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Supporting information for

Naked Eye Colorimetric Sensor for Alcohol Vapor Discrimination and Amplified Spontaneous Emission (ASE) from a Highly Fluorescent Excited-State Intramolecular Proton Transfer (ESIPT) Molecule

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Experimental methods

All reaction materials were obtained from commercial suppliers, and used without further purification.

Synthesis of primary H_2hpi2cfproduct

A mixture of 5-aminoisophthalic acid (5 mmol, 0.905 g) and 5-fluoro-2-hydroxybenzaldehyde (3 mmol, 0.420 g), acetic acid (20 mL) were stirred at 110°C for two hours under the protection of nitrogen. Continued with adding 4, 4'-difluorobenzil (5 mmol, 1.23 g), ammonium acetate (50 mmol, 3.85 g), then the mixture were kept heated and stirred for another 10 hours (Scheme S1). After cooling, the white solid was filtered out, washed by water for several times and then dried at 100°C in air.

Growth of B-, C-, G-form single crystals of H_2hpi2cf

Dissolving 500 mg H_2hpi2cfproduct to the 1 mL heated DMF (160 ^{o}C), then added 15 mL ethanol, natural cooling and resting for one night to afford the colorless B-form block crystals; C- and G-form crystals were obtained by the similar process, merely changed ethanol to methanol (for C-form) and isopropanol (for G-form).

Growth of C1-form single crystals of H_2hpi2cf

Method I (DMF/H_2O layering diffusion): 2 mL water was added to the bottom of a tube, and then, in turn, 4 mL mixture solution (DMF: water, v/v = 50:50) and 2 mL solution of B-H_2hpi2cf (0.1 mmol, 0.0649 g) in DMF were carefully added into the tube. After layering at room temperature for a week, colorless schistose crystals of C1-form with length of several hundreds of micrometers were obtained from the middle liquid layer.

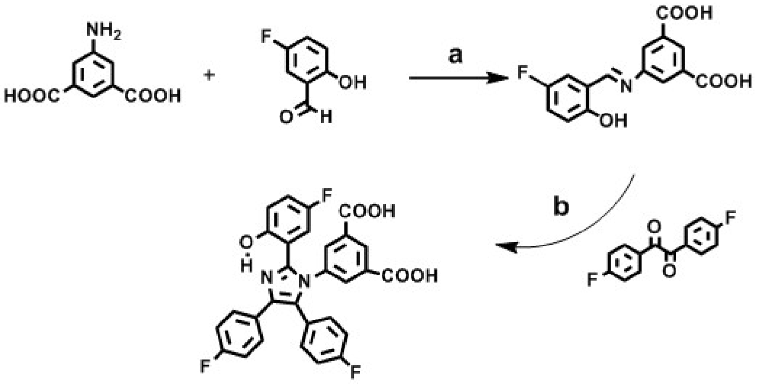
Method II (pure DMF evaporation): 0.15 g H_2hpi2cf of B-form is dissolved in 5 mL N, N-dimethylformamide (DMF) to get the high concentration solution of H_2hpi2cf. Slow evaporation of DMF for a month results in striplike crystals of C1-form with length of several millimeters.

Growth of F-form single crystals of H_2hpi2cf

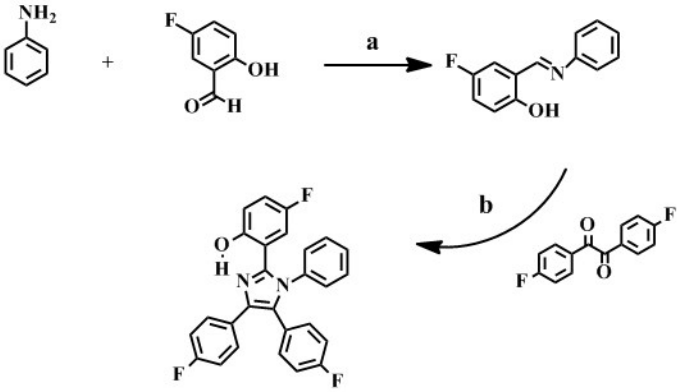
Crystals of C1-form were soaked in water for several weeks, then the original colorless crystals turned to pale yellow and showed much weaker fluorescence, which indicated new crystals were generated.

