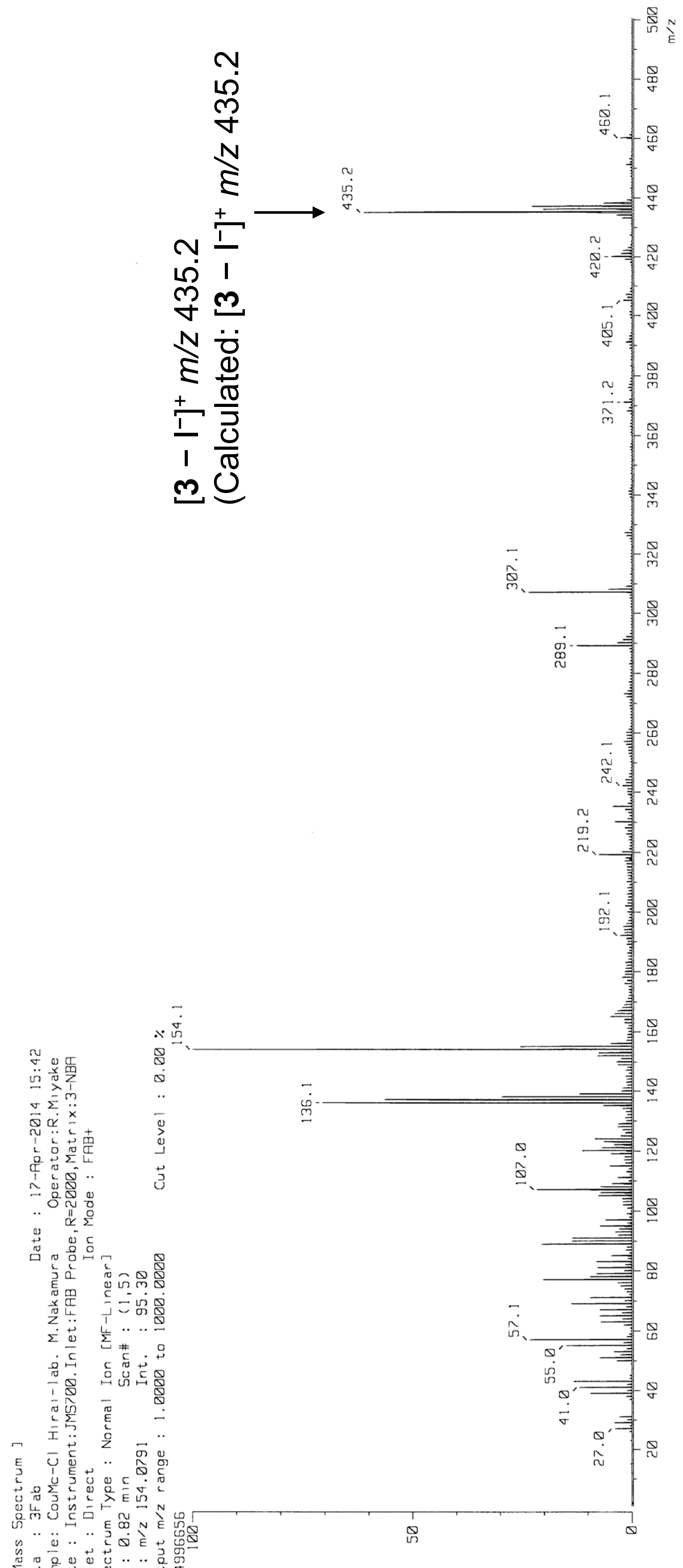
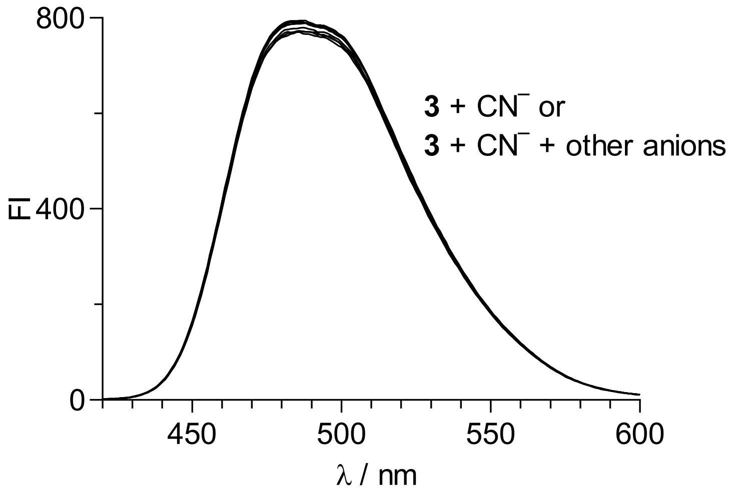


Fig. S6 FAB-MS chart of **3**.

