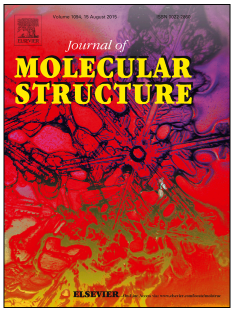

Five new complexes based on 1-phenyl-1*H*-tetrazole-5-thiol: Synthesis, structural characterization and properties

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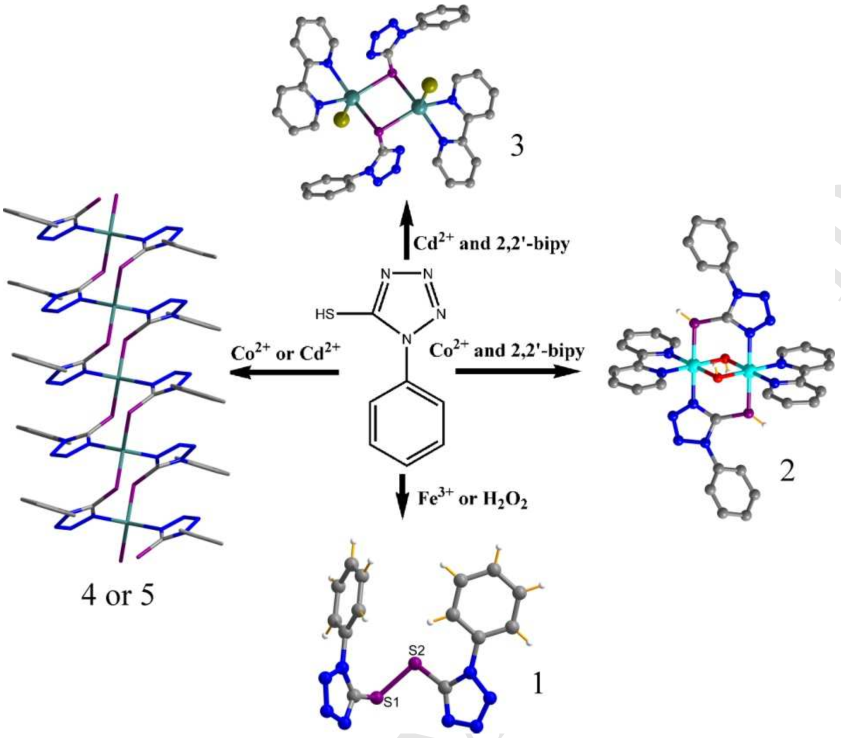

Five new complexes based on 1-phenyl-1H-tetrazole-5-thiol (Hptt) have been isolated and characterized.

Five new complexes based on 1-phenyl-1H-tetrazole-5-thiol: synthesis, structural characterization and properties

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Abstract

Five new complexes based on 1-phenyl-1H-tetrazole-5-thiol (Hptt): 1,1’-diphenyl-5,5’-dithiodi-tetrazole (abbreviated as dptt) (**1**), $\{[Co_2(OH)_2(2,2'\text{-bipy})_2(Hptt)_2]\cdot(ptt)_2\cdot(H_2O)_2\}$(**2**), $[Cd_2I_2(2,2'\text{-bipy})_2(ptt)_2]$ (**3**), $[Co(ptt)_2]_n$ (**4**) and $[Cd(ptt)_2]_n$ (**5**), have been synthesized and fully characterized by elemental analyses, thermogravimetric analysis, powder X-ray diffraction, IR spectra and single-crystal X-ray diffraction. Structural analysis indicated that compound **1** is an organic matter generated from *in situ* oxidative coupling reaction of Hptt ligands under the help of Fe^{3+} ion. In compound **2**, two Hptt ligands adopting μ_2-κN, κS bridging mode and two μ_2-OH^- bridge two Co(2,2'-bipy) fragments into a$[Co_2(OH)_2(2,2'\text{-bipy})_2(Hptt)_2]^{2+}$ core with short Co···Co distance (2.8185(10) Å). In compound **3**, two Cd centers are joined into a dinuclear complex with short Cd···Cd distance (3.9282(14) Å) by two ptt^- aions in μ_2-κS, κS bridging mode. Compounds **4** and **5** are isostructural and both feature one-dimensional (1D) looped chain structures containing 8-membered $[M_2S_2C_2N_2]$ rings (M=Co for **4**, M=Cd for **5**). Variable-temperature magnetic susceptibility measurement of compounds **2** and **4** reveal strong antiferromagnetic interactions between Co centers. The fluorescent properties of compounds **1**, **3** and **5** are investigated in the solid state.

Keywords: coordination polymer; organic sulfur; in situ reaction; crystal structure.

