

## Supporting Information

### Efficient, Broadband Self-Trapped White-Light Emission from Haloplumbate-Based Metal-Organic Frameworks

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## Experiment section

**Materials.** All of the starting reagents and solvents were used as received without further purification unless otherwise indicated. Lead chloride ( $\text{PbCl}_2$ , 99.0%, Aladdin), lead bromide ( $\text{PbBr}_2$ , 99.0%, Aladdin), 2,5-thiophenedicarboxylic acid ( $\text{C}_6\text{H}_4\text{O}_4\text{S}$ , Adamas, 98%), *N,N'*-dimethylformamide (DMF, > 99%, Adamas), dichloromethane ( $\text{CH}_2\text{Cl}_2$ , 99.5%, Greagent) and ethanol (EtOH, 99.7%, Greagent) were used for the solvothermal synthesis of MOFs.

**Synthesis of TMOF-8(Cl).** In a typical solvothermal synthesis, a mixture of 0.139 g  $\text{PbCl}_2$  (0.5 mmol), 0.344 g ( $\text{C}_6\text{H}_4\text{O}_4\text{S}$ , 2 mmol) and 6 mL DMF were added into a 12 mL Teflon-lined autoclave, followed by 30 min vigorous stirring to obtain a transparent solution. The autoclave was then sealed into a stainless-steel vessel and heated statically at 150°C for 72 h. Upon the autoclave cooling to room temperature naturally, the colorless block crystals were isolated by vacuum filtration, rinsed with DMF and anhydrous ethanol extensively, and then dried at 60°C for 10 h (yield: 180.8 mg, ~79% based on Pb). Element analysis: calculated C, 20.93%; H, 2.18%; N, 3.05%; S, 6.98%; found C, 20.86%; H, 2.17%; N, 3.00%; S, 6.91%.

**Synthesis of TMOF-8(Br).** The colorless crystal TMOF-8 (Br) was synthesized in the similar manner as for TMOF-8(Cl). To be specific, a mixture of 0.184 g  $\text{PbBr}_2$  (0.5 mmol), 0.26 g ( $\text{C}_6\text{H}_4\text{O}_4\text{S}$ , 1.5 mmol) and 6 mL DMF were added into a 12 mL Teflon-lined autoclave, followed by 30 min vigorous stirring to obtain a transparent solution. The autoclave was then sealed into a stainless-steel vessel and heated statically at 150°C for 72 h. Upon the autoclave cooling to room temperature naturally, the colorless block crystals were isolated by vacuum filtration, rinsed with DMF and anhydrous ethanol extensively, and then dried at 60°C for 10 h (yield: 181.4 mg, ~72% based on Pb). Element analysis: calculated C, 19.08%; H, 1.99%; N, 2.78%; S, 6.36%; found C, 19.03%; H, 1.95%; N, 2.70%; S, 6.44%.

**Element Analysis (EA).** Elemental analysis for C/H/N/S was performed in a Varian EL III element analyzer.

**Powder X-ray Diffraction (PXRD).** PXRD analysis was performed using a BRUKER D2 PHASER X-ray diffractometer equipped with a Cu sealed tube ( $\lambda = 1.54184 \text{ \AA}$ ) at 30 kV and 10 mA. The diffraction patterns were scanned at ambient temperature, with a scan speed of 1 sec/step, a step size of  $0.02^\circ$  in  $2\theta$ , and a  $2\theta$  range of 5~40°. Simulated powder patterns were calculated by Mercury software using the crystallographic information file from the single-crystal X-ray experiment.

**Single Crystal X-ray Diffraction (SCXRD).** A single crystal of TMOF-8 suitable for X-ray analysis was chosen under an optical microscope (NIKON ECLIPSE LV100N POL), and carefully mounted onto a glass fiber. The crystal structure of the as-prepared single crystal was analyzed by a Bruker SMART APEX II CCD area detector X-ray diffractometer at 276 K, applying a graphite-monochromated Mo- $K_\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) from a fine-focus sealed tube operated at 50 kV and 30 mA. An empirical absorption correction was applied. The data were corrected for Lorentz-polarization effects. The crystal structure was solved by direct

methods and expanded routinely. The model was refined by full-matrix least-squares analysis of  $F^2$  against all reflections. All non-hydrogen atoms were refined with anisotropic thermal displacement parameters. Thermal parameters for hydrogen atoms were tied to the isotropic thermal parameter of the atom to which they are bonded. The used programs included APEX-II v2.1.4,<sup>S1</sup> SHELXTL v6.14,<sup>S2</sup> and DIAMOND v3.1e.<sup>S3</sup> Further details of crystallographic data and structural refinement are summarized in Table S1. Simulated powder patterns were calculated by Mercury software applying the crystallographic information from the SCXRD results.

