Highly sensitive cyanide anion detection with a coumarin-spiropyran conjugate as a fluorescent receptor

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Electronic Supplementary Information (ESI†)

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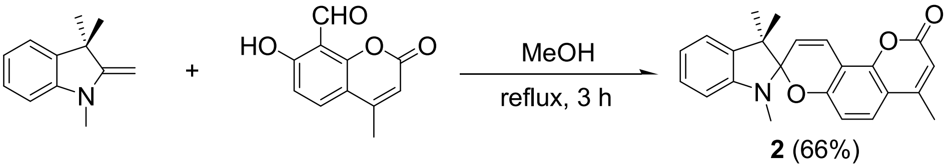
Experimental procedure

Absorption spectra were measured on an UV-visible photodiode-array spectrophotometer (Shimadzu; Multispec-1500) equipped with a temperature controller S-1700.[1] Fluorescence spectra were measured on a JASCO FP-6500 fluorescence spectrophotometer. Time-resolved emission decay analysis was carried out on a PTI-3000 apparatus (Photon Technology International) using a Xe nanoflash lamp filled with N_2.[2] Light irradiations were carried out with a Xe lamp (300 W; Asahi Spectra Co. Ltd.; MAX-302) equipped with 334 nm (light intensity: 69.1 mW m^{-2}), 380 nm (53.8 mW m^{-2}), and 550 nm (32.5 mW m^{-2}) band-pass filters, respectively. ^{1}H and ^{13}C NMR spectra were obtained by a JEOL JNM-GSX270 Excalibur and JNM-AL400 spectrometer. EI- and ESI-MS analysis was performed by a JEOL JMS 700 Mass Spectrometer.

Synthesis

Compound 2 (1,3,3,4′-tetramethylspiro[indoline-2,8′-2*H*,8*H*-pyrano[2,3-*h*]chromen-2-one])



2 (66%)

1,3,3-Trimethyl-2-methylideneindole (161 mg, 0.93 mmol) and 8-formyl-7-hydroxy-4-methylcoumarin (200 mg, 0.98 mmol)[3] were refluxed in MeOH (5 mL) for 3 h under N_2. The resultant was concentrated by evaporation. The crude product was purified by silica gel column chromatography with CH_2Cl_2, affording **2** as a white solid. Yield: 220 mg, 66 %. ^{1}H NMR (270 MHz, acetone-d_6, TMS): δ = 7.53 (d, J = 8.7 Hz, 1H, Ar*H*), 7.42 (d, J = 10.6 Hz, 1H, –CCHC*H*–), 7.18–7.11 (m, 2H, Ar*H*), 6.82 (t, J = 7.4 Hz, 1H, Ar*H*), 6.68 (d, J = 8.7 Hz, 1H, Ar*H*), 6.60 (d, J = 7.6 Hz, 1H, Ar*H*), 6.14 (d, J = 1.0 Hz, 1H, –CC*H*CCH$_3$–), 5.96 (d, J = 10.6 Hz, 1H, –CC*H*CH–), 2.80 (s, 3H, –NC*H*$_3$), 2.42 (d, J = 1.0 Hz, 3H, –CCHCC*H*$_3$–), 1.30 (s, 3H, –C(C*H*$_3$)$_2$), 1.19 ppm (s, 3H, –C(C*H*$_3$)$_2$); ^{13}C NMR (68 MHz, $CDCl_3$, TMS): δ = 160.6, 157.2, 152.7, 149.6, 147.7, 136.2, 127.5, 124.9, 122.4, 121.3, 119.5, 119.3, 112.8, 111.7, 111.3, 107.1, 106.8, 105.4, 52.0, 28.8, 25.8, 20.0, 18.7 ppm; EI-MS: *m/z*: calcd for $C_{23}H_{21}NO_3$: 359.2; found: 359.1 [M^+]; HRMS (EI^+): *m/z*: calcd for $C_{23}H_{21}NO_3$ [M^+]: 359.1521; found: 359.1523.

Nonlinear fitting of the fluorescence titration data[4]

When assuming a 1:1 stoichiometry for interaction between **2** and CN$^-$, the equilibrium is given by the following equation:

$$\mathbf{2}+\mathbf{CN}^- \xleftrightarrow{K_{\text{ass}}} \mathbf{2}\cdot\mathbf{CN}^- \qquad (1)$$

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

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

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

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

Fluorescence intensity is given as follows:[5]

$$I_0 = \Phi_{\mathbf{2}}^{\lambda}[\mathbf{2}]_0 \qquad (4)$$

$$I = \Phi_{\mathbf{2}}^{\lambda}[\mathbf{2}]+\Phi_{\mathbf{2}\cdot\mathbf{CN}^-}^{\lambda}[\mathbf{2}\cdot\mathbf{CN}^-] \qquad (5)$$

$$I_{\max} = \Phi_{\mathbf{2}}^{\lambda}[\mathbf{2}]_{\max}+\Phi_{\mathbf{2}\cdot\mathbf{CN}^-}^{\lambda}[\mathbf{2}\cdot\mathbf{CN}^-]_{\max} \qquad (6)$$

I_0 is the intensity of **2** at 453 nm without anion under UV irradiation, I is the intensity of **2** at 453 nm obtained with CN$^-$ under UV irradiation, and $I_{\max}$ is the intensity of **2** at 453 nm in the presence of excess amount of CN$^-$ under UV irradiation. $\Phi^{\lambda}_{\mathbf{2}}$ and $\Phi^{\lambda}_{\mathbf{2}\cdot\mathbf{CN}^-}$ are the fluorescence quantum yields for **2** and **2–CN**$^-$. By means of eqs 4, 5 and 6, the following equation is obtained:

$$\frac{I_{\max}-I_0}{I-I_0} = \frac{[\mathbf{2}\cdot\mathbf{CN}^-]_{\max}}{[\mathbf{2}\cdot\mathbf{CN}^-]} \qquad (7)$$

With excess amount of CN$^-$, [**2·CN**$^-$]$_{\max}$ is almost equal to [**2**]$_0$. The eq 7 can therefore be replaced as follows:

$$\frac{I_{\max}-I_0}{I-I_0} = \frac{[\mathbf{2}]_0}{[\mathbf{2}\cdot\mathbf{CN}^-]} \qquad (8)$$

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

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

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

Calculation details

Preliminary geometry optimizations were performed using the WinMOPAC version 3.0 software (Fujitsu Inc.) at the semiempirical PM3 level.[6] The obtained structures were fully refined with tight convergence criteria at the DFT level with the Gaussian 03 package,[7] using the B3LYP/6-31G* basis set for all atoms. The excitation energies and the oscillator strength of each structure were calculated by the time-dependent density-functional response theory (TD-DFT)[8] at the same level of optimization using the polarizable continuum model (PCM)[9] with water as a solvent. Cartesian coordinates for the MC form of **2** and **2**–CN$^-$ species are summarized in the end of this ESI†.

