

Chromophore-immobilized luminescent metal-organic frameworks as potential lighting phosphors and chemical sensors

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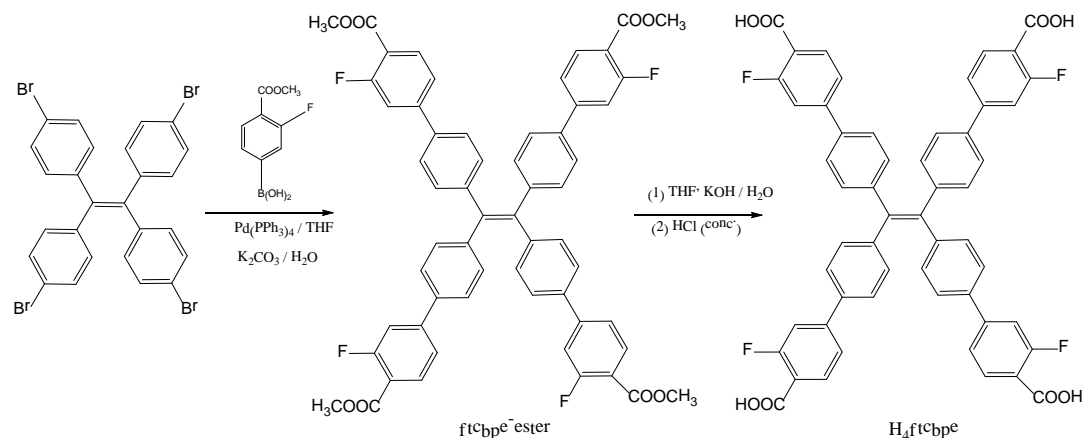
Supporting Information

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S1. Synthesis of *H₄tcbpe-F*

4',4''',4''''',4''''''-(ethene-1,1,2,2-tetrayl)tetrakis((3-fluoro-[1,1'-biphenyl]-4-carboxylic acid)) (*H₄tcbpe-F*) was synthesized by a similar route as that for *H₄tcbpe* (Scheme S1).



Scheme S1. The synthesis of *H₄tcbpe-F*.

As shown in Scheme S1, tetra-(4-bromo-phenyl)ethylene (2.71 g, 4.2 mmol), 3-fluoro-4-(methoxycarbonyl)- phenylboronic acid (5.00g, 25.2 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (0.40g) were added into a 250 ml three-neck bottle. THF and K_2CO_3 aqueous solution (3.0 M, 15 mL) were then added under nitrogen atmosphere at room temperature. The reaction mixture was kept at 90 °C for three days. After cooling to room temperature, the reaction solution was extracted with dichloromethane for three times (100 ml \times 3), and the organic phase was washed with water, dried with anhydrous magnesium sulfate and then subject to flash chromatography using dichloromethane methanol (V:V = 40:1) as fluent. The product F-tcbpe-ester was obtained as green-yellow solid in 63.3% yield (2.50g). ^1H NMR (400 MHz, CDCl_3) δ : 7.90 (t, J = 10.8 Hz), 7.36 (d, 8H, J = 11.2 Hz), 7.28 (m, 8H), 7.12(d, 8H, J = 11.2 Hz), 3.87 (s, 12H).

The tcbpe-F-ester (2.50g, 2.65 mmol) was dissolved in THF (30 mL) and then concentrated KOH solution (3M, 30mL) was added. The mixture was refluxed overnight. After the reaction was completed, the solution was cooled to room temperature and concentrated under reduced pressure. The concentrated solution was acidified with concentrated HCl to precipitate. The mixture was cooled and vacuum filtered and the precipitate was washed with water and dried. The final product *H₄ftcbpe* was obtained as yellow powder in 92.3% yield (2.17g), ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ : 13.26, 7.95 (t, 4H, J = 10.8 Hz), 7.72 (d, 8H, J = 11.2 Hz), 7.66 (m, 8H), 7.23(d, 8H, J = 11.2

Hz), MS (ESI) m/z : 882.9 ($M-H^+$).