(a)



(b)

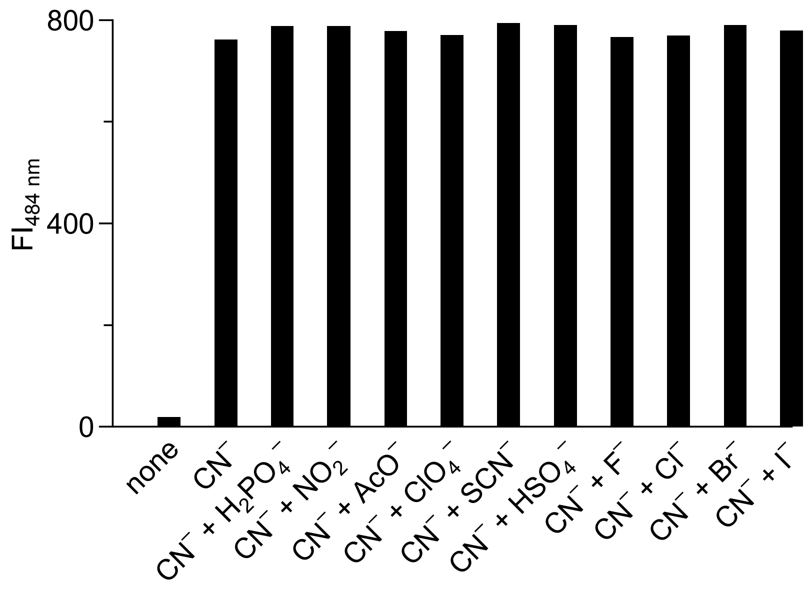


Fig. S7 (a) Fluorescence spectra (λ_{ex} = 415 nm) of **3** (5 μM) measured with 50 equiv of CN^- together with 50 equiv of other respective anions in a buffered water/MeCN mixture (7/3 v/v; CHES 100 mM, pH 9.0) at 25 °C. (b) Fluorescence intensity of the respective solutions.

