Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

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

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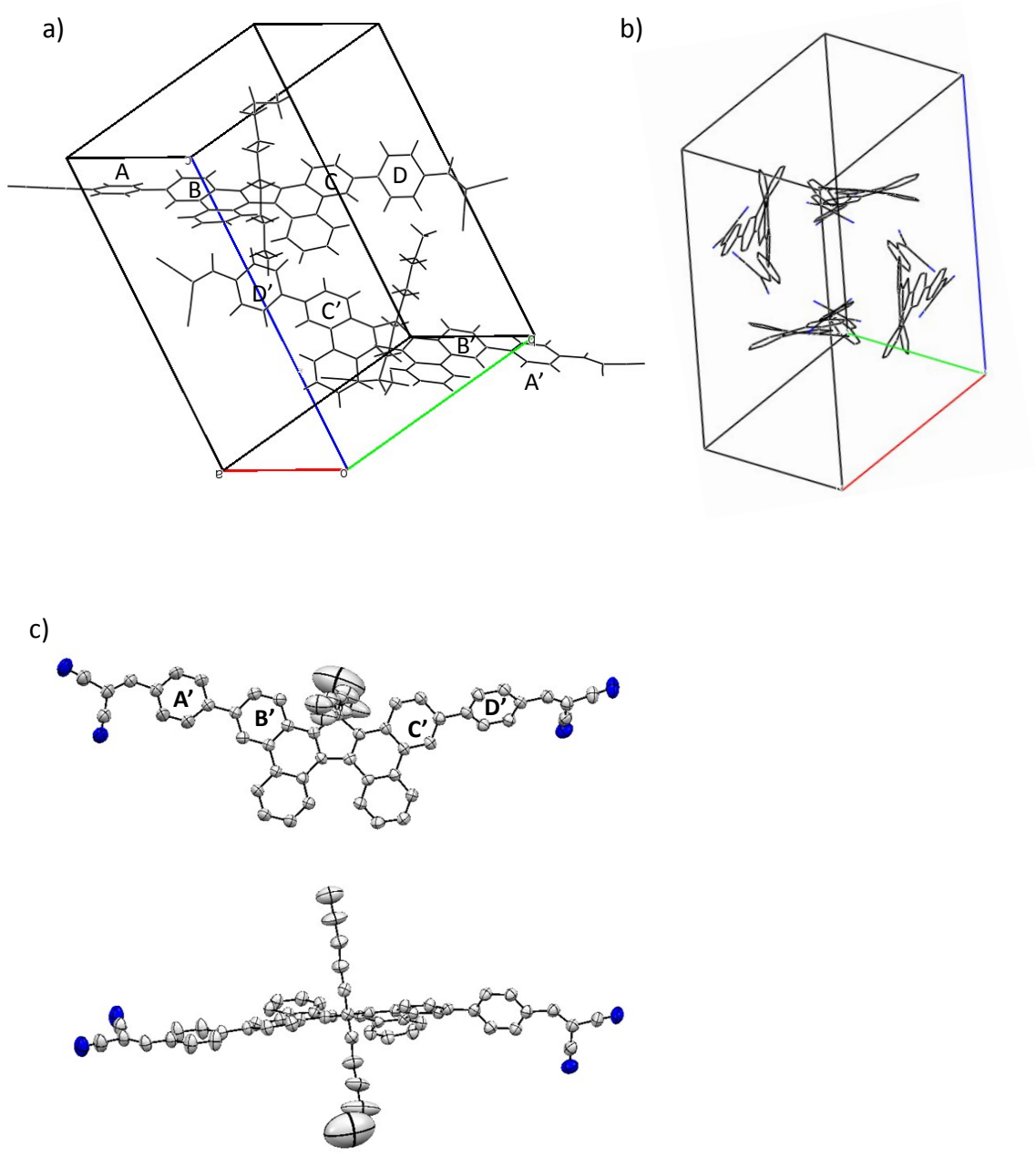


1. X-ray crystal structure of 2a

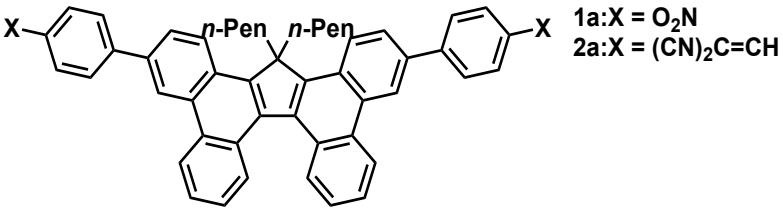
Fig. S1 a) and b) Molecular packing of **2a** in a unit cell. Hydrogen atoms and cocrystallized solvent molecule (acetonitrile) removed for clarity. c) ORTEP drawings of another independent molecule of **2a** with thermal ellipsoids at 50% probability; front and top views.

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 $Mo_{K\alpha}$ ($\lambda = 0.71070$ Å) radiation, Φ and ω scans to a maximum 2θ value of 55.0º. The structures were solved by a direct method using SIR2004.[1] All non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2 using SHELXL97.[2] Hydrogen atoms of **2a** were positioned geometrically and refined using a riding model. All calculations were performed using the WinGX program package.[3] CCDC 1524830 (**2a**, $C_{118}H_{92}N_8 + C_2H_3N$) 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, α = 95.8618(12)º, β = 105.3647(12)º, γ = 91.4814(11)º, V = 4517.3(4) Å^3, Space group = P–1, Z = 2, D_{calc} = 1.220 g/cm^3, 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



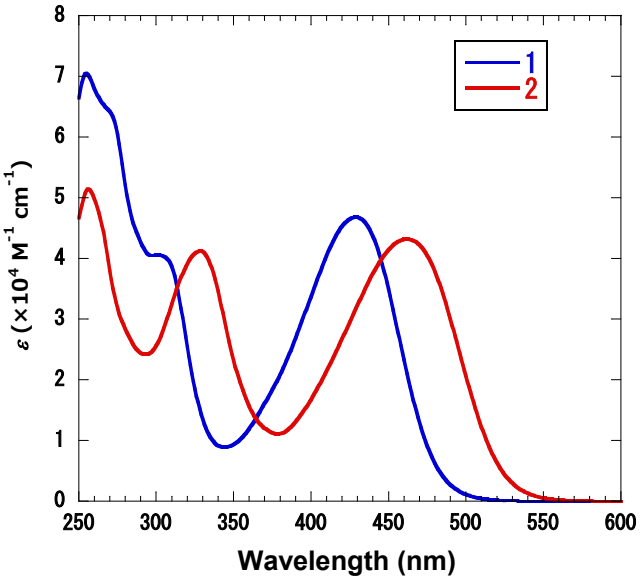


Fig. S2 Absorption spectra of **1a** and **2a** in CH_2Cl_2.