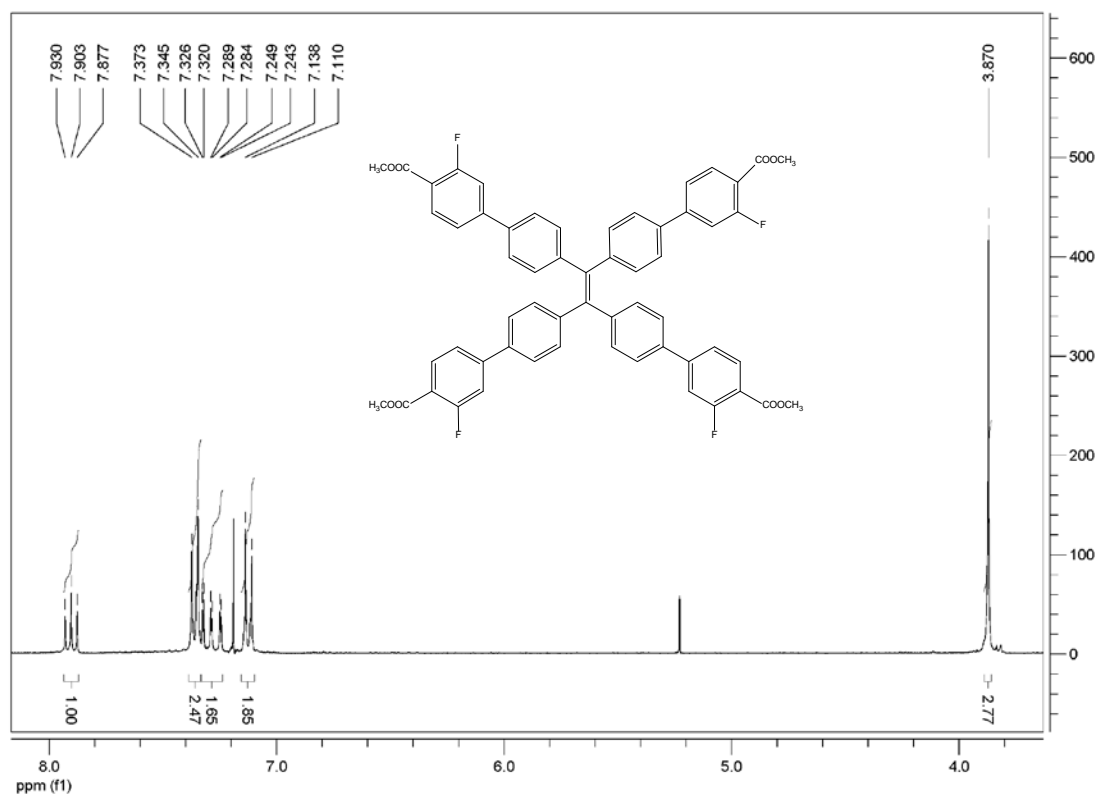


Fig. S1. ^1H NMR of tcbpe-F-ester.

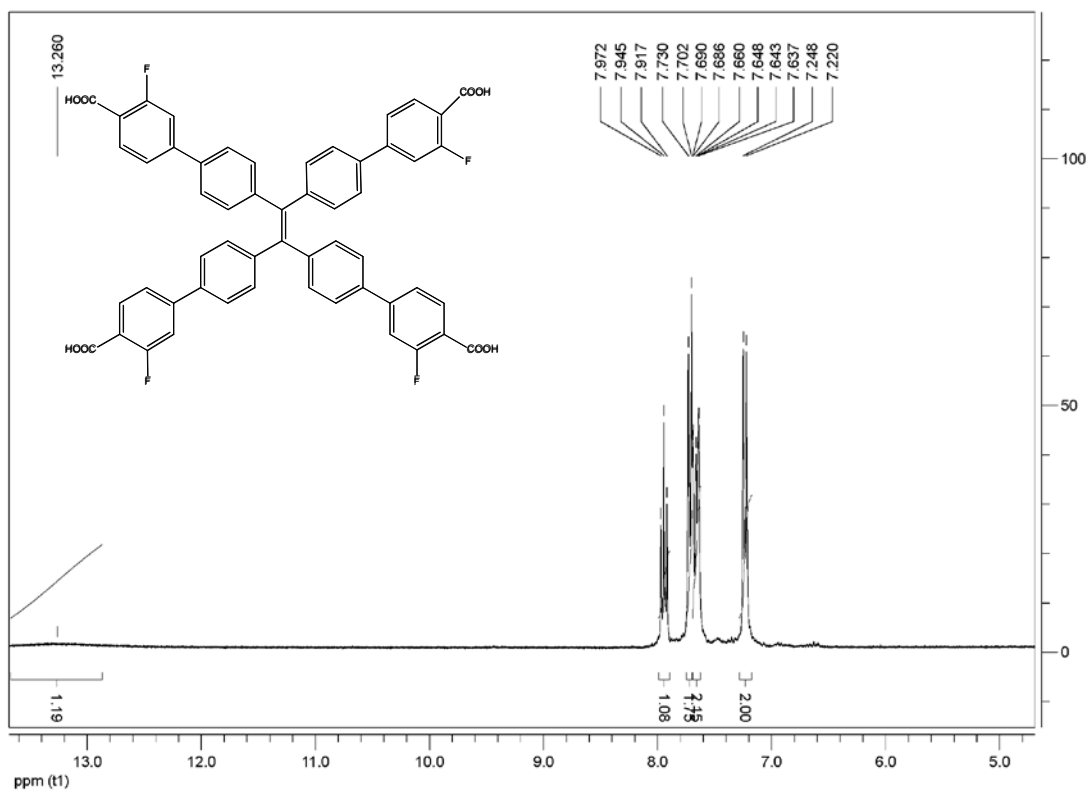


Fig. S2. ^1H NMR of *H4cbpe-F*.

