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A novel 3D Cu(I) coordination polymer based on Cu_6Br_2 and $Cu_2(CN)_2$ SBUs: *in situ* ligand formations and naked-eye colorimetric sensor of NB and 2-NT

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A novel coordination polymer formulated as $[Cu_4Br(CN)(mtz)_2]_n$ (Hmtz = 5-methyl tetrazole) (**1**), has been synthesized under solvothermal condition and characterized by elemental analysis, Infrared (IR) spectroscopy, thermal gravimetric analysis, powder X-ray diffraction and single-crystal X-ray diffraction. Interestingly, Cu(I), CN^- and mtz^- in compound **1** are all generated from *in situ* translation of the original precursors: Cu^{2+}, acetonitrile and 1-methyl-5-mercapto-1,2,3,4-tetrazole (Hmnt). The *in situ* ring-to-ring conversion of Hmnt into mtz^- was found for the first time. Structural analysis reveals that compound **1** is a novel 3D tetrazole-based Cu(I) coordination polymer containing both metal halide cluster Cu_6Br_2 and metal pseudohalide cluster $Cu_2(CN)_2$ second building units (SBUs), which shows an unprecedented (3,6,10)-connected topology. Notably, a pseudo-porphyrin structure with 16-membered rings constructed by four mtz^- anions and four copper (I) ions was observed in compound **1**. The fluorescent properties of compound **1** were investigated in the solid state and in various solvent emulsions, which show that compound **1** is a highly sensitive naked-eye colorimetric sensor for NB and 2-NT (NB= nitrobenzene and 2-NT=2-nitrotoluene).

Introduction:

Luminescent coordination complexes have received considerable attention for potential applications in light-emitting, display devices and chemical sensors.[1] As a fascinating subdiscipline of coordination complexes, copper (I) halide or pseudohalide-based coordination complexes have garnered continuous interest and been extensively explored not only for their diverse topologies but also for their potential application as luminescent materials.[2]

Recently, luminescent sensors for detection of high explosives have drawn more attention owing to homeland security and environmental implications.[1f, 3] Nitroaromatics, which are exemplary explosives or explosive-like molecules, are highly electron deficient and often act as good electron acceptors. Luminescent coordination complexes with electron donors have been proved to be excellent candidates for the detection of nitroaromatic explosives, mainly because the exciton migration between coordination complexes and electron deficient compounds results in coordination complex fluorescence quenching with high sensitivity. To our knowledge, the previous study of coordination complex-based fluorescent sensors for nitroaromatics mainly focused on lanthanide (III) complexes such as Eu and Tb as well as d^{10} transition metal complexes, e. g. Zn and Cd.[1f] However, the related study based on coordination complexes of copper (I) halides or pseudohalides has not been reported yet.

Cu(I) coordination complexes were usually prepared by reaction of Cu(I) and appropriate ligands or by the reaction involved in the *in situ* reduction of Cu(II) into Cu(I) in appropriate solvents under hydro(solvo)thermal conditions. Organic sulfur ligands are frequently used to prepare coordination complexes, not only due to their rich coordination donors but also for their potential *in situ* ligand/metal reactions such as the formation and facile cleavage of S-S bonds,[4] the oxidative cleavage of disulfide bond,[5] the ring-opening reaction of heterocycle [6] and desulfurization.[7] Based on above-mentioned points, we tried to synthesize copper (I) halides or pseudohalides using 1-methyl-5-mercapto-1,2,3,4-tetrazole (Hmnt). Fortunately, a novel Cu(I) coordination polymer with Cu_6Br_2 and $Cu_2(CN)_2$ SBUs, $[Cu_4Br(CN)(mtz)_2]_n$ (Hmtz = 5-methyl tetrazole) (**1**), was synthesized through several *in situ* reactions of reduction of Cu(II), ring-to-ring conversion of organic heterocycle and the formation of cyanide. The possible *in situ* reaction mechanism, network structure, and luminescent property of **1** are carefully studied.

Experimental

Materials and physical measurements

All reagents and solvents for syntheses were commercially available and used as received without further purification. Elemental analysis (C, H, and N) was performed on a Perkin-Elmer 240C elemental analyzer. Infrared (IR) spectra were obtained with KBr Pellets on a Perkin Elmer Spectrum One FT-IR spectrometer in the range 400–4000 cm^{-1}. Powder X-ray diffraction (PXRD) patterns of the samples were recorded by a RIGAKU-DMAX2500 X-ray diffractometer with Cu Kα radiation. Thermal gravimetric analysis (TGA) was carried out in an air stream on a Perkin Elmer TGA-7000 thermogravimetric analyser with a heating rate of $10°C\cdot min^{-1}$. Solid photoluminescence (PL) excitation and emission spectra were performed on a Jobin Yvon Fluoro Max-4 spectrophotometer equipped with 150W xenon lamp as the excitation source at room temperature. Fluorescent spectra of **1**–solvent emulsion were obtained on a LS 55 florescence/phosphorescence spectrophotometer at room temperature.