1. Introduction

Coordination complexes have attracted increasing attention in the field of materials science because of their versatile framework topologies as well as the interesting properties including magnetism, gas sorption, catalysis, optics and molecular sensing **[1-9]**. As is well known, organic ligands play crucial roles in constructing coordination complexes with novel topologies and unique properties **[10-11]**. Recently, organic sulfur ligands such as pyrimidine-2-thiolate,

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2-mercaptoimidazole, 1H-1,2,4-triazole-3-thiol, 1-methyl-1H-imidazole-2-thiolate, 2-mercaptopyridinate, 2-quinolinethiolate, 2-mercaptobenzothiazolate, 5-mercapto-1-methyltetrazolate etc. **[12-21]**, were widely applied to assemble diversities of coordination complexes with unique properties due to their diverse coordination modes and rich redox chemistry such as the cleavage of C-S bonds and the formation of S-S bonds **[21-26]**.

The thiol-substituted heterocycle ligand, 1-methyl-5-mercapto-1,2,3,4-tetrazole (Hmnt), having one soft donor sulfur and three hard donor nitrogen atoms, is a tetrazole-based heterocyclic thioamide, providing more coordination sites for metal ions to form metal coordination complexes. Though some interesting coordination complexes based on Hmnt have been reported **[26-28]**, we found that the higher temperature or oxidizing agents easily result in the decomposition of Hmnt ligand **[21]**. In order to obtain coordination complexes based on mercapo tetrazole, a more stable mercapo tetrazole derivative, 1-phenyl-1H-tetrazole-5-thiol (Hptt), is introduced in the reaction process. Compared with Hmnt, the introduced phenyl unit could improve conjugated effect between benzene ring and tetrazole ring and enhance the stability of the ligand, moreover, the phenyl unit might offer some supramolecuar recognition sites such as $\pi\cdots\pi$, C-H$\cdots\pi$ interactions, which are helpful to stabilize the targeted complexes. To the best of our knowledge, coordination complexes comprised of Hptt are still rare, and most of reported compounds are zero-dimensional oligo species **[29-35]**, moreover, those showing anti-microbial potential have only been recognized recently [**35**]. The above-mentioned analysis implies that there is still much deserving study for such systems.

Following our interests regarding the synthesis of organic sulfur coordination compounds **[19-21]**, Hppt is chosen as an organic linker to construct five new complexes: 1,1'-diphenyl-5,5'-dithiodi-tetrazole (abbreviated as dptt) (**1**), $\{[Co_2(OH)_2(bipy)_2(Hptt)_2]\cdot(ptt)_2\cdot(H_2O)_2\}$(**2**), $[Cd_2I_2(bipy)_2(ptt)_2]$ (**3**), $[Co(ptt)_2]_n$ (**4**) and $[Cd(ptt)_2]_n$ (**5**). Compound **1** is an organic matter generated from *in situ* oxidative coupling reaction of Hptt ligands under the help of Fe^{3+} ion. In compound **2**, two Hptt ligands adopting μ_2-N,S bridging mode and two OH^{-} join two Co centers into a dinuclear complex with short Co$\cdots$Co distance (2.8185(10) Å). In compound **3**, two Cd centers are joined into a dinuclear complex with short Cd$\cdots$Cd distance (3.9282(14) Å)by two ptt^{-} anions inμ_2-S, S bridging mode. Compounds **4** and **5** are isostructural and both feature one-dimensional (1D) looped chain structures. Magnetic properties of compounds **2** and **4** together with fluorescent properties of compounds **1**, **3** and **5** are investigated in the solid state. We hope that the syntheses of compounds **1-5** are helpful to deepen the research of organic sulfur coordination complexes.

2. Experimental Section

2.1. Materials and methods

All reagents and solvents for syntheses were commercially available and used as received without further purification except Hptt ligand, which was purchased from Alfa Aesar and the corresponding purity was higher than 99%. Elemental analysis (C, H, and N) were performed on a Perkin–Elmer 240C elemental analyzer. Infrared (IR) spectra were recorded with KBr Pellets using a Perkin Elmer Spectrum One FT–IR spectrometer in the range of 4000–400 cm^{-1} with the resolution (4.0 cm^{-1}) and the scan's numbers (10). The HNMR spectrum was recorded on a Bruker 400 MHz spectrometer. Powder X–ray diffraction (PXRD) patterns of the samples were recorded by a RIGAKU–DMAX2500 X–ray diffractometer using Cu–Kα radiation (λ = 1.542 Å) with a scanning rate of 10°/min and a step size of 0.02°. Thermal gravimetric analysis (TGA) was carried out in a nitrogen stream on a Perkin Elmer TGA–7000 thermogravimetric analyser with a heating rate of 10 $°C\cdot min^{-1}$. The solid-state photoluminescence spectra were recorded on Jobin Yvon Fluoro Max-4 spectrophotometer equipped with a 150 W xenon lamp as the excitation source at room temperature. Variable-temperature magnetic susceptibility measurements were collected using SQUID magnetometer MPMS XL-7 (Quantum Design) at 1.0 kOe in the temperature range of 2−300 K.