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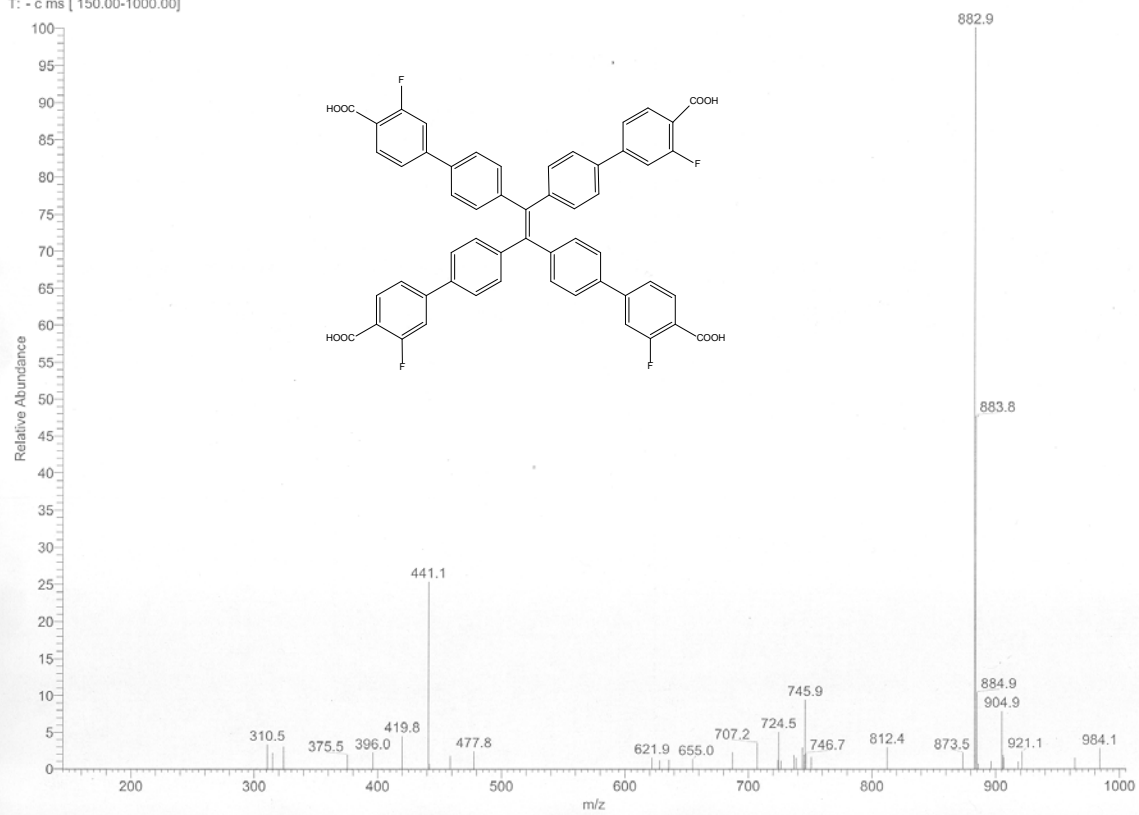


Fig. S3. ESI-MS of H₄tcbpe-F.

S2. Synthesis of $\text{Zn}_2(\text{tcbpe-F})(4,4'\text{-bpy})\cdot x\text{DMA}$ (1) and $\text{Zn}_2(\text{tcbpe-F})(\text{bpee})\cdot x\text{DMA}$ (2)

Synthesis of **1**: $\text{Zn}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$ (0.0110 g, 0.030 mmol), *H₄tcbpe-F* (0.0133 g, 0.015 mmol), 4,4'-bipyridine (0.0047 g, 0.030 mmol), and N,N'-dimethylacetamide (DMA, 5 mL) were added in a 20 mL glass vial. The glass vial was capped and sonicated at room temperature for five minutes until a clear solution was obtained. The sealed glass vial was kept at 100 °C for 72 hours. Transparent pale-yellow single crystals were collected through filtration, washed with DMA, and dried in air. The reaction yield is 60% yield based on Zn^{2+} .

Synthesis of **2**: The synthetic procedure is similar to that of **1**, except the 4,4'-bpy was changed to 4,4'-bipyridyl-ethylene (*bpee*). Yellow cubic single crystals along with crystalline powder were obtained with the yield of 47% based on Zn^{2+} .

S3. Crystallographic data and structural refinement details of 1 and 2.

SCXRD data were collected at 150 K on a D8 goniostat equipped with a Bruker APEXII CCD detector at Beamline 11.3.1 at the Advanced Light Source (Lawrence Berkeley National Laboratory) using synchrotron radiation tuned to $\lambda = 0.7749\text{\AA}$. For data collection frames were measured for duration of 1-s at 0.3° intervals of ω with a maximum 2θ value of $\sim 60^\circ$. The data frames were collected using the program APEX2 and processed using the program SAINT routine within APEX2. The data were corrected for absorption and beam corrections based on the multi-scan technique as implemented in SADABS. CCDC numbers: 1481622, 1484863.

Table S1. Crystallographic data and structural refinement details of compounds **1** and **2**

Parameters	1	2
Empirical formula	$C_{64}H_{36}F_4N_2O_8Zn_2$	$C_{66}H_{38}F_4N_2O_8Zn_2$
Formula weight	1167.69	1193.72
Temperature (K)	150(2)	253(2)
Wavelength (\AA)	0.7749	0.7749
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1
a (\AA)	13.967(5)	16.3170(6)
b (\AA)	15.480(5)	16.8197(7)
c (\AA)	20.893(5)	20.0452(8)
α ($^\circ$)	89.948(5)	89.982(2)
β ($^\circ$)	83.096(5)	85.952(2)
γ ($^\circ$)	89.209(5)	85.919(2)
Volume (\AA^3)	4484(2)	5473.6(4)
Z	2	2
F(000)	1188	1216
Crystal size (mm)	0.08 x 0.06 x 0.04	0.15 x 0.11 x 0.08
Theta range of data collection	1.79 to 25.00	2.811 to 30.739
Index range	-15 \leq h \leq 15	-21 \leq h \leq 21
	-16 \leq k \leq 16	-22 \leq k \leq 22
	-22 \leq l \leq 22	-26 \leq l \leq 26
Total reflection	12121	26224
Data/ Restraints/parameter	12121 / 24 / 568	26224 / 0 / 815
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0965,$ $wR_2 = 0.3234$	$R_1 = 0.0588,$ $wR_2 = 0.3234$
R indices (all data)	$R_1 = 0.1020,$ $wR_2 = 0.3447$	$R_1 = 0.1996,$ $wR_2 = 0.1846$

