

Electronic Supplementary Information (SI) for

**An unusual F-bridged dual-trinuclear Mg–organic framework as
luminescent thermometer for highly efficient low-temperature
detection**

Jian-Wei Zhang, Xi Li, Rui-Ying Yu, Jin-Ping Zhang, Ya Chen* and Jie-Qiong Li*

School of Chemistry and Chemical Engineering, Shangqiu Normal University,
Shangqiu, Henan, 476000, P. R. China.

***Corresponding Authors:**

E-mail: chenya@sqnu.edu.cn (Y. Chen); lijqchem@foxmail.com (J.-Q. Li)

1. Experimental section

1.1 Materials and Methods.

All chemicals used in the syntheses were purchased from commercial sources and were used as received. TGA-DTG curves were performed on a NETZSCH STA 449F5 thermal analyzer in the range of 30-800 °C under nitrogen atmosphere. Powder X-ray diffraction (PXRD) pattern was collected by a Rigaku MiniFlex600 diffractometer with Cu K α ($\lambda = 1.54056 \text{ \AA}$). X-ray photoelectron spectroscopy (XPS) analysis measurement was collected on a Thermo-Scientific ESCALAB Xi+ X-ray photoelectron spectrometer using Al K α source. Elemental analyses of C, H and N were determined with an UNICUBE elemental analyzer. Elemental analyses of samples were performed by using Thermo Fisher Verios G4 equipped and its energy dispersive spectroscopy (EDS) detector. The cooling and heating cycles were recorded an Edinburgh FLS980 fluorescence spectrophotometer. The room luminescent measurements were recorded a Hitachi F-7100 fluorescence spectrophotometer. The temperature-dependent luminescent measurements were recorded a Horiba FluoroMax+ spectrofluorometer.

1.2 Single Crystal X-ray Crystallographic Determination.

The crystal data was recorded at 152.99 (10) K on a Rigaku XtaLAB mini II equipped with graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) for **SQNU-22**. The structure was solved using direct methods and subjected to full-matrix least-squares refinement using the SHELXL-2018/1 crystallographic software package.^{S1,S2} All non-hydrogen atoms were assigned anisotropic displacement parameters and the hydrogen atoms were placed in ideal positions. The highly disordered solvent molecules in the framework were treated using the SQUEEZE program.^{S3} Crystal data of **SQNU-22** was given in Table S1. CCDC number is 2119330 for **SQNU-22**. 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-22 ([Mg₅(μ_3 -F)₂(BDC)₄(DMA)₄] \cdot 2(DMA) \cdot 2(DMPU)]).

Large single crystal preparation: H₂BDC (83.0 mg, 0.5 mmol), and MgCl₂ \cdot 6H₂O (80.0 mg, 0.4 mmol) were mixed in DMA (N,N-dimethylacetamide)/DMPU (1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone) (6.0 mL, 4:2 v/v) in a sealed vial (20 mL). After addition of 28 μ L HFP (1,1,1,5,5,5-hexafluoro-2,4-pentanedione), the vial was

tightly sealed and processed a brief ultrasonication. The mixture was placed in 130 °C oven. After 72 h, the shuttle-like crystals suitable for X-ray diffraction analysis were obtained.

Bulk material preparation: the procedure is similar to that of large single crystal preparation, except that H₂BDC (20.0 mg, 0.12 mmol) and MgCl₂·6H₂O (40.0 mg, 0.2 mmol) were added. The crystals were obtained by filtering and washing several times with fresh DMA, and then dried at room temperature (80.0% yield based on the ligand). The phase purity of sample was checked by powder X-ray diffraction. Anal. Calcd for C₆₈H₉₄F₂Mg₅N₁₀O₂₄: C, 51.15; H, 5.89; N, 8.77%. Found: C, 44.1; H, 4.5; N, 5.0 %.