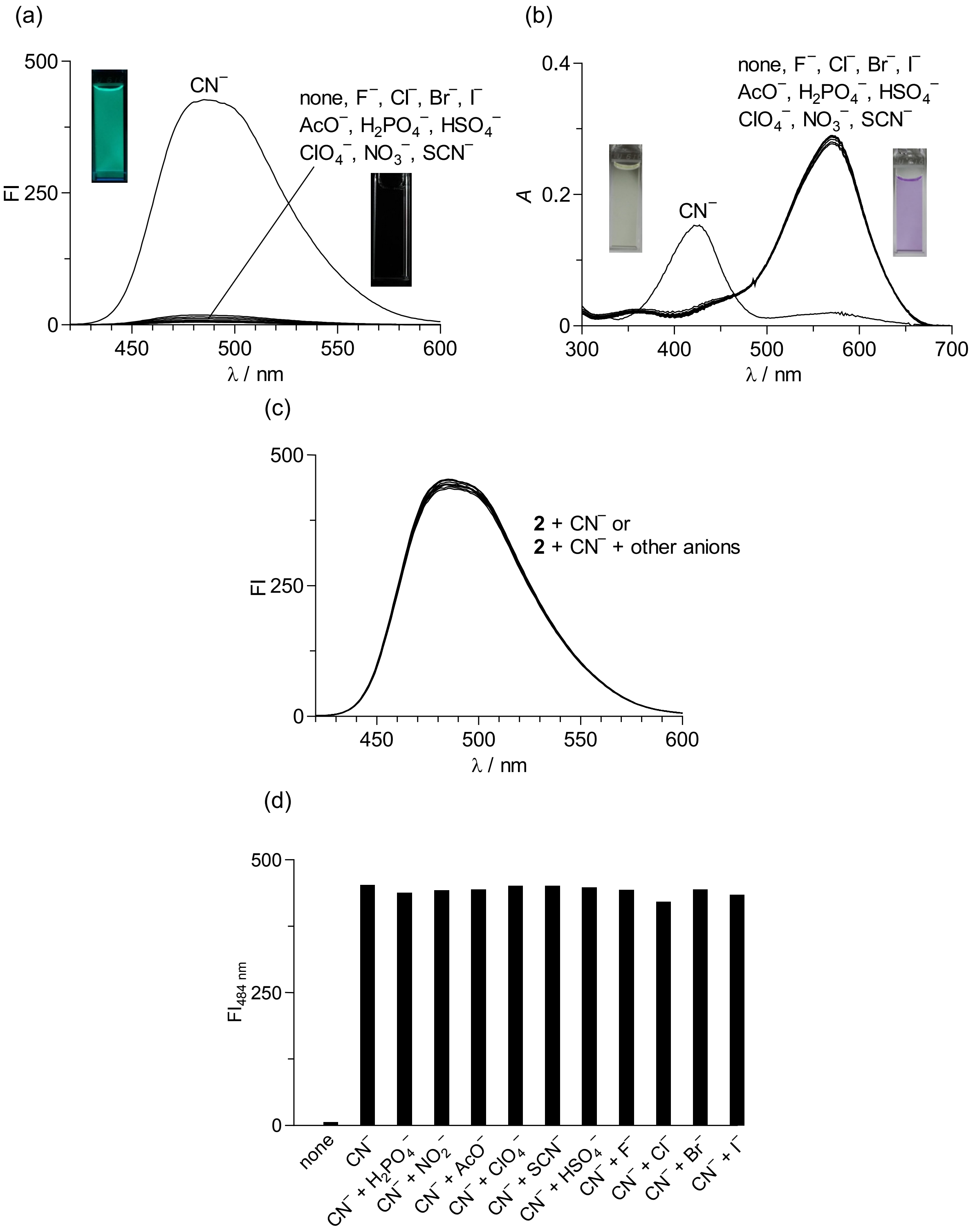


Fig. S8 (a) Fluorescence spectra (λ_{ex}= 415 nm) of **2** (5 μM), measured with 20 equiv of each respective anion in a buffered water/MeCN mixture (7/3 v/v; CHES 100 mM, pH 9.0) at 25 °C. (b) Change in absorption spectra. (c) Fluorescence spectra of **2** measured with 50 equiv of CN^- together with 50 equiv of other respective anions. (d) Fluorescence intensity of the respective solutions.

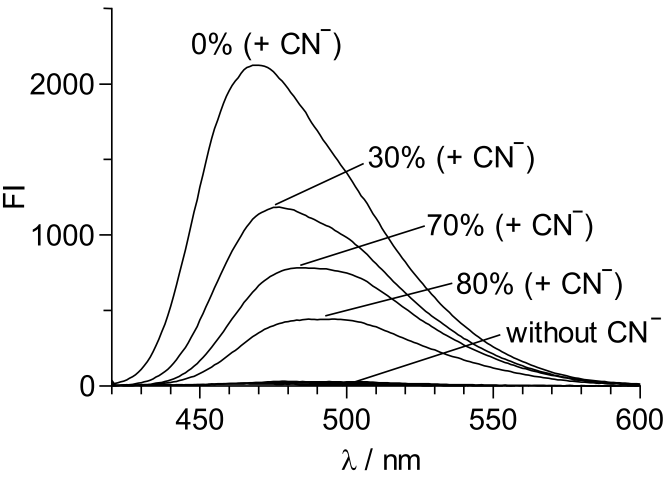


Fig. S9 Fluorescence spectra of **3** (5 μM) measured without or with CN^- (50 equiv) in MeCN solutions (CHES 100 mM, pH 9.0) with different water content (0, 30, 70, and 80%).