Synthesis of primary HPIF and growth of single crystals

A mixture of aniline (5 mmol, 0.465 g) and 5-fluoro-2-hydroxybenzaldehyde (3 mmol, 0.420 g), acetic acid (20 mL) were stirred at 110°C for two hours under the protection of nitrogen. Continued with adding 4, 4'-difluorobenzil (5 mmol, 1.23 g), ammonium acetate (50 mmol, 3.85 g), then the mixture were kept heated and stirred for another 10 hours (Scheme S2). After cooling, the white solid was filtered out, washed by water for several times and then dried at 100°C in air. Dissolving 500 mg HPIF product to the 1 mL heated DMF (160 ^{o}C), then added 10 mL ethanol, natural cooling and resting for one night to afford the colorless HPIF block crystals



Scheme S1. Synthetic route of molecule H_2hpi2cf. *Reagents and conditions:* (a) acetic acid, N_2 atmosphere, 110 ^{o}C, 2 h, 80 %; (b) acetic acid, 4,4’-difluorobenzil, ammonium acetate, 110 ^{o}C, 10 h, 60 %.



Scheme S2. Synthetic route of molecule HPIF. *Reagents and conditions*: (a) acetic acid, N_2 atmosphere, 110 °C, 2 h, 80%; (b) acetic acid, 4,4'-difluorobenzil, ammonium acetate, 110 °C, 10 h, 65%.

Measurements

^{1}H NMR spectra were obtained by Bruker AVANCE III (400 MHz) in DMSO-d_6 solutions. Elemental analysis was carried out using a vario EL cube elemental analyzer. UV-Vis absorption spectra were recorded on a Shimadzu UV-3600 spectrometer. Fluorescence spectra were measured on an Edinburgh FLS980 Photoluminescence Spectrometer. Absolute photoluminescence quantum yields were measured with emission scans that were further processed using the quantum yield wizard provided by the F980 software in the integrating sphere. The fluorescence lifetime experiments were performed in the time-correlated single photo counting (TCSPC) methods by using a 405 nm picoseconds pulsed diode laser with a repetition rate of 10 kMHz as the excitation source. Photographs of fluorescent single crystals were taken by the Fluorescence Stereomicroscope (Leica, German). PXRD measurements were performed on an X-ray powder diffractometer (Rigaku, Japan), operating at 4 kW, 3 mA. For the laser test, the crystal slices were irradiated by the third harmonic (355 nm) of a Nd: YAG (yttrium–aluminum– garnet) laser at a repetition rate of 10 Hz and pulse duration of about 5 ns. The energy of the pumping laser was adjusted by using the calibrated neutral density filters. The beam was focused into a stripe whose shape was adjusted to 2.0 × 0.5 mm by using a cylindrical lens and a slit. The edge emission and PL spectra of the crystals was detected using a Maya2000 Pro CCD spectrometer. The polarization of light emitted from the edge of the crystal was measured by rotating a polarizer. The gain coefficients are measured by adjusting a slit.

Characterization for the compounds

H$_2$hpi2cf: ^{1}H NMR (400 MHz, DMSO-d$_6$) δ: 8.34 (t, J = 1.4 Hz, 1H, carboxyl-H), 7.95 (s, 1H, Ar-H), 7.90 (d, J = 1.5 Hz, 2H, Ar-H), 7.53 – 7.42 (m, 2H, Ar-H), 7.36 – 7.27 (m, 2H, Ar-H), 7.17 (td, J = 16.1, 8.9 Hz, 4H, Ar-H), 7.06 (td, J = 8.6, 3.2 Hz, 1H, Ar-H), 6.93 (dd, J = 9.4, 3.1 Hz, 1H, Ar-H), 6.77 (dd, J = 9.0, 4.9 Hz, 1H, Ar-H).