**Fourier-transform infrared (FT-IR) spectrum.** FT-IR spectra were recorded using a BRUKER ALPHA spectrophotometer with a wavenumber range of 4000~400  $\text{cm}^{-1}$  with a resolution of 2  $\text{cm}^{-1}$ .

**Thermogravimetry Analysis (TGA).** TGA analysis was carried out on a TGA Q500 differential thermal analyzer. The samples were heating in  $\text{N}_2$  stream (60 mL/min) from room temperature to 800°C with a heating rate of 10°C/min.

**Chemical, humidity and thermal stability studies.** ~100 mg of the as-synthesized TMOF-8 were incubated in various organic solvent (including DMF, EtOH, dichloromethane) in air for 24 h. The humidity stability text was carried out in a humidity chamber with different relative humidity (50% RH, 70% RH or 90% RH) for 24 h at 25°C. The samples were exposed into the above conditions for one day before performing PXRD measurements. Thermal stability experiments were carried out by treating TMOF-8 in oven at different temperature for 12 h. After cooling to the room temperature naturally, PXRD characterizations were carried out.

**Ultraviolet-Visible (UV-Vis) Diffuser Reflectance Spectrum.** UV-visible diffuse reflectance spectroscopy was performed on a Agilent Carry 5000 spectrophotometer equipped with an integrating sphere, using 100%  $\text{BaSO}_4$  as reflectance standard for all measurements.

**Steady State Photoluminescence Spectra.** The excitation and emission spectra of both  $\mu\text{m}$ -sized single crystals and the corresponding  $\mu\text{m}$ -sized microcrystals of TMOF-8 were measured on a Horiba Fluorolog setup in reflection geometry (FLUOROLOG-3-11).

**Time-resolved Photoluminescence.** Time-resolved emission data was collected at room temperature using steady state/transient state fluorescence/phosphorescent spectrometer equipped with time-correlated single photon counting (TCSPC) system (FLUOROLOG-3-11). Excitation light with the specific wavelength was provided by an EPL-360PS pulsed diode laser. The average lifetime was calculated according to the following equation:

$$\tau_{avg} = \frac{\sum a_i \tau_i^2}{\sum a_i \tau_i} \quad i=1,2,3\dots$$

where  $a_i$  represents the amplitude of each component and  $\tau_i$  represents the decay time.

**Temperature-Dependent Photoluminescence.** Temperature-dependent emission data of TMOF-

8 was collected applying FLUOROLOG-3-11 steady state fluorescence spectrometer at a series of temperature ranged from 77 K to 298 K.

**Photoluminescence quantum yields (PLQYs).** Absolute PLQY measurements of TMOF-8 were performed on an FLUOROLOG-3-11 steady state/transient state fluorescence/phosphorescent spectrometer with an integrating sphere (BaSO<sub>4</sub> coating) using single photon counting mode. The focal length of the monochromator was 300 mm. Samples were excited at 332 nm light output from a 450 W Xe lamp with 3 mm excitation slits width. Emission spectra of TMOF-8 were guided through a single grating Czerny-Turner monochromator and detected by a Hamamatsu R928P photomultiplier tube using a scan step of 0.2 nm, a scan dwell time of 0.2 s, and an emission slit width of 0.1 mm. The value of PLQYs were calculated according to the following equation:  $\phi = k_f/k_a$ , in which  $k_f$  means the number of emitted photons and  $k_a$  means the number of absorbed photons. Control sample, Rhodamine-101, was measured using the same method to give a PLQY of 95%, which is close to the literature value.

**Raman measurements.** The solid-state Raman spectra were recorded on a CRIAC 20/30PV Technologoes microspectrophotometer with a 514 nm excitation wavelength. Crystals were placed on quartz slides under Krytox oil, and data was collected after optimization of microspectrophotometer.

**Photostability tests.** The photostability study of TMOF-8 was measured by employing a 4W, 365 nm UV lamp as the continuous irradiation source in surrounding environment (~60% relative humidity, room temperature) for a month to test their long-term photostability.