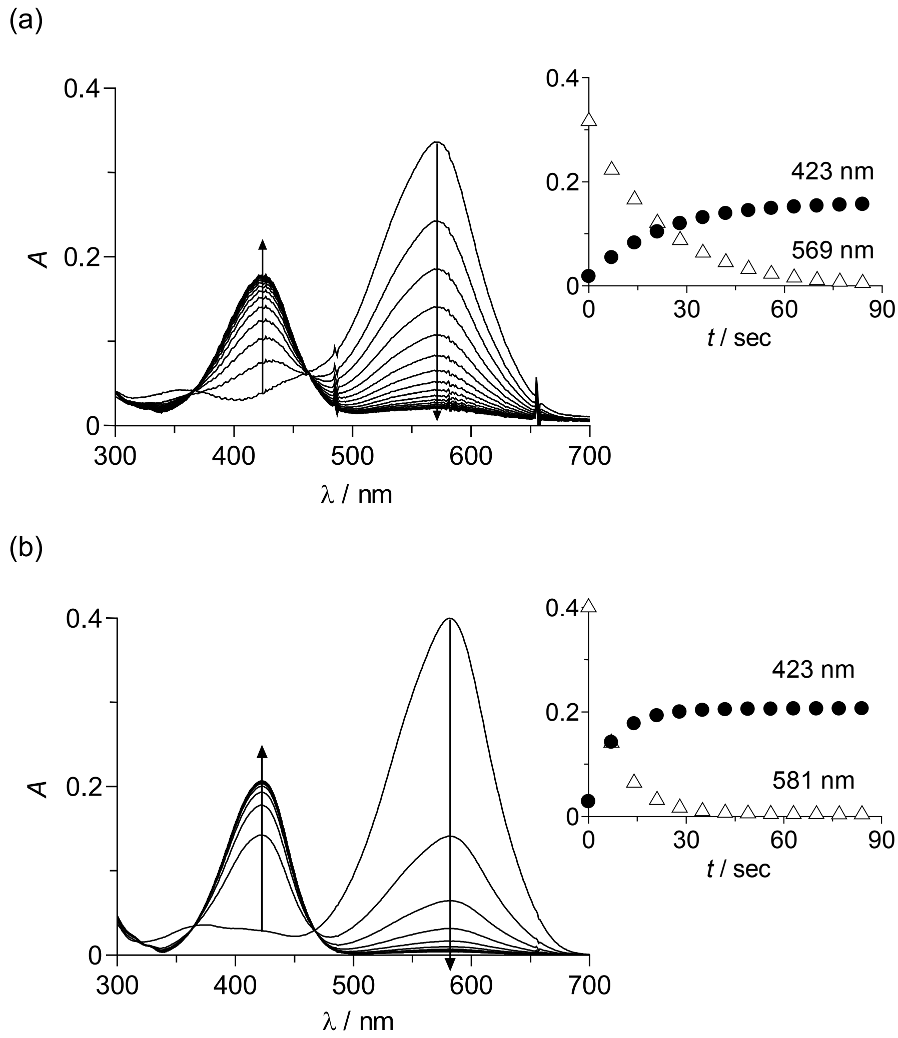


Fig. S10 Time-dependent change in absorption spectra of (a) **2** and (b) **3** (5 μM), measured with 50 equiv of CN^- in a buffered water/MeCN mixture (7/3 v/v; CHES 100 mM, pH 9.0) at 25 °C. (inset) Change in absorbance for respective bands.

