Supporting Information for

A Moisture-Stable Organosulfonate-Based Metal-Organic Framework with Intrinsic Self-Trapped White-Light Emission

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Author Contributions

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Experimental Section

Materials

All starting reagents, materials and solvents were purchased from commercial suppliers (Sigma Aldrich, Fisher Scientific, Alfa Aesar, *et al.*) and used without further purification unless otherwise indicated. Purity of the reagents and the solvents are over 99 % and HPLC grade, respectively. Deionized water was obtained from a BARNSTEAD PACIFIC RO water purification system.

Solvothermal Synthesis of TMOF-7

In a typical synthesis, CdCl₂ (69 mg, 0.3 mmol) and 1,2-ethanedisulfonic acid (68 mg, 0.3 mmol) were adequately dispersed in 10 mL DMF by sonication, followed by transferring the mixtures into a 15 mL Teflon-lined autoclave and heating statically at 120 °C for 72 h. After 72 h, the autoclave was cooled down to room temperature at a rate of 6 °C/h and the colorless block crystals were isolated by centrifugation at 2000 rpm for 5 min. The crystals were then washed with ethanol for three times (10 mL × 3) and dried in air (yield: 94 mg, ~82 % based on Cd). The as-synthetized materials were incubated in 20 mL methanol over a period of 60 hours, in which fresh methanol was changed every 12 hours. The MOFs were evacuated at 150 °C for 6 hours at a pressure of 10⁻² mtorr on a MICROMERITICS ASAP 2020 chemical/physical gas sorption analyzer, giving activated guest-free sample. The high phase purity of TMOF-7 was confirmed by comparing experimental PXRD patterns with theoretical pattern simulated from the single-crystal X-ray diffraction data. Anal. cal. for C₄H₁₂O₆NS₂ClCd: C 12.56, H 3.14, N 3.66, S 16.76 (%); found: C 12.99, H 3.15, N

3.80, S 16.90 (%, activated sample). The μ m-sized microcrystalline powders of TMOF-7 were prepared *via* manual grinding of the bulk crystals.

Powder X-Ray Diffraction (PXRD)

Approximately 20 mg sample of TMOF-7 (pristine or post-treated) were dried in vacuum prior to PXRD analysis. The measurement was carried out on a BRUKER D2 PHASER diffractometer with Cu K α radiation ($\lambda = 1.5418$ Å) at 40 kV, 40 mA and room temperature. The diffraction patterns were scanned with a speed of 1 s/step, a step size of 0.02 ° in 2 θ , and a 2 θ range of 5~40 °. Theoretical PXRD pattern were simulated by using the crystallographic information file collected from the single-crystal X-ray diffraction experiment.

Single Crystal X-Ray Diffraction (SCXRD)

A single crystal of TMOF-7 suitable for X-ray analysis was chosen under an optical microscope (NIKON ECLIPSE LV100N POL), and carefully mounted onto the glass fiber. SCXRD data were collected at 150(2) K using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) from a fine-focus sealed tube operating at 50 kV and 30 mA on a BRUKER D8 VENTURE diffractometer equipped with a PHOTON III detector. The crystal-to-detector distance was set 45 mm. More than half-sphere of data was collected using a combination of phi and omega scans with the scan speeds of 2 s/° for the phi scans and 1 s/° for the omega scans at $2\theta = 0^{\circ}$.

Diffraction data were processed with the APEX3 software package,^[S1] integrated using SAINT, and further corrected for absorption effects using SADABS. Space-group was determined by systematic absences, E-statistics, agreement factors for equivalent reflections, and successful refinement of the structure. The 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 using SHELXTL software package.^[S2] 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 atoms to which they are bonded. Further details for the crystallographic data and structural refinement are summarized in Table S2.

Fourier-Transform Infrared (FT-IR) spectrum

FT-IR spectrum were recorded using a BRUKER ALPHA spectrophotometer with a wavenumber range of $4000 \sim 400 \text{ cm}^{-1}$, a resolution of 4 cm^{-1} , and scan times of 32.

Thermogravimetry Analysis (TGA)

TGA was performed using a NETZSCH STA 409 PC/PG differential thermal analyzer with a platinum crucible. The samples were heated in N₂ stream (60 mL/min) from room temperature to 800 $^{\circ}$ C with a heating rate of 10 $^{\circ}$ C/min.

Chemical and Humidity Resistance Studies

A certain amount of activated TMOF-7 was added to various solvents (DMF, EtOH or acetone) for 24 h. The samples were then filtrated out, washed by EtOH for three times and dried in air. The humidity test was performed by incubating activated TMOF-7 in a chamber at a fixed humidity in the range of 50%~90% RH for 48 h. PXRD patterns and photoluminescence of the samples after humidity treatment were then performed.