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Table S1. Calculated excitation energy (*E*), wavelength (λ), ground to excited state transition electric dipole moments (μ) and oscillator strength (*f*) for low-laying singlet state (S_n) of the MC form of **2** and **2**–CN^-.

	Main orbital transition (CIC[a])	*E* (eV) [λ (nm)]	μ (Debye)				*f*
			μ_x	μ_y	μ_z	μ_{tot}	
2(MC)							
$S_0 \rightarrow S_1$	HOMO–1→LUMO (0.10) HOMO→LUMO (0.62)	2.4279 [510.67]	–3.15	–0.61	0.00	3.2	0.6138
$S_0 \rightarrow S_2$	HOMO–2→LUMO (0.69)	3.0664 [404.33]	0.00	0.00	–0.01	0.0	0.0000
$S_0 \rightarrow S_3$	HOMO–1→LUMO (0.66)	3.1169 [397.78]	2.29	0.19	0.00	2.3	0.4028
2–CN^-							
$S_0 \rightarrow S_1$	HOMO–2→LUMO (–0.13) HOMO→LUMO (0.61) HOMO→LUMO+1 (0.19)	3.2621 [380.07]	–0.20	1.61	0.28	1.6	0.2172
$S_0 \rightarrow S_2$	HOMO→LUMO (–0.17) HOMO→LUMO+1 (0.64)	3.5144 [352.78]	–1.95	–0.42	–0.19	2.0	0.3458
$S_0 \rightarrow S_3$	HOMO–3→LUMO (0.24) HOMO–2→LUMO (0.11) HOMO–1→LUMO (0.63)	3.8167 [324.85]	–0.03	0.55	0.12	0.6	0.0295

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

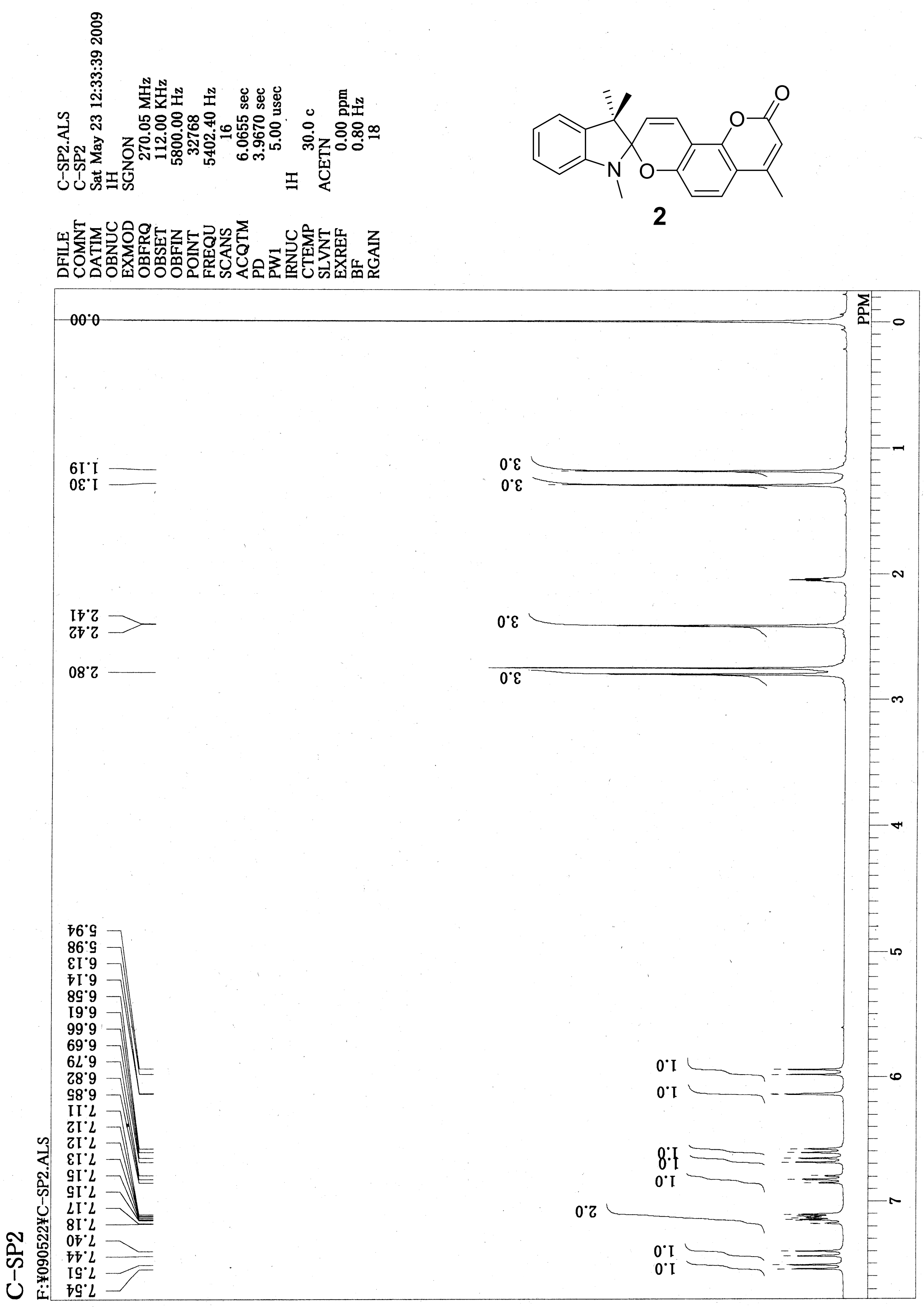

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Fig. S1 ^{1}H NMR chart of **2** (acetone-d_6, 270 MHz).