Anal. Calcd. (%) for B-form ($C_{34}H_{30}F_3N_3O_7$): C, 62.86; H, 4.65; N, 6.47. Found (%): C, 62.68; H, 4.563; N, 6.72. IR (KBr pellet, cm^{-1}): 3471 (-O-H), 3075 (Ar-H), 1705 (-C=O), 1630 (-C=N-), 1510 (C=C), 670, 780 (C-H).

Anal. Calcd. (%) for C1 form ($C_{35}H_{31}F_3N_4O_7$): C, 62.13; H, 4.62; N, 8.28. Found (%): C,62.18; H, 4.561; N, 8.38. IR (KBr pellet, cm^{-1}): 3080 (Ar-H), 1703 (-C=O), 1635 (-C=N-), 1490 (C=C), 770, 650 (C-H).

Anal. Calcd. (%) for C form ($C_{30}H_{21}F_3N_2O_6$): C, 64.06; H, 3.76; N, 4.98. Found (%): C, 64.06; H, 3.708; N, 4.97. IR (KBr pellet, cm^{-1}): 3370, 3200 (-O-H), 1703 (-C=O), 1495 (C=C), 775, 670 (C-H).

Anal. Calcd. (%) for G form ($C_{35}H_{32}F_3N_3O_7$): C, 63.34; H, 4.86; N, 6.33. Found (%): C, 63.33; H, 4.794; N, 6.34. IR (KBr pellet, cm^{-1}): 3470 (-O-H), 3100 (Ar-H), 1705(-C=O), 1635 (-C=N-), 1495 (C=C), 760, 660 (C-H).

Anal. Calcd. (%) for F form: ($C_{29}H_{17}F_3N_2O_5$): C, 65.66; H, 3.23; N, 5.28. Found (%): C, 65.50; H, 3.119; N, 5.28. IR (KBr pellet, cm^{-1}): 3090 (Ar-H), 1705 (-C=O), 1635 (-C=N-), 1500 (C=C), 780, 660 (C-H).

HPIF: ^{1}H NMR (400 MHz, DMSO-d$_6$) δ: 12.15 (s, 1H, hydroxyl-H), 7.57-7.37 (ddd, *J* = 17.0, 10.7, 5.7 Hz, 7H, Ar-H), 7.36-7.30 (dd, *J* = 8.1, 5.7 Hz, 2H, Ar-H), 7.29-7.13 (t, *J* = 8.7 Hz, 4H, Ar-H), 7.05 (td, *J* = 8.5, 2.8 Hz, 1H, Ar-H), 6.92 (dd, *J* = 8.9, 5.0 Hz, 1H, Ar-H), 6.40 (dd, *J* = 10.2, 2.8 Hz, 1H, Ar-H). Anal. Calcd. (%) for $C_{27}H_{17}F_3N_2O$: C, 73.30; H, 3.87; N, 6.33. Found (%): C, 72.92; H, 3.784; N, 6.26.

X-ray Crystallography

Single crystal data collection was performed on a Super Nova X-ray diffractometer system (Agilent Technologies, America) equipped with graphite-monochromated MoKα radiation (λ = 0.71073 Å) or CuKα radiation (λ = 1.54178 Å) at 150 K. Absorption corrections were applied using multiscan technique. All the structures were solved by Direct Method of SHELXS-97 and refined by full-matrix least-squares techniques using the SHELXL-97 program. The hydrogen atoms of the organic ligands were refined as rigid groups. Non-hydrogen atoms were refined with anisotropic temperature parameters.

Table S1 Crystallographic data and structure refinement for crystals B, C1, C, G and F.