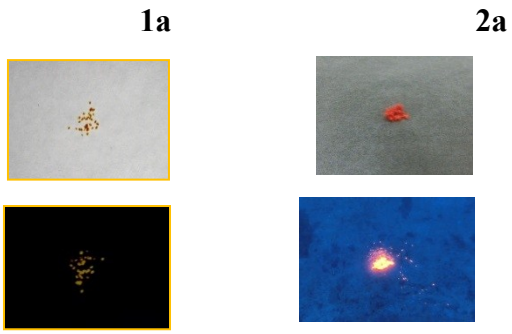


Fig. S3 Colors of **1a** and **2a** under day light (upside) and under a UV (360 nm) lamp (downside).

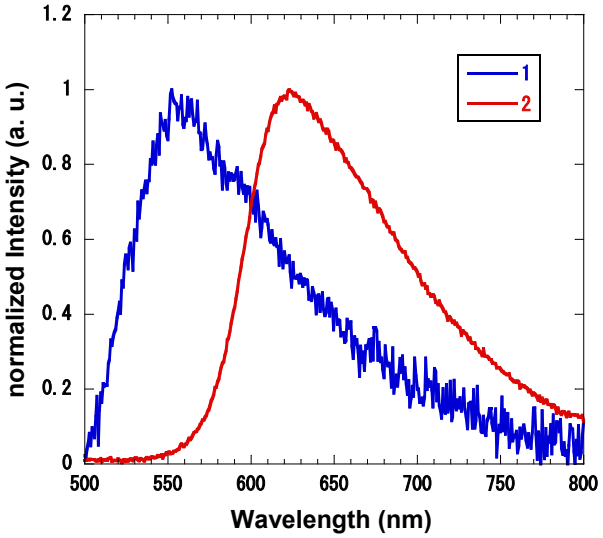


Fig. S4. Normalized fluorescence spectra of **1a** and **2a** in the solid state (powder) (λ_{EX} = 365 nm).

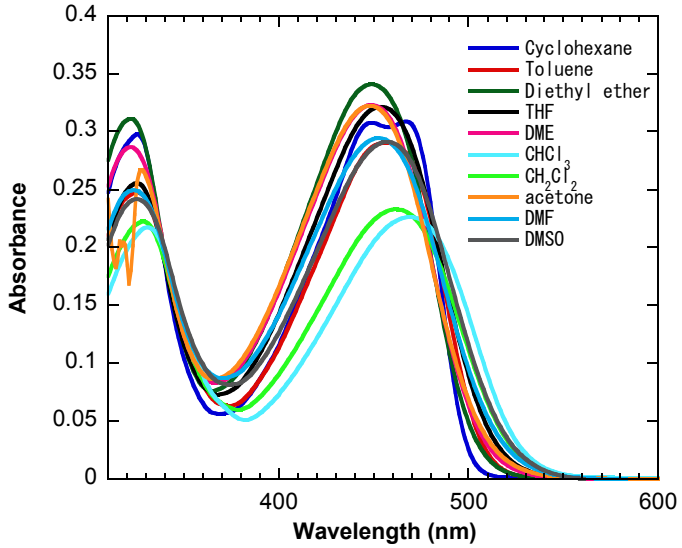


Fig. S5 UV-Vis spectra of **2a** in various solvents.

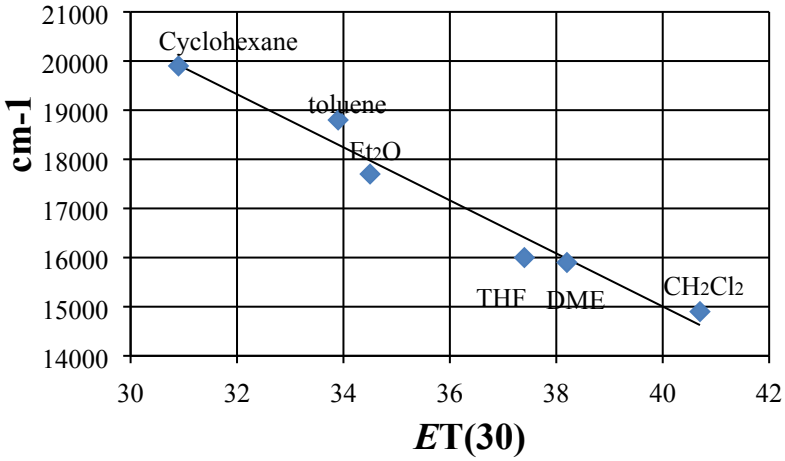
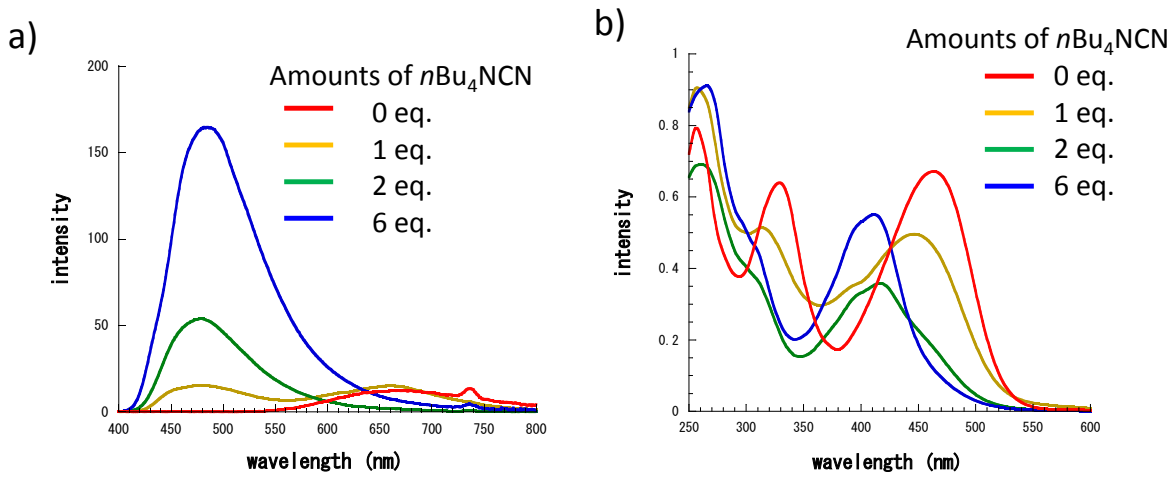