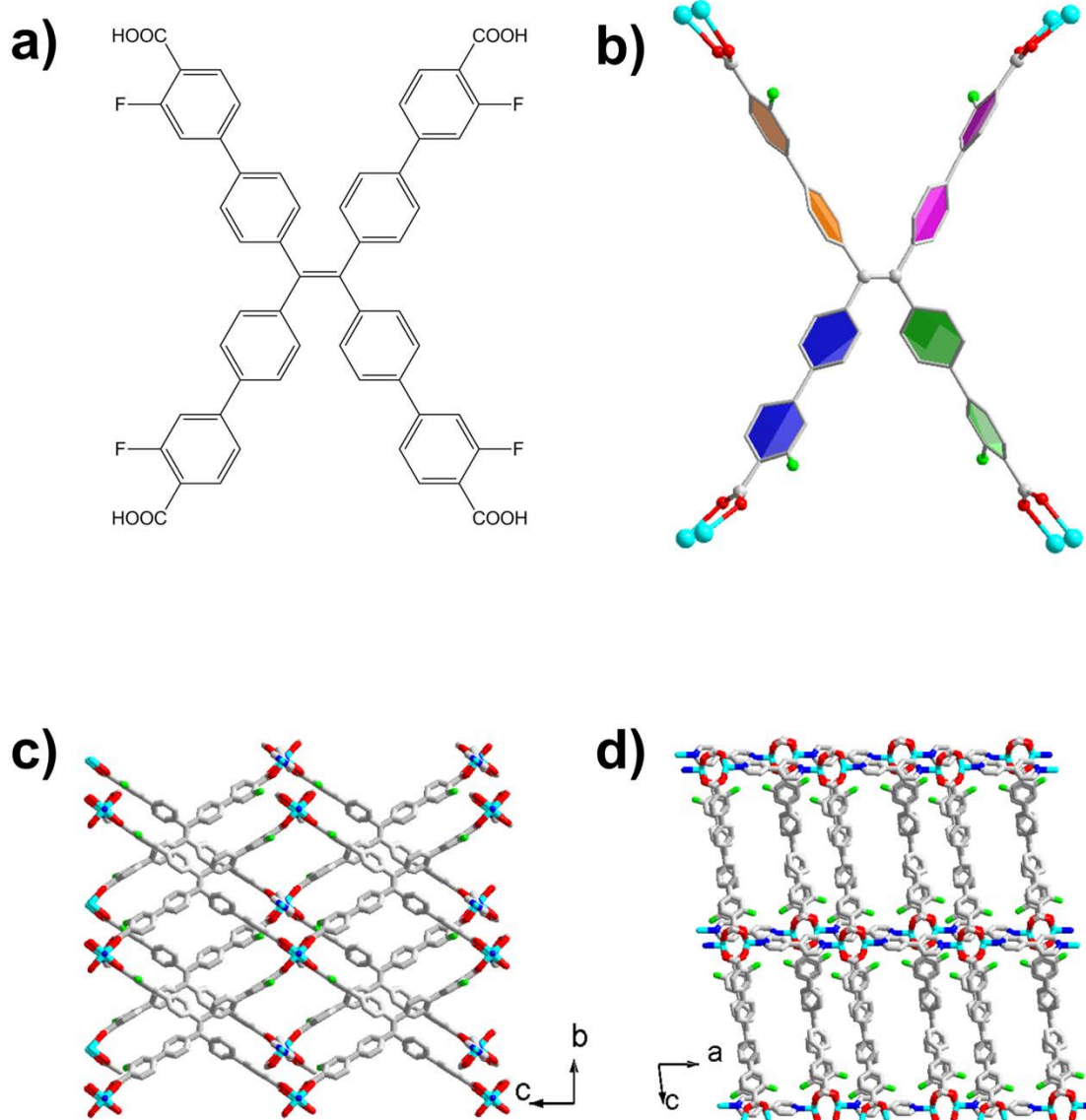


Fig. S4. (a) Chemical structure of $H_4tcbpe-F$; (b) Geometry of the $tcbpe-F$ ligand in **1** emphasizing the benzene ring orientations. The four biphenyl rings are marked with different color (C1-C12, blue, C13-C24, orange, C25-C36, pink, C37-C48, bright green). Hydrogen atoms are omitted for clarity. (c) Framework of **1** viewed along the a -axis. (d) Framework of **1** viewed along the b -axis.

S4. Thermogravimetric analysis (TGA) of compounds 1 and 2

Thermogravimetric analyses (TGA) of **1** and **2** were carried out on a TA Q5000 analyzer. Crystal samples were loaded onto a platinum pan and heated with a ramp rate of 10 °C/min from room temperature to 600 °C under nitrogen flow (20 mL/min).