Cell parameters	Crystal B	Crystal C1	Crystal C	Crystal G	Crystal F
Empirical formula	$C_{34}H_{30}F_3N_3O_7$	$C_{35}H_{31}F_3N_4O_7$	$C_{30}H_{21}F_3N_2O_6$	$C_{35}H_{32}F_3N_3O_7$	$C_{29}H_{17}F_3N_2O_5$
CCDC number	1470803	1470804	1470805	1470806	1470807
Color	colorless	colorless	colorless	colorless	pale yellow
Temperature (K)	150	150	150	150	150
Wavelength (Å)	Mo Kα, 0.71073	Mo Kα, 0.71073	Mo Kα, 0.71073	Mo Kα, 0.71073	Cu Kα, 1.5418
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	P-1	P-1	P-1	P-1	$P2_1/n$
Unit cell dimensions	a = 10.4101(6) Å	a = 10.3694(3) Å	a = 9.4844(5) Å	a = 9.1127(3) Å	a = 14.8457(2) Å
	b= 12.6325(6) Å	b= 12.9551(5) Å	b= 11.9760(6) Å	b= 12.7452(7) Å	b= 20.0452(3) Å
	c = 13.2754(6) Å	c = 13.3347(5) Å	c = 12.6807(6) Å	c = 14.6534(9) Å	c =16.2309(2)Å
	α= 91.976(4) °	α= 87.150(3) °	α= 70.466(4) °	α= 89.060(5) °	α= 90 °
	β= 92.533(4) °	β= 86.739(3) °	β= 70.427(4) °	β= 89.138(4) °	β= 104.788(10) °
	γ= 113.252(5) °	γ= 66.714(3) °	γ= 75.767(4) °	γ= 69.885(4) °	γ= 90 °
Volume (Å^3)	1599.86	1642.03	1264.39	1597.79	4670.09
Z	2	2	2	2	8
Dcalc (g·cm^{-3})	1.349	1.368	1.477	1.379	1.509
Mu (mm^{-1})	0.105	0.911	0.118	0.108	0.118
F(000)	676.0	704.0	580.0	692.0	2176.0
GOF	1.071	1.039	1.001	0.999	1.035
R1(all)	0.0739(4631)	0.0383(5491)	0.0492(3682)	0.0545(3223)	0.0476(6299)
wR2 [$I>2\sigma(I)$]	0.1921(6825)	0.1099(6494)	0.1212(5395)	0.1473(4291)	0.1483(7819)

Table S2 Crystallographic data and structure refinement for crystal HPIF.

Cell parameters	Crystal HPIF
Empirical formula	$C_{27}H_{17}F_3N_2O$
CCDC number	1470813
Color	colorless
Temperature (K)	150
Wavelength (Å)	Cu Kα, 1.5418
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 14.1247(5) Å
	b= 10.5410(4) Å
	c = 14.3333(4) Å
	α= 90 °
	β= 93.617(3) °
	γ= 90 °
Volume (Å^3)	2129.81
Z	4
Dcalc (g·cm^{-3})	1.380
Mu (mm^{-1})	0.103
F(000)	912.0
GOF	1.046
R1(all)	0.0522(3207)
wR2 [I>2σ(I)]	0.1789(5156)