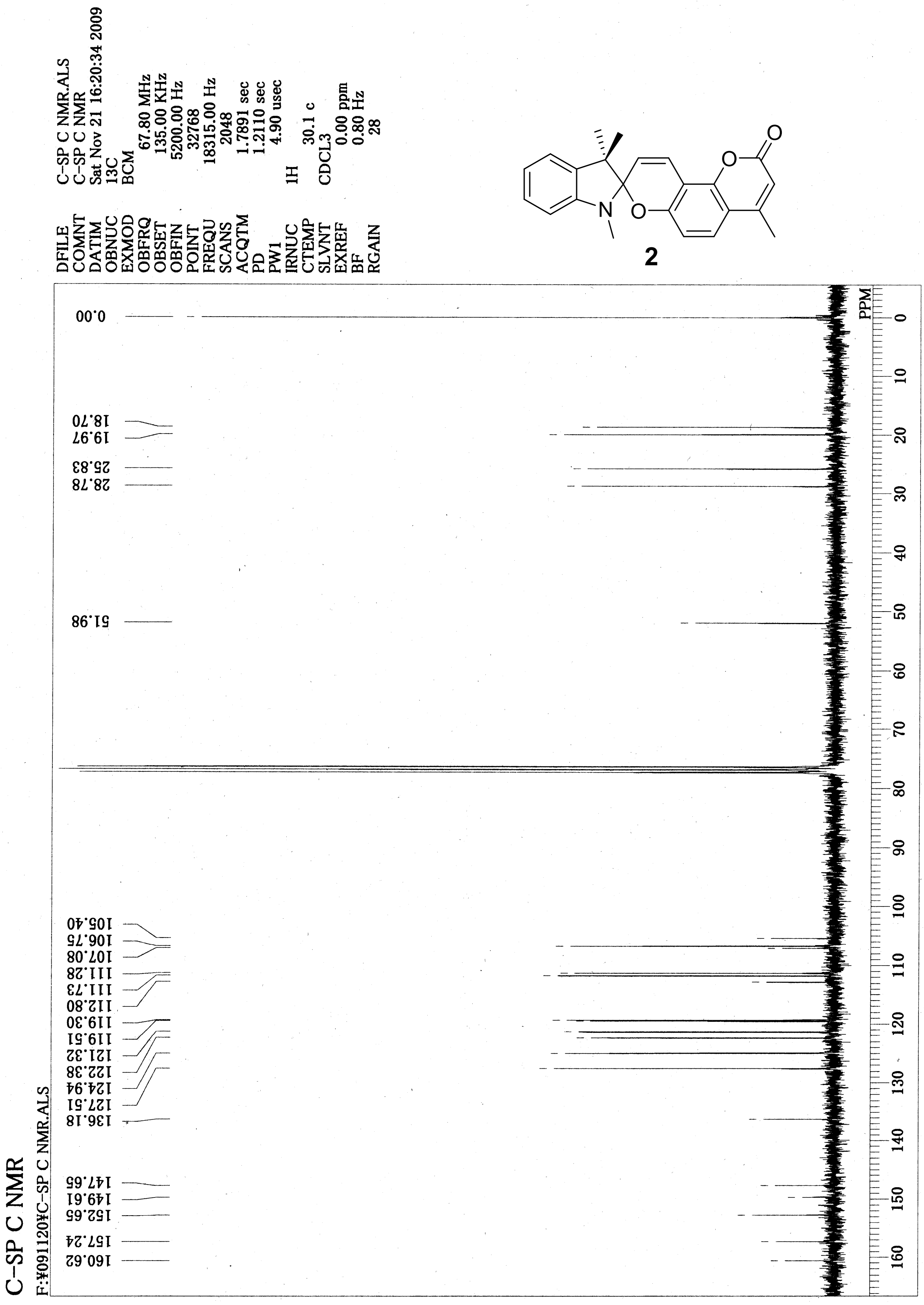
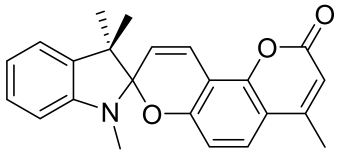


Fig. S2 ^{13}C NMR chart of **2** ($CDCl_3$, 68 MHz).



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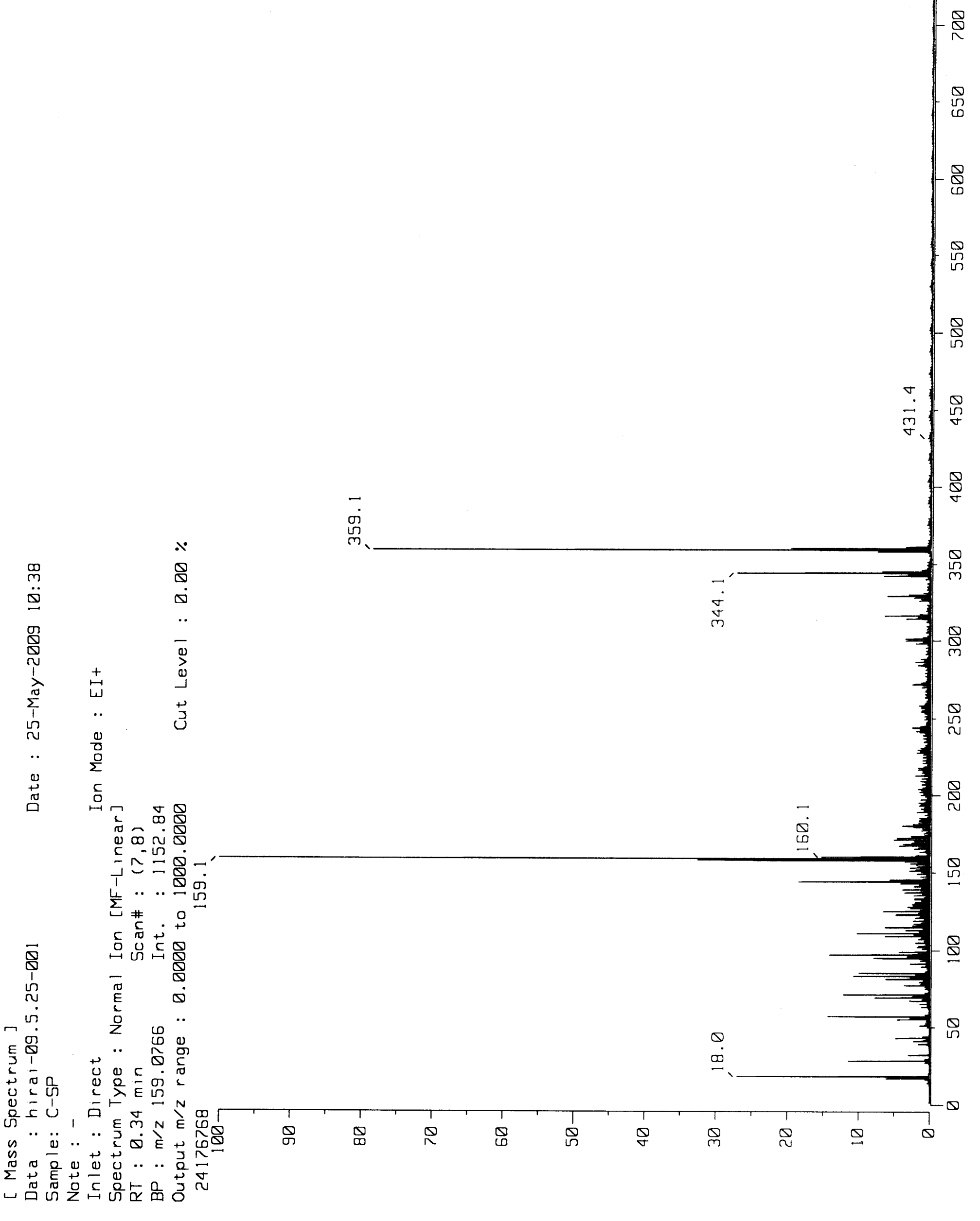


