

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/283746494>

A novel 3D Cu(I) coordination polymer based on Cu₆Br₂ and Cu₂(CN)₂ SBUs: in situ ligand formations and naked-eye colorimetric sensor of NB and 2-NT

ARTICLE *in* DALTON TRANSACTIONS · NOVEMBER 2015

Impact Factor: 4.2 · DOI: 10.1039/C5DT03656A

READS

4

7 AUTHORS, INCLUDING:



Jiang-Feng Song

North University of China

28 PUBLICATIONS 324 CITATIONS

SEE PROFILE



Cui Xiaobing

Jilin University

113 PUBLICATIONS 1,275 CITATIONS

SEE PROFILE



Cite this: DOI: 10.1039/c5dt03656a

A novel 3D Cu(I) coordination polymer based on Cu_6Br_2 and $\text{Cu}_2(\text{CN})_2$ SBUs: *in situ* ligand formation and use as a naked-eye colorimetric sensor for NB and 2-NT[†]

Jiang-Feng Song,^{*a} Yang Li,^a Rui-Sha Zhou,^a Tuo-Ping Hu,^a Yan-Liang Wen,^a Jia Shao^a and Xiao-Bing Cui^{*b}

A novel coordination polymer with the chemical formula $[\text{Cu}_4\text{Br}(\text{CN})(\text{mtz})_2]_n$ (mtz = 5-methyl tetrazole) (**1**), has been synthesized under solvothermal conditions and characterized by elemental analysis, infrared (IR) spectroscopy, thermal gravimetric analysis, powder X-ray diffraction and single-crystal X-ray diffraction. Interestingly, the Cu(I), CN^- and mtz^- in compound **1** are all generated from an *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 $\text{Cu}_2(\text{CN})_2$ secondary 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 fluorescence properties of compound **1** were investigated in the solid state and in various solvent emulsions, the results show that compound **1** is a highly sensitive naked-eye colorimetric sensor for NB and 2-NT (NB = nitrobenzene and 2-NT = 2-nitrotoluene).

Received 18th September 2015,
Accepted 10th November 2015

DOI: 10.1039/c5dt03656a

www.rsc.org/dalton

Introduction

Luminescent coordination complexes have received considerable attention for their potential applications in light-emission, 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 the 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 accep-

tors. 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 the coordination complexes and the electron deficient compounds results in coordination complex fluorescence quenching with high sensitivity. To the best of 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, a related study based on the coordination complexes of copper(I) halides or pseudohalides has not been reported yet.

Cu(I) coordination complexes are usually prepared by the reaction of Cu(I) and appropriate ligands or by a reaction involving 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 bonds,⁵ the ring-opening reaction for heterocycles⁶ and desulfurization.⁷ Based on the above-mentioned points, we tried to synthesize copper(I) halides or pseudohalides using 1-methyl-5-mercapto-1,2,3,4-tetrazole (Hmnt).

^aDepartment of Chemistry, North University of China, Taiyuan, Shanxi 030051, P.R. China. E-mail: jfsong0129@gmail.com

^bCollege of Chemistry and State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Jilin University, Changchun, Jilin 130023, China. E-mail: cuixb@mail.jlu.edu.cn

[†]Electronic supplementary information (ESI) available: Table S1, Fig. S1–S5 and X-ray crystallographic files in CIF format of compound **1** and $\text{Cu}_3(\text{OH})_4\text{SO}_4$. CCDC 1421050. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt03656a

Fortunately, a novel Cu(I) coordination polymer with Cu_6Br_2 and $\text{Cu}_2(\text{CN})_2$ SBUs, $[\text{Cu}_4\text{Br}(\text{CN})(\text{mtz})_2]_n$ (mtz = 5-methyl tetrazole) (**1**), was synthesized through several *in situ* reactions including the reduction of Cu(II), a ring-to-ring conversion of the organic heterocycle and the formation of cyanide. The possible *in situ* reaction mechanism, network structure, and luminescence properties of **1** are carefully studied.

Experimental

Materials and physical measurements

All reagents and solvents for the syntheses were commercially available and used as received without further purification. Elemental analyses (C, H, and N) were 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 $400\text{--}4000\text{ cm}^{-1}$. Powder X-ray diffraction (PXRD) patterns of the samples were recorded using a RIGAKU-DMAX2500 X-ray diffractometer with Cu K α 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 $10\text{ }^\circ\text{C min}^{-1}$. Solid photoluminescence (PL) excitation and emission spectra were obtained using a Jobin Yvon Fluoro Max-4 spectrophotometer equipped with a 150 W xenon lamp as the excitation source at room temperature. Fluorescence spectra of **1**-solvent emulsions were obtained on a LS 55 fluorescence/phosphorescence spectrophotometer at room temperature.