2.2. Synthesis of 1-5

2.2.1. Synthesis of dptt (1)

A mixture of Hptt (0.05mmol), $Fe(NO_3)_3\cdot 9H_2O$ (0.1mmol) was dissolved in 6mL mixed solvents MeOH/H_2O (v : v = 5 : 1), which was stirred in a 15 mL beaker for 30 min at room temperature. Then the above-mentioned mixture was filtered and the filtrate was allowed to slowly concentrate by evaporation at room temperature. After 12h, colorless block crystals were obtained. Yield : 60% (based on Hptt). Elemental anal. Calcd $C_{14}H_{10}S_2N_8$ (354.42): C, 47.47; H, 5.60; N, 31.65. Found: C, 47.40; H, 5.64; N, 31.60. IR Spectrum (cm^{-1}, KBr pellet): 1594 (m), 1496 (s), 1460 (m), 1383 (s), 1265(m), 1226(s), 1095 (m), 1055 (m), 1014 (s), 975 (m), 761 (s), 690 (s), 540 (m), 492 (m). **^{1}H NMR** (400 MHz, [D$_6$]DMSO): δ = 7.57 (2H), 7.65 (4H).

2.2.2. Synthesis of {[$Co_2(OH)_2(bipy)_2(Hptt)_2$]·$(ptt)_2$·$(H_2O)_2$}(2)

A mixture of Hptt (0.1mmol), 2, 2'-bipy (0.1mmol), Co(Ac)$_2$·4H$_2$O (0.1mmol) and MeOH/H$_2$O (v : v = 5 : 1, 6ml) was stirred in a 15 mL beaker for 30 min at room temperature. Then the above-mentioned mixture was allowed to slowly concentrate by evaporation at room temperature. After two days, red crystals were obtained. Yield : 52% (based on Hptt). Elemental anal. Calcd $C_{48}H_{44}Co_2N_{20}O_4S_4$ (1211.13): C, 47.56; H, 3.63; N, 23.12. Found: C, 47.53; H, 3.65; N, 23.10. IR Spectrum (cm^{-1}, KBr pellet): 3459(m) 1598 (s), 1496(s), 1448(m), 1352(m), 1320(m), 1276(m), 1252 (m), 1216 (w), 1154(w), 1093 (m), 1016(m), 762(s), 691(s), 567(m), 483(m).

2.2.3. Synthesis of [$Cd_2I_2(bipy)_2(ptt)_2$] (3)

A mixture of Hptt (0.1mmol), 2, 2'-bipy (0.1mmol), Cd(Ac)$_2$·4H$_2$O (0.1mmol) and KI (0.1mmol) was dissolved in 7mL mixed solvents MeOH/DMF/H$_2$O (v : v = 5 : 1 : 1). Then the resulted mixture was transferred into a Teflon-lined autoclave and kept under autogenous pressure at 80 °C for 3 days. After slowly cooling to room temperature, light yellow crystals were obtained. Yield: 25% (based on Hptt). Elemental anal. Calcd $C_{34}H_{26}Cd_2I_2N_{12}S_2$ (1145.39): C, 35.62; H, 2.27; N, 14.67. Found: C, 35.60; H, 2.26; N, 14.69. IR Spectrum (cm^{-1}, KBr pellet): 1650 (m), 1400 (s), 1238 (m), 1170 (m), 1091 (m), 1051 (m), 1020(m) 754 (m), 680 (m), 561 (m).

2.2.4. Synthesis of [$Co(ptt)_2$]$_n$ (4)

A mixture of Hptt (0.1mmol) and Co(Ac)$_2$·4H$_2$O (0.1mmol) was dissolved in 5mL mixed solvents H$_2$O/DMF (v : v = 4 : 1). Then the resulted mixture was transferred into a Teflon-lined autoclave and kept under autogenous pressure at 80 °C for 3 days. After slowly cooling to room temperature, red crystals were obtained. Yield :32% (based on Hptt). Elemental anal. Calcd $C_{14}H_{10}CoN_8S_2$ (413.35): C, 40.64; H, 2.42; N, 27.10. Found: C, 40.65; H, 2.40; N, 27.08. IR Spectrum (cm^{-1}, KBr pellet): 1594 (w), 1495 (m), 1378 (s), 1316 (m), 1243 (m), 1163 (w), 1095 (m), 1050 (m), 1025 (m), 755 (m), 683 (m), 562(m).

2.2.5. Synthesis of [$Cd(ptt)_2$]$_n$ (5)

A mixture of Hptt (0.1mmol), Fe(NO$_3$)$_3$·9H$_2$O (0.1mmol), CdSO$_4$·8H$_2$O (0.1mmol) and MeOH/H$_2$O (v : v = 5 : 2, 7ml) was stirred in a 15 mL beaker for 30 min at room temperature.

Then the above-mentioned mixture was filtered and the filtrate was allowed to slowly concentrate by evaporation at room temperature. After 3 days, colorless block crystals were obtained. Yield : 34% (based on Hptt). Elemental anal. Calcd $C_{14}H_{10}CdN_8S_2$ (419.83): C, 40.02; H, 2.38; N, 26.68. Found: C, 40.06; H, 2.41; N, 26.72. IR Spectrum (cm^{-1}, KBr pellet): 1594 (w), 1495 (m), 1398 (s), 1314 (m), 1239 (m), 1163 (w), 1089 (m), 1050 (m), 1023 (m), 755 (m), 685 (m), 561(m).