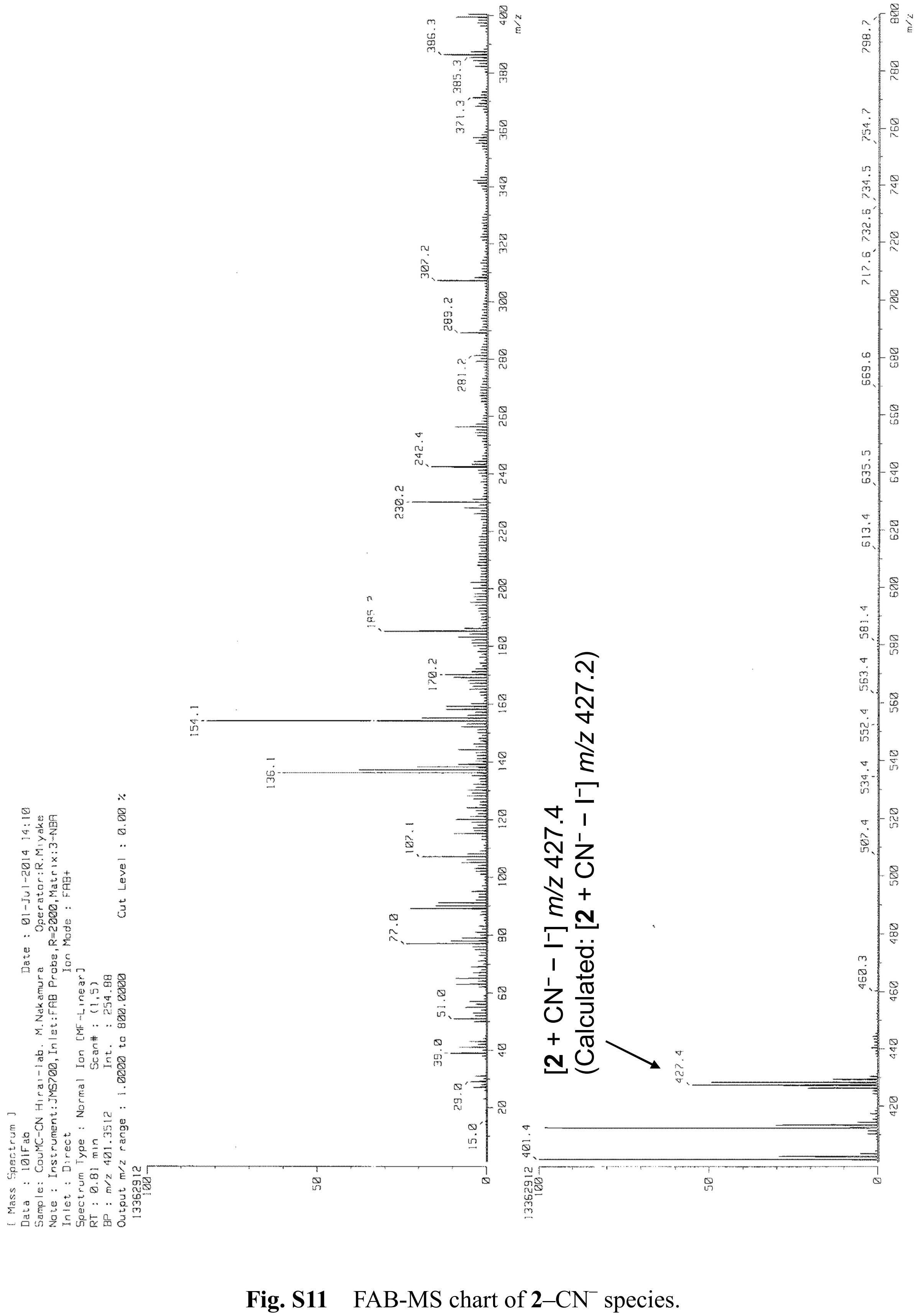


Fig. S11 FAB-MS chart of **2**–CN^- species.