Electrical Conductivity Measurement

Electrical conductivity of a single crystal of TMOF-7 was measured using a CHI 760E electrochemical workstation over a frequency range of 10 Hz~10 MHz with an input voltage amplitude of 500 mV. Silver paste was coated uniformly onto opposite side of the crystal and copper wire electrodes were fixed into the paste (Figure S2). The measurements were taken at room temperature and 50% RH. The resistance (R) was extrapolated by fitting the semicircles of the Niquist plots using a proposed equivalent circuit *via* ZVIEW software package and the conductivity (σ) was acquired by the equation of $\sigma = 1/AR$ where 1 and A represent the length and the cross-section area of the single-crystal, respectively.

Cation Exchange

Appropriately 100 mg TMOF-7 crystals was heated in 120 $^{\circ}$ C oven overnight for adequate activation, and then incubated into DMF solution containing MnCl₂. The concentrations of the solutions range from 0.5 mol % to 2.5 mol % in order to achieve

different degree of cation exchange. The suspension was fixed onto a mechanical shaker at a constant shaking rate of 200 cpm for 6 h to assure sufficient cation exchange. Then, the solids were isolate by filtration, washed by EtOH for three times, and dried in air. Inductively coupled plasma optical emission spectra (ICP-OES, operated on a PERKIN ELMER AVIO 200 ICP-OES spectrometer) was employed to evidence the successful incorporation of Mn^{II} into TMOF-7. TMOF-7 and its derivatives were digested by mixed solvent of D₃PO₄ (36 wt. % in D₂O) and d^6 -DMSO for ¹H NMR measurements.

Elemental Analysis

Elemental analysis (EA) for C/H/N/S was performed using a THERMAL FLASH EA 1112 element analyzer.

Steady State Photoluminescence Spectra

The excitation and emission spectra of both the mm-sized single crystals and μ m-sized microcrystals of TMOF-7 were collected at room temperature using a HITACHI F-7000 spectrophotometer equipped with a 1 kW Xe lamp. The slit width was set 1 mm.

Ultraviolet-Visible (UV-Vis) Diffuser Reflectance Spectrum

The UV-Vis diffuser reflectance spectrum in 200~1000 nm region was recorded at room temperature upon a SHIMADZU UV-2600 spectrometer equipped with integrating sphere. BaSO₄ was used as a reference for 100% reflectance for all measurements. The μ m-sized microscopic powders were packed into the sample cell. Reflectance spectrum were converted to absorption according to the equation:

$$A = 2 - lg(T\%)$$

where A and T represent the absorbance and reflectance, respectively. The Kubelka-Munk plot $[F(\alpha)hv]^{1/2}$ as a function of photon energy (hv) was applied to the absorption spectra and the optical absorption coefficient, $F(\alpha) = A^2/2(1-A)$, is calculated, where A is the absorbance, h is the Planck constant, and v is the frequency of light at a specific wavelength. The extrapolation of the linear region affords the bandgap value for TMOF-7.

Time-Resolved Photoluminescence

Time-resolved emission data was collected at room temperature using an EDINBURGH FLS980 steady state/transient state fluorescence/phosphorescent spectrometer equipped with time-correlated single photon counting (TCSPC) system. Excitation was provided by an EPL-360PS pulsed diode laser. The average lifetime was obtained according to the equation:

$$\tau_{\text{avg}} = \frac{\sum \alpha_i \tau_i^2}{\sum \alpha_i \tau_i} \quad i = 1, 2, 3..$$

where a_i represents the amplitude of each component and τ_i represents their decay time. The instrument response was measured to be ~1 ns FWHM by measuring scattered light from alumina colloidal particles.

Temperature-Dependent Photoluminescence

Temperature-dependent emission data was collected for μ m-sized microscopic powders using the EDINBURGH FLS980 steady state/transient state fluorescence/phosphorescent spectrometer at a series of temperature ranged from 77 K to 477 K.

Photoluminescence Quantum Efficiencies (PLQEs)

Absolute PLQE measurements of TMOF-7 were performed on an EDINBURGH FLS920 steady state/transient state fluorescence/phosphorescent spectrometer with an integrating sphere (BaSO₄ coating) using single photon counting mode. The focal length of the monochromator was 300 mm. Samples were excited using light output from a 450W Xe lamp with 3 mm excitation slits width. Emission from the sample was guided through a single grating Czerny-Turner monochromator and detected by a Hamamatsu R928P photomultiplier tube. The emission was obtained 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 PLQEs were calculated by the equation: $= k_f/k_a$, in which k_f means the number of emitted photons and k_a means the number of absorbed photons. Control sample, Rhadamine-101, was measured using the same method to give a PLQY of 95%, which is close to the literature value.