[Mass Spectrum]
Data : hirai-09.5.25-001 Date : 25-May-2009 10:38
Sample: C-SP
Note : -
Inlet : Direct Ion Mode : EI+
Spectrum Type : Normal Ion [MF-Linear]
RT : 0.34 min Scan# : (7,8)
BP : m/z 159.0766 Int. : 1152.84
Output m/z range : 0.0000 to 1000.0000 Cut Level : 0.00 %

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

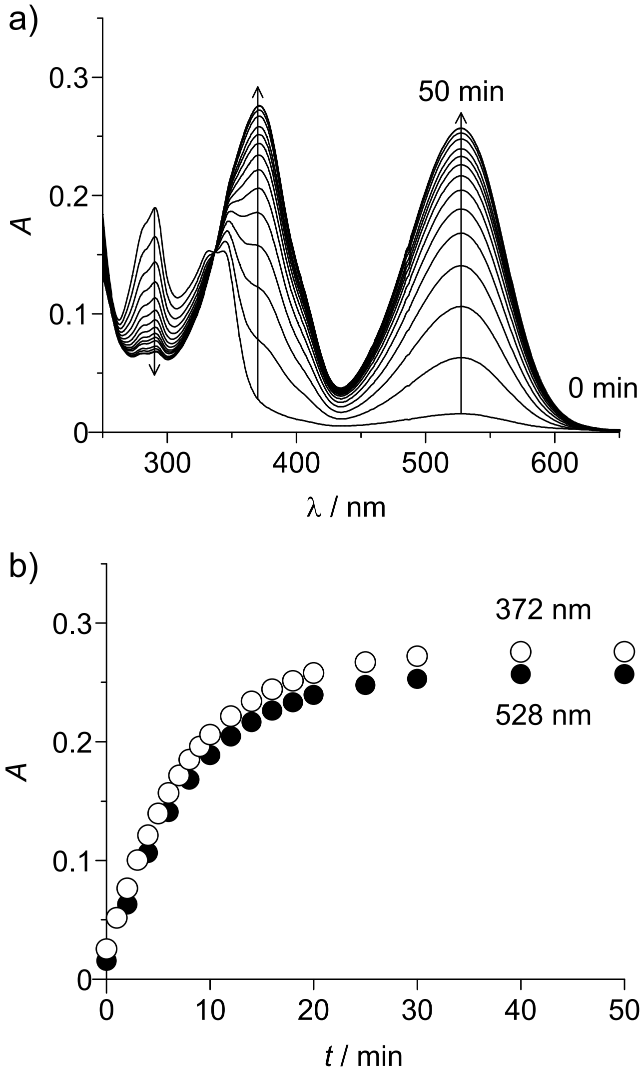


Fig. S4 (a) Time-dependent change in absorption spectra of **2** (10 μM) measured in a buffered water/MeCN mixture (8/2 v/v; CHES 100 mM, pH 9.3) under UV irradiation (334 nm) at 25 °C. (b) Change in absorbance of 372 and 528 nm bands.

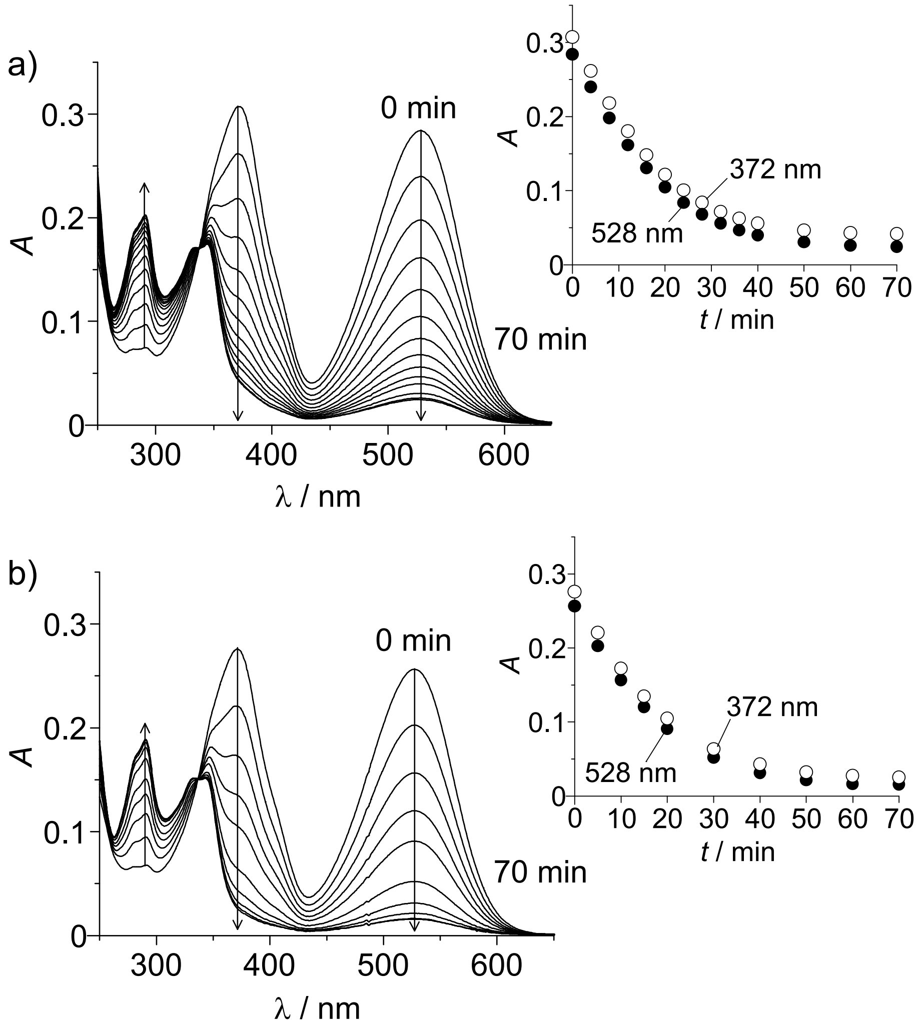


Fig. S5 Time-dependent change in absorption spectra of **2** (10 μM) measured in a buffered water/MeCN mixture (8/2 v/v; CHES 100 mM, pH 9.3) under irradiation of (a) 380 nm and (b) 550 nm monochromatic light at 25 °C.