## Supporting Tables and Figures

**Table S1.** Crystallographic data and structural refinement for TMOF-8.

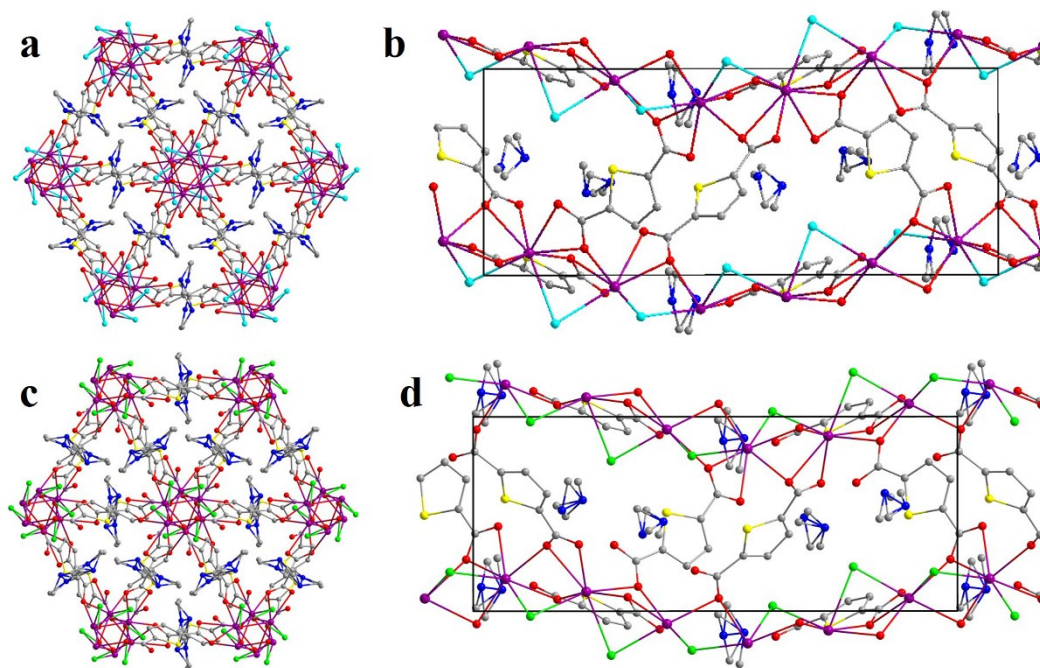
	TMOF-8(Br)	TMOF-8(Cl)
Empirical formula	PbBrC <sub>8</sub> O <sub>4</sub> SH <sub>10</sub> N	PbClC <sub>8</sub> O <sub>4</sub> SH <sub>10</sub> N
Formula weight	503.36	458.87
Temperature (K)	299(2)	296(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	hexagonal	hexagonal
Space group	P6(5)	P6(1)
Unit cell dimensions	<i>a</i> (Å)=10.1079(9) <i>b</i> (Å)=10.1079(9) <i>c</i> (Å)= 21.838(3) $\alpha$ (°)=90 $\beta$ (°)= 90 $\gamma$ (°)=120	<i>a</i> (Å)=10.0345(9) <i>b</i> (Å)=10.0345(9) <i>c</i> (Å)= 21.6691(2) $\alpha$ (°)=90 $\beta$ (°)= 90 $\gamma$ (°)=120
V (Å <sup>3</sup> ), Z	1932.2(4), 6	1889.6(4), 6
Density (calculated) (g cm <sup>-3</sup> )	2.5953	2.420
F(000)	1362.0	1272.0
Crystal size (mm <sup>3</sup> )	0.18×0.21×0.35	0.07×0.10×0.20
$\theta$ range (deg)	2.98 to 27.99	2.53 to 27.57
Limiting indices	-13 ≤ <i>h</i> ≤ 13 -13 ≤ <i>k</i> ≤ 13 -28 ≤ <i>l</i> ≤ 28	-13 ≤ <i>h</i> ≤ 12 -13 ≤ <i>k</i> ≤ 13 -28 ≤ <i>l</i> ≤ 25
Reflections collected	27306	13945
Independent reflections	3015	2806
Absorption correction	Empirical	Empirical
Data/restraints/parameters	3015/37/177	2806/82/175
Goodness-of-fit on F <sup>2</sup>	1.033	1.009
Final R indices [ <i>I</i> >2sigma( <i>I</i> )]	R <sub>1</sub> =0.0210 wR <sub>2</sub> =0.0533	R <sub>1</sub> = 0.0238 wR <sub>2</sub> = 0.0444
R indices (all data)	R <sub>1</sub> =0.0221 wR <sub>2</sub> =0.0539	R <sub>1</sub> = 0.0301 wR <sub>2</sub> = 0.0458

$$R_1 = \sum(|F_o| - |F_c|) / \sum|F_o|; wR_2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)]^2\}^{1/2}$$

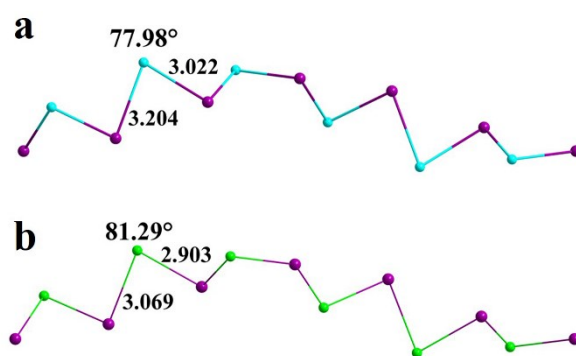
**Table S2.** Photophysical properties of TMOF-8(Cl) and TMOF-8(Br).

