

Supporting Information

Enhancement of the fluorescence properties via introducing the tetraphenylethylene chromophores into a novel Mn–organic framework with a rare $[\text{Mn}_4(\mu_3\text{-OH})_2]$ cluster

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1. Experimental section

1.1 Materials and Methods. All chemicals were obtained from commercial sources and used without further purification. Powder X-ray diffraction (PXRD) patterns were recorded by a Rigaku MiniFlex600 diffractometer (40 kV, 15 mA) using Cu K α ($\lambda = 1.54056 \text{ \AA}$) at room temperature. Thermogravimetric analyses (TGA) were carried out under nitrogen atmosphere using a NETZSCH STA 449C thermal analyzer a heating rate of 8 °C/min. X-ray photoelectron spectroscopy (XPS) analysis measurement was collected on a Thermo-Scientific K-Alpha Plus X-ray photoelectron spectrometer using Al K α source. Solid-state UV-Vis diffuse reflectance spectra measured on a Hitachi U-3900 UV/vis spectrophotometer at room temperature. The luminescence properties were recorded on a Hitachi F-7100 fluorescence spectrophotometer at room temperature. The temperature-dependent luminescent measurements were recorded a Horiba FluoroMax+ spectrofluorometer under different temperatures (80–300 K).

1.2 Single Crystal X-ray Crystallographic Determination. Single crystal X-ray data collection of **SQNU-55** was collected on the Bruker D8 VENTURE PHOTON II diffractometer using graphite-monochromated Mo K α ($\lambda = 0.71073 \text{ \AA}$) at 193 K during data collection. The structure was solved using direct methods and refined by full-matrix least-squares refinement on F^2 using the SHELXL-2018/3 crystallographic software package. All non-hydrogen atoms were refined with anisotropic displacement parameters, and all the hydrogen atoms were placed in ideal positions. For **SQNU-55**, the commands “dfix”, “sadi” and “flat” were used to solve the highly disordered TCPE ligands in framework. The disordered non-coordinated solvents in the pores were removed using SQUEEZE program implemented in PLATON.^{S1} Crystal data and structure refinement details for **SQNU-55** were given in Table S1. The crystal data can be obtained free of charge from the Cambridge Crystallographic Data Centre through www.ccdc.cam.ac.uk/data_request/cif.

1.3 Synthesis of SQNU-55. ($[\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}(\mu_3\text{-OH})(\text{TCPE})(\text{H}_2\text{O})]$). A mixture of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (20 mg, 0.1 mmol) and H_4TCPE (10 mg, 0.02 mmol) was ultrasonically dissolved by *N,N*-diethylformamide (DEF) (3 mL) and CH_3COOH (HAc)(0.4 mL) in a sealed vial (20 mL), and then placed in an oven preheated at 125 °C for 24 h. After cooling to room temperature spontaneously, the light yellow needle crystals were washed several times with fresh DMF and CH_3CN , and then dried in air (65% yield based on the ligand).

2. DFT calculations

2.1 Computational setup. All density functional theory calculations in this work were performed using the Gaussian 09 program suite.⁵² The equilibrium geometries were optimized at the Becke's three-parameter hybrid exchange functional combined with the Lee-Yang-Parr correlation functional (B3LYP)^{53, 54} with 6-31+G(*d*) basis set.^{55,56} On the basis of the optimized ground-state geometries, the absorption spectra were simulated by TD-B3LYP calculations^{57, 58} with the same basis set. The lowest fifty singlet-singlet excitations were calculated respectively to gain insight into the nature of the absorption.

2.2 Absorption spectra and electronic structure. To have a good insight into the UV-vis absorption spectra of H₄TCPE in **SQNU-55** conformation and in free conformation, respectively, their absorption features were calculated on the basis of the optimized ground-state geometries. Referring to Zhou' work,⁵⁹ the conformation of H₄TCPE in **SQNU-55** was obtained by changing four Mn cations to protons and removing other Mn cations connected to the TCPE unit.