Photostability Tests

A 4 W, 365 nm lamp was used as the continuous irradiation source to test the photostability of TMOF-7. Then, steady-state photoemission measurements were

performed for the samples which were irradiated for 14 days in air (~50% relative humidity, room temperature).

Raman Masurements

Solid-state Raman spectra were recorded on a CRIAC 20/30PV full spectrum microspectrophotometer with an above-bandgap excitation wavelength of 785 nm. Crystals were placed on quartz slides under Krytox oil, and data was collected after optimization of microspectrophotometer.

Computational Methods

Density function theory calculations (DFT) were fulfilled by using CP2K package. The system was described by Perdew-Burke-Ernzerhof (PBE) function with Grimme D3 correction. Unrestricted Kohn-Sham DFT has been used as the electronic structure method in the framework of the Gaussian and plane waves method. The Goedecker-Teter-Hutter (GTH) pseudopotentials, DZVP-MOLOPT-SR-GTH basis sets were utilized to describe the molecules. A plane-wave energy cut-off of 500 Ry has been employed. The lattice parameters were fixed at the experimentally measured values while the atomic positions were optimized. Following Franck-Condon principle, the optical excitation and emission energies were obtained by calculating the total energy differences between the excited and the ground states using optimized ground-state and excited-state structures, respectively.

Figures and Tables



Figure S1. Crystallographic view of TMOF-7 along *a*-axis, showing the protonated dimethylamine cations in its pore channel. Hydrogen atoms are omitted for clarity. Cd teal, S yellow, O red, C grey, Cl green, N blue.



Figure S2. a) The approach to measure electrical conductivity of a single crystal of TMOF-7; b) Nyquist plots of a single crystal of TMOF-7 along crystallographic a-axis and along crystallographic b-axis



Figure S3. FTIR spectrum for TMOF-7 before and after chemical treatment, and the characteristic absorption bands (1169 cm⁻¹, 1067 cm⁻¹, 607 cm⁻¹) of sulfonate groups are highlight.



Figure S4. PXRD patterns of TMOF-7 before and after incubation in different solvents. The new peaks highlighted by red squares are likely due to the partial degradation of our MOFs in organic solvents.



Figure S5. Thermogravimetry curve for TMOF-7.



Figure S6. Tauc plot of TMOF-7, in which $(Ahv)^2$ is a function of the photon energy (hv). The extrapolation of the linear region estimates the bandgap value of TMOF-7 is about 4.15 eV.



Figure S7. Photoluminescence excitation and emission of pristine bulk TMOF-7.



Figure S8. Photoluminescence decay of TMOF-7 measured at 298K (monitored at 390 nm).



Figure S9. Photoluminescence decay of TMOF-7 measured at 77K (monitored at 390 nm).



Figure S10. Photoluminescence emission of TMOF-7 before (black) and after (cyan) continuous UV irradiation (310 nm, 67 mW/cm²) for 15 days under ambient condition (~50% RH, room temperature).



Figure S11. Photoluminescence emission of TMOF-7 before (black) and after (blue) incubating in high moisture condition (RH 90 %) for 24 h.



Figure S12. PXRD patterns of TMOF-7 before and after Mn(II) exchange.



Figure S13. ¹H NMR spectra of digested TMOF-7 (black) and TMOF-7-Mn_{0.9} (red), showing slight leaching of dimethylamine species during cation exchange.



Figure S14. Photoluminescence decay of mm/μ m-sized TMOF-7 at 298 K.



Figure S15. Photoluminescence decay of TMOF-7 measured at 298 K (monitored at 489 nm).





 $\Gamma(T) = \Gamma_0 + \Gamma_{\rm LO} (e^{E_{\rm LO}/k_{\rm B}T} - 1)^{-1} + \Gamma_{\rm inh} e^{-E_{\rm b}/k_{\rm B}T}$ (1) The best fit demonstrated a considerable contribution of the electron-phonon coupling [$\Gamma_{\rm LO}$ of 79(2) meV] to the broadening of photoluminescence and phonon energy of 14(1) meV. The latter corresponds to a frequency of 116 cm⁻¹, which resides well in the range of Cd—Cl stretching frequency in TMOF-7 (Figure S17). All of these photophysical studies suggest the high-energy shoulder and the low-energy broadband emission of TMOF-7 are probably attributed to the self-trapped excitons (from electron-phonon coupling in the deformable lattice) and free excitons,

respectively.



