*КРАТКИЕ СООБЩЕНИЯ*

# A 2D BITRIAZOLE-BRIDGING COPPER(II) POLYMER: HYDRO THERMAL SYNTHESIS, CRYSTAL STRUCTURE, AND FLUORESCENCE

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A new 2D metal-organic coordination polymer $[Cu(trtr)_2]_n$ (**1**) (Htrtr = 3-(1,2,4-triazolyl-4-yl)-1H-1,2,4-triazole) is synthesized through the hydrothermal reaction of $Cu(ClO_4)_2$ with Htrtr. The crystal structure of **1** is determined by a direct method from X-ray diffraction data (Rigaku Mercury CCD, Mo$K_\alpha$ radiation). **1** crystallizes in the monoclinic $C2/c$ space group with unit cell parameters: $a = 14.158(2)$ Å, $b = 9.8050(14)$ Å, $c = 11.413(3)$ Å, $\beta = 127.9870(10)°$, $V = 1248.7(4)$ Å$^3$, $Z = 4$, $D_{cal} = 1.775$ g/cm$^3$. **1** features a 2D grid based on the propagation of 28-membered rings, which is further fabricated into a 3D supramolecular framework via the hydrogen bond linkage. The fluorescence of **1** shows a blue emission at 441 nm with a 14 nm red-shift compared to that of free Htrtr, which can be assigned to LMCT.

**K e y w o r d s:** copper(II), crystal structure, fluorescence, 1,2,4-triazole.

Recent decades have witnessed many progresses in the design and synthesis of coordination polymers or metal-organic frameworks (MOFs) due to their potential applications in functional materials [1, 2] as well as intriguing structural architectures and topologies [3—7]. The efforts devoted to MOFs promote the understanding of the structure-property relationship and controlling factors. It consequently attributes to the purposeful design and the controlled synthesis of materials with pre-designed functionalities [8—10]. Though numerous factors affect the final assemblies and functionalities, the most fundamental strategy of MOFs focuses on the selection of metal centers and organic builders [11—13]. 1,2,4-Triazole and its derivatives have been widely utilized as precursors to design MOFs with applications in medicine, biology, and industry. The family of 1,2,4-triazoles, a six π-electron rich system, usually adopts three basic bridging modes ($\mu_2$-$\kappa N^1$:$\kappa N^2$, $\mu_2$-$\kappa N^2$:$\kappa N^4$, and $\mu_3$-$\kappa N^1$:$\kappa N^2$:$\kappa N^4$) to bind metal centers, and thus to fabricate polynuclear complexes and coordination polymers [14—17]. Furthermore, the introduction of π-excessive heterocycles into the structures is one of the important design strategies for heterocycle-based organic fluorescent blue materials [18]. Therefore, we pre-designed an asymmetrical bridging bitriazole ligand 3-(1,2,4-triazolyl-4-yl)-1H-1,2,4-triazole (Htrtr) to construct luminescent MOFs. Herein, the π-excessive asymmetrical bridging Htrtr ligand was prepared and employed in the hydrothermal reaction with $Cu(ClO_4)_2 \cdot 6H_2O$ to produce a new 2D MOF $[Cu(trtr)_2]_n$ (**1**) with its crystal structure and fluorescent property determined.

**Experimental. Materials and physical measurements.** The reagents and solvents were used directly as supplied commercially without further purification, except Htrtr and $Cu(ClO_4)_2 \cdot 6H_2O$. Blue
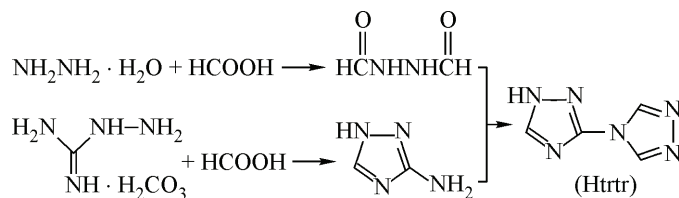
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crystals of $Cu(ClO_4)_2 \cdot 6H_2O$ were crystallized by freezing the concentrated resulting solution of $HClO_4$ reacting with superfluous $Cu_2(OH)_2CO_3$ (**Caution**: great care should be taken in handling $Cu(ClO_4)_2$ in solution or in the dry state since explosions may occur if it contacts with organic or other readily oxidizable substances). The IR spectra were recorded on a Nicolet Magna 750 FT—IR spectrometer with KBr pellets in the range 4000~400 $cm^{-1}$. The 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 measured 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 Htrtr.** Htrtr was prepared by reacting diformylhydrazine (6 mmol, 528 mg) and 3-amino-1H-1,2,4-triazole (6 mmol, 511 mg) in a Teflon-lined stainless steel autoclave in a furnace at 170 °C for 3 days, and then cooled to room temperature. The white crystalline product was isolated and washed with water and ethanol. Yield based on 3-amino-1H-1,2,4-triazole: 656 mg, 80.3 %. The Htrtr ligand partially dissolves in strong polar solvents. Elemental analysis (%) for $C_4H_4N_6$, found (calcd): C, 35.21 (35.30); H, 3.12(2.96); N, 61.83(61.74). IR ($cm^{-1}$, KBr): 3411(s), 1634(s), 1446(w), 1382(w), 1362(w), 1274(w), 1089(s), 1050(s), 881(s), 801(m), 665(w), 437(w).

