



Three coordination compounds based on benzene tetracarboxylate ligand: syntheses, structures, thermal behaviors and luminescence properties

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Abstract. Using 1,2,3,5-benzenetetracarboxylic acid and different pyridyl ligands, three metal-organic coordination compounds, $[\text{Co}(\text{H}_3\text{btec})(1,10\text{-phen})(\text{H}_2\text{O})_3][\text{OH}]\cdot 2\text{H}_2\text{O}$ (**1**), $[\text{Co}_2(\text{btec})(2,2'\text{-bipy})_2(\text{H}_2\text{O})]\cdot \text{H}_2\text{O}$ (**2**), $\{[\text{Co}_{1.5}(\text{H}_2\text{btec})(4,4'\text{-bipy})(\text{H}_2\text{O})_2][\text{Co}_{0.5}(4,4'\text{-bipy})-(\text{H}_2\text{O})_4][\text{OH}]_2\} \cdot 2\text{H}_2\text{O}$ (**3**), ($\text{H}_4\text{btec} = 1, 2, 3, 5\text{-benzenetetracarboxylic acid}$, $1,10\text{-phen} = 1,10\text{-phenanthroline}$, $2,2'\text{-bipy} = 2,2'\text{-bipyridine}$, $4,4'\text{-bipy} = 4,4'\text{-bipyridine}$) were synthesized by hydrothermal method and characterized by elemental analysis, infrared spectroscopy, and single-crystal X-ray diffraction analysis. X-ray crystallographic studies reveal that **1** is a discrete 0D coordination compound, while **2** and **3** possess similar 2D network structures, which show a **sql** network with the point symbol of (4,4). Thermal analysis indicates that compounds **1** and **2** begin to collapse after 350°C. Further, the UV-Vis DRS spectra and solid-state luminescent properties of **1–3** have also been studied.

Keywords. Hydrothermal synthesis; multicarboxylate ligand; coordination polymer; luminescence; thermal behavior.

1. Introduction

Owing to the fascinating topological structures and potential application in magnetism, catalysis and luminescence, considerable attention has been focused on the construction of coordination compounds.^{1–5} Many efforts in this field are focused on the rational design and synthesis of functional molecules and materials.^{6–9} Recently, several synthetic strategies have been successfully applied in the construction of functional coordination compounds, including the use of metal-involved building blocks and multi-functional ligands.^{10–12} It is well-known that the multi-topic organic ligands are good candidates as multi-functional ligands to enrich the structural diversity of coordination compounds, from discrete molecules to multidimensional assemblies.^{13–18} Among the numerous multi-topic organic ligands, benzene polycarboxylic acids (BPCAs), have witnessed the most important development of coordination polymers owing to their rich coordination modes.^{19–22} For

example, tritopic 1,3,5-Benzene-tricarboxylic acid^{23–31} (H_3BTC , also known as trimesic acid) and 1,2,4,5-Benzenetetracarboxylic acid^{32–35} (BTEC) with three and four carboxylic groups, respectively, have been widely introduced into the fabrication of numerous coordination compounds with various structures and different properties. However, the use of 1,2,3,5-Benzenetetracarboxylic acid, which also contains four carboxylic acid groups, in the construction of coordination compounds was explored to a lesser extent. In the last one year, we have reported several new coordination compounds based on 1,2,3,5-Benzenetetracarboxylic acid.^{36–38} Compared with N-containing ligands, 4-carboxyl groups from 1,2,3,5-Benzenetetracarboxylic acid can not only coordinate with metal centers *via* the coordination bonds, but also act hydrogen bonding donor and acceptor. In addition, the completely or partially deprotonated multicarboxylate ligands from 1,2,3,5-Benzenetetracarboxylic acid can adopt various coordination modes with metal centers, which will give