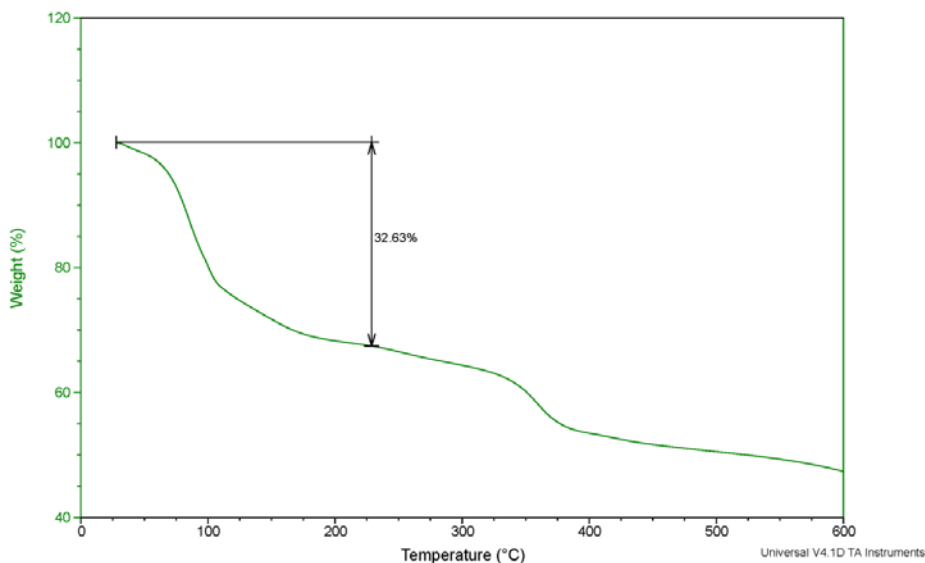


Fig. S5. TG profile for **1**.

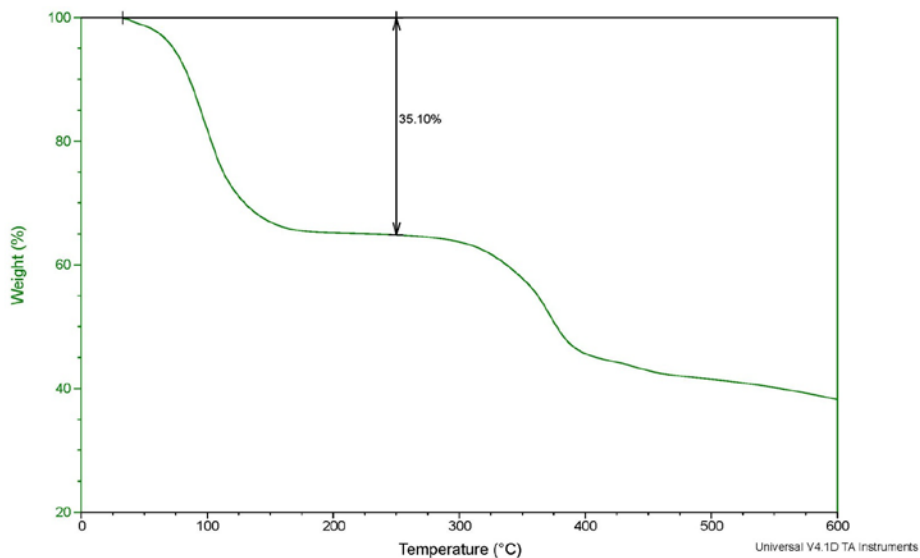


Fig. S6. TG profile for **2**.

S5. Power X-ray diffraction (PXRD) analysis of 1, 2 and selected solvent exchanged samples

Powder X-ray diffraction (PXRD) patterns were recorded on a Ultima IV with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). The data were collected at room temperature in a 2θ range of $3\text{-}55^\circ$ with a scan speed of 2 deg/min and operating power of 40 kV and 40 mA .