Preparation of $[\text{Cu}_4\text{Br}(\text{CN})(\text{mtz})_2]_n$ (**1**)

A mixture of $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (14.50 mg, 0.5 mmol), Hmnt (11.60 mg, 1.0 mmol) and KBr (12.0 mg, 1.0 mmol) was dissolved in 5 mL mixed solvents $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ ($v:v = 4:1$), then the blue-black suspension was transferred into a Teflon-lined autoclave and kept under autogenous pressure at $140\text{ }^\circ\text{C}$ 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 $\text{C}_5\text{H}_6\text{BrCu}_4\text{N}_9$ (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-K α radiation, graphite monochromator) at room temperature with a ω -scan mode. An 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, with 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**

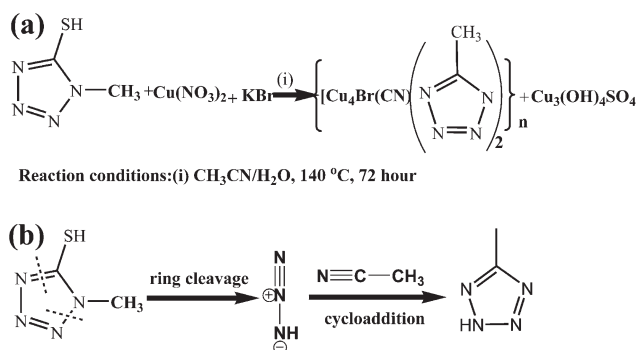
Compound	1
Empirical formula	$\text{C}_5\text{H}_6\text{BrCu}_4\text{N}_9$
Formula weight	526.26
Crystal system	Orthorhombic
Space group	<i>Pnmm</i>
<i>a</i> , Å	13.043(3)
<i>b</i> , Å	8.1888(16)
<i>c</i> , Å	11.148(2)
Volume (Å ³)	1190.7(4)
<i>Z</i>	4
$\rho_{\text{calc}}/\text{g cm}^{-3}$	2.936
Absorption coef./ mm^{-1}	10.399
θ range ($^\circ$)	3.09–27.48
Crystal size (mm^3)	$0.35 \times 0.28 \times 0.21$
Reflections collected	10 841
Unique reflections (R_{int})	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

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

Results and discussion

Synthesis of compound **1**

Colourless block-like crystals of compound **1** were obtained by the solvothermal reaction of $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, KBr and Hmnt in mixed solvents $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ at $140\text{ }^\circ\text{C}$. 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 formula was $\text{Cu}_3(\text{OH})_4\text{SO}_4$. If $\text{Cu}(\text{NO}_3)_2$ was substituted by CuSO_4 , CuCl_2 or $\text{Cu}(\text{Ac})_2$, 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 reaction from the corresponding metal salts and sodium azide; unfortunately, no product **1** was isolated. According to Scheme 1a, several *in situ* reactions were involved in the formation of compound **1**, (1) Cu(II) was par-



Scheme 1 (a) Synthesis of compound **1** (b) *in situ* formation of the mtz.

tially reduced into Cu(I), (2) Hmnt was desulfurized and the corresponding thiol was oxidized into SO_4^{2-} ; (3) an *in situ* ring-to-ring conversion of Hmnt into mtz occurred; and (4) the cyanide was formed. Although *in situ* reactions such as the metal reduction reaction and the 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 values (about 3), HNO_3 and Cu^{2+} are helpful for the desulfurization and the 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 , $\text{CH}_3\text{CH}_2\text{OH}$, DMF and CHCl_3 etc.

Crystal structure of compound 1

A single-crystal X-ray diffraction analysis revealed that the asymmetric unit of compound **1** consists of four crystallographically independent Cu(I) ions, each of which is located at a twofold axis with an occupancy of 0.5, half a bromide, half a cyanide and one mtz^- . All of the copper(I) ions exhibit similar tetrahedral geometries except for the Cu3 ion which 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 $\mu_4\text{-Br}^-$ anion and three nitrogens from two independent mtz^- anions and one CN^- anion with a 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 a Cu–Br distance of 2.7056(15) Å and a Cu–N distance of 1.894(4) Å. Cu4 is coordinated by two nitrogens from two independent mtz^- anions and two $\mu_4\text{-Br}^-$ anions with a Cu–N distance of 1.955(4) Å and a Cu–Br distance of 2.7515(11) Å. Both the 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.