2.3. Crystal structure determination

X-ray diffraction data of compounds **1-5** were collected on a Bruker SMART CCD area-detector diffractometer (MoKα radiation, graphite monochromator) at room temperature with ω-scan mode. Adsorption corrections were applied using the SADABS routine. The structure was solved by direct methods and refined by full-matrix least squares on F^2 using SHELXTL 97 software **[36]**. Non-hydrogen atoms were refined anisotropically. All carbon-bound hydrogen atoms were refined using a riding model. All calculations were carried out using SHELXTL 97. For **2**, the disordered lattice water molecule was treated by performing split and occupancies refinement of the disordered atoms, and the corresponding hydrogen atoms were not located in a difference Fourier map. The crystallographic data and pertinent information are given in table 1; selected bond lengths and angles in table S1.

3. Results and discussion

3.1. Synthesis of compounds 1-5

The Hptt ligand was easily solved in common organic solvents such as methanol, ethanol, acetonitrile and DMF. A series of experimental results show that compound **1** can be synthesized in the presence of Fe^{3+} or H_2O_2, however, at the same reaction conditions, *in situ* oxidative coupling reaction based on Hmnt didn’t occur. The crystals of compound **1** are difficult to dissolve in common solvents as methanol, ethanol, acetonitrile, acetone and DMF at room temperature, so we also tried to synthesize the coordination complexes based on compound **1** through one-pot reaction under the help of oxidizing agents such as Fe^{3+} or H_2O_2, only compound **5** was obtained, however, no targeted products were isolated to date. When metal ions (Co^{2+} or Cd^{2+}) react with Hptt ligands, compounds **4** and **5** with 1D chains were obtained, however, when chelating 2, 2'-bipy with strong coordination activity was introduced into the reaction system, compounds **2** and **3** with binuclear structures were obtained, indicating the terminally chelating ligands have an important influence on the topology structures. Compounds **2-5** are very stable in air and insoluble in common solvents such as H_2O, CH_3OH, CH_3CH_2OH, CH_3CN, DMF, DMSO and $CHCl_3$ *etc*.

3.2. Crystal structure

3.2.1. Crystal structure of compound 1

A single crystal X-ray diffraction analysis revealed that compound **1** is crystallized in the triclinic space group, *P-1*. The asymmetric unit of compound **1** is composed of one dptt molecule, which generated from *in situ* oxidative coupling reaction of two ptt^- ligands (**Fig.1**). The S-S distance is 2.0311(10) Å in dptt molecule, which is shorter than those in the photo-responsive organodirhodium complexes with active S-S bonds **[37]**. The dihedral angles between the tetrazole and phenyl rings in two ptt units are 42.708(83) and 54.540(87)° respectively. The C-S distances of compound **1** are in the range of 1.7489(24)-1.7571(20) Å, which are shorter than the typical C-S bonds (1.82 Å), indicating that the sulfur atom has double bond character **[38]**. The dptt molecules were packed into a 3D supramolecular network thorough $\pi\cdots\pi$ interactions between ptt units (**Fig. S1**).

3.2.2. Crystal structure of compound 2

Compound **2** crystallizes in the monoclinic space group, *P2₁/n*. The asymmetric unit contains one Co (II) ion, one OH^-, one ptt^- anion, one lattice water and one Hptt molecule. The Co center shows an octahedral geometry where the basal plane is occupied by two oxygens and two nitrogens from two symmetrical equivalent OH^- anions and one 2, 2'-bipy molecule, and the axial positions are occupied by one nitrogen and one sulfur from two Hptt molecules (**Fig. 2**). The Co-O/N bond distances around Co range from 1.8915(35) Å to 2.20224(37) Å, and the Co-S distance is 2.2446 (17) Å. Notably, ptt^- anions uncoordinates with Co center but acts as counter anions. The C-S bond distances in Hptt and ptt^- are 1.6884(50) and 1.6868(56) Å respectively, which are shorter than that of compound **1**, and their dihedral angles between the tetrazole and phenyl rings are 54.15 and 67.48°, respectively.

Two Hptt ligands adopting μ_2-κN, κS bridging mode and two μ_2-OH^- bridge two Co(2,2'-bipy) fragments into a$[Co_2(OH)_2(2,2'\text{-bipy})_2(Hptt)_2]^{2+}$ core with short Co$\cdots$Co distance

(2.8185(10) Å), interestingly, two Co(2,2'-bipy) fragments and two μ$_2$-O are all coplanar. The $[Co_2(OH)_2(2,2'\text{-bipy})_2(Hptt)_2]^{2+}$ core interact with two ptt$^-$ anions into a neutral molecule, $[Co_2(OH)_2(2,2'\text{-bipy})_2(Hptt)_2]\cdot(ptt)_2$, in which several supramolecuar recognition sites based on π···π interactions are observed (**Fig. S2**). The $[Co_2(OH)_2(2,2'\text{-bipy})_2(Hptt)_2]\cdot(ptt)_2$ molecules are packed into a 3D supramolecular network with a 1D abnormal channel, in which lattice water molecules are filled (**Fig. 3)**.