Material	$\lambda_{\text{abs}}(\text{nm})^{\text{a}}$	$\lambda_{\text{em}}(\text{nm})^{\text{b}}$	$(x, y)^{\text{c}}$	$T_c(\text{K})^{\text{d}}$	$\tau_{\text{av}}(\text{ns})^{\text{e}}$	PLQY <sup>f</sup>
TMOF-8(Cl)	354	487	(0.21, 0.37)	12199	0.97	12 %
TMOF-8(Br)	371	487	(0.22, 0.39)	10717	1.05	15 %

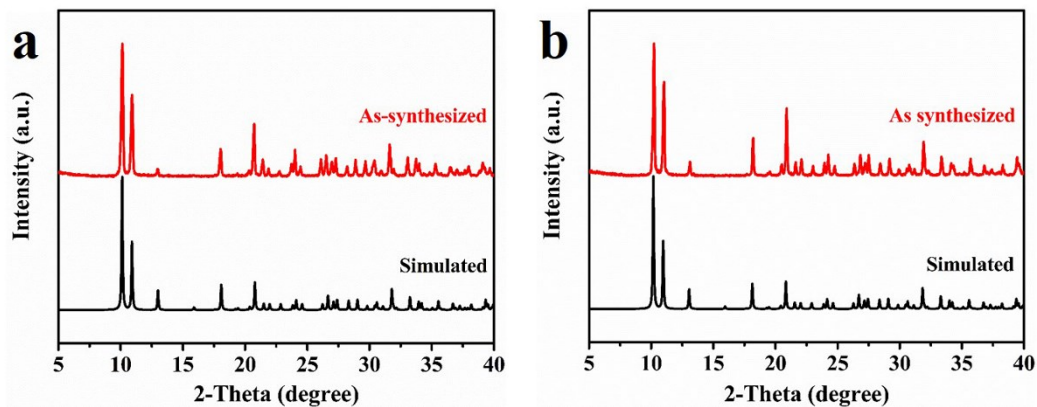
<sup>a</sup>  $\lambda_{\text{abs}}$  is the absorption edge; <sup>b</sup>  $\lambda_{\text{em}}$  is the maximum emission wavelength; <sup>c</sup>  $(x, y)$  is the chromatic coordinates; <sup>d</sup>  $T_c$  is the color temperature; <sup>e</sup>  $\tau_{\text{av}}$  is the photoluminescence lifetime at room temperature; <sup>f</sup> PLQY is photoluminescence quantum yield.



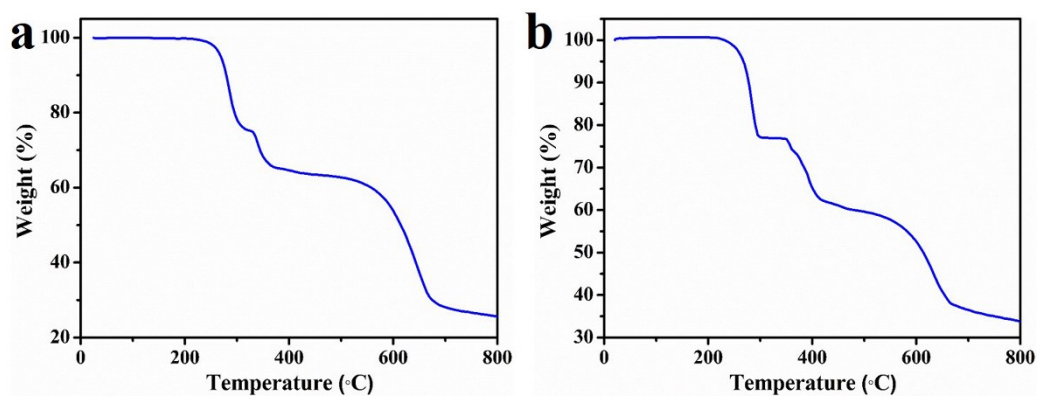
**Figure S1.** Crystallographic view of TMOF-8(Br) (a-b) and TMOF-8(Cl) (c-d) along c-axis and b-axis, showing protonated dimethylamine ( $(\text{CH}_3)_2\text{NH}_2^+$ ) cations residing in the 1D pore channels. Hydrogen atoms are omitted for clarity. Pb purple, Br turquoise, Cl green, S yellow, O red, C grey, N blue.