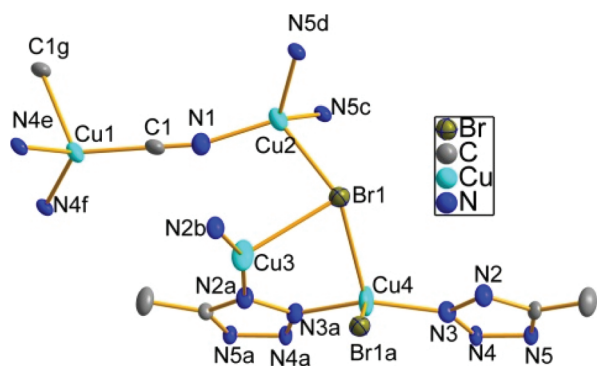


Fig. 1 Coordination environments of Cu(I) in compound **1**.

Each of the four mtz^- anions interacts with two Cu2 and two Cu4 ions to generate a pseudo-porphyrin structure with 16-membered rings, in which the mtz^- anions and the Cu(I) ions are coplanar with a largest deviation of 0.69° (Fig. 2a). The carbon atom of the CN^- bridges two Cu1 ions into a

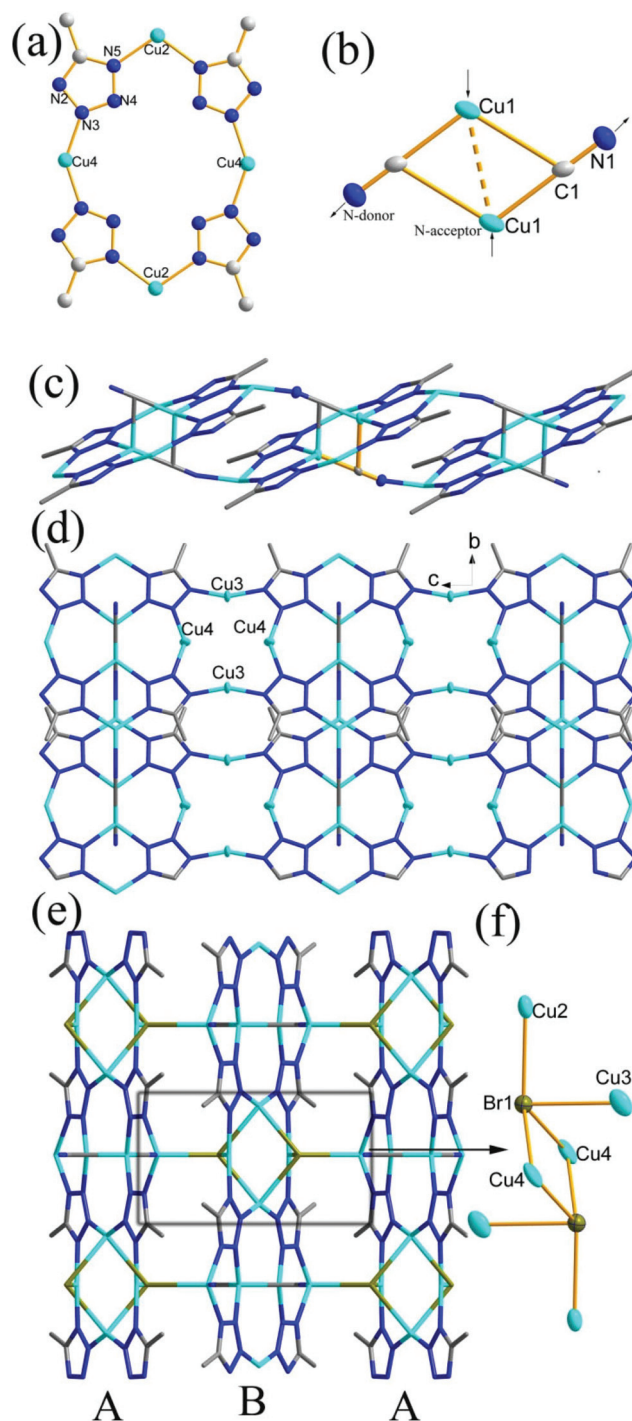


Fig. 2 (a) The pseudo-porphyrin structure, (b) the $(\text{CuCN})_2$ SBU, (c) the 1D polymer chain constructed by pseudo-porphyrin structures and $(\text{CuCN})_2$ SBUs, (d) the 2D layer, (e) the 3D network with ABAB layers, (f) the Cu_6Br_2 SBU.