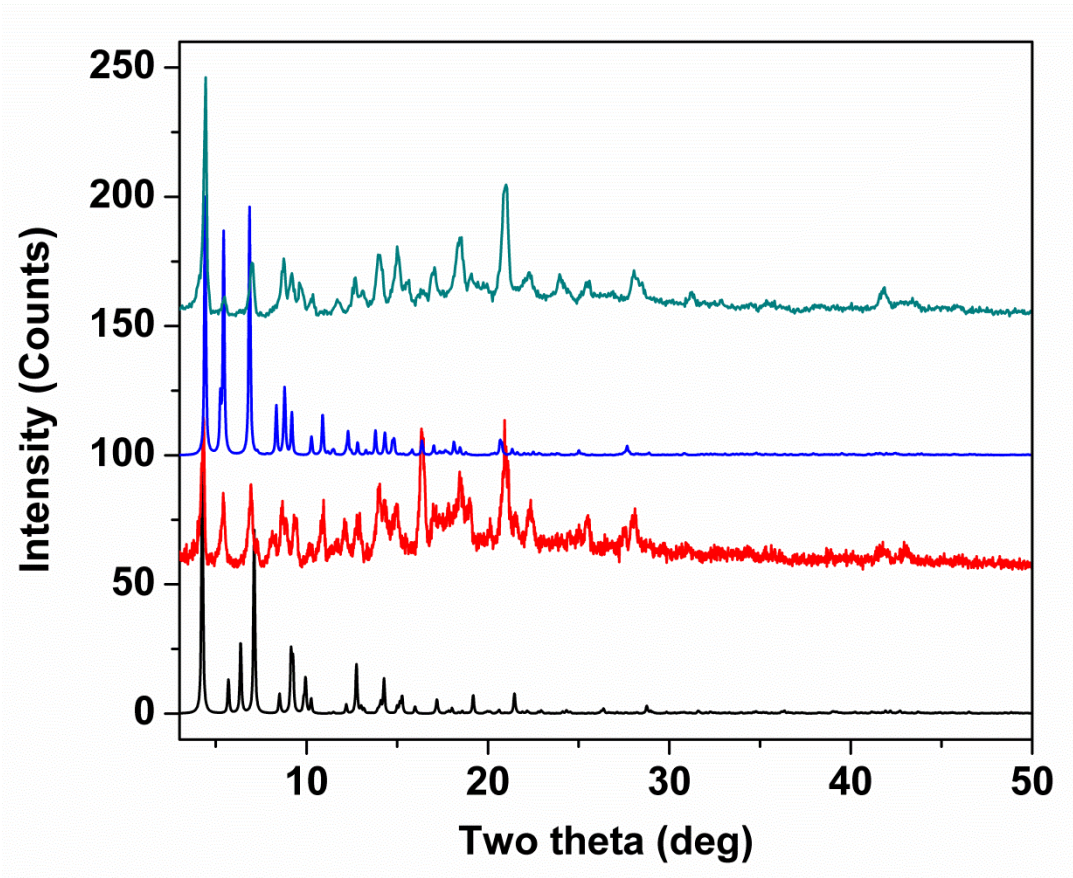


Fig. S7. PXRD patterns. From bottom to top: simulated 1, as-made 1, simulated 2, as-made 2.

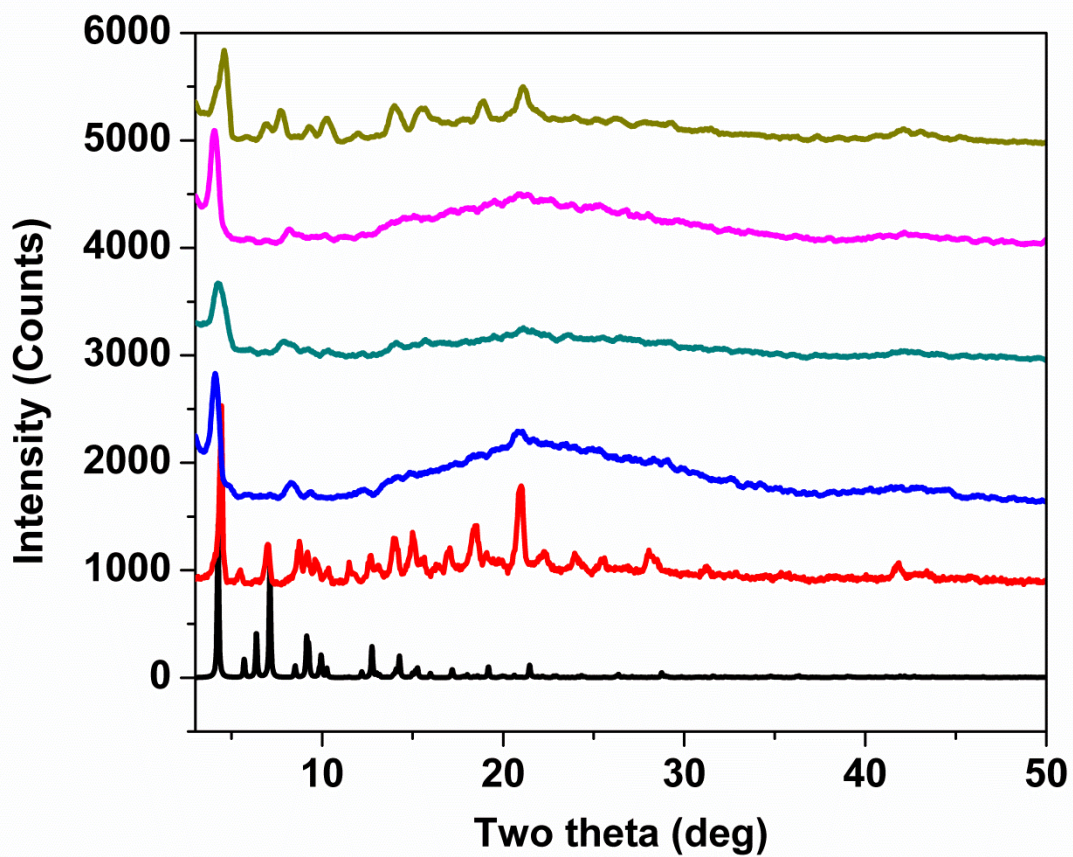


Fig. S8. PXRD patterns: **1** and **1** exchanged with non-aromatic solvents. From bottom to top: simulated **1**, as-made **1**, **1** exchanged with acetone, **1** exchanged with CH₂Cl₂, **1** exchanged with acetonitrile, **1** exchanged with n-hexane.