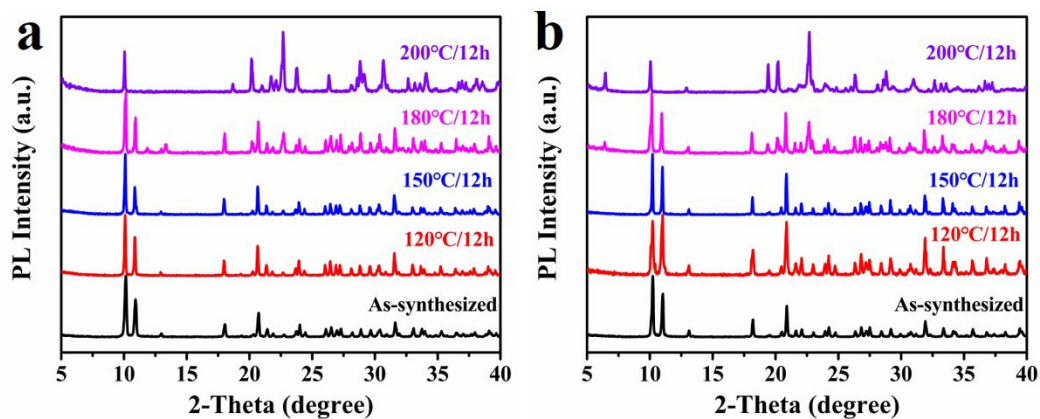
**Figure S2.** Crystallographic view of Pb-X (X=Cl, Br) single chains in TMOF-8. Pb purple, Br turquoise, Cl green.



**Figure S3.** Simulated XRD patterns from the single-crystal data and PXRD patterns of TMOF-8(Br) (a) and TMOF-8(Cl) (b).