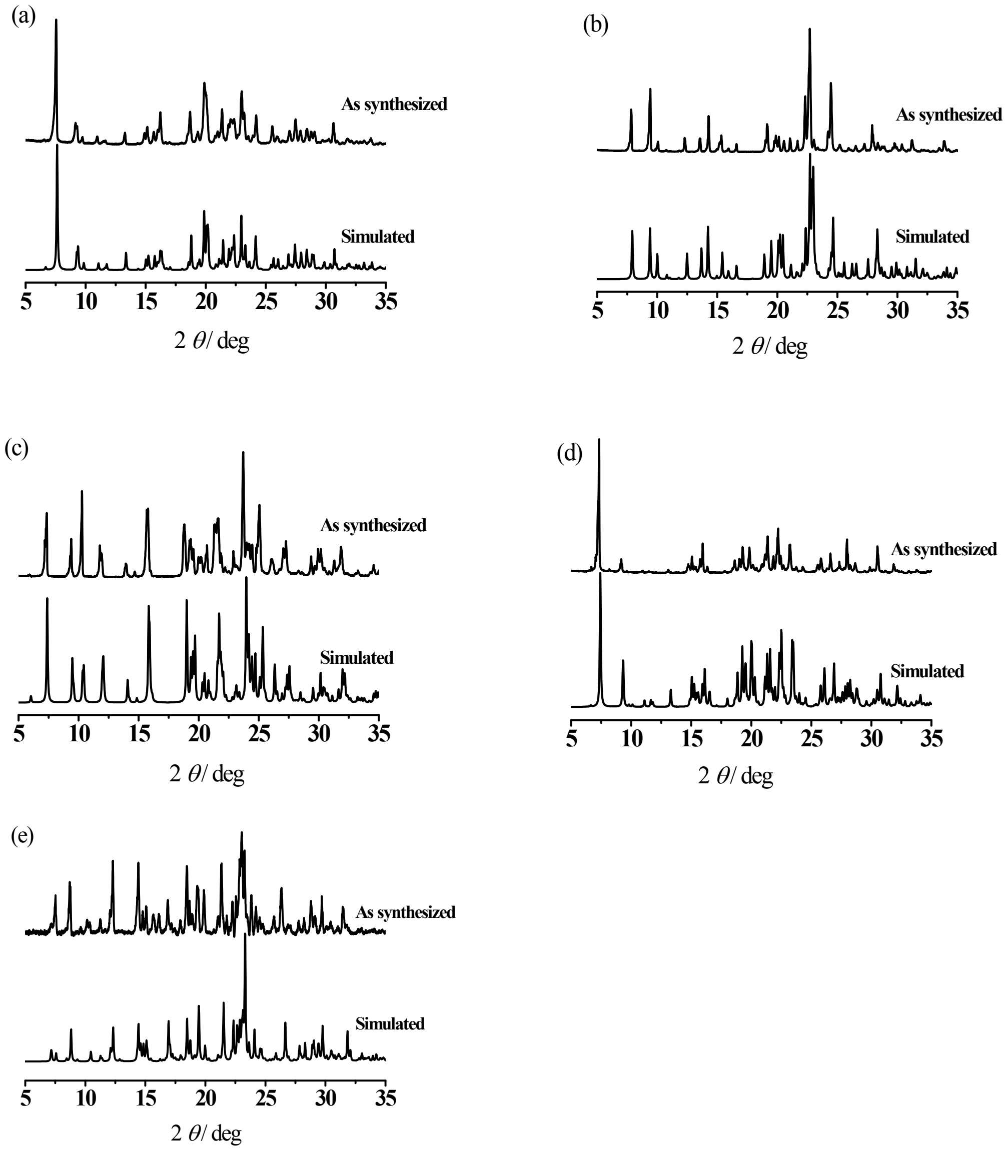
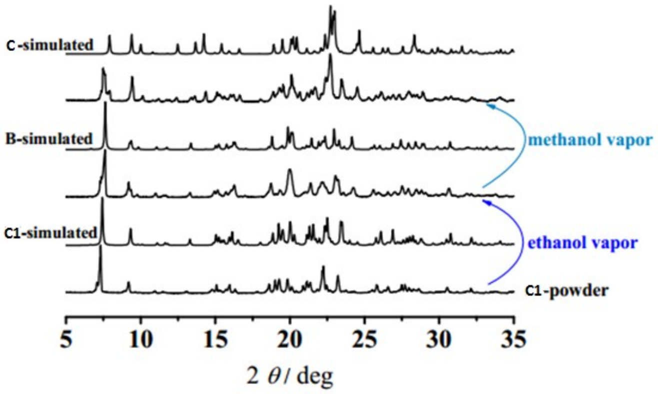
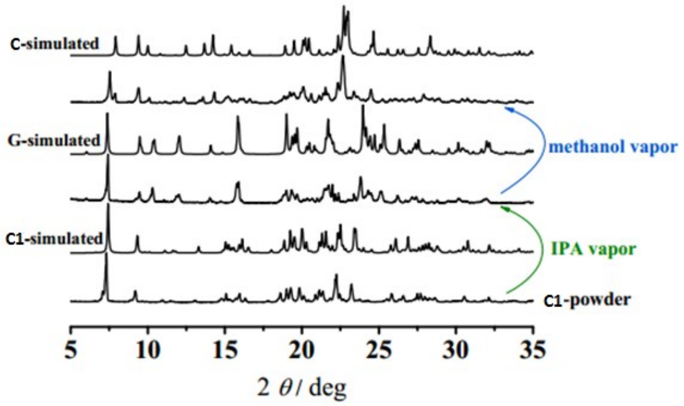