$\text{Cu}_2(\text{CN})_2$ SBU with a short $\text{Cu}\cdots\text{Cu}$ distance of 2.5048(19) Å (Fig. 2b), which is shorter than the sum of their van der Waals radii (2.80 Å), indicating that strong $\text{Cu}\cdots\text{Cu}$ interactions exist in compound **1**. It's worth noting that $\text{Cu}_2(\text{CN})_2$ serves as both a N-donor and N-acceptor, which coordinates to both Cu(I) ions and N atoms. Each $\text{Cu}_2(\text{CN})_2$ 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 centers) is coordinated by the mtz^- anions from the pseudo-porphyrin ring. Interestingly, the two Cu(I) ions of the $\text{Cu}_2(\text{CN})_2$ dimers and the ring of the pseudo-porphyrin are almost coplanar with a largest deviation of 5.79°. The 1D chain of pseudo-porphyrin rings is coordinated by 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) ions (Cu3 and two Cu4) of the 12-membered ring and one Cu2 ion from the adjacent layer forming a Cu_4Br tetramer and joining the 2D layers into a 3D network (Fig. 2e). Interestingly, two Cu_4Br tetramers formed by sharing two Cu4 ions are joined into a Cu_6Br_2 SBU (Fig. 2f). Each Cu_6Br_2 SBU connects two $\text{Cu}_2(\text{CN})_2$ 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 $\text{Cu}_2(\text{CN})_2$ SBUs have rarely been reported up to now. Notably, two kinds of 2D layer are alternately arranged in an ABAB fashion along the *a* axis to form a nonporous 3D network, which differs from the frameworks of the reported tetrazole-based Cu(I) coordination polymers by the *in situ* reactions of NaN_3 , $\text{Cu}(\text{NO}_3)_2$ (or CuCN) and acetonitrile, $\{[\text{Cu}(\text{mtz})] \cdot 0.17\text{H}_2\text{O}\}_n$, $[\text{Cu}(\text{mtz})]$, $\{[\text{Cu}_2(\mu_3\text{-mtz})_2(\text{CN})][\text{Na}(\text{CH}_3\text{CN})]\}_n$ and $\{[\text{Cu}_4(\mu_3\text{-Hmtz})_2(\text{CN})_3](\text{OH})\}_n$, which are all porous.¹⁴

From the perspective of network topology, each mtz^- interacting with one $\text{Cu}_2(\text{CN})_2$ and two Cu_6Br_2 SBUs can be regarded as a 3-connected node; each $\text{Cu}_2(\text{CN})_2$ SBU interconnecting two Cu_6Br_2 SBUs and four MTZ^- anions can be regarded as a 6-connected node; however, each Cu_6Br_2 SBU interconnecting two $\text{Cu}_2(\text{CN})_2$ SBUs and eight MTZ^- anions can be regarded as a 10-connected node. So the framework of compound **1** may be simplified into a 3-nodal net with the Schläfli symbol $\{3 \cdot 4 \cdot 5\}_4 \{3^4 \cdot 4^4 \cdot 5^4 \cdot 6^3\}_3 \{3^4 \cdot 4^4 \cdot 8^{20} \cdot 9^{14} \cdot 10^3\}$ (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 $\text{Cu}_2(\text{CN})_2$ and Cu_6Br_2 SBUs, are joined into a 3D network by the mtz^- anions.

Characterization

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

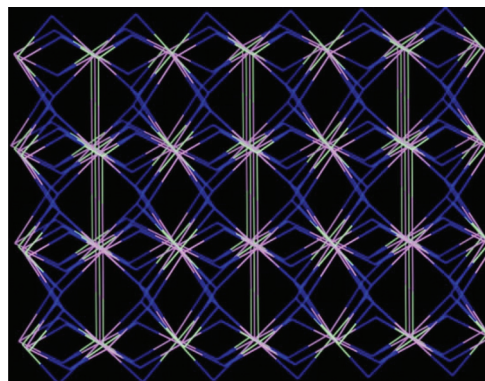


Fig. 3 The topology network of compound **1**.

which may be assigned to the bridging cyanide stretching vibration.

Thermogravimetric analysis was performed to explore the thermal stability of compound **1** (Fig. S2†). The TG-DTG curves indicate that compound **1** is stable up to 365 °C. In the temperature range of 365–420 °C, the weight loss of 31.67% is attributed to the removal of the 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 the Br^- anions (calculated 15.21%).