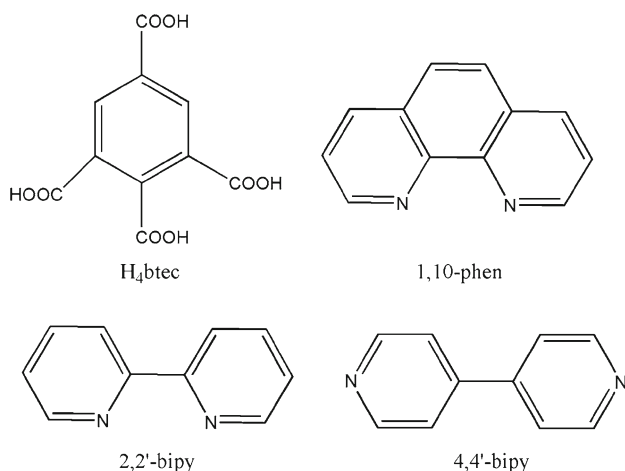
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numerous possibilities to the final structures of coordination compounds.

From the synthetic point of view, several critical factors, such as metal/ligand ratio, solvent polarity, kinds of the organic ligands, and the counter ions, have more influence on the structures and properties of coordination compounds. For example, the participation of different types of ligands during the synthetic process is a useful approach to the structural diversity of coordination compounds. Therefore, the combination of 1,2,3,5-Benzenetetracarboxylic acid (H_4btec) with other kind of ligands may also increase the variety of structures and topologies. In this regard, H_4btec -based coordination compounds possibly possessing distinctive architectures and applicable functions can be achieved by using the N-containing auxiliary ligands, such as 2,2'-bipyridine (2,2'-bipy), 1,10-phenanthroline (1,10-phen), and 4,4'-bipyridine (4,4'-bipy) (Scheme 1).

Herein, we report the hydrothermal synthesis of three coordination compounds based on 1,2,3,5-Benzenetetracarboxylic acid and three different N-containing auxiliary ligands (1,10-phen, 2,2'-bipy, and 4,4'-bipy). All three compounds $[Co(H_3btec)(1,10\text{-phen})(H_2O)_2][OH] \cdot 3H_2O$ (**1**), $[Co_2(btec)(2,2'\text{-bipy})_2(H_2O)] \cdot H_2O$ (**2**), and $\{[Co_{1.5}(H_2btec)(4,4'\text{-bipy})(H_2O)_2][Co_{0.5}(4,4'\text{-bipy})(H_2O)_4][OH]_2\} \cdot 2H_2O$ (**3**) have been characterized by elemental analysis, infrared spectroscopy, and single-crystal X-ray diffraction analysis. X-ray crystallographic studies reveal that **1** is a discrete 0D coordination compound, while **2** and **3** exhibit the 2D network structures with a **sql** topology. Thermogravimetric analysis indicates that the main structures of the compounds **1** and **2** begin to collapse after 350°C. Moreover, the thermal properties, UV-Vis analysis and photoluminescent properties of compounds **1–3** have been studied.



Scheme 1. Structure of H_4btec and bipyridyl ligands.

2. Experimental

2.1 Materials and physical measurements

All the chemicals were commercially available and used without further purification. Elemental analyses for C, H and N were performed with a Perkin Elmer 240C system. Infrared spectra were recorded in the range of 400–4000 cm^{-1} with a Nicolet Nexus 470 spectrometer (Germany) with samples as KBr disks. The powder X-ray study was recorded on a XD-3 diffractometer equipped with a sealed tube $Cu K\alpha$ X-ray radiation (generator power settings: 35 kV and 20 mA) and a DTex Ultra detector using the parallel beam geometry (5° primary and 80° terminated, 3° divergence slit with 10 mm height limit slit). Thermogravimetric analysis (TGA) measurements were carried out with a Perkin Elmer Pyris 1 system under nitrogen purge at a heating rate of $10^\circ C min^{-1}$. Ultraviolet-Visible spectra (UV-Vis) were recorded on a Varian Cary 5000 Spectrophotometer, corrected by $BaSO_4$. The fluorescence measurements were performed on ground powder samples at room temperature using an Edinburgh analytical instrument FLS920.