Preparation of $[Cu_4Br(CN)(MTZ)_2]_n$ (1)

A mixture of $Cu(NO_3)_2·6H_2O$ (14.50 mg, 0.5 mmol), Hmnt (11.60 mg, 1.0 mmol) and KBr (12.0 mg, 1.0 mmol) was dissolved in 5mL mixed solvents CH_3CN/H_2O (v : v = 4 : 1), then the blue-black suspension was transferred into a Teflon-lined autoclave and kept under autogenous pressure at 140°C for 3 days. After slow cooling to room temperature, transparent colourless crystals of **1** and a spot of green crystals were obtained. Yield: 45% (based on Cu). Elemental anal. Calcd $C_5H_6BrCu_4N_9$ (526): C, 11.41; H, 1.14; N, 23.96. Found: C, 11.45; H, 1.12; N, 23.89. IR data (KBr, cm^{-1}): 3019(w), 2088(m), 1507(m), 1399(s), 1170(m), 1146(m), 1043(w), 711(m), 663(m).

Single Crystal Structure Determination.

The crystal structures were determined by single-crystal X-ray diffraction. Reflection data were collected on a Bruker SMART CCD area-detector diffractometer (Mo-Kα radiation, graphite monochromator) at room temperature with ω-scan mode. Empirical adsorption correction was applied to all data using SADABS. The structure was solved by direct methods and refined by full-matrix least squares on F^2 using SHELXTL 97 software. [8] Non-hydrogen atoms were refined anisotropically. All C-bound H atoms were refined using a riding model. All calculations were carried out using SHELXTL 97 and PLATON.[9] The crystallographic data and pertinent information are given in Table 1; selected bond lengths and angles in Table S1. The CCDC reference number is 1421050 for the title compound.

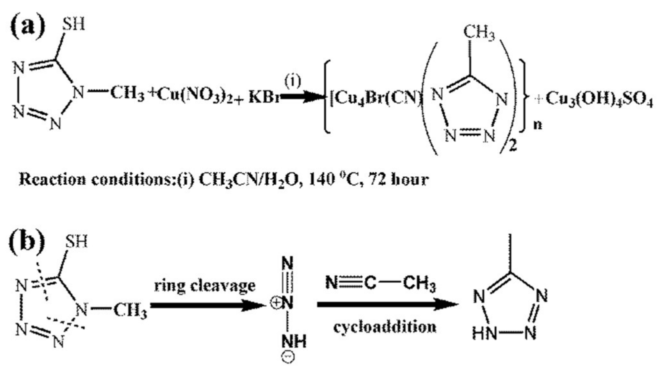
Table 1 Crystal and structure refinement data for compound **1**

Compound	**1**
Empirical formula	$C_5H_6BrCu_4N_9$
Formula weight	526.26
Crystal system	Orthorhombic
Space group	*Pnnm*
a, Å	13.043(3)
b, Å	8.1888(16)
c, Å	11.148(2)
Volume (Å^3)	1190.7(4)
Z	4
ρ_{calc}/gcm^{-3}	2.936
Absorption coef./mm^{-1}	10.399
θ range (°)	3.09 - 27.48
Crystal size (mm^3)	0.35 x 0.28 x 0.21
Reflections collected	10841
Unique reflections (Rint)	1431(0.0859)
Completeness	99.6 %
Goodness-of-fit on F^2	1.111
R_1, wR_2 [$I>2\sigma(I)$]^a	0.0402, 0.0790
R_1, wR_2 (all data)	0.0581, 0.0853

^{a} $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR = [\Sigma w(F_o^2 - F_c^2)_2/\Sigma w(F_o^2)^2]^{1/2}$