Fig. S1 Comparisons between simulated XRD patterns for crystals (a) B, (b) C, (c) G, (d) C1, and (e) F according to the single-crystallographic data and XRD patterns of their grinding samples.



a)



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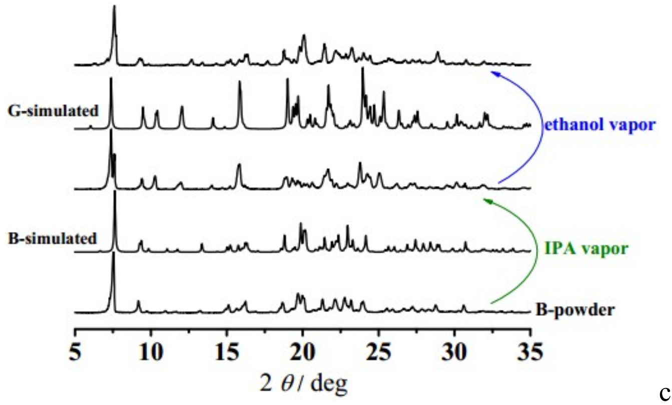
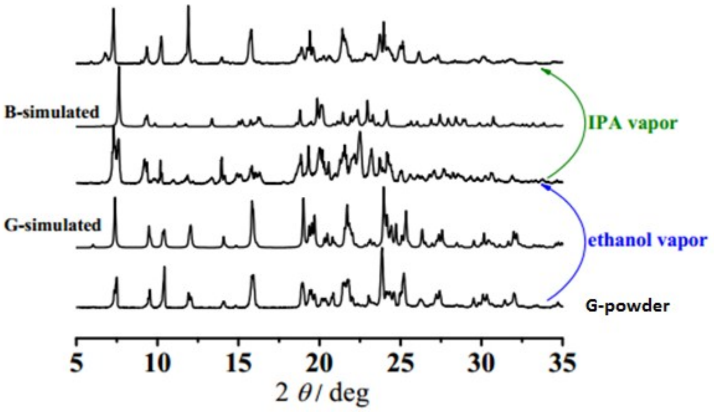


c)



d)

Fig. S2 (a)-(d) PXRD showing the reversible changes among different forms of H_2hpi2cf species upon alcohol vapor fuming. (a) C1→B→C, (b) C1→G→C, (c) B→G→B, (d) G→B→G.