**Synthesis of $[Cu(trtr)_2]_n$.** $Cu(ClO_4)_2 \cdot 6H_2O$ (0.1 mmol, 37.0 mg) and Htrtr (0.2 mmol, 27.2 mg) were mixed with 10 ml of $H_2O$ in a 25-ml Teflon-lined stainless-steel autoclave. The mixture was heated at 180°C for 3 days in a furnace and then cooled with a step of 10°C/d to room temperature, thus to obtain blue block crystals of **1**. Yield based on Htrtr: 7.1 mg, 21.4 %. Elemental analysis found (calcd): C, 28.98(28.79); H, 1.65(1.81); N, 50.19(50.36). IR data (in KBr, $cm^{-1}$): 3151(br, m), 3119(m), 2361(m), 1654(s), 1557(m), 1498(w), 1436(w), 1373(s), 1307(w), 1288(w), 1251(w), 1212(w), 1154(w), 1120(m), 1066(w), 1035(w), 975(w), 884(w), 734(w), 669(w), 491(w).

**Structural determination and refinement.** Data collection for compound **1** was performed on a Rigaku Mercury CCD diffractometer with graphite monochromated Mo$K_\alpha$ radiation ($\lambda = 0.71073$ Å). The intensity data were collected at 20 °C and corrected for Lorentz and polarization effects as well as for absorption by the ω scan technique and reduced using the CrystalClear program [19]. The structure was solved by the direct method using the SHELXTL$^{TM}$ package and refined by the full-matrix least-squares technique on $F^2$ [20]. All non-hydrogen 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 the calculated positions bonded to their carrier atoms. Crystallographic data and the selected bond distances and angles for compound **1** are respectively listed in Tables 1 and 2. The CIF file containing complete information on the studied structure was deposited with CCDC, deposition number 678168, and is freely available upon request from the following web site: www.ccdc.cam.ac.uk/data_request/cif.

**Results and discussion.  Synthesis.** Htrtr was prepared through three condensation reactions (Scheme 1), including the syntheses of diformylhydrazine [21] (m.p. = 155—157 °C, yield: 84.0 %),



Scheme 1. Synthetic route of 3-(1,2,4-triazolyl-4-yl)-1H-1,2,4-triazole (Htrtr)

3-amino-1H-1,2,4-triazole (m.p. = 158—159 °C, yield: 92.0 %) [22], and Htrtr (m.p. = 324—325 °C) [23, 24]. Htrtr comprises of two asymmetric rigid triazole rings: one coming from 3-amino-1H-1,2,4-triazole and the newborn one taking the place of —$NH_2$. Because of Htrtr possessing five donor sites, it is reasonably expected to easily assemble a variety of multidimensional frameworks. However, our continuous studies seem not to agree with this. Also, the survey based on the Cambridge Structural

*Crystallographic characteristics, details of the experiment and structure refinement for compound* **1**

| | |
|---|---|
| Empirical formula | $C_8H_6CuN_{12}$ |
| Molecular weight | 333.79 |
| Crystal system | Monoclinic |
| $a, b, c$, Å; β, deg. | 14.158(2), 9.8050(14), 11.413(3);  127.9870(10) |
| $V$, Å$^3$ | 1248.7(4) |
| $Z$; $Dc$, mgm$^{-3}$ | 4; 1.775 |
| μ, mm$^{-1}$ | 1.765 |
| Crystal dimensions, mm | 0.490×0.276×0.213 |
| θ scanning range, deg. | 2.77—28.25 |
| Number of meas. / indep. reflections | 4577 / 1523 |
| $R$(int) | 0.0175 |
| Number of reflections with $I > 2\sigma(I)$ | 1432 |
| Number of refined parameters | 96 |
| GOOF on $F^2$ | 0.965 |
| $R$ factor, $I > 2\sigma(I)$ | |
| $R_1$; $wR_2$ | 0.0206; 0.0514 |
| $R$ factor (over all $I_{hkl}$) | |
| $R_1$; $wR_2$ | 0. 24; 0.052602 |
| Residual electron density (max / min), e/Å$^3$ | 0.178 / –0.320 |

Database gave a few examples: three extended frameworks [25—27] and four mononuclear compounds [28—31]. The rarity of Htrtr-containing compounds is most likely to be caused by that it almost immediately produces insoluble precipitates. However, a hydro/solvothermal method can effectively overcome the solubility problem. The reaction and cooling times play an important role in obtaining crystals.