Results and discussion

Synthesis of compound 1



Scheme 1 (a) Synthesis of compound **1** (b) *In situ* formation of the Hmtz

Colourless block-like crystals of compound **1** were obtained by the solvothermal reaction of $Cu(NO_3)_2·6H_2O$, KBr and Hmnt in mixed solvents CH_3CN/H_2O at 140 °C. Except for **1**, the product was also mixed with some larger green crystalline phase, which was determined by single-crystal diffraction and its corresponding chemical formulas was $Cu_3(OH)_4SO_4$. If $Cu(NO_3)_2$ is substituted by $CuSO_4$, $CuCl_2$ or $Cu(Ac)_2$, compound **1** was not obtained, indicating that NO_3^- plays an important role in the formation of compound **1**. Similarly, in the absence of the solvent acetonitrile, compound **1** was also not obtained. On the other hand, we also tried to synthesize compound **1** by the direct reactions from corresponding metal salts and sodium azide; unfortunately, no products of **1** were isolated. According to Scheme 1a, several *in situ* reactions were involved in the formation of compound **1**, (1) Cu (II) was partially reduced into Cu(I), (2) Hmnt was desulfurized and the corresponding thiol were oxidized into SO_4^{2-}; (3) *in situ* ring-to-ring conversion of Hmnt into mtz; (4) formation of the cyanide. Although *in situ* reactions such metal reduction reaction, transformation of organic sulfur to SO_4^{2-} as well as the formation of cyanide from the cleavage of acetonitrile have been reported before,[7b,10] the *in situ* ring-to-ring conversion of Hmnt into mtz was found for the first time. The possible *in situ* formation mechanism for mtz^- is depicted in Scheme 1b: Under high temperature and lower pH value (about 3), HNO_3 and Cu^{2+} are helpful for the desulfurization and opening of the heterocycle of Hmnt.[11] The targeted mtz^- was prepared by the [2 + 3] cycloaddition reaction of the azide and the solvent acetonitrile.[12] Compound **1** was very stable in air and insoluble in common solvents such as H_2O, CH_3CN, CH_3OH, CH_3CH_2OH, DMF and $CHCl_3$ *etc*.

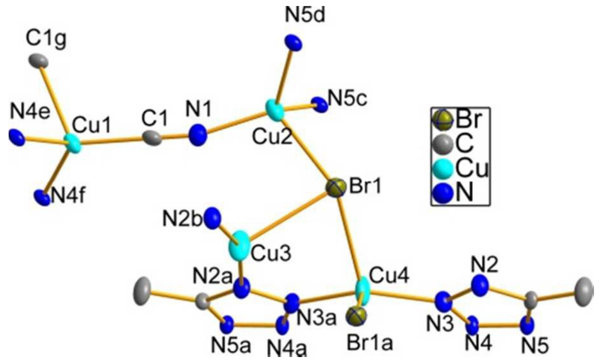


Fig.1 Coordination environment of Cu (I) in compound **1**

Crystal structure of compound 1

A single-crystal X-ray diffraction analysis revealed that the asymmetric unit of compound **1** consists of four crystallographically Cu (I) ions, each of which is located at a twofold axis with occupancy of 0.5, half a bromide, half a cyanide and one MTZ$^-$. All the copper (I) ions exhibit similar tetrahedral geometries except that Cu3 ion is in a distorted triangular planar coordination environment (**Fig. 1**). Cu1 is bound to two nitrogens from two independent MTZ$^-$ anions and two carbons from two independent CN$^-$ anions with Cu-N distances of 2.012(4) Å and Cu-C distances of 1.940(8)-2.430(8) Å. Cu2 is coordinated by a μ_4-Br$^-$ anion and three nitrogens from two independent MTZ$^-$ and one CN$^-$ anions with Cu-Br distance of 2.6777(14) Å and Cu-N distances of 1.936(6) - 2.035(4) Å. Cu3 is bound to one bromide and two nitrogens from two independent MTZ$^-$ anions with Cu-Br distance of 2.7056(15) Å and Cu-N distances of 1.894(4) Å. Cu4 is coordinated by two nitrogens from two independent MTZ$^-$ anions and two μ_4-Br$^-$ anions with Cu-N distances of 1.955(4) Å and Cu-Br distances of 2.7515(11) Å. Both MTZ$^-$ and Br$^-$ anions coordinate to four Cu (I) ions in a μ_4 coordination mode, however, each cyanide as a bridging ligand interacts with three Cu (I) ions in a μ_3 coordination mode.