The measurements were carried out as follows: UV light (334 nm) was irradiated to the solution containing **2** for 30 min. The spectral measurements were then started under irradiation of the respective monochromatic light. (Inset) Change in absorbance of 372 and 528 nm bands.

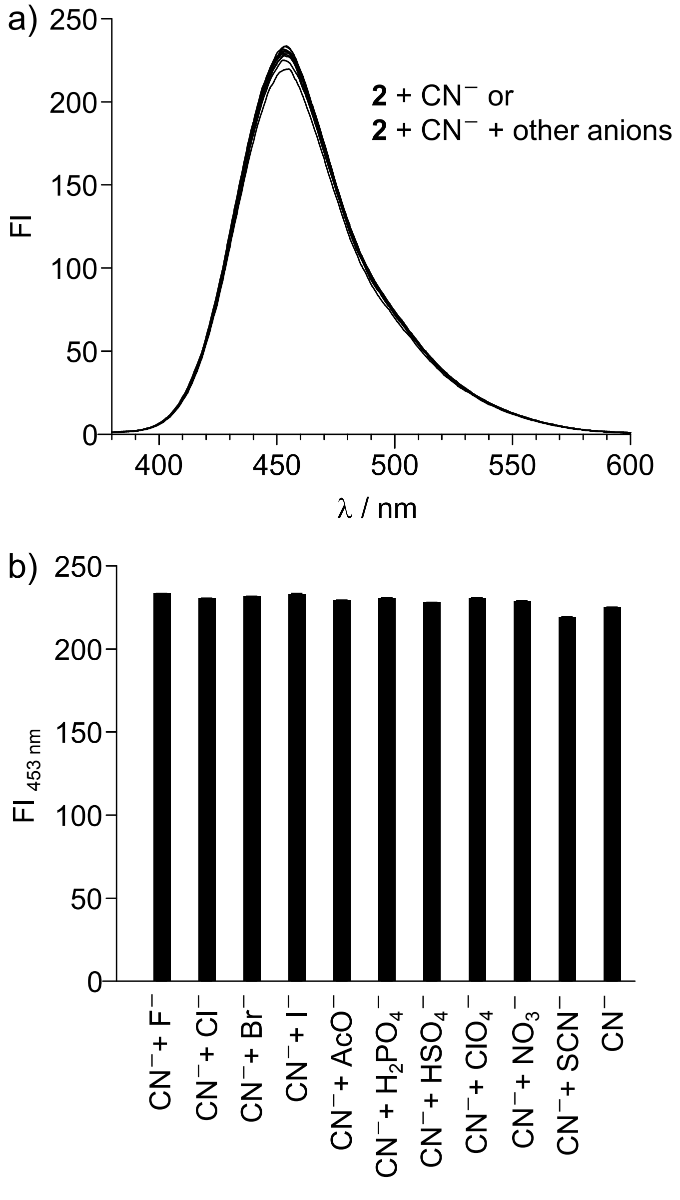


Fig. S6 (a) Fluorescence spectra (λ_{ex} = 309 nm) of **2** (10 μM) measured with 50 equiv of CN^- together with 50 equiv of other respective anions in a buffered water/MeCN mixture (8/2 v/v; CHES 100 mM, pH 9.3) under UV irradiation (334 nm) at 25 °C. The fluorescence measurements were carried out after the solution was stirred for 30 min under UV irradiation. (b) Fluorescence intensity of the respective solutions.

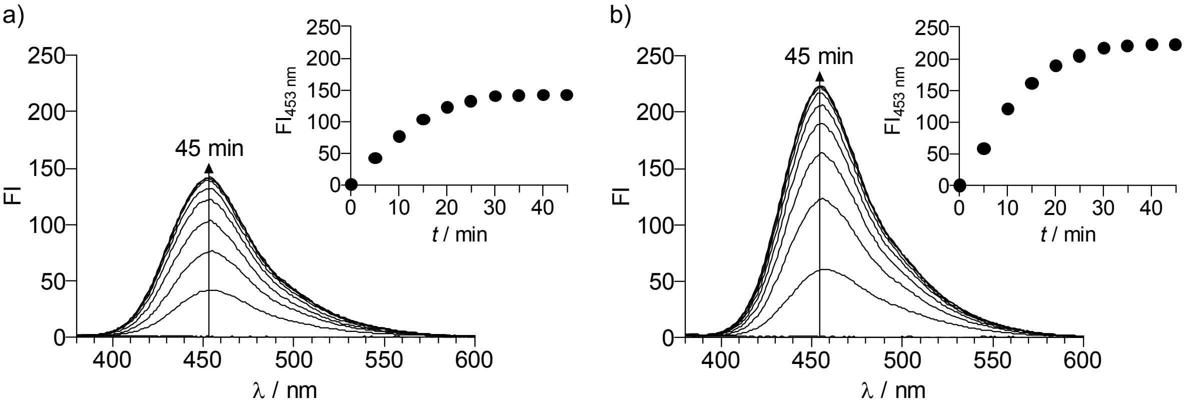


Fig. S7 Time-dependent change in the fluorescence spectra (λ_{ex} = 309 nm) of **2** (10 μM) measured after addition of (a) 10 equiv or (b) 50 equiv of CN^- in a buffered water/MeCN mixture (8/2 v/v; CHES 100 mM, pH 9.3) under UV irradiation (334 nm) at 25 °C. (Inset) Change in fluorescence intensity at 453 nm.