**Description of crystal structure.** Compound **1** crystallizes in a monoclinic *C*2/*c* space group, which features a 2D layered structure. The asymmetric unit of **1** comprises of a half- occupancy Cu(II) atom and a deprotoned trtr⁻ ligand. The one positive charge on the half- occupancy Cu(II) atom is balanced by one trtr⁻ ligand. The coordination geometry of Cu1 is a tetrahedron constructed by N11A, N11B, N21, and N21C (*A* = *x*–1/2, *y*–1/2, *z*; *B* = –*x*+3/2, *y*–1/2, –*z*+1/2; *C* = –*x*+1, *y*, –*z*+1/2) from four separated trtr⁻ entities with Cu—N bond distances of 1.9667(7) and 2.0150(10) Å (Fig. 1). The trtr⁻ ligand acts as a rod-like spacer with μ₂-1κN: 1′κN mode to bind two Cu1 centers. Four trtr⁻ alternately connect four Cu1 centers to form a 28-membered ring, whose fuse further generates a 2D layer along

*Selected bond distances* (Å) *and angles* (deg.) *for compound* **1**

| Bond | $d$ | Angle | ω | Angle | ω |
|---|---|---|---|---|---|
| Cu1—N11A | 1.9667(7) | N11A—Cu1—N11B | 119.49(5) | N21—Cu1—N21C | 112.41(6) |
| Cu1—N21 | 2.0150(10) | N11A—Cu1—N21 | 106.93(4) | C15—N11—Cu1D | 133.92(8) |
| | | N11B—Cu1—N21 | 105.62(4) | N12—N11—Cu1D | 118.54(6) |
| | | N11A—Cu1—N21C | 105.62(4) | C25—N21—Cu1 | 128.83(6) |
| | | N11B—Cu1—N21C | 106.93(4) | N22—N21—Cu1 | 122.23(6) |

Symmetry code: *A* = *x*–1/2, *y*–1/2, *z*;  *B* = –*x*+3/2, *y*–1/2, –*z*+1/2;  *C* = –*x*+1, *y*, –*z*+1/2; *D* = *x*+1/2, *y*+1/2, *z*.
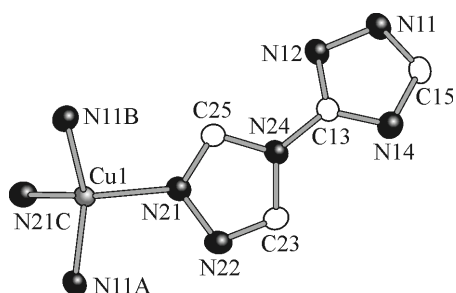
*Fig. 1.* Coordination sphere of Cu1 in compound **1**.
Symmetry code: $A = -x+1, y, -z+1/2$; $B = -x+1/2, y-1/2, -z+1/2$; $C = x+1/2, y-1/2, z$

the *ab* plane (Fig. 2, *a*), and its topological drawing exhibits a simple (4, 4) net with trtr⁻ and Cu(II) respectively as two- and four-connecting nodes (Fig. 2, *b*). The neighboring interlaced 2D layers are further connected by weak C15—H···π (the centroid of the newborn triazole ring) interactions of 3.715 Å into a 3D supramolecular framework (Fig. 3). The dihedral angle between the two triazole rings in **1** twists to 28.92°, much larger than 2.35° in the free Htrtr ligand, exhibiting the twisting configuration of trtr⁻ fits the space requirements of metal, thus to decrease the spatial resistance of trtr⁻.