2. DFT calculations

2.1 Computational Setup

All density functional theory calculations in this work were performed using the Gaussian 09 program suite.⁵⁴ The equilibrium geometries were optimized at the Becke's three-parameter hybrid exchange functional combined with the Lee-Yang-Parr correlation functional (B3LYP)^{55,56} with 6-31+G(*d*) basis set^{57,58} for the non-metal atoms and LANL2DZ of Hay and Wadt [a,b] for Mg atoms. A relativistic effective core potential (ECP) was employed to represent the core electrons of Mg atoms. The vibrational frequencies were calculated at the same level to identify the stationary points with zero. The absorption spectra were simulated by TD-B3LYP calculations^{59,60} with the same basis set. The lowest fifty singlet-singlet excitations were calculated respectively to gain insight into the nature of the absorption.

Table S1. Crystal data and structure refinements of **SQNU-22**.

Formula	C ₆₈ H ₉₄ F ₂ Mg ₅ N ₁₀ O ₂₄
Formula weight	1595.08
Temperature (K)	152.99 (10)
Crystal system	Orthorhombic
Space group	<i>Cmca</i>
<i>a</i> (Å)	16.7917(8)
<i>b</i> (Å)	15.9499(8)
<i>c</i> (Å)	24.5755(13)
α (deg)	90.00
β (deg)	90.00
γ (deg)	90.00
Volume(Å ³)	6582.0(6)
Z	4
$d_{\text{calcd.}}$ (g·cm ⁻³)	1.610
μ (mm ⁻¹)	0.167
<i>F</i> (000)	3368
Reflections collected/unique	14591/3127
<i>R</i> _{int}	0.0881
Data/restraints/parameters	3127/139/234
GOF on <i>F</i> ²	1.053
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b [<i>I</i> > 2σ(<i>I</i>)]	0.0522, 0.1372
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b (all data)	0.0725, 0.1471