Each of four MTZ$^-$ anions interacts with two Cu2 and two Cu4 ions to generate a pseudo-porphyrin structure with 16-membered rings, in which MTZ$^-$ anions and Cu (I) ions are coplanar with the largest deviation of 0.69^o (**Fig. 2a**). The carbon atom of CN$^-$ bridges two Cu1 ions into a $Cu_2(CN)_2$ SBU with short Cu···Cu distances of 2.5048(19)Å (**Fig. 2b**), which is shorter than the sum of their van der Waals radii (2.80 Å), indicating that the strong Cu···Cu interactions exist in compound **1**. It's worthy to note that $Cu_2(CN)_2$ serves as both N-donor and N-acceptor, which coordinates to both Cu(I) ions and N atoms. each $Cu_2(CN)_2$ SBU vertically goes through a 16-membered pseudo-porphyrin ring and the N-donor (N1 atom) interacts with two Cu2 ions from two adjacent pseudo-porphyrin rings to join the pseudo-porphyrins into a 1-D chain structure (**Fig. 2c**), however, its N-acceptor (copper meters) is coordinated by MTZ$^-$ anions from pseudo-porphyrin ring. Interestingly, two Cu(I) ions of $Cu_2(CN)_2$ dimers and ring of pseudo-porphyrin are almost coplanar with the largest deviation of 5.79^o. The 1D chain of pseudo-porphyrin rings coordinated to Cu3 ions into a 2D layer with 12-membered rings constructed by four MTZ$^-$ anions and four copper ions (**Fig. 2d**). Two Br$^-$ ions are located equidistantly above and below the 12-membered ring, each of which coordinates to three Cu(I) (Cu3 and two Cu4) of the 12-memebered ring and one Cu2 ion from the adjacent layer into a Cu_4Br tetramer and joined the 2D layers into a 3D network (**Fig. 2e**). Interestingly, two Cu_4Br tetramers by sharing two Cu4 ions are joined into a Cu_6Br_2 SBU (**Fig. 2f**). Each Cu_6Br_2 SBU connects two $Cu_2(CN)_2$ SBUs and eight MTZ$^-$ anions into a 3D network, though the coordination complexes based on copper (I) halide SBUs such as Cu_4I_4 clusters have been reported,[13] the related report containing both metal halide cluster Cu_6Br_2 and metal pseudohalide cluster $Cu_2(CN)_2$ SBUs are rarely reported up to now. Notably, two kinds of 2D layers are alternately arranged in an ABAB fashion along *a* axis to form a nonporous 3D network, which differs from the porous frameworks of the reported tetrazole-based Cu(I) coordination polymers by the *in situ* reactions of NaN_3, $Cu(NO_3)_2$ (or CuCN) and acetonitrile, $\{[Cu(mtz)]\cdot 0.17H_2O\}_n$, [Cu(mtz)], $\{[Cu_2(\mu_3\text{-}mtz)_2(CN)][Na(CH_3CN)]\}_n$ and $\{[Cu_4(\mu_3\text{-}Hmtz)_2(CN)_3](OH)\}_n$, which are all porous.[14]