**Fluorescence.** Compound **1** and free Htrtr show luminescent features in the solid-state fluorescent spectra at room temperature (Fig. 4). Excitation of **1** with $\lambda_{ex} = 370$ nm produces blue fluorescence at 441 nm, implying **1** may have potential application in organic blue fluorescent materials with its emission locating in the blue light region (435—480 nm). Compared to the free Htrtr ligand (emission at 427 nm with $\lambda_{ex} = 360$ nm), the emission of **1** with a 14 nm red-shift can be assigned as a ligand-to-metal charge transfer (LMCT). It is significantly different from that of [Cd(trtr)₂]ₙ (emission
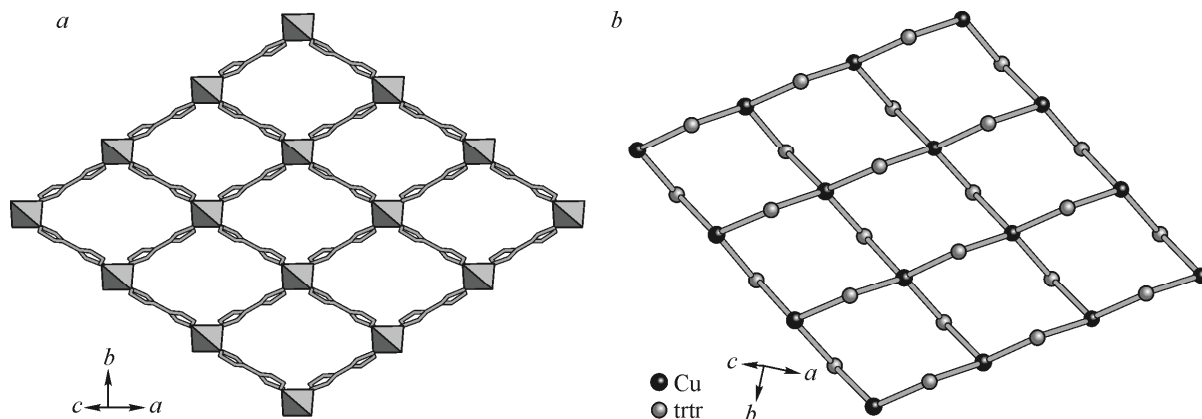


*Fig. 2.* (*a*) 2D layer in **1** constructed from the growth of the 28-membered rings (light tetrahedron: CuN₄); (*b*) The topological (4,4) net of the 2D layer
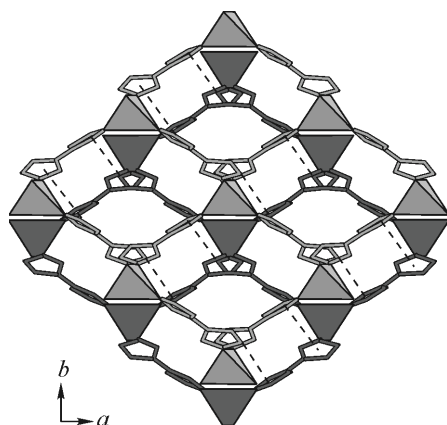


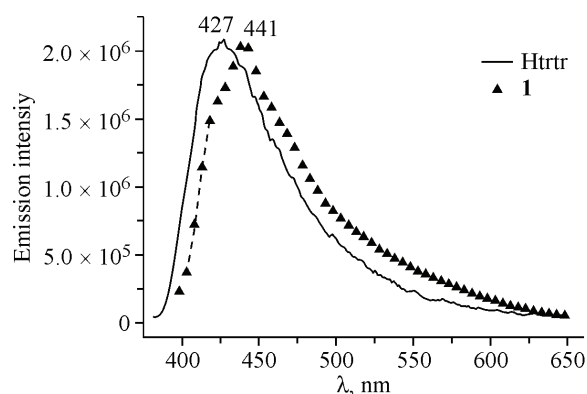*Fig. 3.* 3D supramolecular framework of **1** constructed from 2D layers connected by C15—H···π interactions



*Fig. 4.* Solid-state emission spectra of compound **1** ($\lambda_{ex} = 370$ nm) and the free ligand Htrtr ($\lambda_{ex} = 360$ nm) recorded at room temperature

at 426 nm with $\lambda_{ex} = 350$ nm) [25] and the allomer $[Zn(trtr)_2]_n$ (emission at 424 nm with $\lambda_{ex} = 366$ nm) [ 27 ]. The comparison of **1** and reported $[Cd(trtr)_2]_n$ and $[Zn(trtr)_2]_n$ shows the disturbance of completely filled $d^{10}$ configurations of Cd(II) and Zn(II) to the $\pi$ orbital of triazole rings to be much less than that of the $d^9$ configuration of Cu. Therefore, it proves that metal centers are not only the key factor in fabricating frameworks [ 12, 13 ], but an important source for imparting a particular physical property [ 32—34 ]. Further systemic investigations in the effect of metal centers on the luminescent properties may give more help in searching for blue emission molecular materials.

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