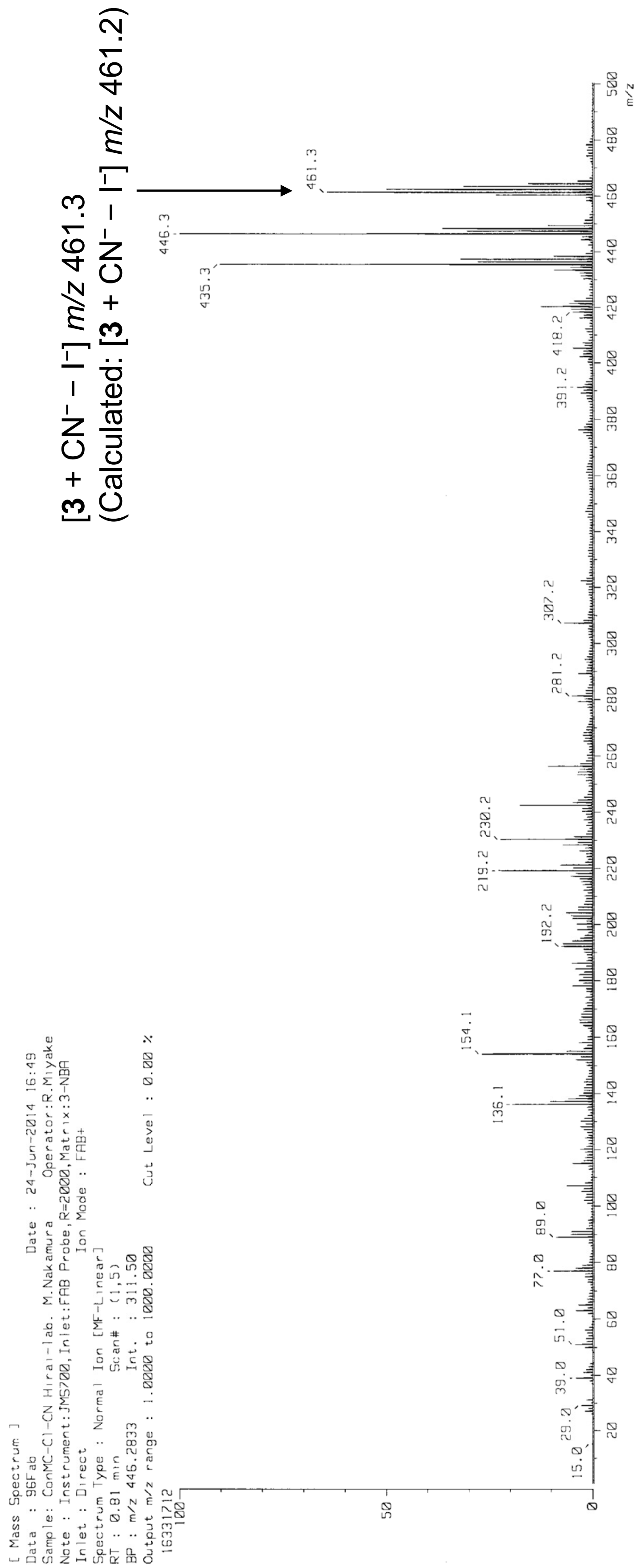


Fig. S12 FAB-MS chart of **3**–CN^- species.

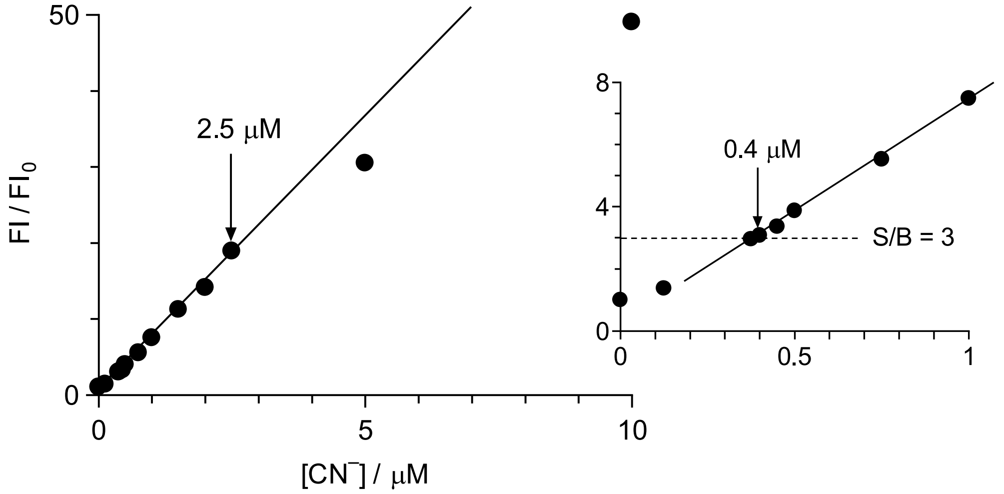


Fig. S13 Change in the ratio of fluorescence intensity (λ_{ex}= 415 nm; λ_{em}= 484 nm) of **2** (5 μM) as a function of CN^- concentration in a water/MeCN mixture (7/3 v/v; pH 9.0) at 25 °C.