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

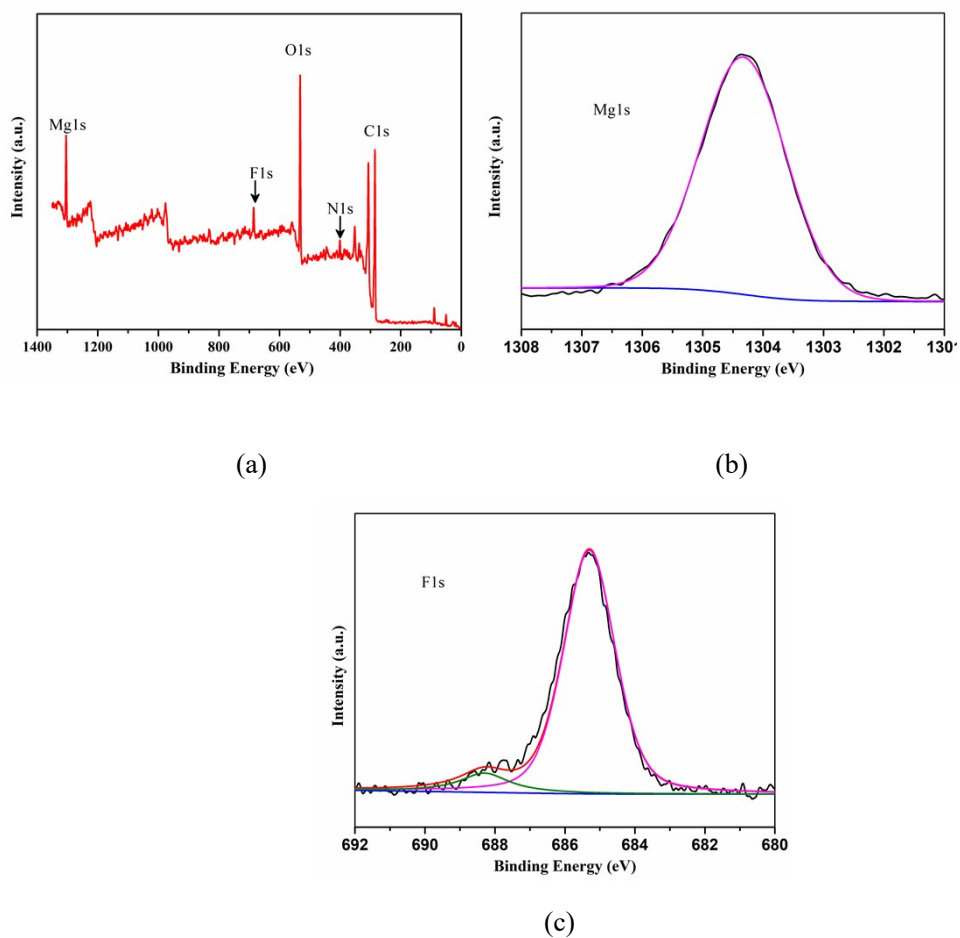


Fig. S1 XPS pattern of **SQNU-22**: (a) survey; (b) Mg1s and (c) F1s.

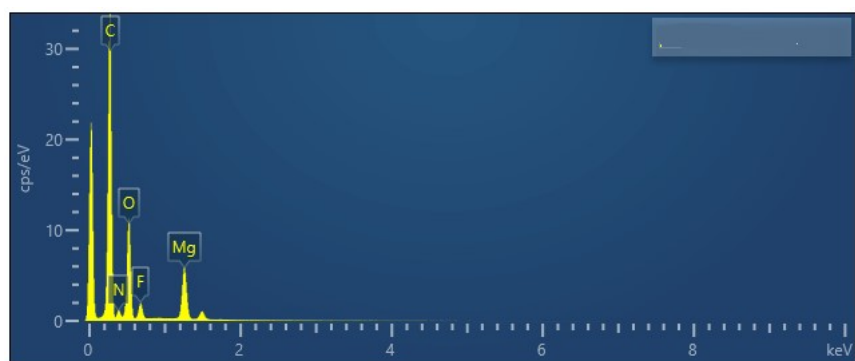


Fig. S2 Energy dispersive spectroscopy (EDS) of **SQNU-22**.

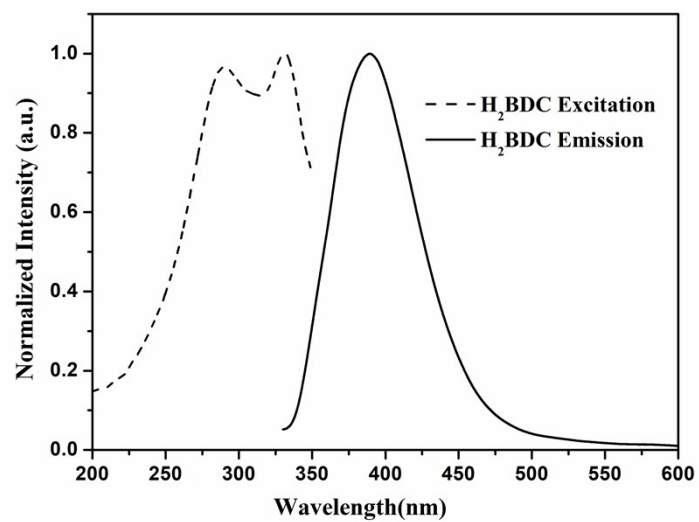


Fig. S3 Excitation and emission spectra of the free H₂BDC ligand.

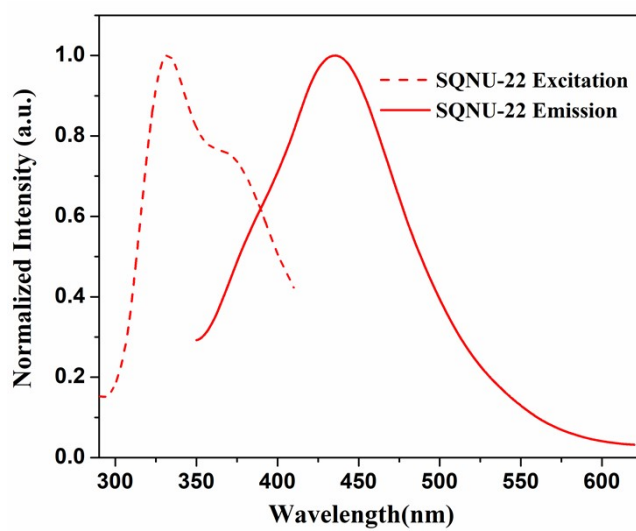


Fig. S4 Excitation and emission spectra of SQNU-22.