Luminescence properties

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) systems, especially the Cu–CN and Cu–X (Cl, Br, I) analogues,^{14b,16} the emissions of compound **1** are tentatively attributed to the combination of $[\text{Cu}/\text{mtz}]$, $[\text{Cu}/\text{CN}]$, and $[\text{Cu}/\text{Br}]$ ligand-to-metal charge transfers (LMCT) and d–s transitions by Cu(I)/Cu(I) interactions.

To examine the potential of **1** for the sensing of small molecules, 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), methanol, dichloromethane (CH_2Cl_2), ethanediol, methanol, H_2O , nitrobenzene (NB) and 2-nitrotoluene (2-NT), and the corresponding PL spectra were measured after treating the emulsions by ultrasonication for approximately 30 min. The emission spectra of compound **1** dispersed in different solvents ($\lambda_{\text{ex}} = 330 \text{ nm}$) were shown in Fig. 5, which reveals that the maximum emission peaks for all of the 1-solvent emulsions have red-shifted by 30 nm due to the solvent effect, compared with the solid-state emissions. The intensities of the PL spectra for all of the emulsions are

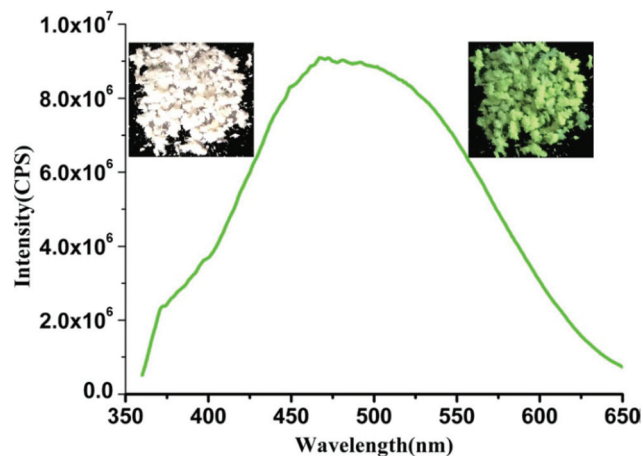


Fig. 4 Solid-state emission spectrum of compound 1. Inset are the photoimages of compound 1 under daylight (left) and UV illumination (right) at 330 nm.

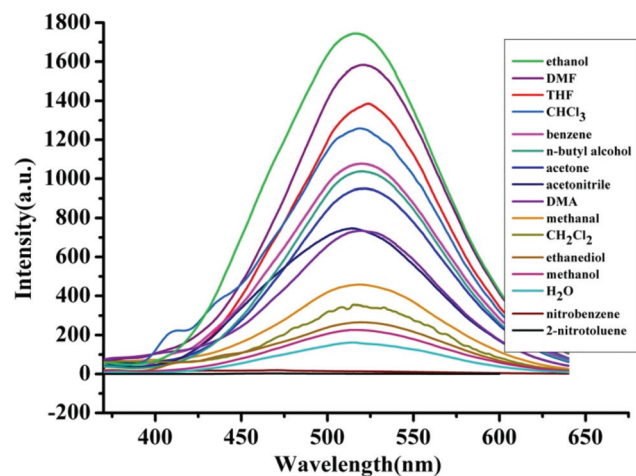


Fig. 5 Emission spectra of compound 1 in different solvents when excited at 330 nm (DMF = *N,N*-dimethylformamide, THF = tetrahydrofuran, CHCl_3 = trichloromethane, DMA = dimethylacetamide, CH_2Cl_2 = dichloromethane).

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, resulting in nearly 100% photoluminescence quenching. Such solvent-dependent luminescence properties are helpful for the sensing of nitroaromatics.

To investigate its potential application as a chemosensor for the detection of nitroaromatics, compound 1 was dispersed in 1-ethanol as the standard emulsion, the analyte molecule content (0.1 mol L^{-1}) was gradually increased while the emissive response was monitored. The changes in fluorescence intensity of the 1-ethanol emulsion were measured upon the addition of different volumes of 0.1 mol L^{-1} solutions of analytes such as NB, 2-NT, 2,4-dinitrochlorobenzene (DNCB) and