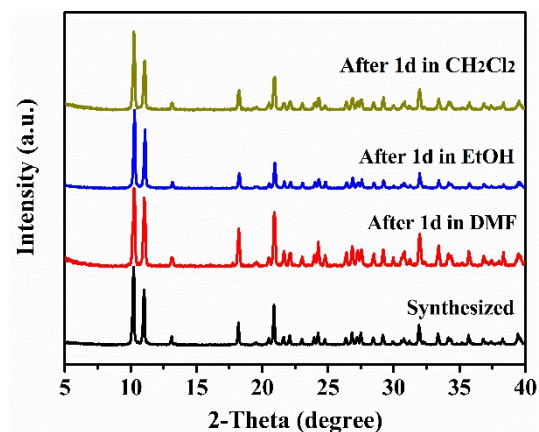


**Figure S4.** Thermogravimetric analysis of TMOF-8(Br) (a) and TMOF-8(Cl) (b) in  $N_2$  flow.

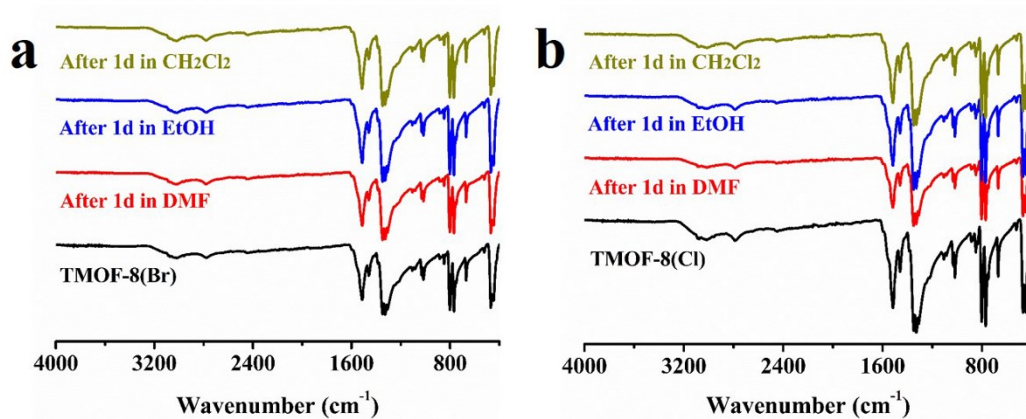


**Figure S5.** PXRD patterns of TMOF-8(Br) (a) and TMOF-8(Cl) (b) after thermal treatment in air.

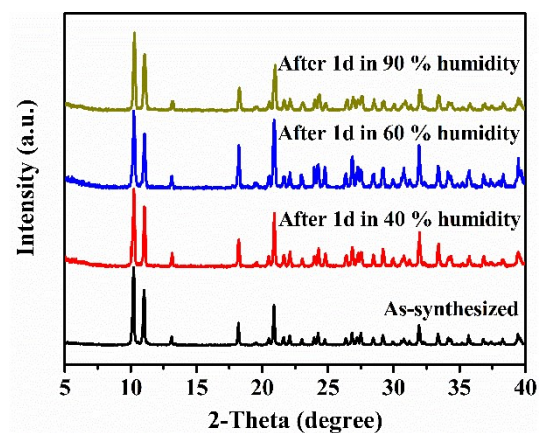




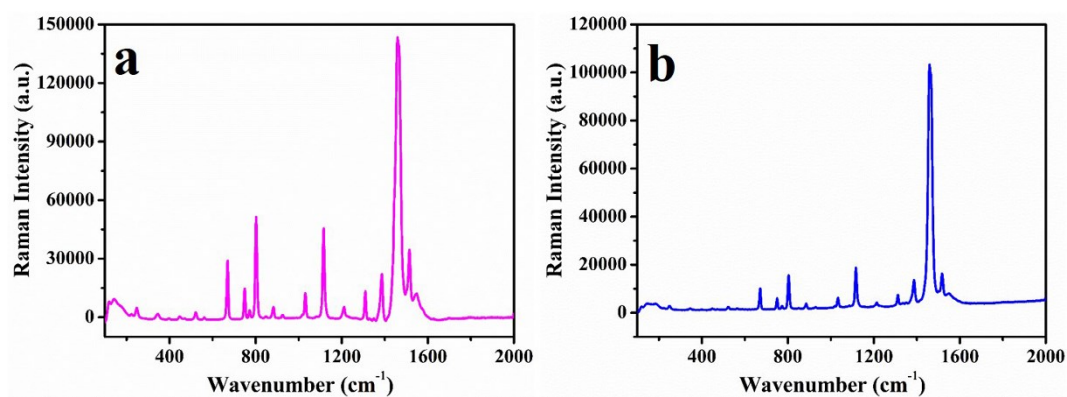
**Figure S6.** PXRD patterns of TMOF-8(Cl) before and after incubation in different solvents for 24 h.



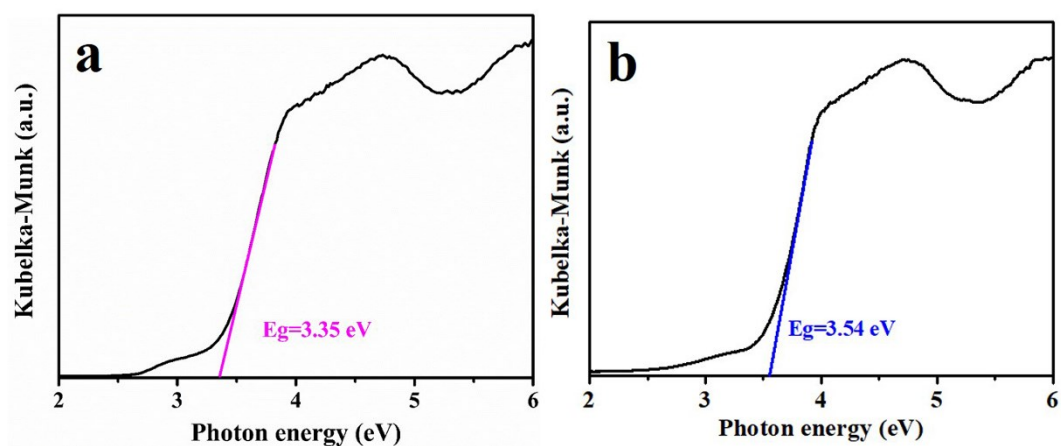
**Figure S7.** FTIR spectrum for TMOF-8(Br) (a) and TMOF-8(Br) (b) before and after different chemical treatment.



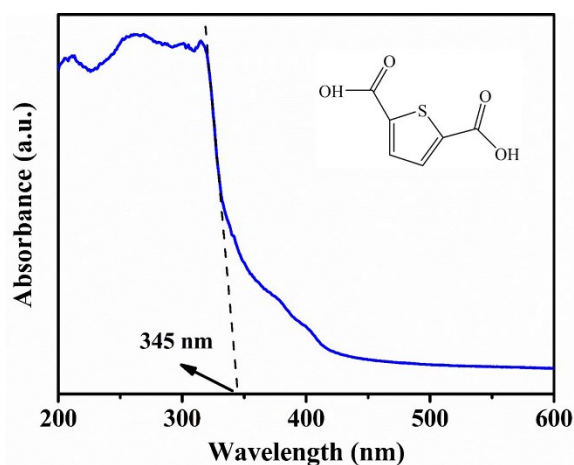
**Figure S8.** PXRD patterns of TMOF-8(Cl) before and after 24 h in different relative humidity.