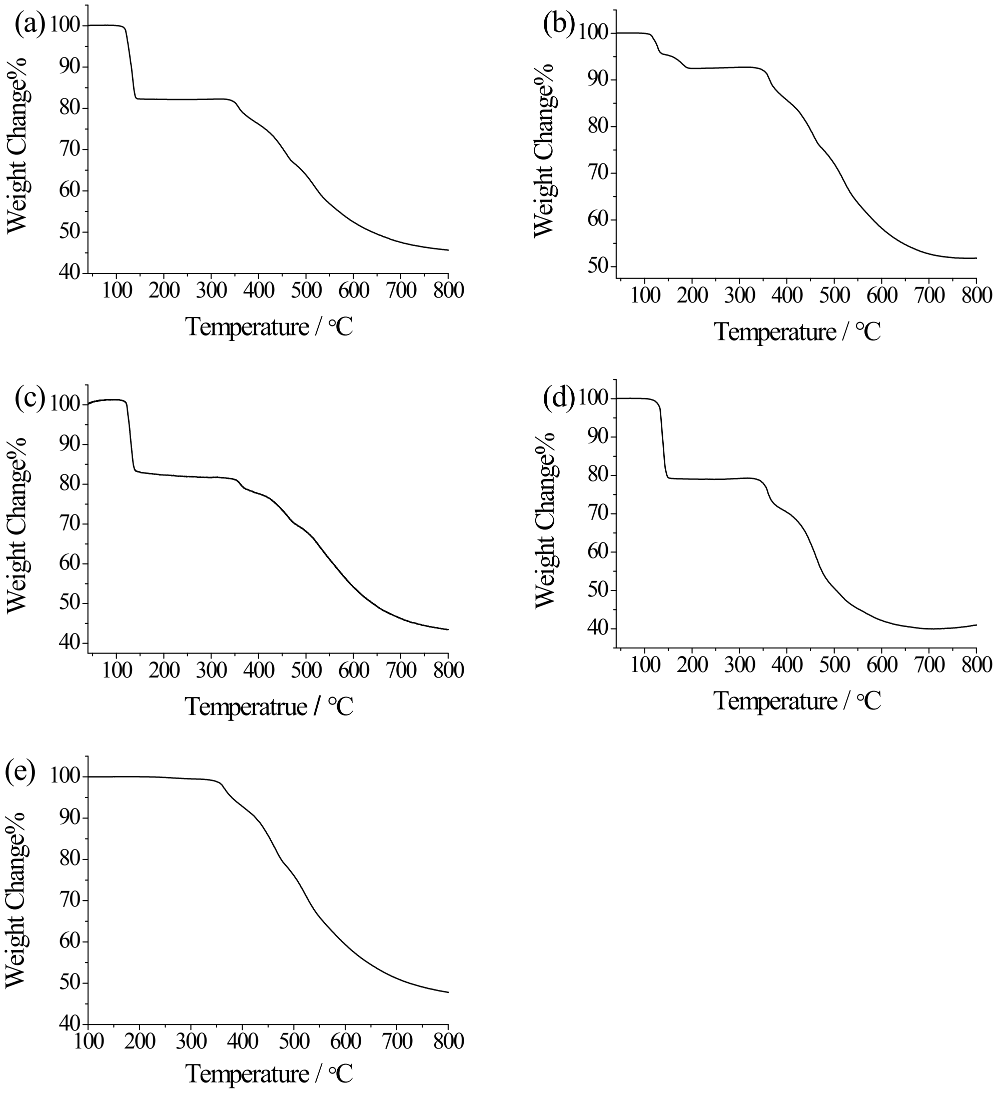


Fig. S3 TG curves for (a) B-form, (b) C-form, (c) G-form (d) C1-form, and (e) F-form, respectively.

For the four forms of H_2hpi2cf species, the first continuous weight loss respectively starting from 82 °C to 145 °C (for B), 82 °C to 148 °C (for C), 102 °C to 146 °C (for G) and 82 °C to 147 °C (for C1), due to the removal of the solvent molecules. The calculated and experimentally found solvent weight loss which considers the EA results are listed as follow.

Formula	Molecular weight	Solvent molecules and weight	Calculated weight loss	Found weight loss
$C_{34}H_{30}F_3N_3O_7$ (B)	649	DMF+EtOH, 119	18.3%	17.8%
$C_{30}H_{21}F_3N_2O_6$ (C)	562	MeOH, 32	5.7%	5.1%
$C_{35}H_{32}F_3N_3O_7$ (G)	663	*i*PrOH+DMF, 133	20.1%	18.5%
$C_{35}H_{31}F_3N_4O_7$ (C1)	676	2DMF, 146	21.6%	20.5%

