

Hydrothermal Synthesis, Structure and Fluorescence of a New Triazole-bridging Zinc(II) 2D Layered Framework

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Metal-organic frameworks (MOFs) are of considerable interest due to their potential applications in the areas of ion-exchange, sorption, catalysis and nonlinear optics. Their diversified structural features greatly rely on the selection of the metal centers, organic building blocks, and the reaction pathways.¹ The selection of organic building blocks exhibiting various connection fashions is the most effective strategy to assemble MOFs.² Complexes containing heterocyclic π -conjugated 1,2,4-triazole moiety are one of the most extensively explored systems, whose researches lead to some molecular functional materials, such as magnetic materials,³ photochemically driven molecular devices,⁴ information storage,⁵ molecular recognition media,⁶ and supramolecular devices.⁷ 1,2,4-Triazole ring being a 6-electron π -excessive system, its emission region locates near blue light, implying that 1,2,4-triazole derivatives can act as a carrier to investigate the possibility in the design strategies for the heterocycle-based organic blue emission molecular materials.⁸

3-Amino-1H-1,2,4-triazole (Htr) is chosen as the organic building blocks in the presented work, which is a two-connecting neutral ligand or three-connecting (deprotonated) anionic ligand in the construction of MOFs. Its coordination chemistry is helpful in the studies of the "simple high-symmetry" structures and new topological networks.⁹ Though Htr can be purchased from commercial sources or synthesized in laboratories, the examples of the complexes containing Htr is not rich as expected.^{6a,10} Therefore, our interest is in the investigation of fabricating metal-organic frameworks with desired optical properties. Herein, a 2D layered compound, $[\text{Zn}_2(\text{tr})_2(\text{OAc})_2]_n$ (**1**), was yielded from the hydrothermal reaction of Htr with $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, whose structure and fluorescence were characterized.

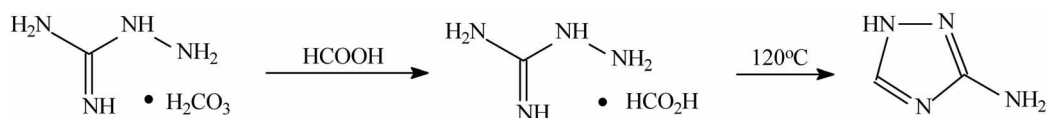
Experimental Section

Materials and Physical Measurements. The reagents and solvents were used directly as supplied commercially without further purification except Htr synthesized as

standard literature procedure (Scheme 1, m.p. = 158-159 °C).¹¹ The IR spectrum was recorded on a Nicolet Magna 750 FT-IR spectrometer with KBr pellet in the range 4000-400 cm^{-1} . Elemental analysis of C, H and N was carried out on a Vario EL III elemental analyzer. The solid-state fluorescent excitation and emission spectra were performed on a FluoroMax-3 spectrophotometer at room temperature with excitation and emission slits at 5.0 nm, increment 1.0 nm and integration time 0.1 s.

Synthesis of $[\text{Zn}_2(\text{tr})_2(\text{OAc})_2]_n$ (1**).** $\text{Zn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.1 mmol, 22.0 mg) and Htr (0.2 mmol, 17.0 mg) were mixed with 10 mL H_2O in a 25 mL Teflon-lined stainless-steel autoclave. The mixture was heated at 170 °C for 3 days in a furnace and then naturally cooled to obtain block colorless crystals. Yield based on Zn: 7.8 mg, 37.6%. Elemental analysis found (calcd) for $\text{C}_8\text{H}_{12}\text{N}_8\text{O}_4\text{Zn}_2$: C, 23.23 (23.15); H, 2.85 (2.91); N, 27.11 (27.00). IR data (in KBr, cm^{-1}): 3391 (m), 3337 (m), 2362 (m), 1622 (s), 1598 (s), 1551 (s), 1525 (m), 1393 (m), 1321 (m), 1224 (m), 1074 (m), 1020 (w), 942 (w), 779 (w), 683 (m), 484 (m).