Fig S6 Correlation of peak emission wavenumber with solvent polarity parameter $E_T(30)$ (correlation: R2=0.969).

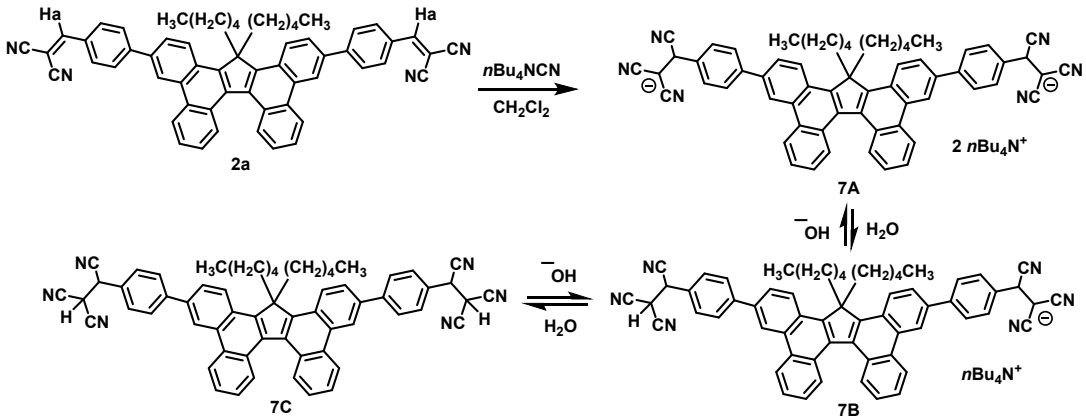
3. Ion and molecular sensing experiments



3-1. Cyanide ion sensing experiments

Fig. S7 Fluorescence and absorption spectra of **2a** (1×10^{-5} M) in the presence of none, 1 eq, 2 eq and 6 eq of nBu$_4$NCN in CH_2Cl_2. These spectra were measured after 30 min.

When an excess amount of nBu$_4$NCN (~10^{-2} M) was added to the NMR sample solution of **2a** (~10^{-3} 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 nBu$_4$NCN to **2a**.

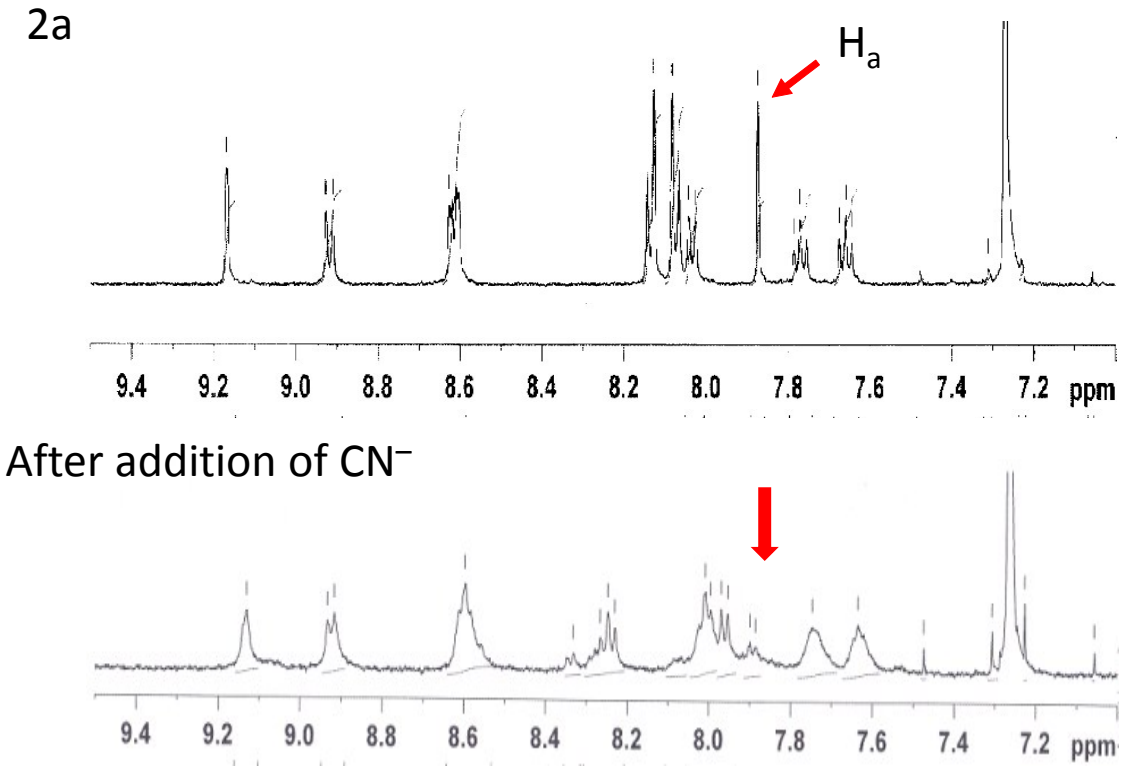
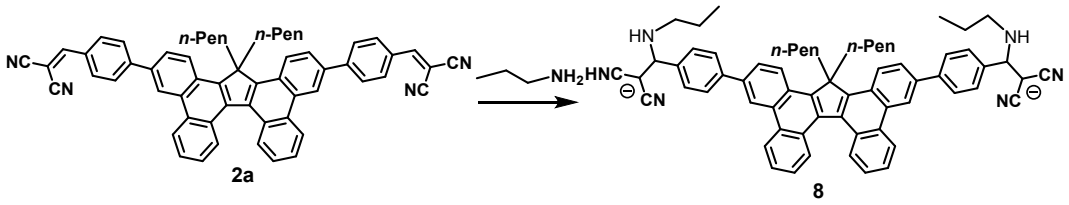


Fig. S8 ^{1}H-NMR spectra of **2a** (~10^{-3} M) before and after adding an excess amount of nBu$_4$NCN in $CDCl_3$.