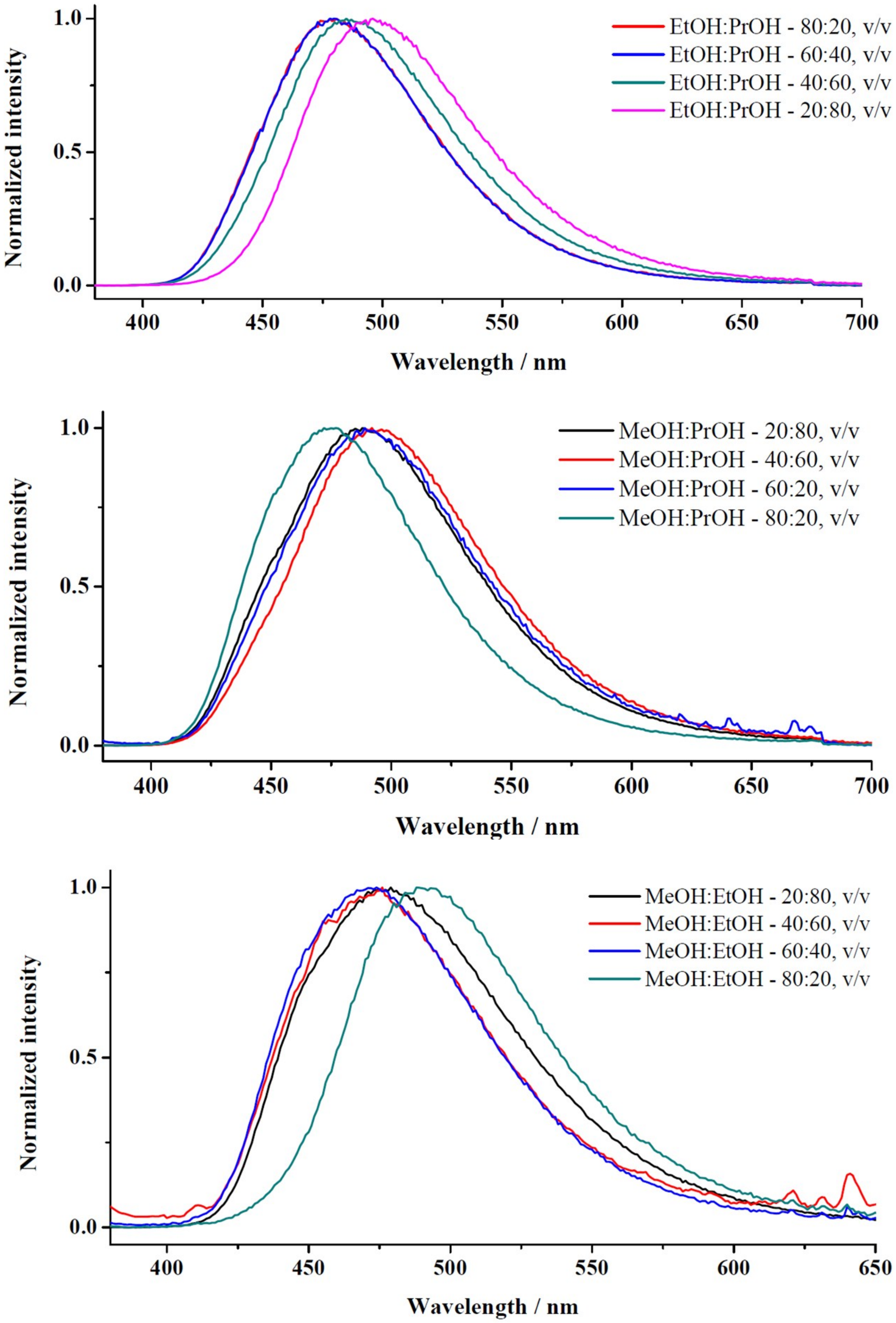


Fig. S4 Emission spectra of H_2hpi2c samples exposed to the mixed alcohol solvents with different ratios.