2.2 Preparation of $[Co(H_3btec)(phen)(H_2O)_3][OH] \cdot 2H_2O$ (**1**)

A mixture of $Co(NO_3)_2 \cdot 6H_2O$ (0.0292 g, 0.1 mmol), H_4btec (0.0127 g, 0.05 mmol), 1,10-phen (0.018 g, 0.1 mmol), H_2O (3 mL) was placed in a 10 mL vial, and the pH value was adjusted to 4.0 by addition of 1 M NaOH solution. The vial was sealed in a Teflon-lined stainless steel vessel, heated at $120^\circ C$ for three days, and then it was gradually cooled to room temperature. The pink plate crystals were obtained in 68% yield. Elemental Anal. Calc. for $C_{22}H_{20}N_2O_{14}Co$ (595.34): C, 44.34; H, 3.36; N, 4.70%; Found: C, 44.18; H, 3.41; N, 4.69%. IR (KBr pellet) ν/cm^{-1} : 3486w, 3248m, 3012w, 1722s, 1595s, 1431s, 1372s, 1205w, 1072w, 937w, 856m, 824s, 780m, 683m, 651w, 624w, 490w, 457w.

2.3 Preparation of $[Co_2(btec)(2,2'\text{-bipy})_2(H_2O)] \cdot H_2O$ (**2**)

The preparation of **2** was similar to that for compound **1**, except that 2,2'-bipy (0.0156 g, 0.1 mmol) was used instead of 1,10-phen and the pH value was adjusted to 5.0. The pink crystals were obtained in 65% yield. Elemental Anal. Calc. for $C_{30}H_{19}N_4O_{10}Co_2$ (713.35): C, 50.47; H, 2.66; N, 7.85%; Found: C, 50.60; H, 2.65; N, 7.83%. IR (KBr pellet) ν/cm^{-1} : 3544w, 2959w, 1629s, 1580s, 1475s, 1426s, 1340s, 1223m, 1081m, 1032m, 1001w, 946m, 872m, 816m, 785m, 743s, 620m, 558w, 527m.

2.4 Preparation of $\{[Co_{1.5}(H_2btec)(4,4'\text{-bipy})(H_2O)_2][Co_{0.5}(4,4'\text{-bipy})(H_2O)_4][OH]_2\} \cdot 2H_2O$ (**3**)

The preparation of **3** was similar to that for compound **1**, except that 4,4'-bipy (0.0156 g, 0.1 mmol) was used instead

Table 1. Crystallographic data for coordination compounds **1–3**.

| Compounds | 1 | 2 | 3 |
|---|---|--|--|
| Formula | C ₂₂ H ₂₀ N ₂ O ₁₄ Co | C ₃₀ H ₁₉ N ₄ O ₁₀ Co ₂ | C ₃₀ H ₂₈ N ₄ O ₁₈ Co ₂ |
| Formula weight | 595.34 | 713.35 | 850.44 |
| <i>T</i> (K) | 293(2) | 293(2) | 293(2) |
| Crystal system | orthogonal | Monoclinic | Monoclinic |
| Space group | <i>Pbca</i> | <i>P2₁/c</i> | <i>C2</i> |
| <i>a</i> (Å) | 24.137(5) | 19.607(4) | 19.477(4) |
| <i>b</i> (Å) | 7.4424(15) | 9.806(2) | 11.397(2) |
| <i>c</i> (Å) | 26.882(5) | 14.521(3) | 15.884(3) |
| α (°) | 90 | 90 | 90 |
| β (°) | 90 | 98.70(3) | 93.10(3) |
| γ (°) | 90 | 90 | 90 |
| <i>V</i> (Å ³) | 4829.0(17) | 2759.8(10) | 3520.8(12) |
| <i>Z</i> | 8 | 4 | 4 |
| <i>D</i> _{calc} (g/cm ³) | 1.61 | 1.714 | 1.566 |
| <i>M</i> (Mo <i>K</i> α) (mm ⁻¹) | 0.789 | 1.273 | 1.026 |
| θ Range (°) | 3.03–25.35 | 3.14–25.35 | 3.26–26.02 |
| <i>F</i> (000) | 2360 | 1440 | 1656 |
| Total reflections | 12746 | 11148 | 14218 |
| Unique reflections | 4374 | 5006 | 6647 |
| <i>R</i> _{int} | 0.0680 | 0.0869 | 0.0503 |
| Goodness of fit | 1.154 | 1.159 | 0.954 |
| <i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)] | 0.0749/0.1389 | 0.0904/0.1445 | 0.0422/0.0650 |
| <i>R</i> ₁ , <i>wR</i> ₂ (all data) | 0.0938/0.1482 | 0.1363/0.1664 | 0.0527/0.0684 |
| $\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e · Å ⁻³) | 0.523/−0.611 | 0.602/−0.514 | 0.409/−0.471 |