Figure S17. Raman spectrum of TMOF-7.

Table	S1 .	Photophysical	properties	of	TMOF-7	before	and	after	the	Mn^{2+}
incorpo	oratio	on.								

Material	х	У	FWHM (nm)	CCT (K)	CRI	PLQE (%)
TMOF-7	0.28	0.34	230	8497	82	11
TMOF-7-Mn _{0.3}	0.30	0.35	225	6720	86	7
TMOF-7-Mn _{0.6}	0.36	0.37	219	4297	92	8
TMOF-7-Mn _{0.9}	0.38	0.38	202	3862	88	11

Material	PLQE (%)	CRI	Reference
TJU-3	1.8	78	Angew. Chem. Int. Ed. 2017, 56, 14411.
TJU-4	11.8	68	Angew. Chem. Int. Ed. 2017, 56, 14411.
TJU-5	2.0	N.A.	Angew. Chem. Int. Ed. 2017, 56, 14411.
TJU-6	5.4	N.A.	Chem. Sci. 2018, 9, 1627.
TJU-7	1.8	N.A.	Chem. Sci. 2018, 9, 1627.
TMOF-5(Cl)	6~8	85	Angew. Chem. Int. Ed. 2019, 58, 7818.
TMOF-5(Br)	1.5	89	Angew. Chem. Int. Ed. 2019, 58, 7818.
(N-MEDA)PbBr ₄	0.5	85	J. Am. Chem. Soc. 2014, 136 , 1718.
(EDBE)PbBr ₄	9	84	J. Am. Chem. Soc. 2014, 136 , 13154.
(EDBE)PbCl ₄	2	81	J.Am. Chem. Soc. 2014, 136 , 13154.
(PEA) ₂ PbCl ₄	<1	84	Chem. Mater. 2017, 29, 3947.
(API)PbCl ₄	<1	93	J. Mater. Chem. C 2018, 6, 1171.
(MPenDA)PbBr ₄	3.4	91	Chem. Commun. 2018, 54 , 4053.
(CyBMA)PbBr ₄	1.5	N.A.	ChemSusChem 2017, 10, 3765.
α-(DMEN)2PbBr4	N.A.	73	J.Am. Chem. Soc. 2017, 139 , 5210.
(HMTA)3Pb2Br7	7	N.A.	Chem. Sci. 2017, 8, 8400.
(H2DABCO)Pb2Cl6	2.5	96	Chem. Sci. 2015, 6, 7222.
$(C_6H_{18}N_2O_2)Pb_{0.95}Mn$	12.5	85	Chem. Mater. 2019, 31 , 5788.
$_{0.05}\mathrm{Br}_4$			
(BAPP)Pb ₂ Br ₈	1.5	87	<i>Adv. Mater.</i> 2019, 31 , 1807383.
(TDMP)PbBr ₄	45	75	Adv. Mater. 2019, 31 , 1807383.

Table S2. Photoluminescence parameters of recently reported intrinsic white-light emitters.

Identification code	TMOF-7				
Empirical formula	C ₄ H ₁₂ O ₆ NS ₂ ClCd				
Formula weight	382.12				
Temperature	150 (2) K				
Wavelength	0.71073 Å				
Crystal system	triclinic				
Space group	<i>P</i> -1				
Unit cell dimensions	a = 8.0898 (9) Å α = 113.630(4) °				
	b = 8.7429 (11) Å β = 100.423(4) °				
	$c = 9.3861 (11) \text{ Å} \gamma = 106.839(4)^{\circ}$				
Volume	547.71 (11) Å ³				
Z	2				
Density (calculated)	2.317 g/cm ³				
F (000)	376				
Crystal size	$0.23 \times 0.13 \times 0.10 \text{ mm}^3$				
θ range for data collection	3.048 ~ 27.552 °				
Limiting indices	$-10 \le h \le 10, -11 \le k \le 10, 0 \le l \le 12$				
Reflections collected	2521				
Independent reflections	2409				
Completeness to $\theta = 26.73^{\circ}$	100%				
Absorption correction	empirical				
Data / restraints / parameters	2521/0/142				
Goodness-of-fit on F^2	1.190				
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0180, wR_2 = 0.0480$				
R indices (all data)	$R_1 = 0.0199, wR_2 = 0.0468$				
Largest diff. peak and hole	0.407 and -0.565 eÅ ⁻³				

 Table S3. Crystallographic data and structural refinement for TMOF-7.

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. Lee, J.; Koteles, E. S.; Vassell, M. O., Phys. Rev. B 1986, 33: 5512-5516.