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# **Supporting Information**

### A New Fluorophore Displaying Remarkable Solvatofluorochromism and Solid State Light Emission, and Serving as a Turn-on Fluorescent Sensor for Cyanide Ion

Yusuke Kimura,<sup>a</sup> Ikumi Kawajiri,<sup>a</sup> Masanori Ueki,<sup>a</sup> Takayuki Morimoto,<sup>a</sup> Jun-ich Nishida,<sup>a</sup> Hiroshi Ikeda,<sup>\*b,c</sup> Mirai Tanaka,<sup>b</sup> and Takeshi Kawase<sup>\*a</sup>

<sup>a</sup>Department of Materials Science and Chemistry, Graduate School of Engineering, University of Hyogo, 2167 Shosha, Himeji, Hyogo 671-2280

<sup>b</sup>Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, 1-1 Gakuen-cho, Naka-ku, Sakai, Osaka 599-8531

<sup>c</sup>The Research Institute for Molecular Electronic Devices (RIMED), Osaka Prefecture University, 1-1 Gakuen-cho, Naka-ku, Sakai, Osaka 599-8531, Japan

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### 1. X-ray crystal structure of 2a

Fig. S1 a) and b) Molecular packing of 2a in a unit cell. Hydrogen atoms and cocrystallized solvent molecule (acetonitrile) removed for clarity. c) ORTEP drawings of another independent molecule of 2a with thermal ellipsoids at 50% probability; front and top views.

X-ray crystallography: Single crystals of 2a suitable for X-ray analysis were obtained by slow

evaporation from a toluene solution. X-ray diffraction data were collected on a Rigaku RAXIS-RAPID Imaging Plate with graphite-monochromated Mo<sub>Ka</sub> ( $\lambda = 0.71070$  Å) radiation,  $\Phi$  and  $\omega$  scans to a maximum  $2\theta$  value of 55.0°. The structures were solved by a direct method using SIR2004.<sup>1</sup> All non-hydrogen atoms were refined anisotropically by full-matrix least-squares on  $F^2$  using SHELXL97.<sup>2</sup> Hydrogen atoms of **2a** were positioned geometrically and refined using a riding model. All calculations were performed using the WinGX program package.<sup>3</sup> CCDC 1524830 (2a, C<sub>118</sub>H<sub>92</sub>N<sub>8</sub>  $+ C_2H_3N$ ) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

**2a**: Crystal system = triclinic, a = 13.8813(6) Å, b = 14.4392(7) Å, c = 23.5317(11) Å,  $\alpha = 95.8618(12)^{\circ}$ ,  $\beta = 105.3647(12)^{\circ}$ ,  $\gamma = 91.4814(11)^{\circ}$ , V = 4517.3(4) Å<sup>3</sup>, Space group = P-1, Z = 2,  $D_{calc} = 1.220$  g/cm<sup>3</sup>, T = 200, R1 [ $I > 2\sigma$  (I)] = 0.0714, wR2 (all) = 0.2407, F = 0.938. Refl/param. = 20530/1183 (CCDC 1524830).

### 2. Optical properties



Fig. S2 Absorption spectra of 1a and 2a in CH<sub>2</sub>Cl<sub>2</sub>.



Fig. S3 Colors of 1a and 2a under day light (upside) and under a UV (360 nm) lamp (downside).



Fig. S4. Normalized fluorescence spectra of 1a and 2a in the solid state (powder) ( $\lambda_{EX} = 365$  nm).



Fig. S5 UV-Vis spectra of 2a in various solvents.



**Fig S6** Correlation of peak emission wavenumber with solvent polarity parameter  $E_T(30)$  (correlation: R2=0.969).

#### 3. Ion and molecular sensing experiments



#### 3-1. Cyanide ion sensing experiments

**Fig. S7** Fluorescence and absorption spectra of **2a** ( $1 \times 10^{-5}$  M) in the presence of none, 1 eq, 2 eq and 6 eq of *n*Bu<sub>4</sub>NCN in CH<sub>2</sub>Cl<sub>2</sub>. These spectra were measured after 30 min.

When an excess amount of  $nBu_4NCN$  (~10<sup>-2</sup> M) was added to the NMR sample solution of **2a** (~10<sup>-3</sup> M), the fluorescence color was changed from reddish orange to blue-green color (Fig. S7). The NMR spectral change was disclosed in Fig. S8. The NMR spectrum of the cyanide adduct (Fig. 8) showed broad signals, because the cyanide adduct **7A** would exist as an equilibrium mixture with the monoanion **7B** and the neutral species **7c** owing to the presence of water as a contamination (Scheme S1).



Scheme S1 Addition of *n*Bu<sub>4</sub>NCN to 2a.