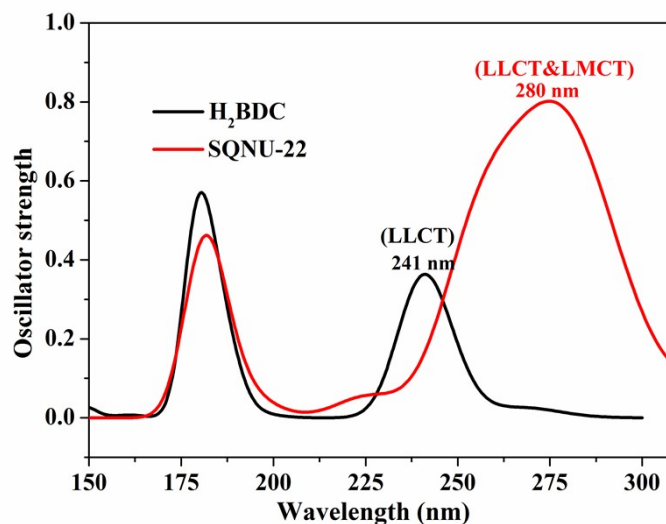


Fig. S5 Simulated the UV-vis absorption spectra of H_2BDC and $SQNU-22$.

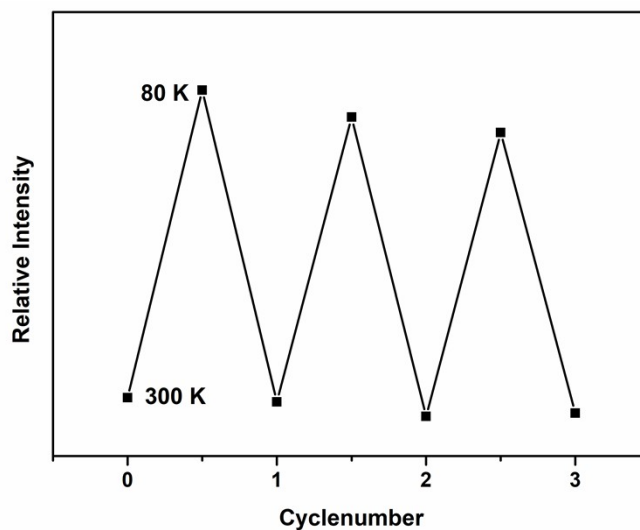


Fig. S6 The cooling and heating cycles of $SQNU-22$.

References

- S1 M. C. Burla, R. Caliendo, M. Camalli, B. Carrozzini, G. L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, D. Siliqi and R. Spagna, *J. Appl. Cryst.*, 2007, **40**, 609–613.
- S2 O. V. Dolomanov, L. J. Bourhis, R. J., Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339–341.
- S3 A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7–13.
- S4 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y.

Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, Revision A.02, Gaussian, Inc., Wallingford CT, 2009.

- S5 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648–5652.
- S6 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785–789.
- S7 W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257–2261.
- S8 M. J. Frisch, J. A. Pople and J. S. Binkley, *J. Chem. Phys.*, 1984, **80**, 3265–3269.
- S9 T. Helgaker and P. Jørgensen, *J. Chem. Phys.*, 1991, **95**, 2595–2601.
- S10 K. L. Bak, P. Jørgensen, T. Helgaker, K. Ruud and H. J. A. Jensen, *J. Chem. Phys.*, 1993, **98**, 8873–8887.