X-ray Crystallography. Data collection for the compound was performed on Rigaku Mercury CCD diffractometer equipped with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). Intensity data were collected by the narrow frame method at 293 K and corrected for Lorentz and polarization effects as well as for absorption by the ω scan technique and reduced using CrystalClear program.¹² The structure was resolved by direct method using SHELXTLTM package of crystallographic software and refined by full-matrix least-squares technique on F^2 .¹³ All nonhydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms attached to C atoms were located at geometrically calculated positions and refined with isotropic thermal parameters included in the final stage of the refinement on calculated positions bonded to their carrier atoms. Crystallographic data, and the selected bond distances and angles for compound **1** are respectively listed in Table 1 and 2.



Scheme 1. The synthetic route of 3-amino-1H-1,2,4-triazole.

Table 1. Crystallographic and Refinement Data

| | |
|--|--|
| Empirical formula | C ₈ H ₁₂ N ₈ O ₄ Zn ₂ |
| Color and Habit | colorless block |
| Crystal Size (mm) | 0.3 × 0.2 × 0.1 |
| Crystal system | Orthorhombic |
| Space group | <i>Pna</i> 2 ₁ |
| <i>a</i> (Å) | 9.822(3) |
| <i>b</i> (Å) | 15.69(3) |
| <i>c</i> (Å) | 9.501(3) |
| <i>V</i> (Å ³) | 1464(3) |
| <i>Z</i> | 4 |
| <i>F</i> _w | 415.00 |
| <i>D</i> _{calc} (Mgm ⁻³) | 1.883 |
| <i>μ</i> (mm ⁻¹) | 3.308 |
| <i>F</i> (000) | 832 |
| <i>θ</i> (°) | 3.25 to 25.49 |
| Reflections measured | 8950 |
| Independent reflections | 2641 (<i>R</i> _{int} = 0.0351) |
| Observed Reflection [<i>I</i> > 2σ(<i>I</i>)] | 2373 |
| Final <i>wR</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)] | 0.0320, 0.0846 |
| <i>R</i> ₁ , <i>wR</i> ₂ indices (all) | 0.0366, 0.0882 |
| <i>S</i> | 1.031 |
| (Δ/ <i>σ</i>) _{max/min} | 0.172/0.025 |
| (Δρ) _{max/min} (eÅ ⁻³) | 0.761, -0.393 |

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

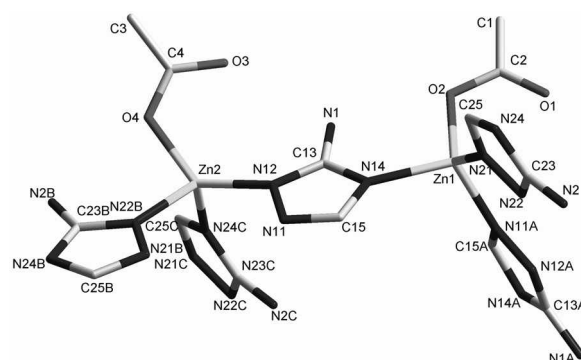
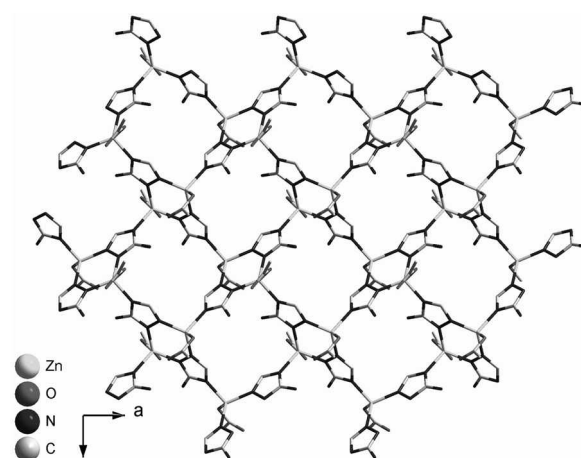
Table 2. Selected Bond Distances (Å) and Angles (°)

| | |
|---------------------------|----------------------------|
| Zn1-O2 = 1.924(4) | Zn2-O4 = 1.941(3) |
| Zn1-N21 = 1.981(2) | Zn2-N12 = 1.979(2) |
| Zn1-N11A = 2.016(3) | Zn2-N24B = 1.995(2) |
| Zn1-N14 = 2.045(2) | Zn2-N22C = 2.009(3) |
| O2-Zn1-N21 = 121.36(10) | O4-Zn2-N12 = 130.09(11) |
| O2-Zn1-N11A = 110.88(13) | O4-Zn2-N24B = 104.07(11) |
| N21-Zn1-N11A = 109.18(10) | N12-Zn2-N24B = 107.04(10) |
| O2-Zn1-N14 = 100.25(10) | O4-Zn2-N22C = 96.44(13) |
| N21-Zn1-N14 = 105.75(10) | N12-Zn2-N22C = 109.83(10) |
| N11A-Zn1-N14 = 108.27(10) | N24B-Zn2-N22C = 107.53(11) |