3-2. *n*-Propylamine (nPrNH$_2$) sensing experiments



Scheme S2 Addition of nPrNH$_2$ to **2a**.

When an excess amount of nPrNH$_2$ (~10^{-2} M) was added to the NMR sample solution of **2a** (~10^{-3} 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$_2$.

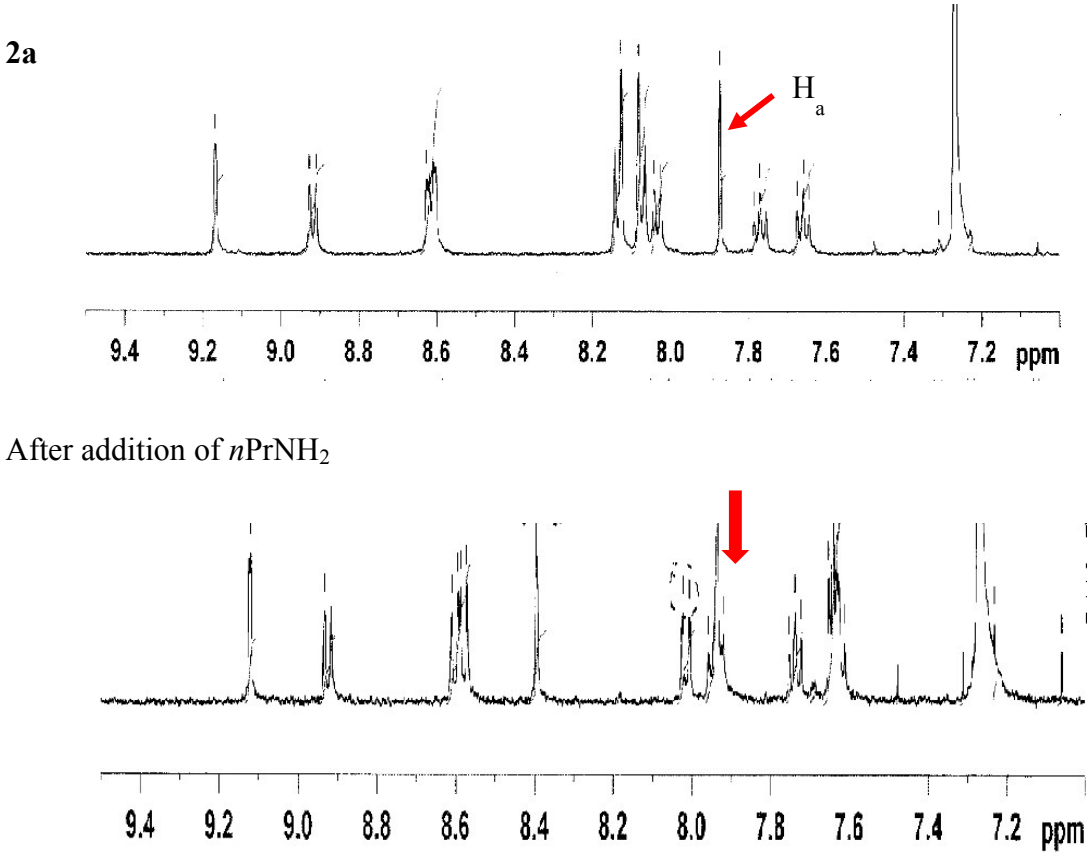


Fig S9 ^{1}H-NMR spectra of **2a** (~10^{-3} M) before and after adding an excess amount of *n*PrNH$_2$ in CDCl$_3$.

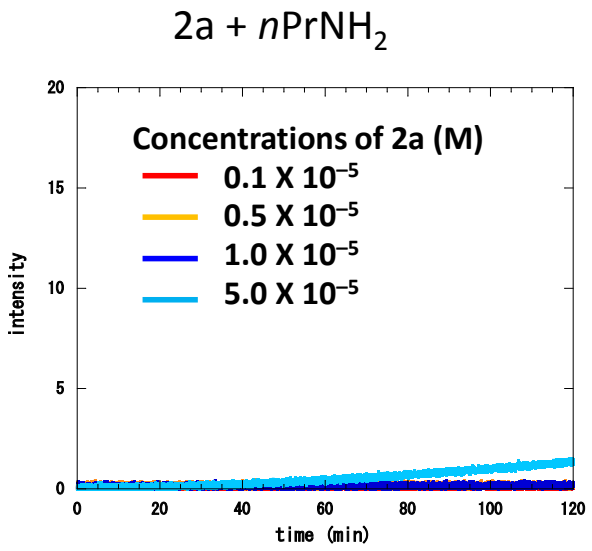


Fig. S10 Time- and concentration-dependent fluorescence intensity change at 478 nm of **2a** (0.1, 0.5, 1 and 5 × 10^{-5} M) in the presence of excess amount of nBu$_4$NF and nPrNH$_2$ in CH_2Cl_2.