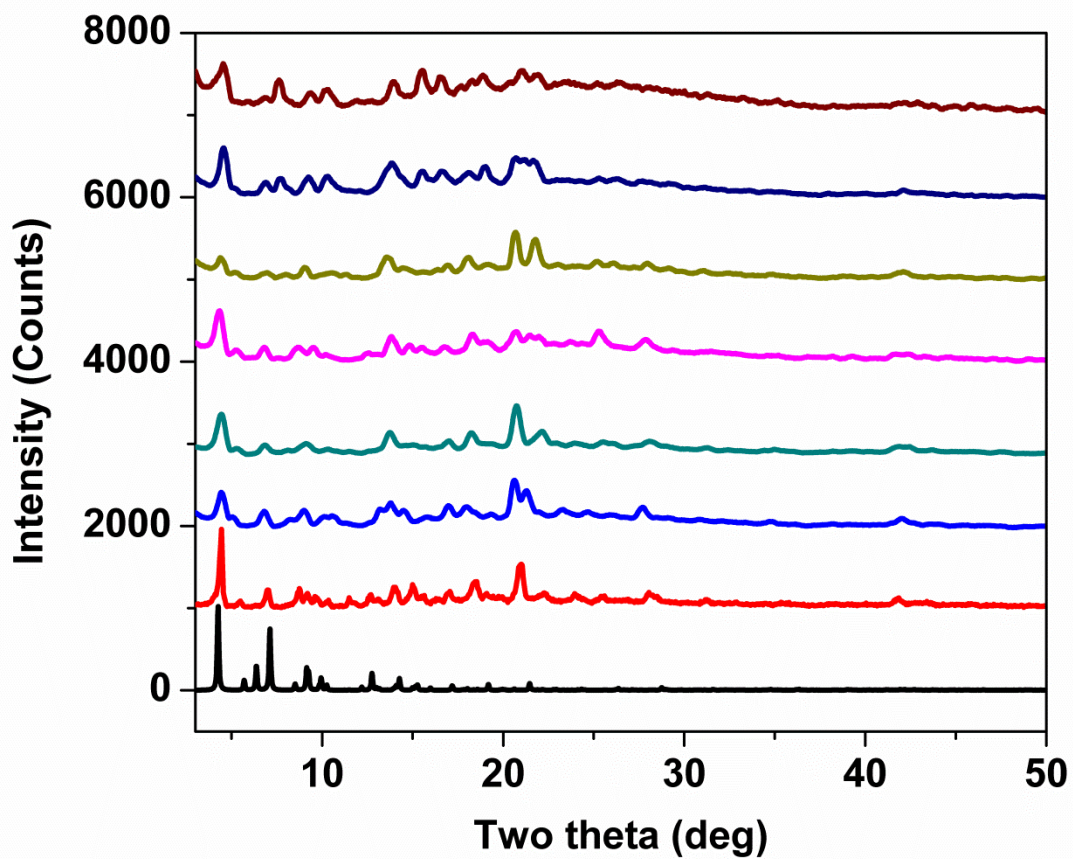


Fig. S9. PXRD patterns: **1** and **1** exchanged with aromatic solvents. From bottom to top: simulated **1**, as-made **1**, **1** exchanged with 1,2,4-trimethyl-benzene, **1** exchanged with anisole, **1** exchanged with nitro-benzene, **1** exchanged with 4-Cl-toluene, **1** exchanged with p-xylene, **1** exchanged with toluene.

S6. Photoluminescence (PL) spectrum of 2 and CIE coordinates of selected compounds