3.2.3. Crystal structure of compound 3

A single crystal X-ray diffraction analysis revealed that compound **3** crystallized in the monoclinic space group, *P2$_{1/}$n*. The asymmetric unit consists of one Cd (II) ion, one I$^-$ and one ptt$^-$ anion. The Cd center with square pyramidal coordination environment is bound to two nitrogens from one chelating 2,2'-bipy, two sulfurs from two independent ptt$^-$ ligands and one I$^-$ anion (**Fig. 4**). The Cd-N distances range from 2.3267(30) Å to 2.3292(26) Å, and the Cd-S distances are 2.6395(10)-2.7504(11) Å, while the Cd-I distance is 2.7553(6) Å, and selected bond lengths and angles in Table S1.

Two [CdI(2,2'-bipy)]fragments are bridged by two ptt$^-$ anions in μ_2-1 κS : 2 κS coordination modes into a neutral dinuclear molecule, $[Cd_2I_2(2,2'\text{-bipy})_2(ptt)_2]$,in which a four-membered ring of $Cd_2S_2$with short Cd···Cd distance (3.9282(14) Å) is observed. Notably, two 2,2'-bipy molecues, two ptt$^-$and two I$^-$ anions are all on the opposite sides of M_2S_2 rings so as to lower the steric exclusion effect.

3.2.4. Crystal structure of compounds 4 and 5

Compounds **4** and **5** have the same crystal system, space group and isomorphic framework, so only the structure of **5** will be described in detail as a representative example. The asymmetric unit of compound **5** contains a Cd ion and a μ_2-ptt$^-$ ligand. The cadmium center located on a twofold rotation axis is bounded to two S atoms and two N atoms from four independent ptt$^-$ ligands (**Fig. 5a**), showing a distorted tetrahedral geometry with Cd-S and Cd-N distances of 2.5029(23) Å and 2.2456(70) Å, respectively.

The ptt$^-$ ligand adopting a μ_2-κN, κS coordination mode bridges two Cd centers into a one-dimensional (1D) looped chain along the c axis (**Fig. 5b**), in which a 8-membered ring of

[$Cd_2S_2C_2N_2$] is observed and the Cd···Cd distance is 4.1763(9) Å. Then the 1D chains are interdigitated with each other into a 2D supramolecular layer via the π-π interactions among the neighboring phenyl rings along the bc plane (**Fig. 5c and 5d**). Compared with compounds **2 -5**, we found that the terminally chelating ligands have an important influence on the topology structures.

3.3. Characterization

The experimental PXRD patterns of compounds **1-5** are shown in **Fig. S3**, which matched well with the corresponding simulated ones from their X-ray single-crystal diffraction data, as indicated that the phase purities of the synthesized bulk materials. The IR spectra of compounds **1-5** as well as Hptt ligand are shown in **Fig.6**. Compound **2** with a broad peak at around 3459 cm^{-1} reveals the presence of the stretching vibrations of O-H bonds. In compounds **1-5**, the peak at about 3063 cm^{-1} belongs to the C-H stretching of aromatic rings. The peaks at 2220–2781 cm^{-1} in Hptt ligand and compound **2** are attributed to the S-H stretching, however, the corresponding peaks were absent in the spectra of compounds **1** and **3-5**, indicating that the Hptt ligands are deprotonated. The characteristic peaks at 1497 and 1463 cm^{-1} are assigned as the symmetric stretching of C=C and C=N bonds, and 1320 cm^{-1} characteristic band corresponds to their asymmetric stretching. The peaks appeared at 1100-985 cm^{-1} in Hptt ligand and compounds **1-5** correspond to the typical region for C=S double bonds. The peaks at 760-650 cm^{-1} are attributed to the C-H bending vibration of aromatic rings.

To examine the thermal stability of compounds **1-5**, their thermal behaviors were investigated under nitrogen atmosphere. The thermogravimetric analysis (TGA) revealed that the decomposition temperature of compound **2** (84.3 ^{o}C) is much lower than that of the other compounds due to the water molecules in the supramolecular channels. Compounds **1** and **3** start to decompose at 210 °C, in comparison, compounds **4** and **5** are more stable and the corresponding decomposition temperatures were 255 °C (**Fig. S4**).

3.4. The fluorescence curve of compounds 1, 3 and 5

The solid-state photoluminescence properties of compounds **1, 3, 5** together with 2, 2-bipy and Hptt ligands were investigated at room temperature. The luminescence spectra of compounds

1, **3** and **5**, which are very similar in terms of position and band shape, all exhibit blue light emission with the maximum at 415 nm when excited at 254 nm, similar to that of the Hptt ligand but different from that of 2, 2-bipy. So the emission bands of compound **1**, **3** and **5** are attributed to the intraligand emission state, which may be due to $\pi \longrightarrow \pi^*$ *or* $n\text{-}\pi^*$ transition of the Hptt ligands. Notably, the fluorescence intensity of compound **3** is much higher than the free Hptt ligands, which may be attributed to the co-ligand (2, 2'-bipy) resulting in a more rigid structure.