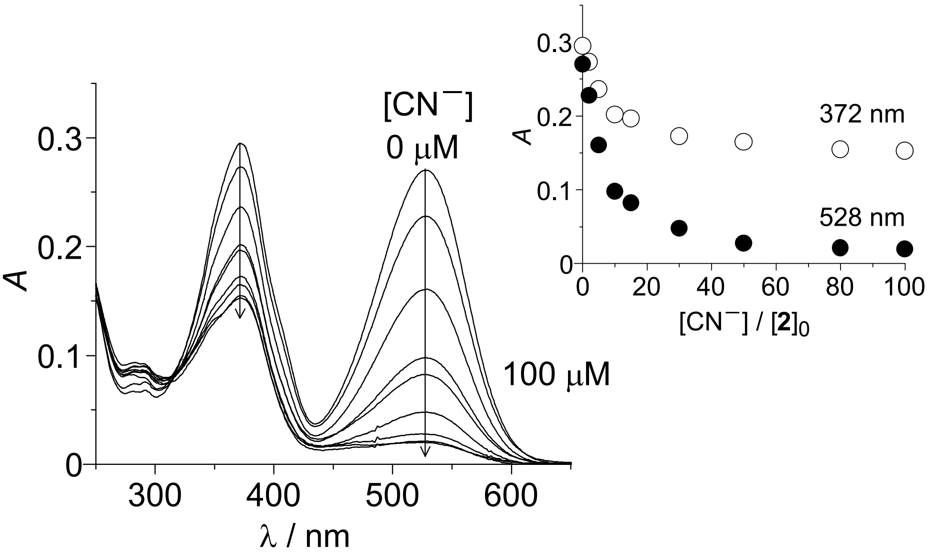
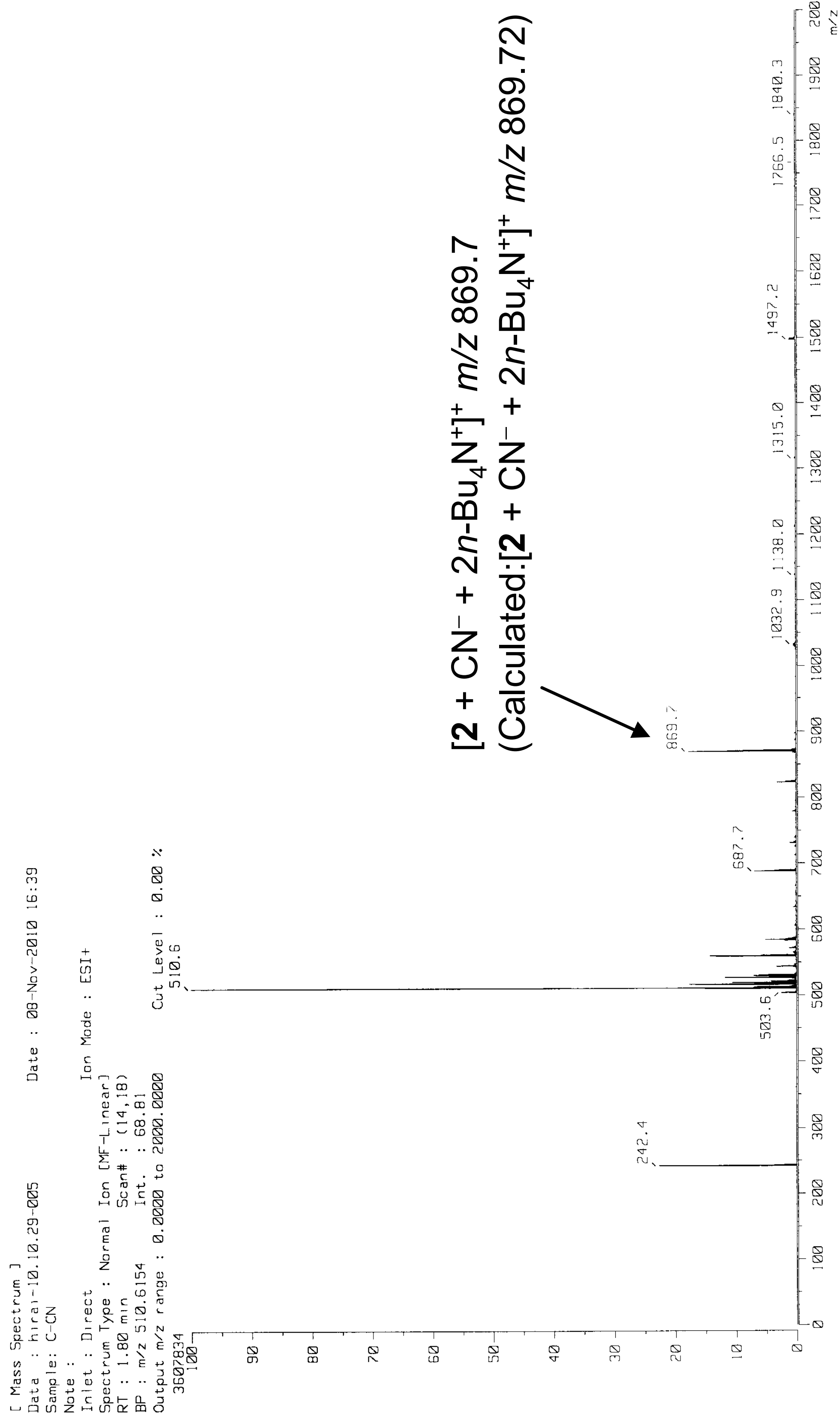


Fig. S8 Absorption titration of **2** (10 μM) with CN^- in a buffered water/MeCN mixture (8/2 v/v; CHES 100 mM, pH 9.3) under UV irradiation (334 nm) at 25 °C. Each spectrum was obtained after stirring the solution for 30 min with UV irradiation. (Inset) Change in absorbance of 372 and 528 nm bands.



[**2** + CN$^-$ + 2*n*-Bu$_4$N$^+$]$^+$ *m/z* 869.7
(Calculated:[**2** + CN$^-$ + 2*n*-Bu$_4$N$^+$]$^+$ *m/z* 869.72)

Fig. S9 ESI-MS chart of a MeCN solution containing of **2** and 2 equiv of *n*-Bu$_4$N$^+$ salt of CN$^-$ obtained after UV irradiation (334 nm).