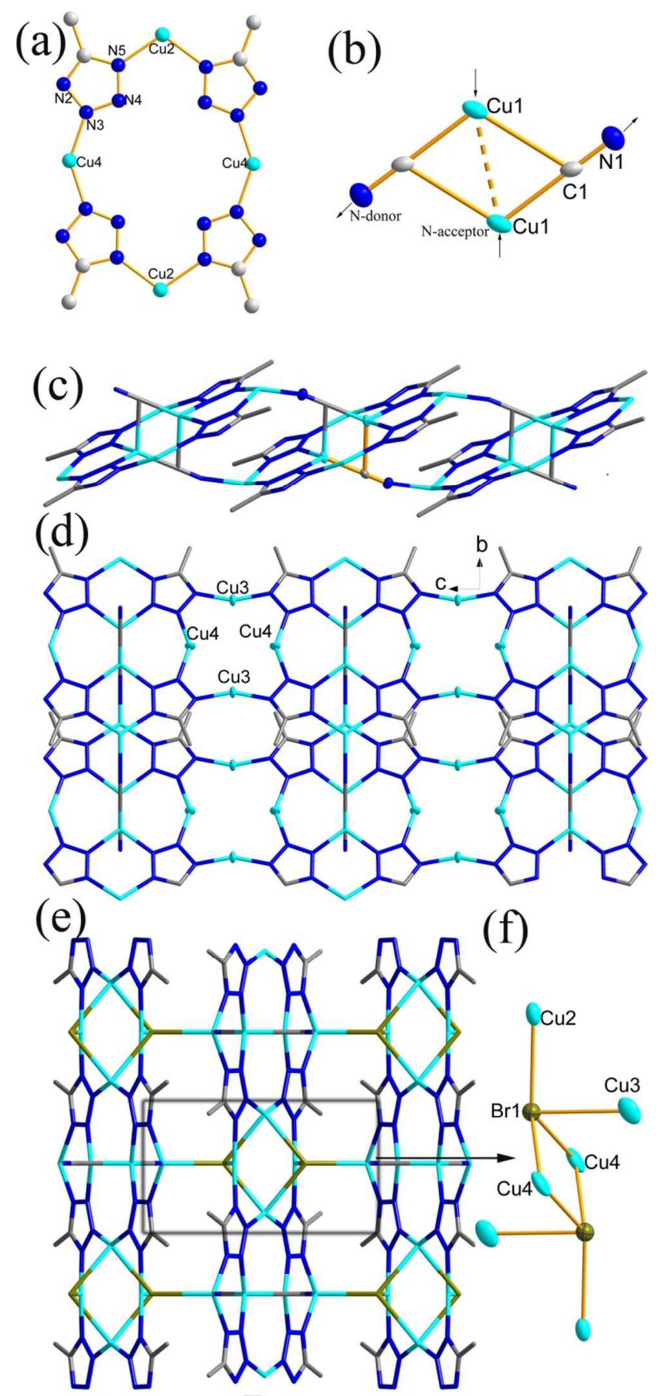


Fig. 2 (a) the pseudo-porphyrin structure, (b) the $(CuCN)_2$ SBU, (c) the 1D polymer chain constructed by pseudo-porphyrin structures and $(CuCN)_2$ SBUs, (d) the 2D layer, (e) the 3D network with ABAB layers, (f) Cu_6Br_2 SBU

From the perspective of network topology, each MTZ$^-$ interacting with one $Cu_2(CN)_2$ and two Cu_6Br_2 SBUs can be regarded as a 3-connected node; each $Cu_2(CN)_2$ SBU interconnecting two Cu_6Br_2 SBUs and four MTZ$^-$ anions can be regarded as a 6-connected nodes; however, each Cu_6Br_2 SBU interconnecting two $Cu_2(CN)_2$ SBUs and eight MTZ$^-$ anions can be regarded as a 10-connected nodes. So the framework of compound **1** may be simplified into a 3-nodal net with Schlafli symbol $\{3.4.5\}_4\{3^4.4^4.5^4.6^3\}\{3^4.4^4.8^{20}.9^{14}.10^3\}$ (**Fig. 3**), which shows an unprecedented (3,6,10)-connected topology net determined by *TOPOS*.[15] From the topology net, two kinds of 1D chains, which are constructed from $Cu_2(CN)_2$ and Cu_6Br_2 SBUs, are joined into a 3D network by MTZ anions.

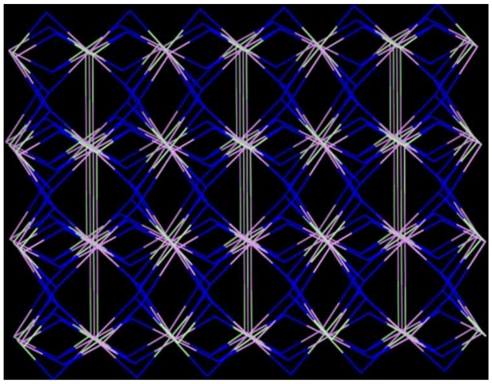


Figure 3 The topology network of compound **1**

Characterization

The PXRD showed that the experimental pattern of compound **1** is consistent well with the simulated one generated from single-crystal X-ray diffraction data (**Fig. S1**), indicating that the phase purity of the synthesized crystalline products. The IR spectrum of **1** showed a medium peak at 2088 cm^{-1}, which may be assigned to the bridging cyanide stretching vibration.

Thermogravimetric analysis was performed to explore their thermal stability of compound **1** (**Fig. S2**). The TG-DTG curves indicate that compound **1** is stable until 365 °C. In the temperature range of 365-420 °C, the weight loss of 31.67% is attributed to the removal of MTZ^- and CN^- anions (calcd 31.56%). From 420 to 436 °C, the weight is apparently increasing, which corresponds to the oxidation of Cu (I). Then the resulting complex further decomposes at about 436 °C, and the weight loss of 13.44% is due to the removal of Br^- anions (calculated 15.21).

Luminescence property

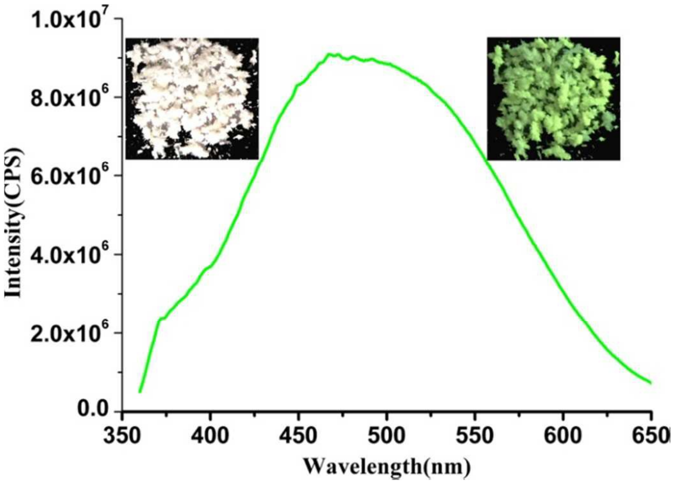


Fig. 4 Solid-state emission spectrum of compound **1**.Insets are the photoimages of compound **1** under daylight (Left) and UV illumination (Right) at 330 nm, respectively.