3.5. The Magnetic properties of compounds 2 and 4

Variable-temperature magnetic susceptibilities for compounds **2** and **4** were measured in the temperature range of 2–300 K under a 1000 Oe applied field. The χ_mT of per Co(II) ion *versus* T curves are shown in **Fig.S5** and **Fig.S6**, the χ_mT values at 300 K for compounds **2** and **4** are 2.13 and 2.28 $cm^3 \cdot K \cdot mol^{-1}$, respectively, which are higher than the spin-only value of 1.875 $cm^3 \cdot K \cdot mol^{-1}$ for Co^{II} ion (Co^{II}, S = 3/2 and g = 2.0), indicating the spin-orbit coupling contribution of high-spin Co^{II}. For compound **2**, the χ_mT curve decreases successively with a decrease in temperature and reach a minimum at 5.97 K (0.40 $cm^3 \cdot K \cdot mol^{-1}$), and then increase to a maximum value (0.44 $cm^3 \cdot K \cdot mol^{-1}$ at 4.93 K). Further cooling, χ_mT values sharply drops at 2 K (0.15 $cm^3 \cdot K \cdot mol^{-1}$). The increase of the χ_mT at low temperatures is probably due to spin-canting behaviors **[39, 40]**. In χ_m^{-1} *versus* T curve, the magnetic susceptibilities data follow the Curie−Weiss law ($\chi_m = C/(T - \theta)$) above 30 K with Curie constant C = 2.44 $cm^3 \cdot K \cdot mol^{-1}$ and the Weiss constant $\theta = -45.38$ K. For compound **4**, the χ_mT values decrease continuously along with the decreasing temperature and reach a minimum of 0.073 $cm^3 \cdot K \cdot mol^{-1}$ at 2 K, and the corresponding Curie and Weiss constants in the range of 50-300K are 2.70 $cm^3 \cdot K \cdot mol^{-1}$ and −45.60 K, respectively. The larger negative value of θ and the decrease of χ_mT indicate strong antiferromagnetic interactions between Co (II) centers in compounds **2** and **4** **[41]**.

4. Conclusion

Five new compounds based on Hptt ligand have been synthesized under solvothermal conditions and fully characterized. Compound **1** is an organic matter generated from *in situ* oxidative coupling reaction of Hptt ligands. Compounds 2 and 3 are both dinuclear compounds in the presence of chelating 2,2'-bipy ligand, interestingly, compounds **4** and **5** are isostructural and both feature one-dimensional (1D) looped chain structures without chelating 2,2'-bipy ligand. The results revealed that the terminally chelating 2,2'-bipy ligand has an important influence on the synthesis and structural diversification of the targeted complexes. Compounds **2** and **4** reveal strong antiferromagnetic interactions between Co centers, however, compounds **1**, **3** and **5** display blue light emission in the solid state. These compounds are promising materials for magnetic and fluorescent applications. The further research for the construction of new coordination compounds based on dptt ligand is underway in our laboratory.

Acknowledgments

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Appendix A. Supplementary material

Table S1, Figure S1-S8 and CCDC numbers 1495558-1495562 for compounds **4, 5, 1, 2, 3** contain the supplementary crystallographic data. 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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Table 1 Crystal data and structure refinement for compounds **1-5**.

Complex	**1**	**2**	**3**	**4**	**5**
Empirical formula	$C_{14}H_{10}N_8S_2$	$C_{48}H_{44}Co_2N_{20}O_4S_4$	$C_{34}H_{26}Cd_2I_2N_{12}S_2$	$C_{14}H_{10}CoN_8S_2$	$C_{14}H_{10}CdN_8S_2$
Formula weight	354.42	1211.13	1145.39	413.35	466.85
Crystal system	triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*P-1*	$P2_1/n$	$P2_1/n$	*C2/c*	*C2/c*
a, Å	7.2986(15)	11.873(2)	8.9617(18)	25.0104(16)	27.746(5)
b, Å	9.3495(19)	13.022(3)	22.559(5)	8.9264(5)	9.1090(18)
c, Å	11.977(2)	18.089(4)	9.7089(19)	7.2366(4)	7.4584(15)
α, deg	80.43(3)	90	90	90.00	90.00
β, deg	89.36(3)	93.35(3)	102.36(3)	96.828(5)	102.88(3)
γ, deg	74.60(3)	90	90	90.00	90.00
Volume ($Å^3$)	776.5(3)	2792.1(10)	1917.3(7)	1604.14(17)	1638.9(6)
Z	2	2	2	4	4
ρ_{calc}/gcm^{-3}	1.516	1.441	1.984	1.712	1.892
Absorption coef./mm^{-1}	0.358	0.806	2.871	1.346	1.603
θ range (^{o})	3.09 to 27.48	3.13 to 25.15	3.34 to 27.48	3.28 to 25.35	3.38 to 27.48
Crystal size (mm^3)	0.45 x 0.37 x 0.27	0.45 x 0.35 x 0.20	0.58 x 0.15 x 0.10	0.35 x 0.25 x 0.20	0.22x 0.18 x 0.18
Reflections collected	7665	20507	18526	2901	7733
Unique reflections (*R*int)	3524 (Rint = 0.0213)	4956 (Rint = 0.0782)	4386 (Rint = 0.0336)	1463 (Rint = 0.0473)	1877 (Rint = 0.0229)
Completeness	98.9%	99.1 %	99.7 %	99.6 %	99.7 %
Goodness-of-fit on F^2	1.051	1.072	1.100	0.948	1.114
R indexes $[I>2\sigma(I)]^{[a]}$	R_1 = 0.0406 wR_2 = 0. 1010	R_1 =0.0655 wR_2 = 0.1902	R_1= 0.0313 wR_2 = 0.0574	R_1= 0.0497 wR_2 = 0.1060	R_1= 0.0230 wR_2 = 0.0565
R (all data)$^{[a]}$	R_1 = 0. 0572 wR_2 = 0. 1136	R_1 =0.0943 wR_2 = 0.2108	R_1= 0.0405 wR_2= 0.0600	R_1= 0.0725 wR_2 = 0.1172	R_1= 0.0249 wR_2= 0.0571