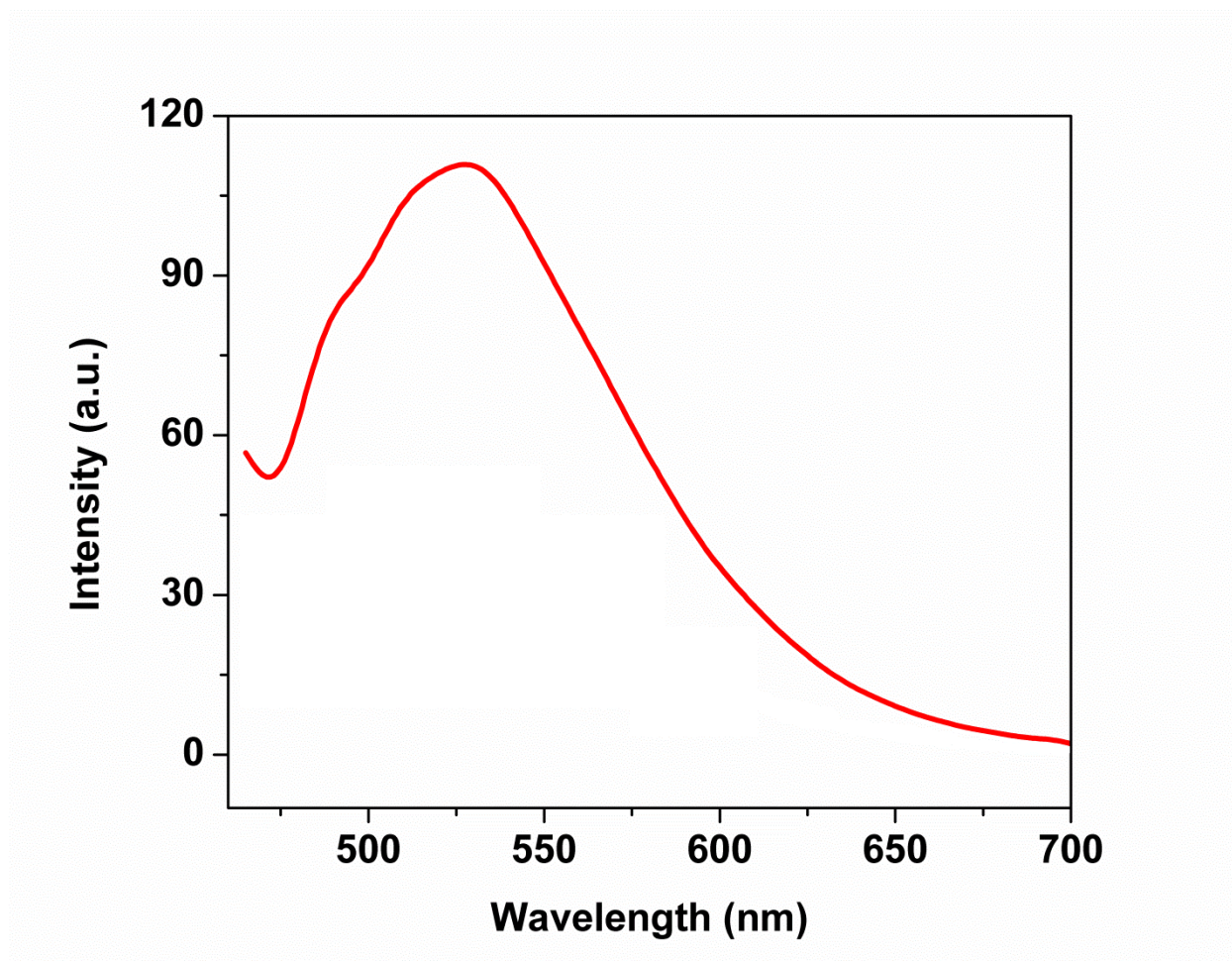


Fig. S10. Photoluminescence (PL) spectrum of 2. $\lambda_{ex} = 455$ nm.

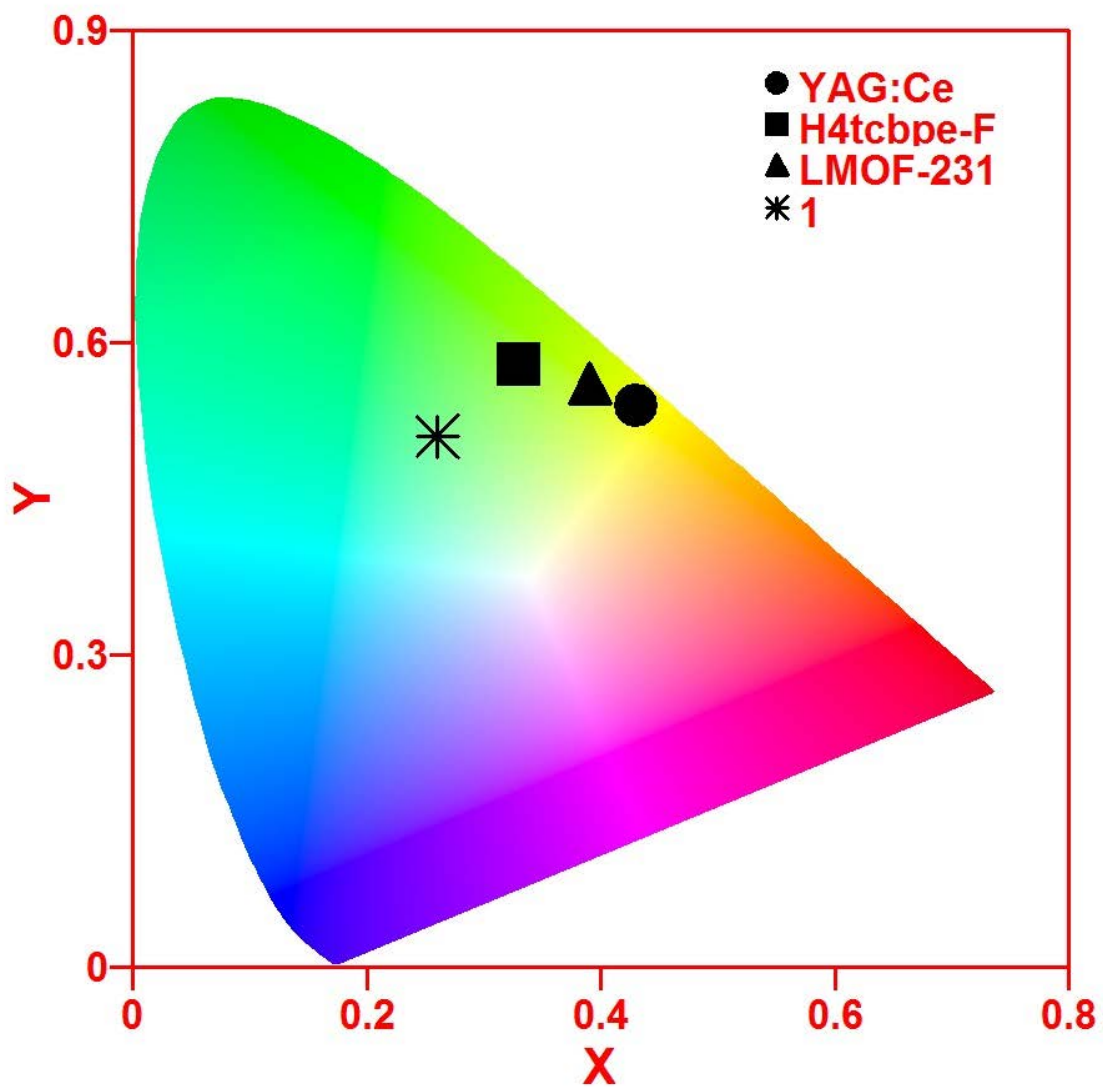


Fig. S11. CIE coordinates of selected compounds.