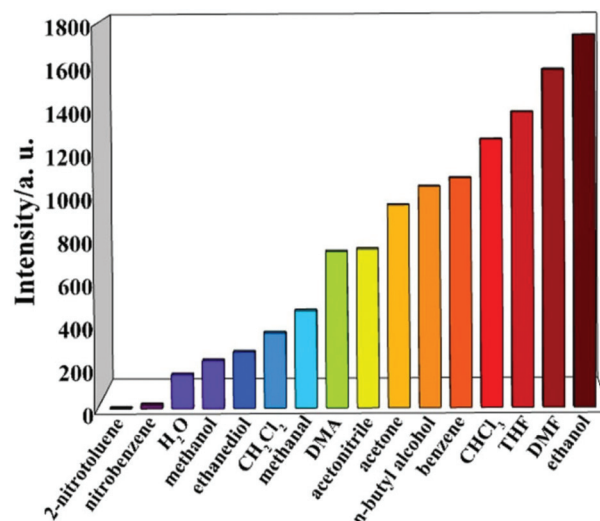


Fig. 6 Emission intensities of compound 1 in different solvents when excited at 330 nm (DMF = *N,N*-dimethylformamide, THF = tetrahydrofuran, CHCl_3 = trichloromethane, DMA = dimethylacetamide, CH_2Cl_2 = dichloromethane).

2,4,6-trinitrophenol (TNP). With the addition of 20 μL NB to the 1-ethanol emulsion, the corresponding emission intensity attenuated by approximately 93.35% (Fig. 7a), and the emission spectra were nearly completely quenched (98.35%) after the addition of 40 μL NB (molar ratio: 1.05:1 for NB: compound 1). Though 2-NT also exhibited a substantial quenching efficiency, a lower detection sensitivity than that for

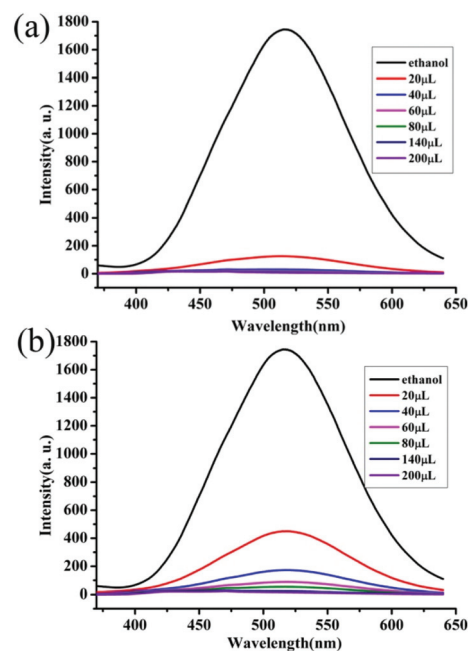


Fig. 7 Fluorescence titration of compound 1 dispersed in ethanol by gradual addition of 0.1 M solution of analytes in ethanol, (a) NB, (b) 2-NT.

NB was observed because the addition of 80 μL 2-NT results in a 97.08% quenching efficiency of the emission spectra (Fig. 7b). Notably, the fluorescence intensity of the 1-ethanol emulsion was almost unchanged upon the 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.

The absence of 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 resulting in the photoluminescence response. Because the finely dispersed particles with larger specific surface areas and surface tension in the 1-ethanol emulsion will be in close contact with the analyte molecules, the fluorescence quenching observed is presumably due to the photoinduced electron transfer from the excited electron rich MOF to the electron deficient analytes adsorbed on the surface of the MOF particles. Although the specific quenching mechanism for the sensing of the 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 $-\text{NO}_2$ group in the nitroaromatics.^{3b,e} The fine particles of the 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 the analytes before the PL measurement, effectively simplifying the troublesome procedures of dissolving, activation and analyte-exchange for normal PL quenching MOFs.

To prepare a naked-eye colorimetric sensor for NB and 2-NT molecules, we tried to prepare a fluorescence membrane of compound **1** on 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 target glass substrates, (Fig. 8a) which showed bright green

fluorescence under UV-light (Fig. 8b). When pure ethanol was dropped on the fluorescence membrane, the corresponding green fluorescence was not quenched, however, the fluorescence totally disappeared upon the addition of 50 μL 0.1 mol L^{-1} NB, that is, the bright green fluorescence was changed to the dark state of the film (Fig. 8c). It is worth noting that the fluorescence of the membrane was recovered after 10 seconds, this is most likely because the NB molecules are gathered into the oil particles and move away from the surface of the membrane with the evaporation of the ethanol. A similar phenomenon was also observed in the sensing of 2-NT (Fig. S5†). In conclusion, the membrane demonstrated fast and efficient fluorescence quenching upon the addition of 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 mtz-based coordination complexes. The title compound shows a potential application as an efficient, convenient and easily recycled chemosensor for NB and 2-NT molecules. 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

This work was supported by the National Natural Science Foundation of China (no: 21201155), the Natural Science Young Scholars Foundation of Shanxi Province (no: 2012021007-5 and 2013021008-6), Program for the Top Young Academic Leaders of Higher Learning Institutions of Shanxi and 131 Talent Plan of Higher Learning Institutions of Shanxi, respectively.