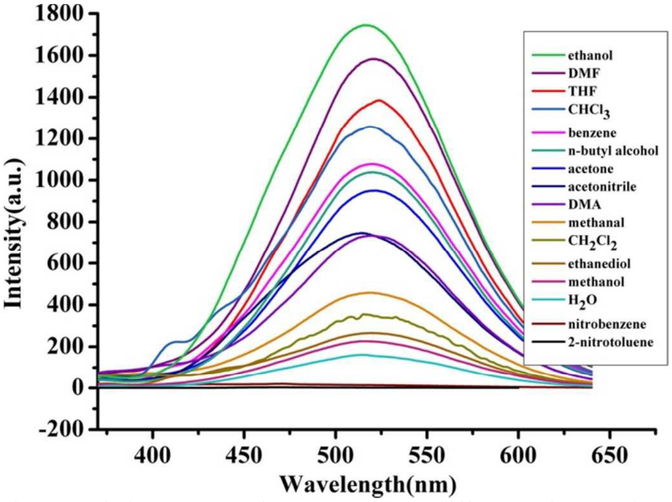


Fig. 5 Emission spectra of compound 1 in different solvents when excited at 330 nm (DMF = N, N-dimethylformamide, THF = tetrahydrofuran, $CHCl_3$ = Trichloromethane, DMA = Dimethylacetamide, CH_2Cl_2 = Dichloromethane).

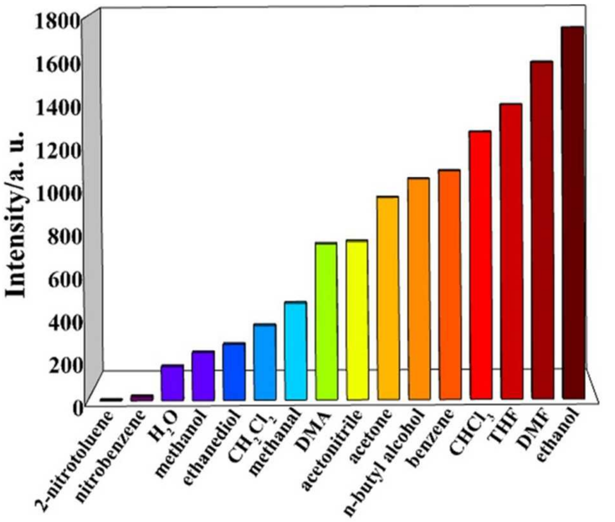


Fig. 6 Emission intensities of compound 1 in different solvents when excited at 330 nm (DMF = N,N-dimethylformamide, THF = tetrahydrofuran, $CHCl_3$ = Trichloromethane, DMA = Dimethylacetamide, CH_2Cl_2 = Dichloromethane).

The fluorescence properties of compound **1** were investigated in the solid state and in various solvent emulsions at room temperature. The solid-state photoluminescence behaviour of compound 1 exhibits strong green light emission with the maximum at 485 nm when excited at 330 nm (**Fig. 4**). According to the related luminescence of copper (I) system, especially Cu-CN and Cu-X (Cl, Br, I) analogues,[14b, 16] the emission of compound **1** are tentatively attributed to the combination of [Cu/MTZ], [Cu/CN], [Cu/Br] ligand-to-metal charge transfer (LMCT) and d–s transitions by Cu(I)/Cu(I) interactions.

To examine the potential of **1** for the sensing of small molecules, the **1**–solvent emulsions were prepared by immersing 2.0 mg powders of **1** into 4.00 mL of ethanol, N, N-dimethylformamide (DMF), tetrahydrofuran (THF), trichloromethane ($CHCl_3$), benzene, n-butyl alcohol, acetone, acetonitrile, dimethylacetamide (DMA), methanal, dichloromethane (CH_2Cl_2), ethancdiol, methanol, H_2O, nitrobenzene (NB) and 2-nitrotoluene (2-NT), and the corresponding PL spectra were measured after treated by ultrasonication for approximately 30 min before testing. The emission spectra of compound **1** dispersed in different solvents (λex = 330 nm) were shown in **Fig. 5**, which revealed that the maximum emission peaks for all of **1**–solvent emulsions have red-shifted by 30 nm due to the solvent effect, compared with the solid-state emission. The intensities of PL spectra for all of the emulsions are largely dependent on the solvent molecules (**Fig. 6**). Perhaps most significantly, ethanol exhibits the most significant enhancing effect, while NB and 2-NT were the most effective quenchers, which nearly result in the 100% photoluminescence quenching. Such solvent-dependent luminescence properties are helpful for the sensing of nitroaromatics.