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

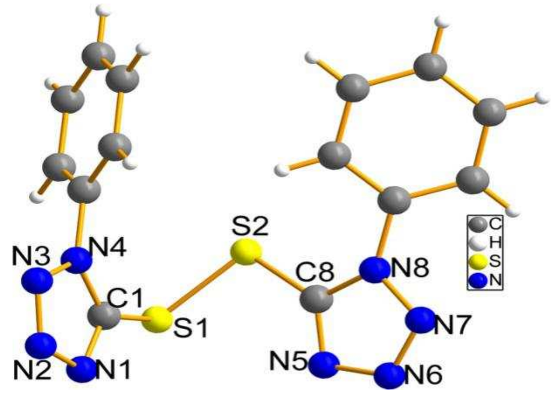

Fig.1 The coordination environment of compound **1**

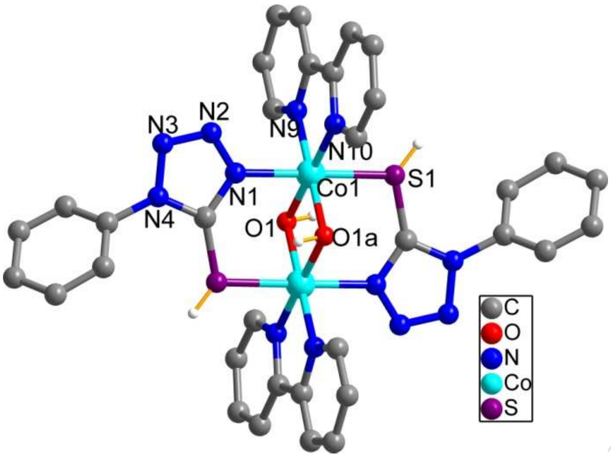

Fig.2 The coordination environment of Co centers in compound **2**

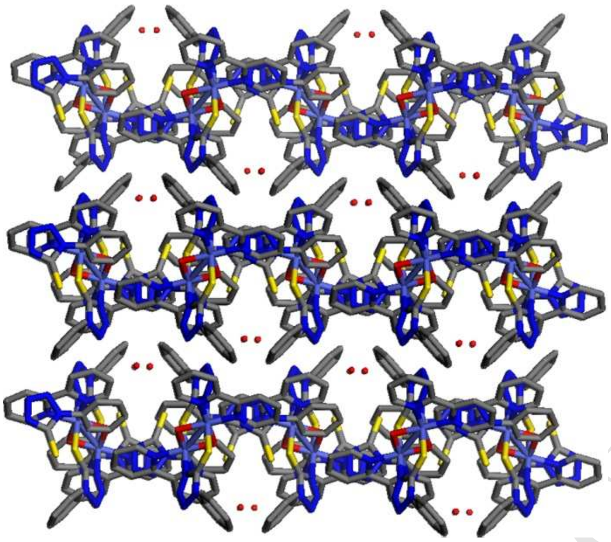

Fig. 3 The 3D supramolecular network of compound **2**

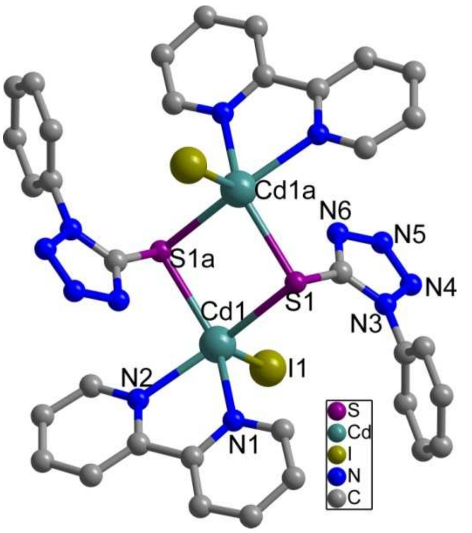

Fig. 4 The coordination environment of Cd in compound **3**

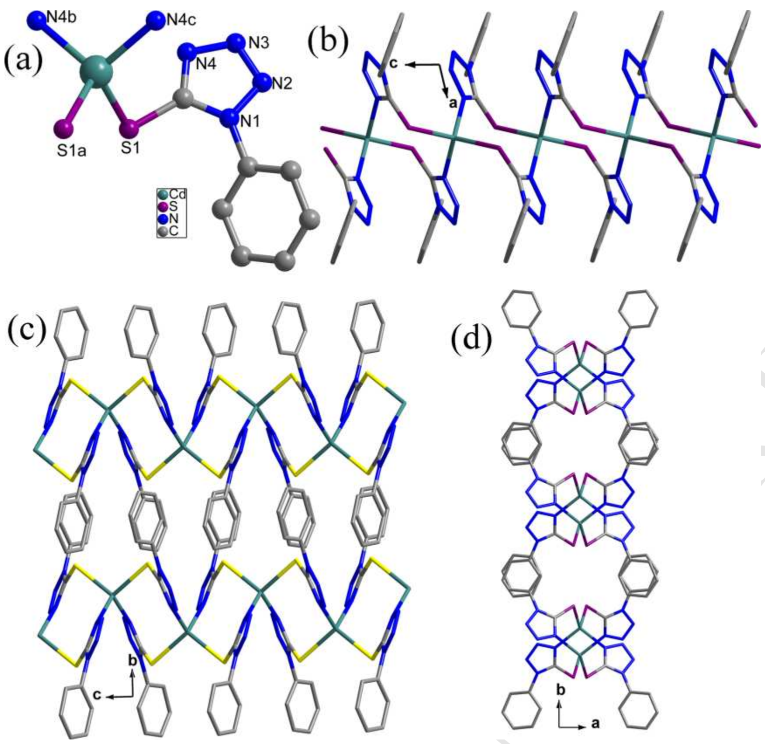

Fig. 5 (a) Coordination environment of Cd, (b) the1D looped chain along the c axis, (c) the 2D supramolecular layer *via* the π-π interactions along the bc plane, (d) the 2D supramolecular layer along the ab plane for **5**.