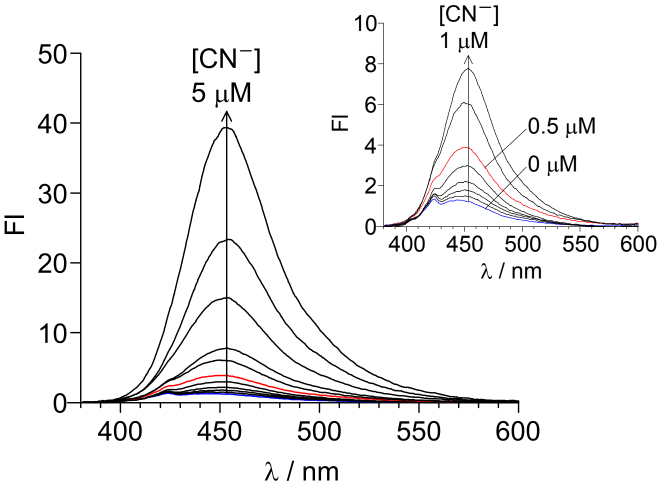


Fig. S10 Change in fluorescence spectra (λ_{ex} = 372 nm) of **2** (10 μM) during titration with CN^- in a buffered water/MeCN mixture (8/2 v/v; CHES 100 mM, pH 9.3) under UV irradiation (334 nm) at 25 °C. The spectra at each CN^- concentration were obtained after stirring the solution for 30 min under UV irradiation. The blue and red spectra were obtained with 0 and 0.5 μM CN^-.

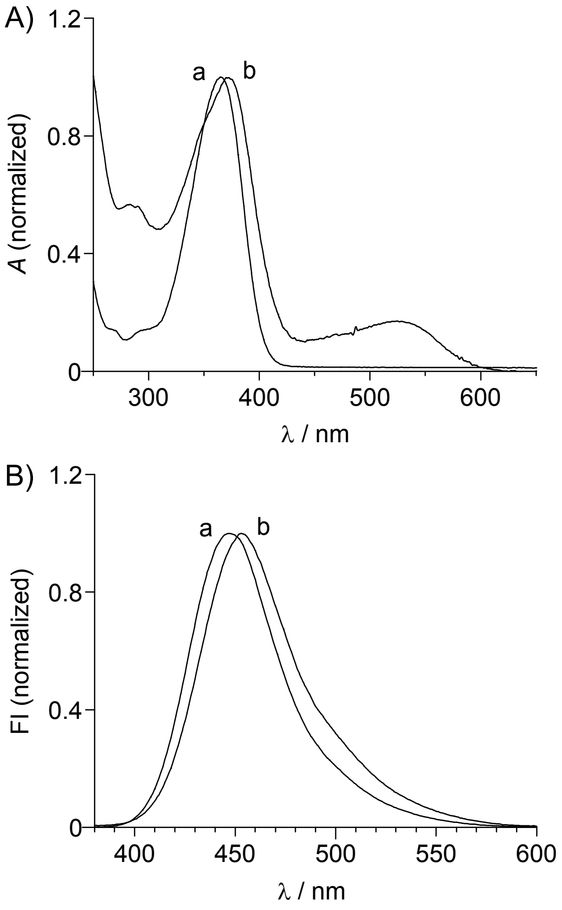
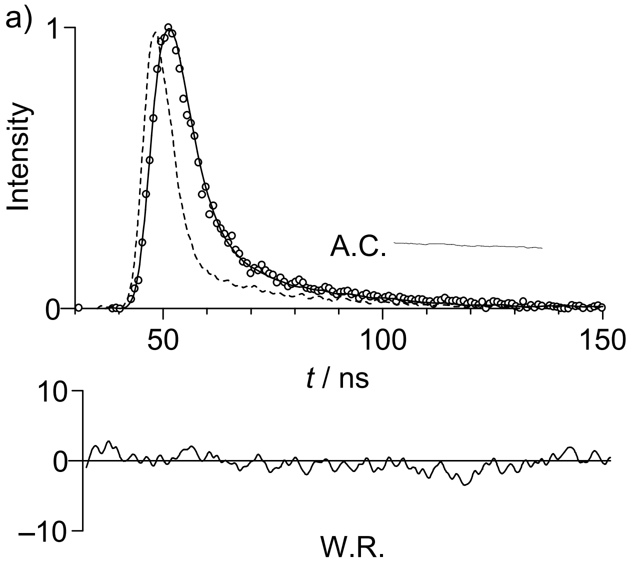
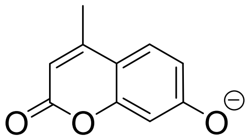
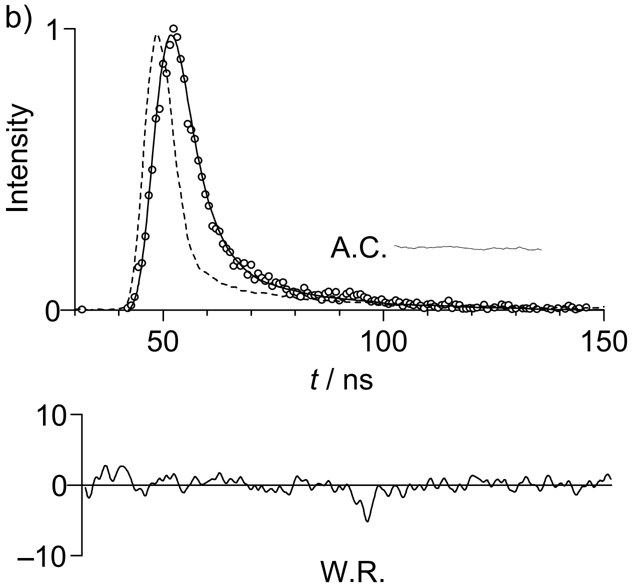


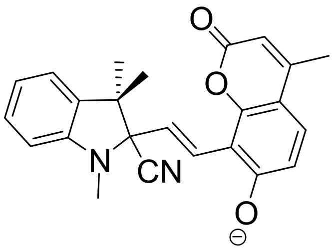
Fig. S11 (A) Absorption spectra of (a) 7-hydroxy-4-methylcoumarin (10 μM) in a water/MeCN mixture (8/2 v/v; pH 12.8) and (b) **2** (10 μM) measured with 50 equiv of CN^- in a water/MeCN mixture (8/2 v/v; CHES 100 mM, pH 9.3) under UV irradiation (334 nm) at 25 ºC. (B) Normalized fluorescence spectra of (a) 7-hydroxy-4-methylcoumarin (λ_{ex} = 320 nm) and (b) **2** (λ_{ex} = 309 nm) with 50 equiv of CN^- under UV irradiation at 25 ºC. The spectrum (b) was obtained after stirring the solution for 30 min under UV irradiation.