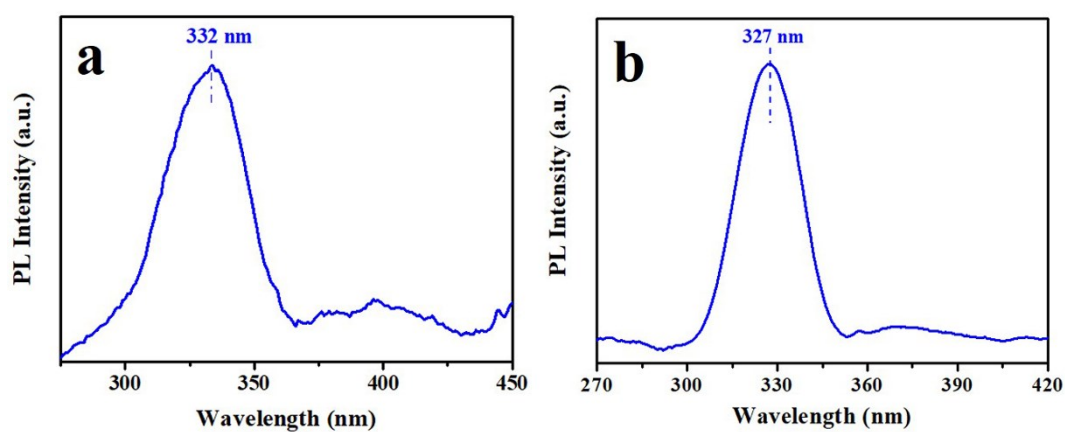
**Figure S9.** Raman spectra of TMOF-8(Br) (a) and TMOF-8(Cl) (b).



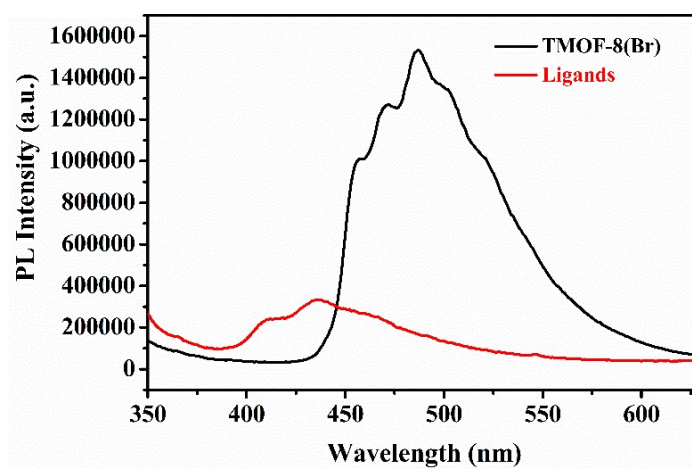
**Figure S10.** Kubelka-Munk plot of TMOF-8(Br) (a) and TMOF-8(Cl) (a). The extrapolation of the linear region estimates the bandgap value of  $\sim 3.35$  eV and  $\sim 3.54$  eV for TMOF-8(Br) and TMOF-8(Cl), respectively.



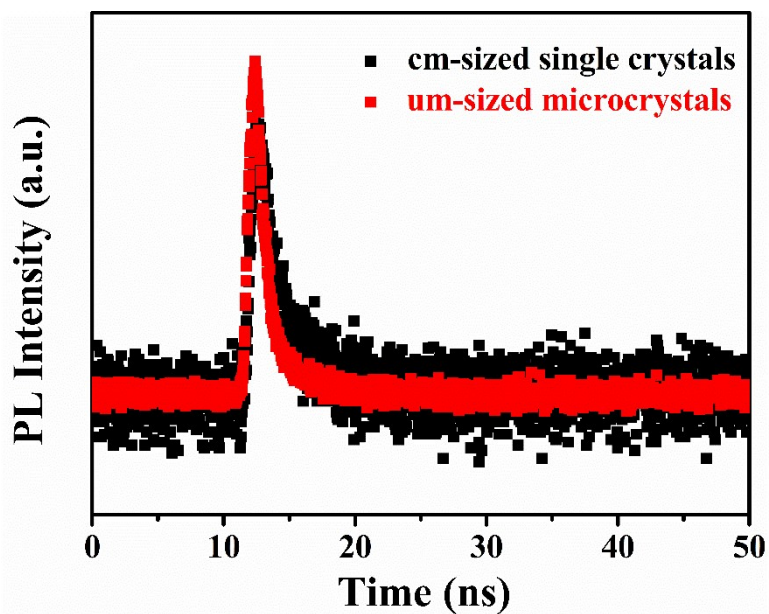
**Figure S11.** The absorption spectrum of the free organic ligands, which has an absorption edge of 345 nm.