Symmetry codes: *A* = -*x*+2, -*y*, *z*+1/2; *B* = *x*+1, *y*, *z*; *C* = -*x*+2, -*y*, *z*-1/2.

Results and Discussion

Description of Crystal Structure. The crystallographic analysis reveals that [Zn₂(trr)₂(OAc)₂]_n (**1**) crystallizes in the orthorhombic non-central group *Pna*2₁. The asymmetrical unit of **1** includes two independent zinc(II) atom, two deprotonated trr⁻ and two OAc⁻. The two positive charges on each Zn²⁺ centre are balanced by one OAc⁻ and one trr⁻. Each zinc(II) center locates in a slight distorted tetrahedron geometry with three nitrogen atoms from three separate trr⁻ ligands lying on their basal sites with Zn-N distances ranging from 1.979(2) to 2.045(2) Å, and the apical position occupied by a oxygen atom from a OAc⁻ anion (Figure 1). Slight difference between Zn1 and Zn2 is that Zn1 comprises of two triazole rings of N11 and one of N21; while for Zn2, one of N11 and two of N21. The trr⁻ ligands both adopt

**Figure 1.** The coordination sphere of zinc atoms with atom labels. Hydrogen atoms are omitted for clarity.**Figure 2.** The 2D layered framework in **1**.

$\mu_3-1\kappa N: 2\kappa N: 4\kappa N$ coordination mode to coordinate with three Zn²⁺ centers to form two sorts of 6- and 16-membered rings. With their 1- and 2-positioned nitrogen atoms, two trr⁻ ligands connect Zn1 and Zn2 centers into a 6-membered hexagonal ring [Zn₂N₄]. The neighboring hexagonal rings [Zn₂N₄] are further linked through the residual 4-positioned N atoms of triazole moieties to form a non-planar 16-membered ring. Subsequently, the fuse of the two sorts of edge-sharing rings produces a 2D layer along the *ac* plane (Figure 2). There exists a hydrogen bonding (N2-H...O4 = 2.941(4) Å, 134.7°) in the inner of the 2D layer. A T...π stacking interaction is shaped between C3 and the centroid of the triazole ring (N11) with the minimum distance of 3.397 Å. Through the C3-H...π stacking interaction, the neighboring 2D layers are further connected into a 3D supramolecular architecture stacking as -ABAB- fashion (Figure 3).

Compared to our previous work [Zn(trr)Cl]_n,^{10c} some hints can be found. There are many differences between [Zn(trr)Cl]_n and **1**, such as the compositions of the asymmetrical unit, the space group (orthorhombic non-central *Pna*2₁ in **1** and orthorhombic *Pbca* in [Zn(trr)Cl]_n), and the reaction conditions (hydrothermal reaction at 170 °C for **1** and mild diffusion method at room temperature for [Zn(trr)Cl]_n). However, because of the same $\mu_3-1\kappa N: 2\kappa N: 4\kappa N$ coordination mode of trr⁻, the two skeleton frameworks are both

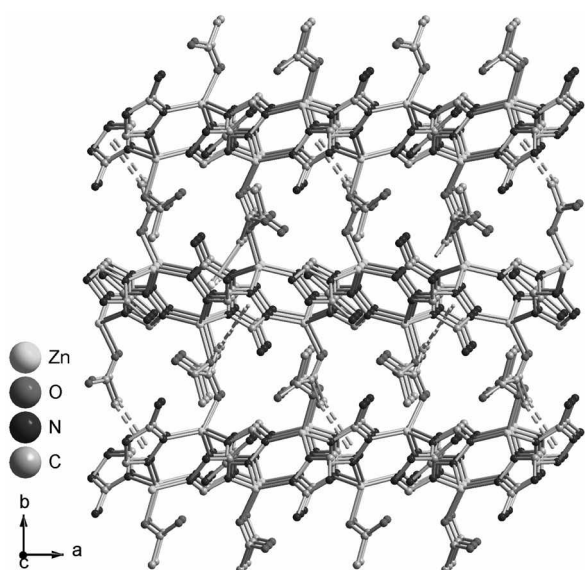


Figure 3. The 3D supramolecular architecture constructed from the linkage of C3-H... π stacking interaction with the 2D layers.