The calculated results show that the maximum and strongest absorption wavelength of H₄TCPE in free configuration is located at 373 nm, which is in good agreement with the experimental data at 377 nm (Fig. S4). This absorption peak is predominantly attributed to the transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), i.e., HOMO → LUMO. While the maximum singlet absorption band of H₄TCPE in **SQNU-55** is centered at 392 nm, which shows a distinct deviation from the experimental result at 348 nm (Fig. S4). This may be because that the absorption peak of 348 nm measured by experiment is the absorption wavelength with the strongest oscillator strength (see Figure S4). However, the intensity of the calculated absorption of 392 nm is not the strongest ($f = 0.14$). According to the calculated wavelengths, the experimentally measured peak of 348 nm is more likely to correspond to the calculated second singlet-singlet excitation (S_2) with 334 nm. The reasons for this proposal are that the simulated absorption spectra at 334 nm possesses strongest intensity ($f = 0.17$) and reproduces the experimental spectra well within acceptable error. The peak at 334 nm is mainly contributed by HOMO → LUMO+1.

Table S1. Crystal data and structure refinements of **SQNU-55**.

Formula	C ₃₀ H ₁₆ Mn ₂ O ₁₀
Formula weight	646.31
Temperature (K)	193
Crystal system	Tetragonal
Space group	<i>I</i> -4
<i>a</i> (Å)	18.1333(11)
<i>b</i> (Å)	18.1333(11)
<i>c</i> (Å)	12.5930(13)
α (deg)	90.00
β (deg)	90.00
γ (deg)	90.00
Volume(Å ³)	4140.8(7)
Z	4
<i>d</i> _{calcd.} (g·cm ⁻³)	1.037
μ (mm ⁻¹)	0.649
<i>F</i> (000)	1304
Reflections collected/unique	15085 / 3659
<i>R</i> _{int}	0.0582
Data/restraints/parameters	3659 / 696 / 331
GOF on <i>F</i> ²	1.067
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b [<i>I</i> > 2σ(<i>I</i>)]	0.1493, 0.3100
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b (all data)	0.2286, 0.3491

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

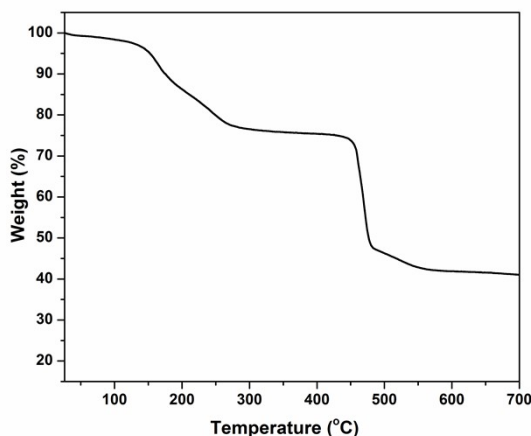


Fig. S3 TGA curve of **SQNU-55**.

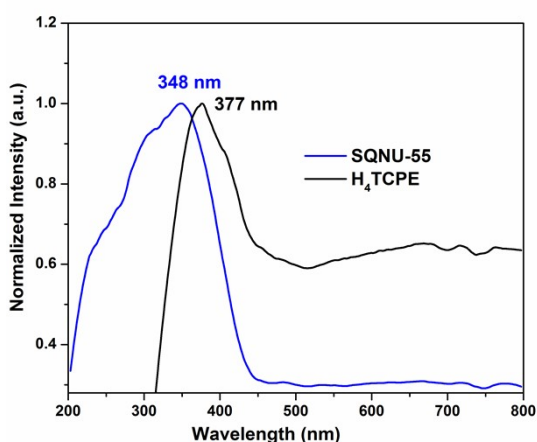


Fig. S4 The solid-state UV-Vis absorption spectra of **SQNU-55** and ligand H_4TCPE at room temperature.

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