3-3. Fluoride ion sensing experiments

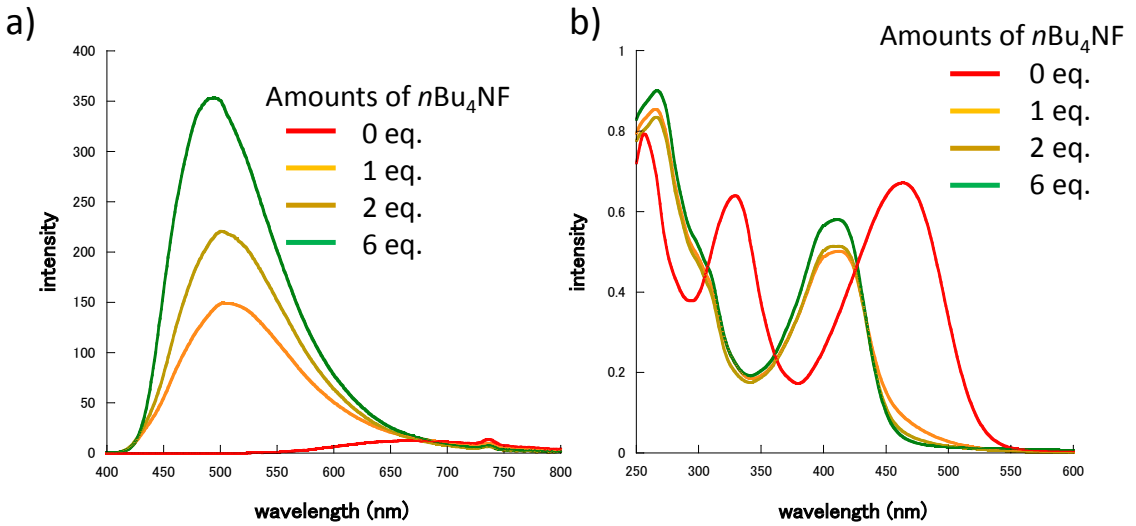


Fig S11 Fluorescence and absorption spectra of **2a** (1× 10^{-5} M) in the presence of none, 1 eq, 2 eq and 6 eq of nBu$_4$NF in CH_2Cl_2. These spectra were measured after 30 min.

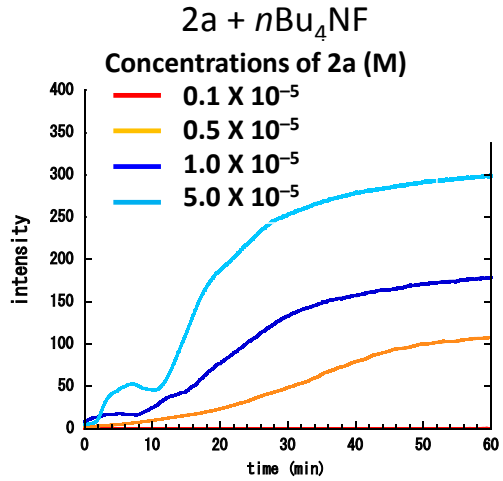
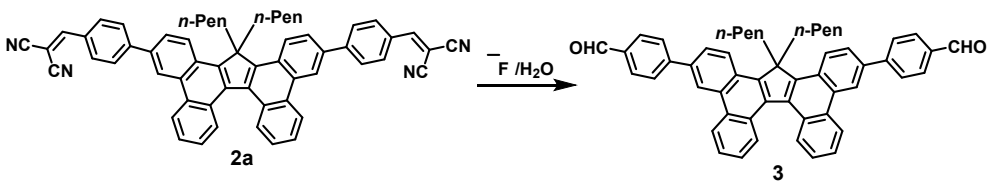


Fig S12 Time- and concentration-dependent fluorescence intensity change at 478 nm of **2a** (0.1, 0.5, 1 and 5 × 10^{-5} M) in the presence of excess amount of nBu$_4$NF in CH_2Cl_2.



Scheme S3 Retro-Knoevenagel condensation of **2a**.

4. NMR spectra of 2a and 3 in $CDCl_3$

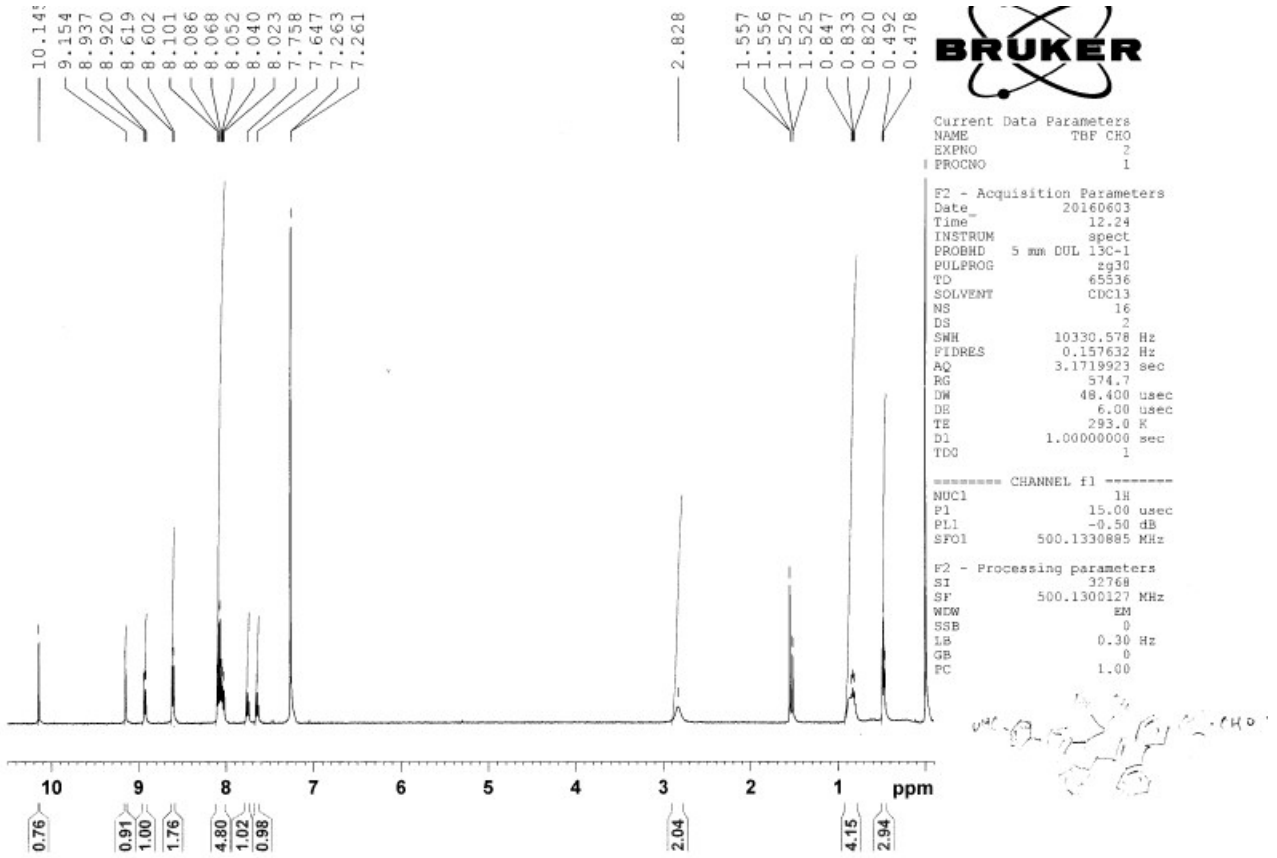


Fig. S13 ^{1}H-NMR spectrum of **3**.