2D layers comprising of very similar 6- and 16-membered rings. When tr^- adopts another common mode of μ_2 -1 κ N:4 κ N in $[\text{Mn}(\text{Htrr})_2(\text{OAc})_2]_n \cdot n\text{H}_2\text{O}$, it tends to form a 2D layer containing single 16-membered rings.¹⁴ It indicates the coordination mode of tr^- plays a more significant role in the structural constructions than other factors.

For their potential applications in heterocycle-based organic blue emission molecular materials, 1,2,4-triazoles have been used as basic materials to search possible luminescent materials. In this work, the solid-state electronic emission spectrum of **1** shows blue fluorescence at around 443 nm by excited the solid sample at 344 nm recorded at room temperature (Figure 4). Compared to the free ligand Htrr (emission at 427 nm with $\lambda_{\text{em}} = 350$ nm), the blue emission peak with small blue-shift of 16 nm can be assigned to $\pi \cdots \pi^*$ intra-ligand transition of tr^- , which is different from that in $[\text{Zn}(\text{trr})\text{Cl}]_n$ (416 nm with $\lambda_{\text{em}} = 350$ nm) and $[\text{Mn}(\text{Htrr})_2(\text{OAc})_2]_n \cdot n\text{H}_2\text{O}$ (419 nm with $\lambda_{\text{ex}} = 360$ nm). The

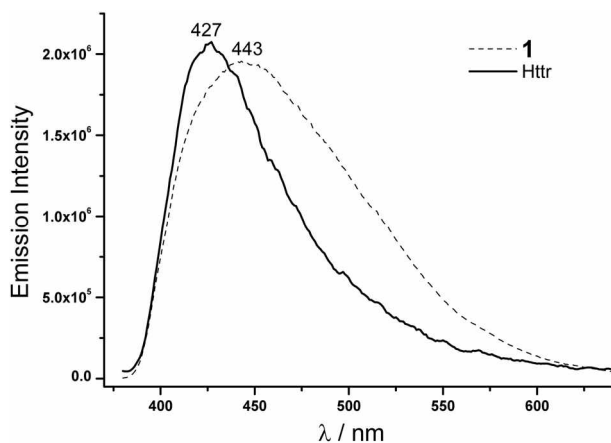


Figure 4. The solid-state electronic emission spectra of compound **1** ($\lambda_{\text{ex}} = 344$ nm) and the free ligand Htrr ($\lambda_{\text{ex}} = 360$ nm) recorded at room temperature.

comparison exhibits the coordination of metal centers have a subtle effect on the emission bands. Due to the emission peak of **1** locating in the region of blue ray (435–480 nm), it may be regarded as a potential candidate for organic blue emission materials. Otherwise, it leaves space to improve through adjusting the metal centers to tune emission bands for the further systematic experiments.

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Supporting Information. Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC-698908). The data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