Notes and references

- (a) M. D. Allendorf, C. A. Bauer, R. K. Bhakta and R. J. T. Houk, *Chem. Soc. Rev.*, 2009, **38**, 1330–1352; (b) K. Binnemans, *Chem. Rev.*, 2009, **109**, 4283–4374; (c) L. D. Carlos, R. A. Ferreira, V. de Zea Bermudez, B. Julian-Lopez and P. Escrivano, *Chem. Soc. Rev.*, 2011, **40**, 536–549; (d) Y. Cui, Y. Yue, G. Qian and B. Chen, *Chem. Rev.*, 2011, **112**, 1126–1162; (e) J. Rocha, L. D. Carlos, F. A. Paz and D. Ananias, *Chem. Soc. Rev.*, 2011, **40**, 926–940; (f) Z. Hu, B. J. Deibert and J. Li, *Chem. Soc. Rev.*, 2014, **43**, 5815–5840; (g) L. V. Meyer, F. Schonfeld and K. Muller-Buschbaum, *Chem. Commun.*, 2014, **50**, 8093–8108; (h) F. Y. Yi, J. P. Li, D. Wu and Z. M. Sun, *Chem. – Eur. J.*, 2015, **21**, 11475–11482; (i) S. Y. Zhang, W. Shi, P. Cheng

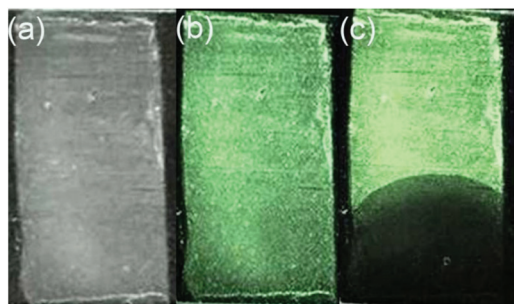


Fig. 8 The film of compound **1** on the glass substrate (a) under daylight, (b) under UV illumination, (c) after the addition of 50 μL 0.1 mol L^{-1} NB under UV illumination.