To investigate its potential application as chemosensor for the detection of nitroaromatics, compound **1** was dispersed in 1-ethanol as the standard emulsion, while the analyte molecule content (0.1molL^{-1}) was gradually increased to monitor the emissive response. The changes in fluorescence intensity of 1-ethanol emulsion were measured with addition of different volumes of 0.1molL^{-1} solution of analytes such as NB, 2-NT, 2, 4-Dinitrochlorobenzene (DNCB) and 2, 4, 6-Trinitrophenol (TNP). With the addition of 20μL NB to 1- ethanol emulsion, the corresponding emission intensity attenuated by approximately 93.35% (**Fig. 7a**), and emission spectra were nearly completely quenched (98.35%) until the addition of 40 uL NB (molar ratio: 1.05 : 1 for NB : compound **1**). Though 2-NT also exhibited substantial quenching efficiency, the lower detection sensitivity than NB was observed because the addition of 80 uL 2-NT results in 97.08% quenching efficiency of emission spectra (**Fig. 7b**). Notably, the fluorescence intensity of the 1-ethanol emulsion was almost unchanged upon addition of analytes such as DNCB and TNP (**Fig. S3 and S4**). These data clearly demonstrate the high selectivity and sensitivity of compound **1** towards NB and 2-NT over other nitroaromatics.

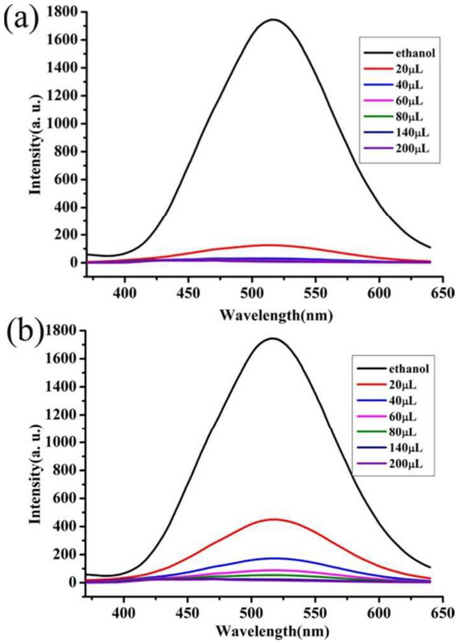


Fig. 7 Fluorescence titration of compound **1** dispersed in ethanol by gradual addition of 0.1 M solution of analytes in ethanol, (a) NB, (b) 2-NT

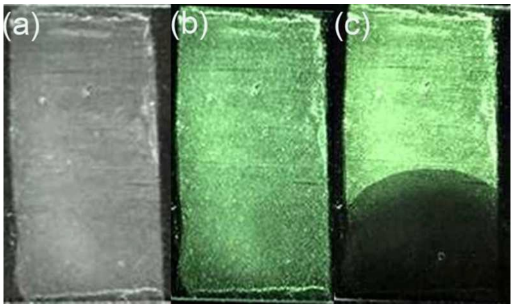


Fig. 8 The film of compound **1** on the glass substrate (a) under daylight, (b) under UV illumination, (c) after the addition of 50 uL 0.1molL^{-1} NB under UV illumination

The absence of the effective porosity in compound **1** rules out the possibility of the encapsulation of the analytes during the sensing process. Therefore, the quenching mechanism might be quite different from those of host–guest interactions, that is, the interactions between the analyte molecules encapsulated in the pores and the host framework results in the photoluminescence response. Because the fine dispersed particles with larger specific surface area and surface tension in 1-ethanol emulsion will be close contact with the analyte molecules, the fluorescence quenching observed is presumably due to the photoinduced electron transfer from the excited MOF with rich electrons to the electron deficient analytes adsorbed on the surface of the MOF particles. Although the specific quenching mechanism for the sensing of nitroaromatics is still not clear, two factors may play an important role: the dispersible nature of the sample in different solvents and the electron deficient nature of the –NO$_2$ group in nitroaromatics.[3b,3e] The fine particles of 1-ethanol emulsion could be regenerated and reused by centrifuging the dispersed solution after use and washing several times with ethanol. Moreover, compound 1 will be a particularly convenient and excellent detector of NB and 2-NT, not only due to its high thermal stability, but also because the as-synthesized samples were simply dispersed into analytes before the PL measurement, as effectively simplifies the troublesome procedures of dissolving, activation and analyte-exchange for normal PL quenching MOFs.