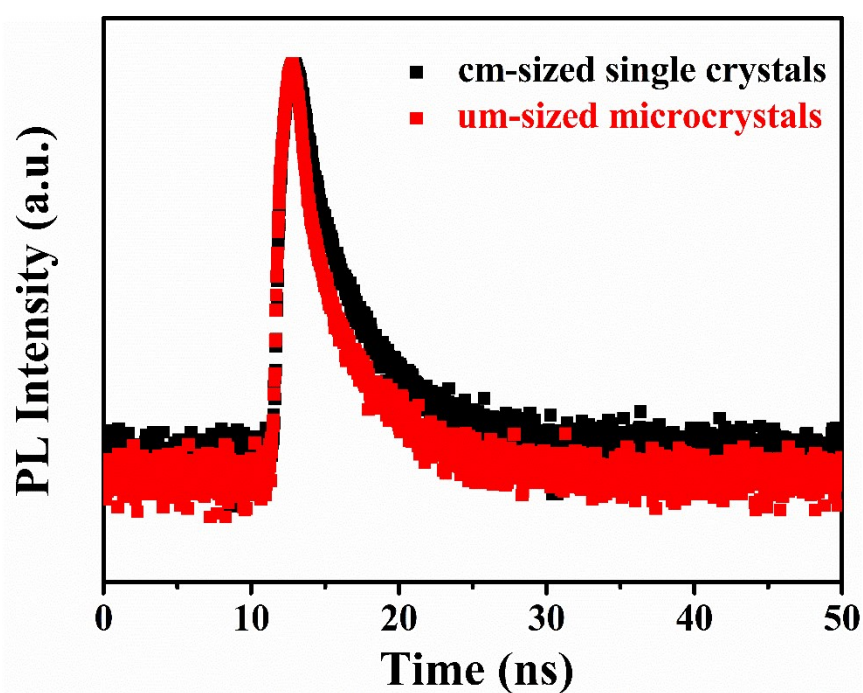
**Figure S12.** The excitation spectra of TMOF-8(Br) (a) and TMOF-8(Cl) (b) measured at room temperature.



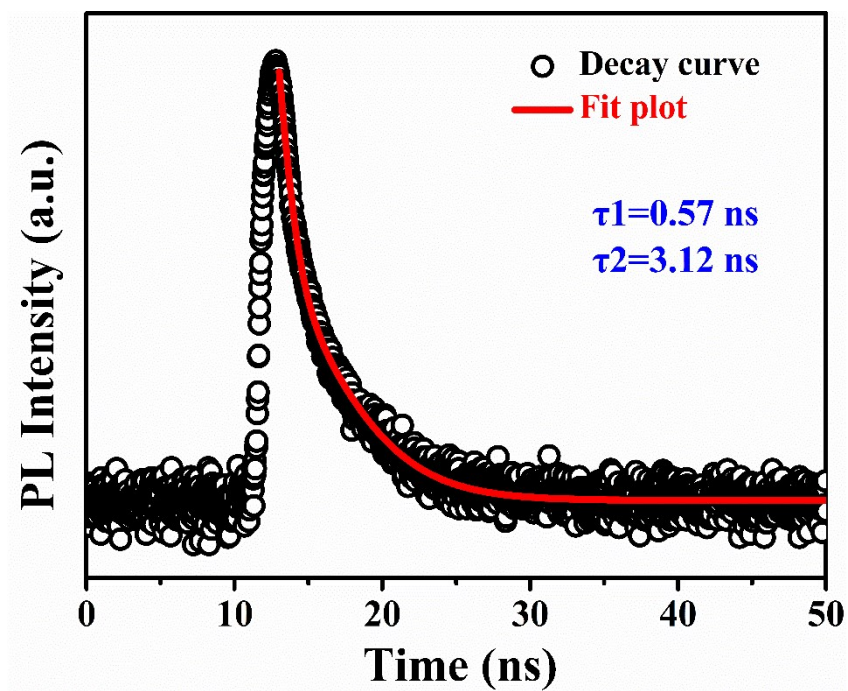
**Figure S13.** The emission spectra of TMOF-8(Br) and the free ligands (the excitation wavelength=332 nm, slit width=2 nm).



**Figure S14.** Photoluminescence decay curve of cm-sized TMOF-8(Br) single crystals (black) and  $\mu\text{m}$ -sized microcrystals (red) at 298 K.



**Figure S15.** Photoluminescence decay curve of cm-sized TMOF-8(Cl) single crystals (black) and  $\mu\text{m}$ -sized microcrystals (red) at 298 K.



**Figure S16.** Photoluminescence decay of TMOF-8(Cl) measured at room temperature.

## References

- S1. *APEX-II, 2.1.4*, Bruker-AXS: Madison, WI, 2007.
- S2. *SHELXTL, Crystal Structure Determination Package*, Bruker Analytical X-ray Systems Inc.: Madison, WI, 1995~99.
- S3. Brandenburg, K.; Putz, H., Diamond, *Crystal Impact*, Bonn, Germany, 2007.