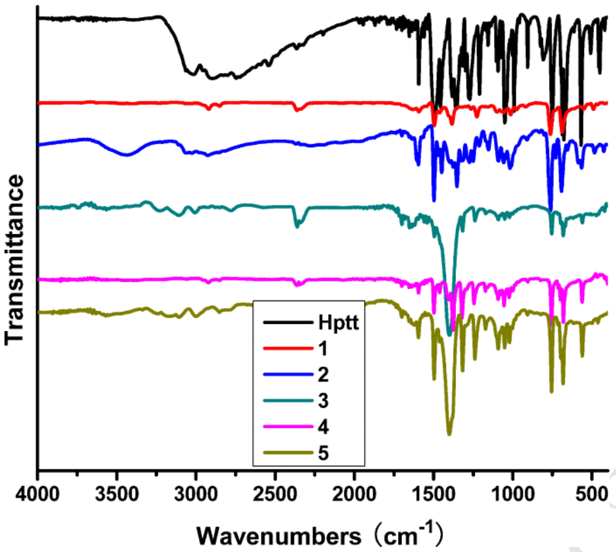

Fig. 6 The IR spectra of compounds **1-5** and Hptt ligand

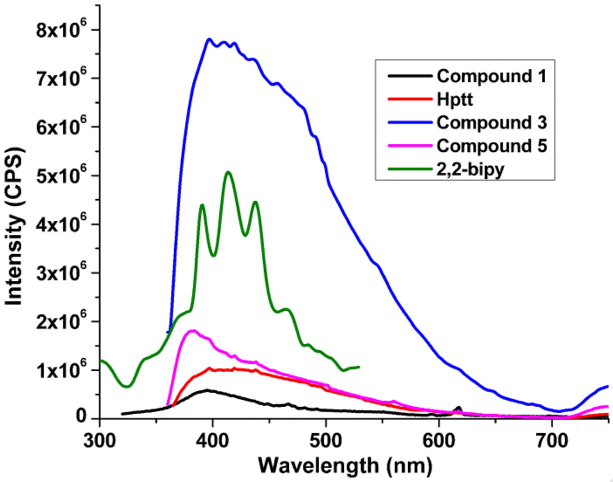

Fig. 7 The fluorescence spectra of compounds **1, 3**, **5** as well as Hptt and 2,2-bipy ligands in solid state at room temperature.

- Five new compounds based on Hptt have been isolated and characterized.
- The magnetic properties of compounds **2** and **4** were described.
- Photoluminescence properties of compounds 1, 3 and 5 have been studied.
- The chelating ligands have an important influence on topology structures.