**Fig. S8** <sup>1</sup>H-NMR spectra of **2a** ( $\sim 10^{-3}$  M) before and after adding an excess amount of *n*Bu<sub>4</sub>NCN in CDCl<sub>3</sub>.

3-2. *n*-Propylamine (*n*PrNH<sub>2</sub>) sensing experiments



Scheme S2 Addition of *n*PrNH<sub>2</sub> to 2a.

When an excess amount of  $nPrNH_2$  (~10<sup>-2</sup> M) was added to the NMR sample solution of **2a** (~10<sup>-3</sup> M), the fluorescence color was changed from reddish orange to blue (Fig. S7). The NMR spectral change was illustrated in Fig. S10. The NMR spectrum of the adduct showed clear signals. It probably due to the formation of the corresponding dianion **8** in the presence of an excess amount of  $nPrNH_2$ .



**Fig S9** <sup>1</sup>H-NMR spectra of **2a** ( $\sim$ 10<sup>-3</sup> M) before and after adding an excess amount of *n*PrNH<sub>2</sub> in CDCl<sub>3</sub>.

# $2a + nPrNH_2$



**Fig. S10** Time- and concentration-dependent fluorescence intensity change at 478 nm of **2a** (0.1, 0.5, 1 and  $5 \times 10^{-5}$  M) in the presence of excess amount of *n*Bu<sub>4</sub>NF and *n*PrNH<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub>.



3-3. Fluoride ion sensing experiments

**Fig S11** Fluorescence and absorption spectra of **2a** ( $1 \times 10^{-5}$  M) in the presence of none, 1 eq, 2 eq and 6 eq of *n*Bu<sub>4</sub>NF in CH<sub>2</sub>Cl<sub>2</sub>. These spectra were measured after 30 min.



**Fig S12** Time- and concentration-dependent fluorescence intensity change at 478 nm of **2a** (0.1, 0.5, 1 and  $5 \times 10^{-5}$  M) in the presence of excess amount of *n*Bu<sub>4</sub>NF in CH<sub>2</sub>Cl<sub>2</sub>.



Scheme S3 Retro-Knoevenagel condensation of 2a.



Fig. S14 <sup>13</sup>C-NMR spectrum of 3.





### 4. IR spectra of 3 and 2a.

E'--? 731.05 759.98 788.91 819.77 842.92 1168.9 1211.34 1305.95 HIE 00 0.916 3.608 0.311 8.739 0.551 4.051 7.829 2.189 3.276 0.583 54.788 19.946 58.963 12.657 56.61 35.674 18.304 49.946 50.955 53.933 52.437 51.373 42.36 3.726 2.579 54.163 32.027 44.664 105 43.325 9.864 50.128 5.417 41.941 60.164 27.837 12.805 18.747 17.283 16.699 64.492 79.529 3.505 19.472 11.114 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 ST. NewY 90 1305.85 1386.86 1438.94 1458.23 1496.81 1570.11 1600.97 1697.41 2858.6 2941.54 2956.97 1.202 0.9 0.965 13.669 28.611 0.327 5.563 0.816 75 60 45 1999.81 30 165.90 15 0-040 5 0 000 3500 3000 20130628 PenTBF CHO 500 1/cm 750 2500 2000 1750 1500 1250 1000 コメント: 20130828 PenTBF CHO 日時; 2013/08/28 13:53:39 積算: Fig. S17 IR spectrum of 3. 1 SHIMADZU 補正高 24.291 E<sup>-</sup>-9 756.12 821.7 1195.91 1222.91 1394.58 1419.68 1496.81 1550.82 1560.46 1581.68 1602.9 2227.86 1602.9 2227.86 1602.9 2227.86 1602.9 2227.86 1602.9 2227.86 1602.9 2227.86 1002.9 2251.19 63.66 62.259 65.427 73.796 73.522 74.6 63.663 53.852 56.137 16.937 55.349 58.162 73.19 62.5 66.246 1.16 1.851 1.64 1.472 0.229 0.368 0.536 0.707 0.138 7.28 0.927 2.517 1.522 1.059 0.478 28.664 22.39 14.538 3.983 6.248 10.065 8.979 3.827 46.42 19.527 31.942 9.401 7.879 4.856 120 3 4 5 6 7 8 9 10 11 12 13 14 15 \$T 105 90 75 25 60 156.12 821.70 227.96 45 30

() SHIMADZU

Fig. S18 IR spectrum of 2a.

2500

2000

4000 3500 3000 20130828 PenTBF CN2

コメント: 20130828 PenTBF CN2

15

1000

1250

1750

積算;

1500

日時: 2013/08/28 14:17:40

750

500 1/cm

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