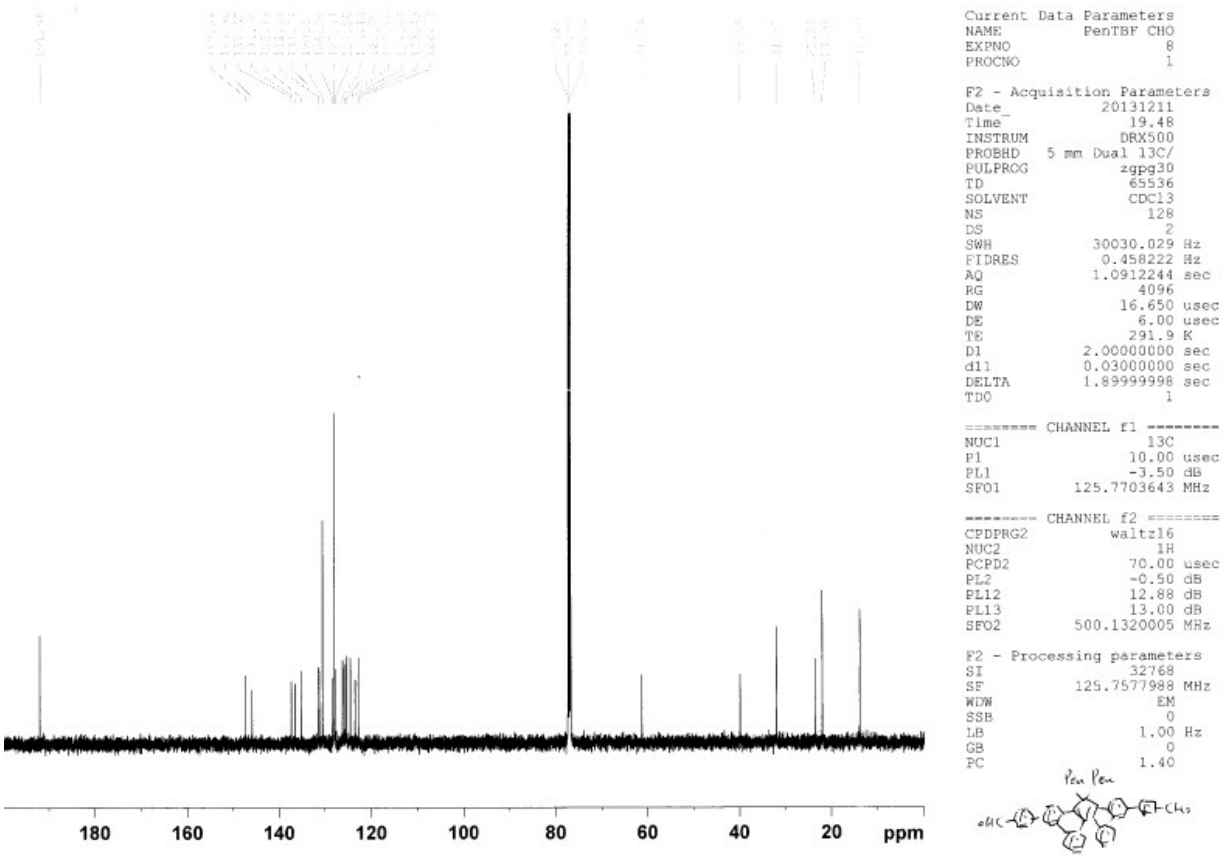


Fig. S14 ^{13}C-NMR spectrum of **3**.