To prepared naked-eye colorimetric sensor of NB and 2-NT molecules, we try to prepare a fluorescence membrane of compound **1** on the glass substrates by spraying the 1-ethanol emulsion onto the substrate surface and letting it dry in the air. The fine powders of compound **1** were deposited on the targeted glass substrates, (**Fig. 8a**) which show bright green fluorescence under UV-light (**Fig. 8b**). When pure ethanol was dropped on the fluorescence membrane, the corresponding green fluorescence were not quenched, however, the fluorescence totally disappeared upon the addition of 50 uL 0.1molL^{-1} NB, that is, bright green fluorescence was changed to the dark state of the film (**Fig. 8c).** It is worth noting that fluorescence of the membrane was recovered after 10 seconds, this is most likely because of NB molecules are gathered into the oil particles and move away from the surface of the membrane with the evaporation of ethanol. Similar phenomenon was also observed in the sensing of 2-NT (**Fig. S5)**. In conclusion, the membrane demonstrated fast and efficient fluorescence quenching to both NB and 2-NT.

Conclusions

In summary, a novel 3D nonporous tetrazole-based Cu(I) coordination polymer with an unprecedented (3,6,10)-connected topology net has been developed through *in situ* ring-to-ring conversion of Hmnt into mtz, providing a new way to synthesize Hmtz-based coordination complexes. The title compound shows efficient, convenient and easily recycled chemosensor for NB and 2-DT molecules. The further research for the construction of new architectures through *in situ* ring-to-ring conversion of Hmnt into mtz is underway in our laboratory.

Acknowledgements

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Notes and references

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† Table S1, Fig. S1, S2, S3 S4, S5 and X-ray crystallographic files in CIF format of compound **1** and $Cu_3(OH)_4SO_4$. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk/data_request/cif.

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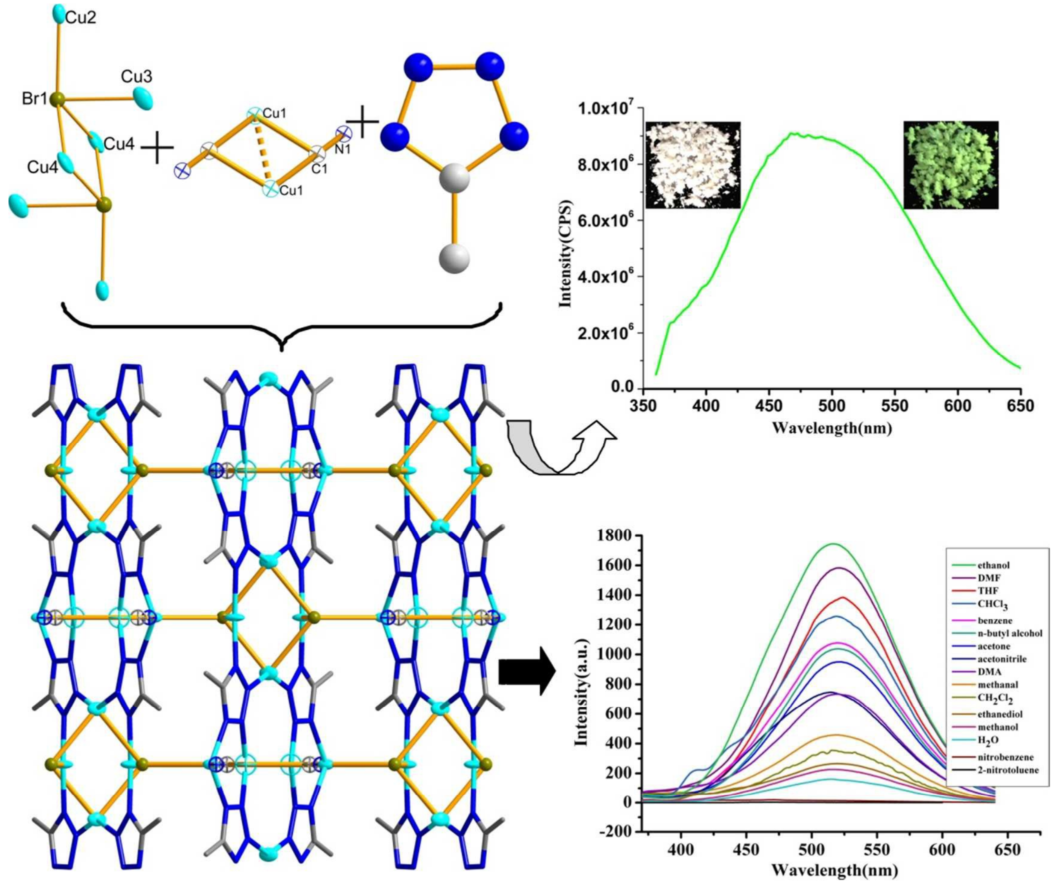

A novel 3D Cu(I) coordination polymer based on Cu_6Br_2 and $Cu_2(CN)_2$ SBUs displays strong green light emission and sensing properties of nitrobenzene and 2-nitrotoluene