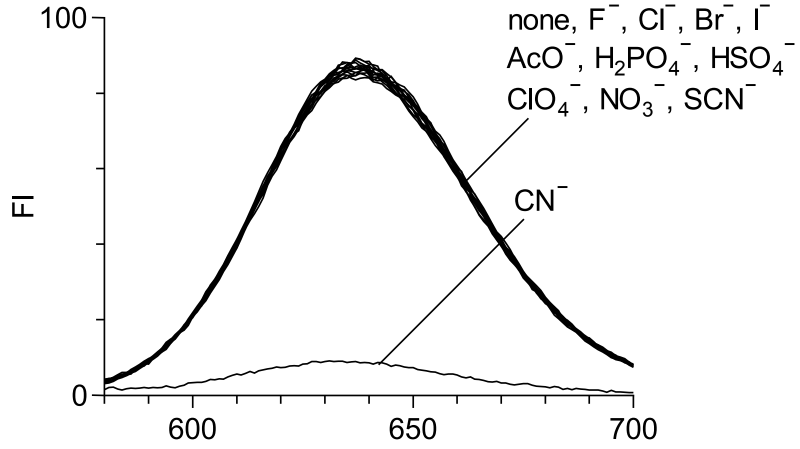
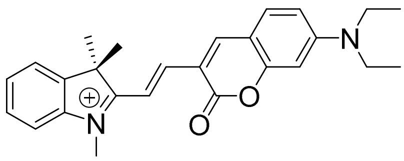
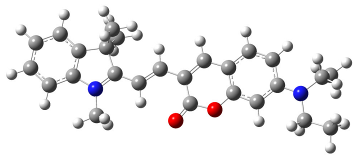


Fig. S14 Fluorescence spectra of **3** (5 μM) measured in a water/MeCN mixture (7/3 v/v; pH 9.0) by excitation at 570 nm with different anions (50 equiv).

Cartesian Coordinates (in Å) of **2**





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
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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
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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
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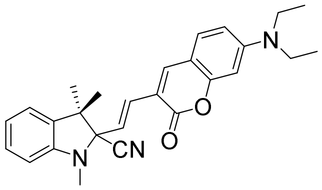
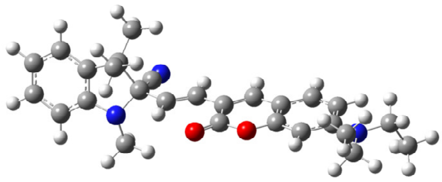
N	6.623139	0.005319	-0.218524	H	8.270179	-0.762075	1.906312
C	7.629056	-1.066939	-0.156843	H	6.994833	-1.980421	1.723653
C	7.050354	1.416676	-0.080082	H	8.694733	2.765102	-0.190123
C	7.900847	-1.570109	1.265345	H	9.168643	1.19518	0.462149
C	8.538267	1.685456	-0.286072	H	8.87761	1.389607	-1.284209
O	0.070005	2.358533	0.093976				

Cartesian Coordinates (in Å) of **2**–CN^{-}





C	3.413382	0.329081	0.05296	N	3.620996	2.975486	-0.020414
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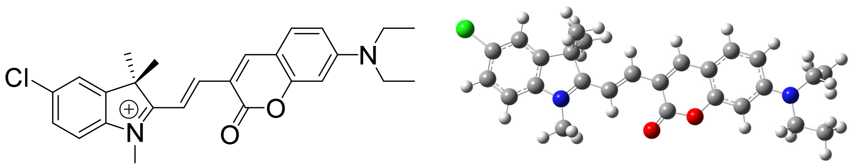
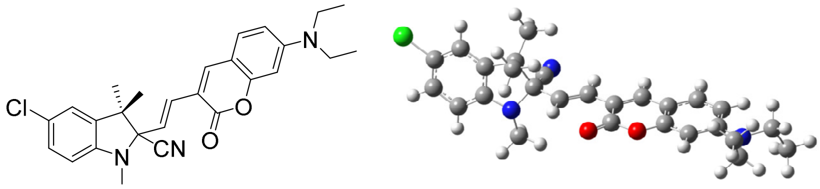
C	0.900786	0.657359	-0.058713	H	1.055483	1.694849	-0.360577
C	-0.51156	0.292644	0.016059	H	-1.16085	2.231601	-0.592395
C	-1.47426	1.229445	-0.293954	H	-3.627233	2.871137	-0.854666
C	-2.860816	0.944313	-0.243089	H	-5.970065	2.247222	-0.710385
C	-3.257902	-0.350798	0.147719	H	-4.789168	-1.765106	0.525035
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 **3**



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 **3**–CN^-



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				