species	τ / ns (a / %)	χ^2
7-hydroxy-4-methylcoumarin	4.1 (100)	1.59

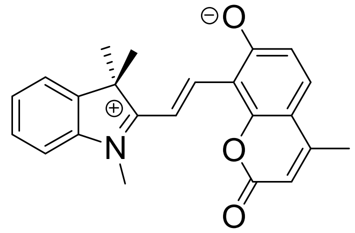




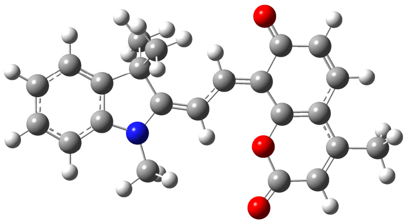
species	τ / ns (a / %)	χ^2
2–CN$^-$	4.1 (100)	1.70

Fig. S12 (a) Fluorescence decay of 7-hydroxy-4-methylcoumarin in a water/MeCN mixture (8/2 v/v; pH 12.8) (λ_{ex} = 337 nm, λ_{em} = 448 nm). (b) Fluorescence decay of **2** measured with 50 equiv of CN$^-$ in a buffered water/MeCN mixture (8/2 v/v; CHES 100 mM, pH 9.3) (λ_{ex} = 337 nm, λ_{em} = 453 nm). The measurement was carried out after stirring the solution for 30 min under UV irradiation (334 nm). Shown as insert are the decay times (τ / ns) and the normalized pre-exponential factors (a). For judging the quality of the fit, chi-squares (χ^2), autocorrelation functions (A.C.), and weighted residuals are also shown.

Cartesian Coordinates (in Å) of the MC form of 2

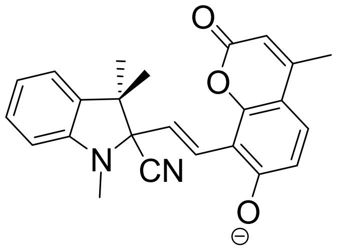


2(MC)

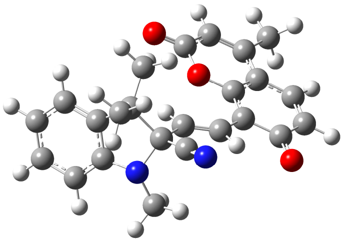


C	-6.451241	0.084195	0.000283	C	4.997946	-0.958784	0.000151
C	-6.248171	-1.297289	-0.000054	O	2.384103	-3.443427	0.000146
C	-4.958498	-1.840753	-0.000270	C	6.498228	-0.811588	0.000311
C	-3.885766	-0.952631	-0.000109	H	-7.461314	0.482759	0.000474
C	-4.072492	0.434100	0.000241	H	-7.102803	-1.967847	-0.000156
C	-5.356235	0.959396	0.000412	H	-4.818863	-2.916714	-0.000553
N	-2.503472	-1.225194	-0.000367	H	-5.516331	2.034570	0.000660
C	-1.761249	-0.076250	-0.000054	H	0.094176	-1.090129	-0.000033
C	-2.718543	1.128750	0.000204	H	-0.009994	1.997732	-0.000301
C	-0.375526	-0.117164	-0.000035	H	5.732248	1.708894	0.000141
C	0.453979	1.015960	-0.000186	H	4.231239	3.657319	-0.000131
C	1.844796	1.118876	-0.000198	H	-1.587478	2.496377	1.303842
C	2.774272	0.029384	-0.000109	H	-2.654695	1.380952	2.178669
C	4.155544	0.209283	0.000017	H	-3.338797	2.758496	1.299067
C	4.655740	1.562682	0.000017	H	-1.587939	2.496937	-1.303258
C	3.838259	2.645670	-0.000115	H	-3.339311	2.758671	-1.298229
C	2.383468	2.513374	-0.000268	H	-2.655005	1.381483	-2.178234
C	-2.556693	1.992008	1.275864	H	-1.299329	-2.710291	-0.887599
C	-2.557040	1.992353	-1.275302	H	-2.721499	-3.301321	-0.001582
C	-1.923088	-2.560752	-0.000451	H	-1.300921	-2.711175	0.887666
O	1.638258	3.503675	-0.000441	H	5.033026	-3.104942	0.000327
O	2.241905	-1.217786	-0.000112	H	6.987098	-1.789169	0.000198
C	3.005578	-2.401978	0.000116	H	6.842589	-0.258144	0.882422
C	4.430285	-2.203832	0.000197	H	6.842768	-0.257848	-0.881539

Cartesian Coordinates (in Å) of the **2**–CN^- species



2–CN^-



C	-4.236827	-2.787822	0.813799	O	1.270259	-3.191172	-0.821694
C	-4.256412	-2.113148	2.033707	C	5.875640	-1.956937	0.211110
C	-3.760469	-0.807876	2.152144	C	-1.997038	2.495962	-0.945681
C	-3.251958	-0.186113	1.008788	N	-2.092289	3.564605	-1.390399
C	-3.226650	-0.861736	-0.225198	H	-4.609694	-3.806252	0.745644
C	-3.716496	-2.152743	-0.326458	H	-4.648577	-2.610019	2.918540
N	-2.733781	1.099562	0.879912	H	-3.762210	-0.303192	3.113505
C	-1.908891	1.134545	-0.378374	H	-3.685136	-2.679064	-1.277576
C	-2.685883	0.072313	-1.298626	H	-0.360366	-0.327881	0.099275
C	-0.475211	0.725896	-0.122278	H	0.438107	2.621443	-0.270238
C	0.590928	1.553591	-0.111480	H	5.847658	0.655105	0.629401
C	1.994787	1.241489	0.110789	H	4.926448	2.937771	0.805640
C	2.561896	-0.030757	0.007889	H	-3.555893	1.430563	-2.790932
C	3.948280	-0.293033	0.181188	H	-4.526236	1.272245	-1.314099
C	4.782728	0.824743	0.482766	H	-4.493726	-0.050022	-2.496097
C	4.282138	2.090735	0.583349	H	-1.324716	0.148050	-2.994668
C	2.867221	2.392077	0.398877	H	-2.370572	-1.279355	-2.960468
C	-3.888356	0.728707	-2.018383	H	-0.969706	-1.182031	-1.878983
C	-1.775585	-0.601964	-2.334776	H	-1.923337	2.818936	1.732600
C	-2.253444	1.824173	2.042895	H	-1.414454	1.324073	2.548254
O	2.431951	3.561671	0.489120	H	-3.077847	1.948432	2.753721
O	1.718268	-1.070620	-0.302537	H	3.860605	-3.662605	-0.432838
C	2.134032	-2.388876	-0.501974	H	6.058583	-3.025722	0.063821
C	3.531830	-2.637476	-0.300487	H	6.221963	-1.686701	1.216617
C	4.411579	-1.630608	0.027008	H	6.500746	-1.402820	-0.500384