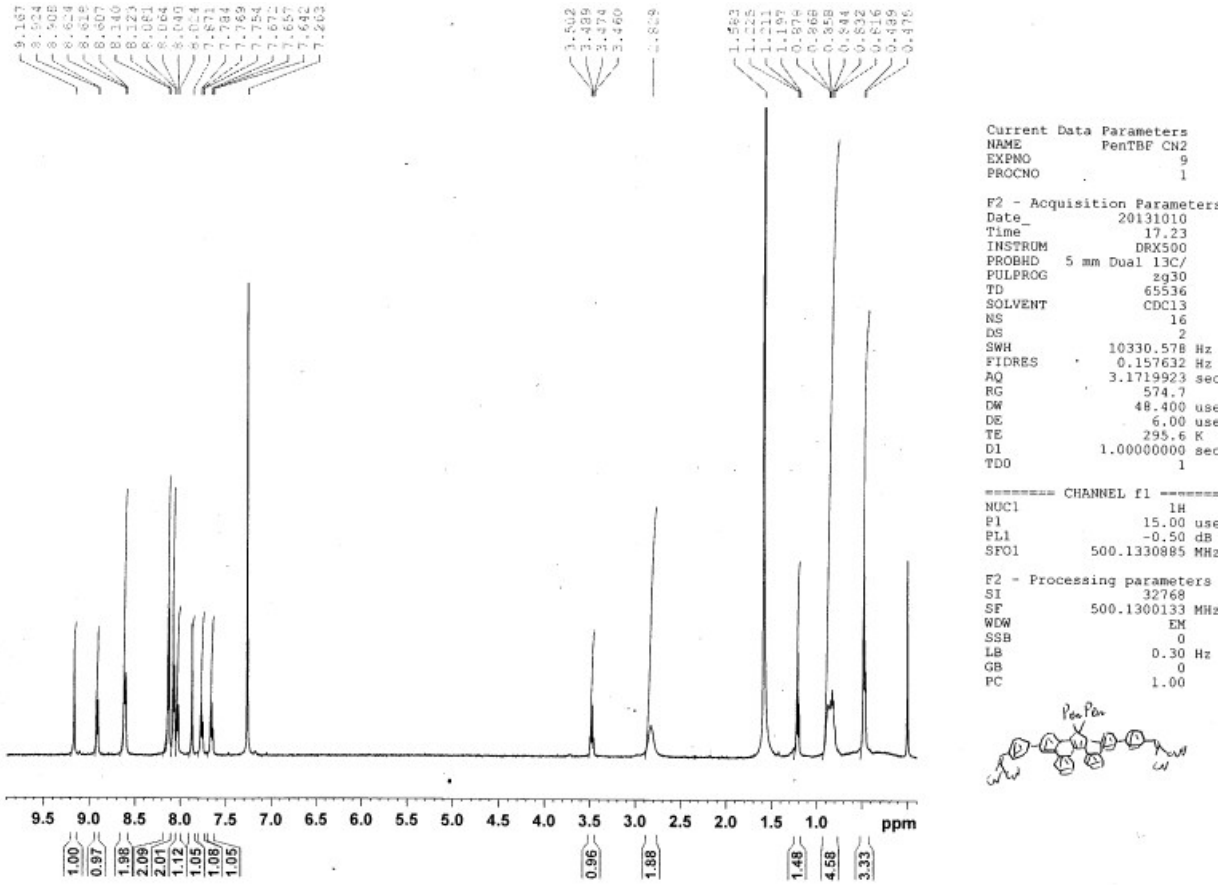


Fig. S15 ^{1}H-NMR spectrum of **2a**.

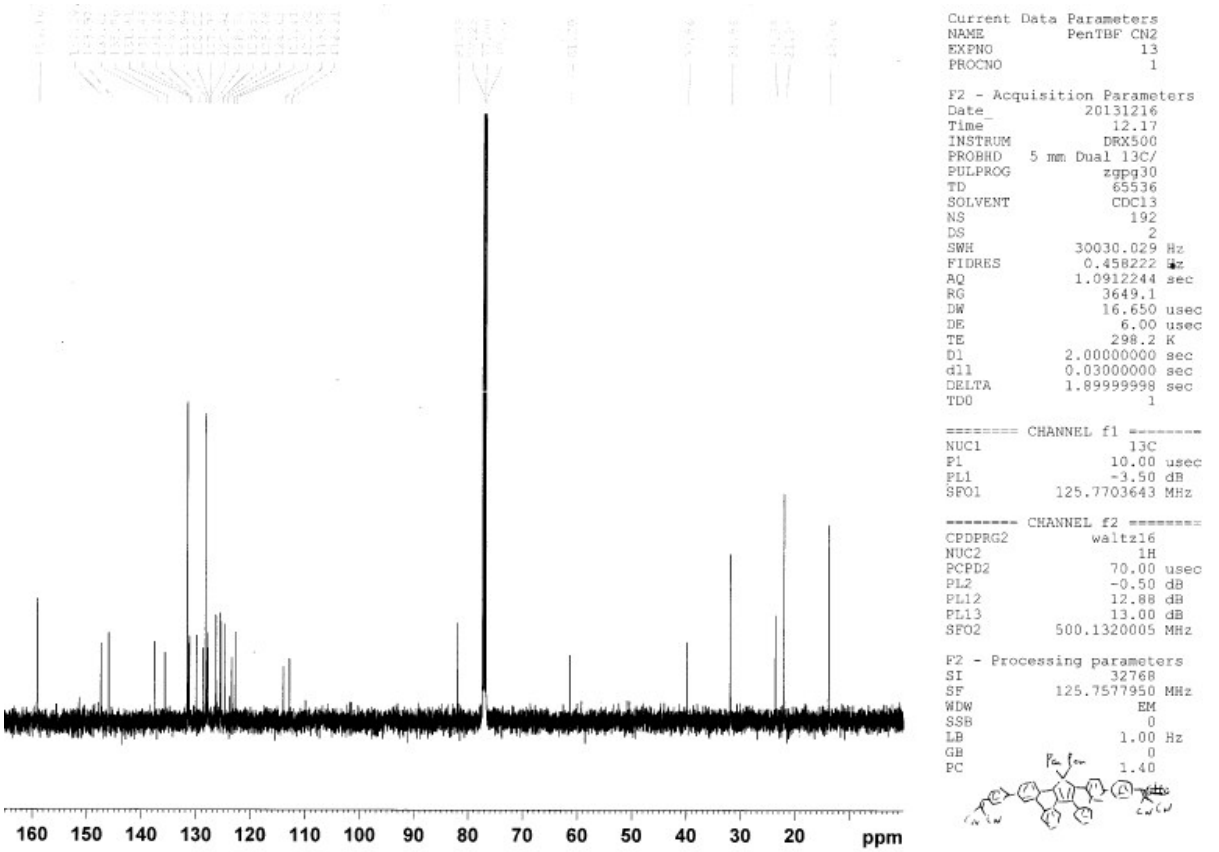


Fig. S16 ^{13}C-NMR spectrum of **2a**.