- and M. J. Zaworotko, *J. Am. Chem. Soc.*, 2015, **137**, 12203–12206.
- 2 (a) Y. Kang, F. Wang, J. Zhang and X. Bu, *J. Am. Chem. Soc.*, 2012, **134**, 17881–17884; (b) J. H. Wang, M. Li, J. Zheng, X. C. Huang and D. Li, *Chem. Commun.*, 2014, **50**, 9115–9118; (c) Y. Yu, X. M. Zhang, J. P. Ma, Q. K. Liu, P. Wang and Y. B. Dong, *Chem. Commun.*, 2014, **50**, 1444–1446; (d) X. Zhang, W. Liu, G. Z. Wei, D. Banerjee, Z. Hu and J. Li, *J. Am. Chem. Soc.*, 2014, **136**, 14230–14236; (e) J. F. Liu, X. Min, J. Y. Lv, F. X. Pan, Q. J. Pan and Z. M. Sun, *Inorg. Chem.*, 2014, **53**, 11068–11074; (f) W. Liu, Y. Fang, G. Z. Wei, S. J. Teat, K. Xiong, Z. Hu, W. P. Lustig and J. Li, *J. Am. Chem. Soc.*, 2015, **137**, 9400–9408.
 - 3 (a) A. J. Lan, K. H. Li, H. H. Wu, D. H. Olson, T. J. Emge, W. Ki, M. C. Hong and J. Li, *Angew. Chem., Int. Ed.*, 2009, **48**, 2334–2338; (b) B. Gole, A. K. Bar and P. S. Mukherjee, *Chem. Commun.*, 2011, **47**, 12137–12139; (c) C. Zhang, Y. Che, Z. Zhang, X. Yang and L. Zang, *Chem. Commun.*, 2011, **47**, 2336–2338; (d) H. Xu, F. Liu, Y. Cui, B. Chen and G. Qian, *Chem. Commun.*, 2011, **47**, 3153–3155; (e) M. Guo and Z.-M. Sun, *J. Mater. Chem.*, 2012, **22**, 15939; (f) Y. N. Gong, L. Jiang and T. B. Lu, *Chem. Commun.*, 2013, **49**, 11113–11115; (g) H. Wang, W. T. Yang and Z. M. Sun, *Chem. – Asian. J.*, 2013, **8**, 982–989; (h) X. Q. Wang, L. L. Zhang, J. Yang, F. L. Liu, F. N. Dai, R. M. Wang and D. F. Sun, *J. Mater. Chem. A*, 2015, **3**, 12777–12785; (i) F. Y. Yi, Y. Wang, J. P. Li, D. Wu, Y. Q. Lan and Z. M. Sun, *Mater. Horiz.*, 2015, **2**, 245–251; (j) W. Xie, S. R. Zhang, D. Y. Du, J. S. Qin, S. J. Bao, J. Li, Z. M. Su, W. W. He, Q. Fu and Y. Q. Lan, *Inorg. Chem.*, 2015, **54**, 3290–3296.
 - 4 (a) Y.-L. Wang, N. Zhang, Q.-Y. Liu, Z.-M. Shan, R. Cao, M.-S. Wang, J.-J. Luo and E.-L. Yang, *Cryst. Growth Des.*, 2011, **11**, 130–138; (b) N. Yuan, T. Sheng, J. Zhang, C. Tian, S. Hu, X. Huang, F. Wang and X. Wu, *CrystEngComm*, 2011, **13**, 5951; (c) J. Wang, S.-L. Zheng, S. Hu, Y.-H. Zhang and M.-L. Tong, *Inorg. Chem.*, 2007, **46**, 795–800; (d) Y.-N. Zhang, Y.-Y. Wang, L. Hou, P. Liu, J.-Q. Liu and Q.-Z. Shi, *CrystEngComm*, 2010, **12**, 3840.
 - 5 Y. Bu, F. Jiang, S. Zhang, J. Ma, X. Li and M. Hong, *CrystEngComm*, 2011, **13**, 6323.
 - 6 J.-K. Cheng, J. Zhang, P.-X. Yin, Q.-P. Lin, Z.-J. Li and Y.-G. Yao, *CrystEngComm*, 2010, **12**, 1024–1026.
 - 7 (a) J. K. Cheng, Y. B. Chen, L. Wu, J. Zhang, Y. H. Wen, Z. J. Li and Y. G. Yao, *Inorg. Chem.*, 2005, **44**, 3386–3388; (b) J.-K. Cheng, Y.-G. Yao, J. Zhang, Z.-J. Li, Z.-W. Cai, X.-Y. Zhang, Z.-N. Chen, Y.-B. Chen, Y. Kang, Y.-Y. Qin and Y.-H. Wen, *J. Am. Chem. Soc.*, 2004, **126**, 7796–7797.
 - 8 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 2008, **64**, 112–122.
 - 9 A. L. Spek, *PLATON, Molecular Geometry Program*, University of Utrecht, The Netherlands, 1999.
 - 10 X.-M. Zhang, R.-Q. Fang and H.-S. Wu, *J. Am. Chem. Soc.*, 2005, **127**, 7670–7671.
 - 11 C. M. Bian, X. Dong, X. Zhang, Z. Zhou, M. Zhang and C. Li, *J. Mater. Chem. A*, 2015, **3**, 3594–3601.
 - 12 H. Zhao, Z. R. Qu, H. Y. Ye and R. G. Xiong, *Chem. Soc. Rev.*, 2008, **37**, 84–100.
 - 13 (a) S. Z. Zhan, M. Li, X. P. Zhou, J. H. Wang, J. R. Yang and D. Li, *Chem. Commun.*, 2011, **47**, 12441–12443; (b) M. Hashimoto, S. Igawa, M. Yashima, I. Kawata, M. Hoshino and M. Osawa, *J. Am. Chem. Soc.*, 2011, **133**, 10348–10351.
 - 14 (a) T. Wu, B.-H. Yi and D. Li, *Inorg. Chem.*, 2005, **44**, 4130–4132; (b) Z. Li, M. Li, S.-Z. Zhan, X.-C. Huang, S. W. Ng and D. Li, *CrystEngComm*, 2008, **10**, 978.
 - 15 V. A. Blatov, A. P. Shevchenko and V. N. Serezhkin, *J. Appl. Crystallogr.*, 2000, **33**, 1193.
 - 16 X. He, C.-Z. Lu, C.-D. Wu and L.-J. Chen, *Eur. J. Inorg. Chem.*, 2006, **2006**, 2491–2503.