References

- (a) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *101*, 1629. (b) Matsuda, R.; Kitaura, R.; Kitagawa, S.; Kubota, Y.; Belosludov, R. V.; Kobayashi, T. C.; Sakamoto, H.; Chiba, T.; Takata, M.; Kawazoe, Y.; Mita, Y. *Nature* **2005**, *436*, 238. (c) Sun, W. W.; Cheng, A. L.; Jia, Q. X.; Gao, E. Q. *Inorg. Chem.* **2007**, *46*, 5471.
- (a) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853. (b) Melanie, A. P.; Darren, W. J. *Chem. Soc. Rev.* **2007**, *36*, 1441.
- (a) Gültlich, P.; Hauser, A.; Spierring, H. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2024. (b) Kahn, O.; Kröber, J.; Jay, C. *Adv. Inorg. Chem.* **1992**, *4*, 718.
- (a) Browne, W. R.; O'Connor, C. M.; Hughes, H. P.; Hage, R.; Walter, O.; Doering, M.; Gallagher, J. F.; Vos, J. G. *J. Chem. Soc., Dalton Trans.* **2002**, 4048. (b) Potts, K. T. *Chem. Rev.* **1961**, *61*, 87.
- (a) Chun, H.; Dybtsev, D. N.; Kim, H.; Kim, K. *Chem. Eur. J.* **2005**, *11*, 3521. (b) Fletcher, A. J.; Thomas, K. M.; Rosseinsky, M. J. *J. Solid State Chem.* **2005**, *178*, 2491. (c) Rowsell, J. L. C.; Yaghi, O. M. *J. Am. Chem. Soc.* **2006**, *128*, 1304.
- (a) Zhai, Q. G.; Wu, X. Y.; Chen, S. M.; Zhao, Z. G.; Lu, C. Z. *Inorg. Chem.* **2007**, *46*, 5046. (b) Bradshaw, D.; Claridge, J. B.; Cussen, E. J.; Prior, T. J.; Rosseinsky, M. J. *Acc. Chem. Res.* **2005**, *38*, 273.
- (a) Huang, X. H.; Sheng, T. L.; Xiang, S. C.; Fu, R. B.; Hu, S. M.; Li, Y. M.; Wu, X. T. *Inorg. Chem.* **2007**, *46*, 497. (b) Xiang, S. C.; Wu, X. T.; Zhang, J. J.; Fu, R. B.; Hu, S. M.; Zhang, X. D. *J. Am. Chem. Soc.* **2005**, *127*, 16352. (c) Evans, O. R.; Lin, W. *Acc. Chem. Res.* **2002**, *35*, 511. (d) Wu, C. D.; Hu, A.; Zhang, L.; Lin, W. *J. Am. Chem. Soc.* **2005**, *127*, 8940.
- (a) Abbotto, A.; Beverina, L.; Bozio, R.; Facchetti, A.; Ferrante, C.; Pagani, G. A.; Pedron, D.; Signorini, R. *Org. Lett.* **2002**, *4*, 1495. (b) Kido, J.; Ohtaki, C.; Hongawa, K.; Okuyama, K.; Nagai, K. *Jpn. J. Appl. Phys.* **1993**, *32*, L917.
- Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. *Nature* **2003**, *423*, 705.
- (a) Su, C. Y.; Goforth, A. M.; Smith, M. D.; Pellechia, P. J.; zur Loye, H. C. *J. Am. Chem. Soc.* **2004**, *126*, 3576. (b) Zhang, J. P.; Lin, Y. Y.; Zhang, W. X.; Chen, X. M. *J. Am. Chem. Soc.* **2005**, *127*, 14162. (c) Liu, B.; Zhou, Z. Q.; Zhang, X. C.; Zhang, X. Y. *Inorg. Chem. Commun.* **2007**, *10*, 1095. (d) Li, W.; Jia, H. P.; Ju,

- Z. F.; Zhang, J. *Cryst. Growth Des.* **2006**, *6*, 2136. (e) Park, H.; Krigsfeld, G.; Teat, S. J.; Parise, J. B. *Cryst. Growth Des.* **2007**, *7*, 1343. (f) Sanchez, C.; Salas, J. M.; Quiros, M.; Sanchez, M. P. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2004**, *60*, m370. (g) Zhai, Q. G.; Wu, X. Y.; Chen, S. M.; Lu, C. Z.; Yang, W. B. *Cryst. Growth Des.* **2006**, *6*, 2126.
11. Horning, E. C.; *Organic Syntheses*, CV3; John Wiley & Sons: New York, 1955; p 95.
 12. Rigaku, *CrystalClear 1.3.6*, Software User's Guide for the Rigaku R-Axis, Mercury and Jupiter CCD Automated X-ray Imaging System; Rigaku Molecular Structure Corporation: Utah, USA, 2002.
 13. Siemens *SHELXTLTM Version 5 Reference Manual*; Siemens Energy & Automation Inc.: Madison, Wisconsin, USA, 1994.
 14. Liu, B.; Chen, Y. H.; Zhang, X. C. *Inorg. Chem. Commun.* **2008**, *11*, 965.
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