4. IR spectra of 3 and 2a.

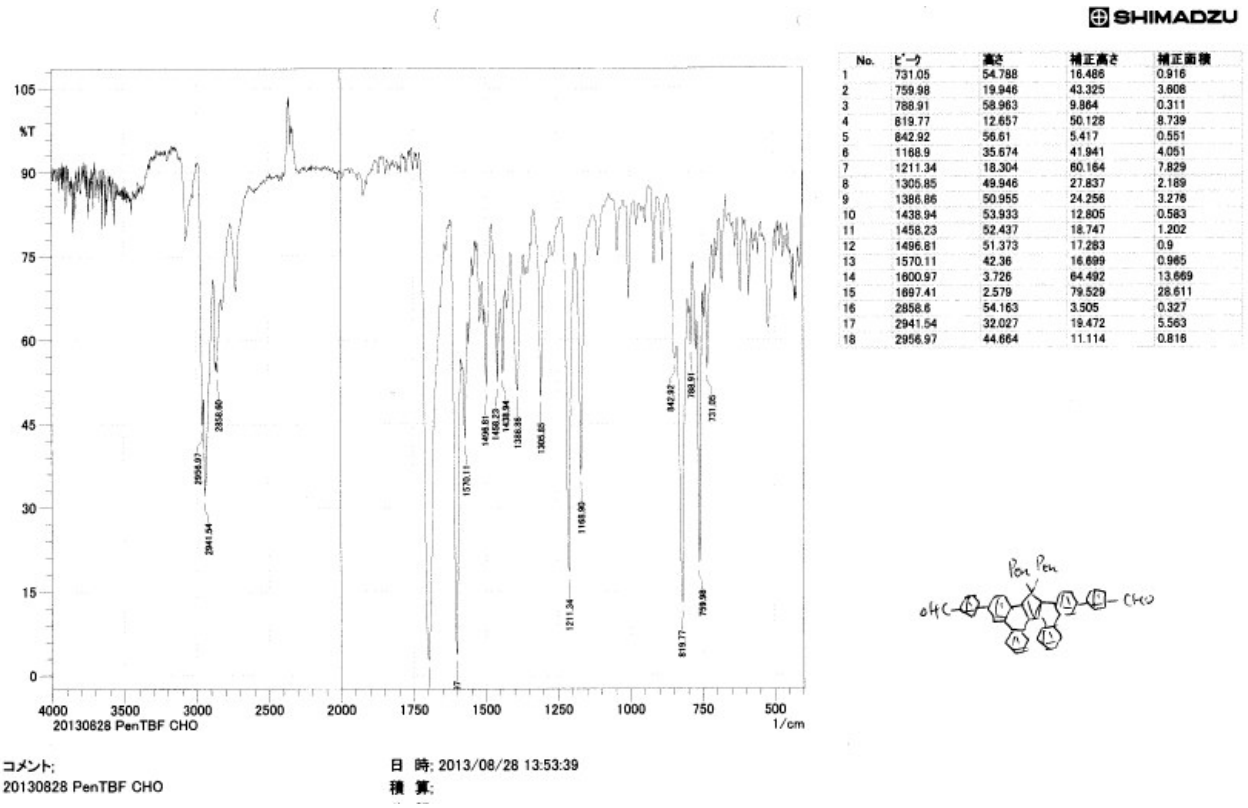


Fig. S17 IR spectrum of **3**.

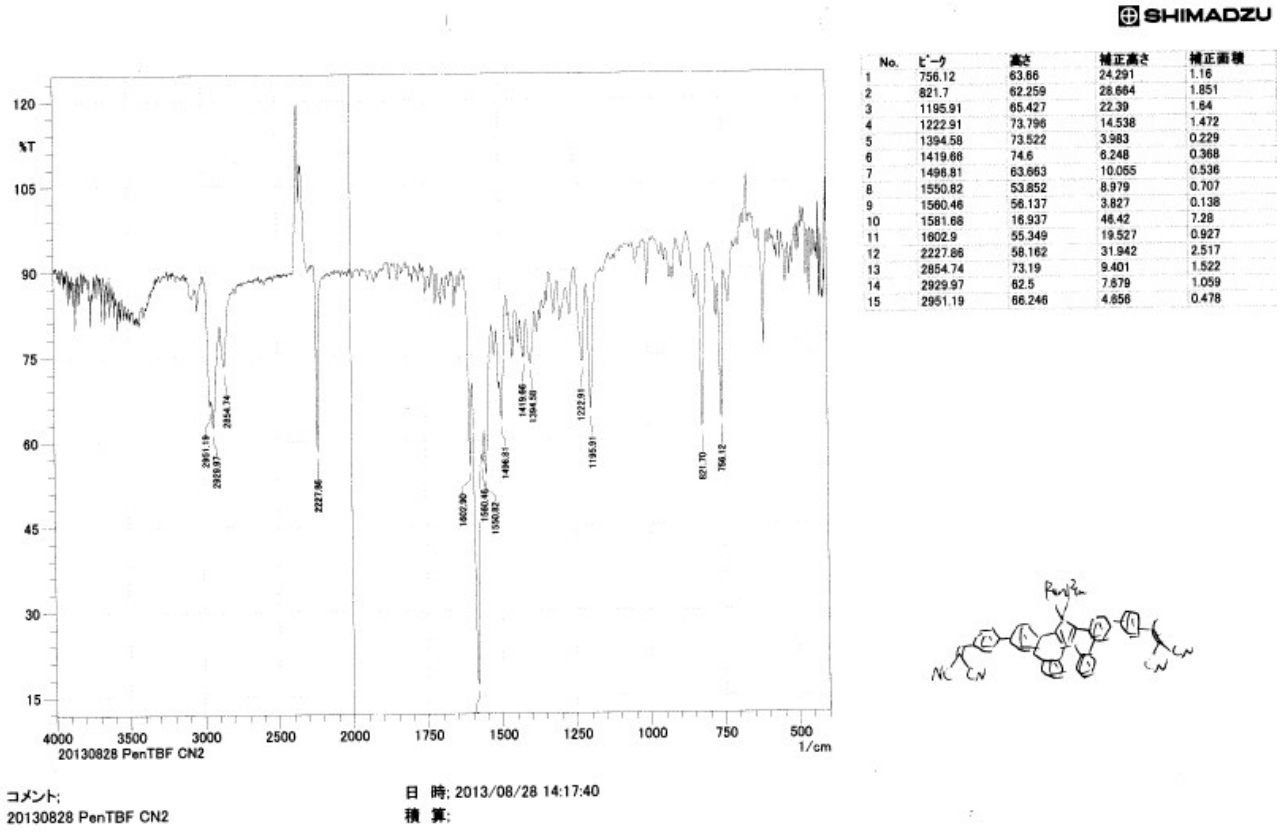


Fig. S18 IR spectrum of **2a**.

5. References

[1] M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **2005**, *38,* 381–388.

[2] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112–122.

[3] L. J. Farrugia, *J. Appl. Crystallogr*. **1999**, *32*, 837–838.