of 1,10-phen. The block-like crystals of **3** (54% yield) were obtained intermixed with a few colorless crystals. Elemental Anal. Calc. for C₃₀H₂₈N₄O₁₈Co₂ (850.44): C, 42.33; H, 3.28; N, 6.58%; Found: C, 42.61; H, 3.33; N, 6.55%. IR (KBr pellet) ν /cm⁻¹: 3159m, 2458w, 1714s, 1589m, 1480w, 1405m, 1226s, 1204s, 1072m, 976m, 822m, 805m, 743w, 650m, 569m, 523w.

2.5 Crystal structure determination

Suitable single crystals of compounds **1–3** were carefully selected under an optical microscope and glued to thin glass fibers. The diffraction data were collected on a Siemens SMART CCD diffractometer with graphite-monochromated Mo-*K*α radiation ($\lambda = 0.71073$ Å) at 298 K. An empirical absorption correction was applied using the SADABS program.³⁹ The structures were solved by direct methods and refined by full-matrix least-squares methods on *F*² by using the *SHELX-97* program package.⁴⁰ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of btec phenyl ring and pyridyl ligands were generated geometrically. The crystallography details for the structures determination of compounds **1–3** are presented in Table 1.

3. Results and Discussion

3.1 Synthesis and characterization

Attempts to obtain suitable crystals for X-ray diffraction analysis from the reaction of H₄btec and cobalt(II)

metal salts with N-containing auxiliary ligands under the solvent diffusion method failed due to quick precipitation. It is well known that hydrothermal or solvothermal synthesis can provide an efficient method for the crystallization of coordination compounds,^{10,41–43} and this strategy was adopted for the reaction of H₄btec and cobalt(II) metal salts in water with NaOH as base and pyridyl as auxiliary ligands. Structure difference in compounds **1–3** may be attributed to the different coordination modes of H₄btec ligand as well as different steric hindrance of bipyridyl ligands. Among these compounds, cobalt(II) ions show similar octahedral coordination geometry, while the H₄btec ligands exhibit three different coordination modes. The X-ray powder diffraction (XRPD) has also been applied to check the phase purity of the bulk samples in the solid state. For compounds **1** and **2**, the measured XRD patterns closely matched the simulated patterns, which were generated from the results of single-crystal diffraction data, indicative of pure products (see Figures S1 and S2 in the Supplementary Information). When compared to the simulated patterns based on the single crystal data of compound **3**, the experimental pattern was also in agreement with the calculated diffractogram (see Figure S3 in SI). The powder X-ray diffraction results were in good agreement with the simulated pattern from single X-ray diffraction thus confirm pure phase.

3.2 Crystal structures

3.2a Crystal structure of 1: Compound **1** crystallizes in the orthogonal system with *Pbca* space group. Single-crystal X-ray diffraction analysis reveals that compound **1** consists of one crystallographically unique Co(II) cation, one H_3btec^- anion, one phen ligand, three coordinated water molecules, one OH^- ion and two free water molecules (Figure S4 in SI).: In compound **1**, each Co(II) cation shows a distorted octahedral geometry $[CoN_2O_4]$, which is surrounded by two nitrogen atoms from the chelating 1,10-phen ligand, one carboxylate oxygen atom from H_3btec^- ligand, and three oxygen atoms from coordinated water molecules (Figure 1). The H_4btec ligand here is partly deprotonated, which is in agreement with the IR data in which strong absorption peaks around 1720 cm^{-1} for $-COOH$ are observed. The H_3btec^- ligand bridges one Co^{2+} ion with the μ_1 -coordination mode. The Co–N bond length falls in the range of $2.115(4)$ – $2.127(5)$ Å, while the Co–O

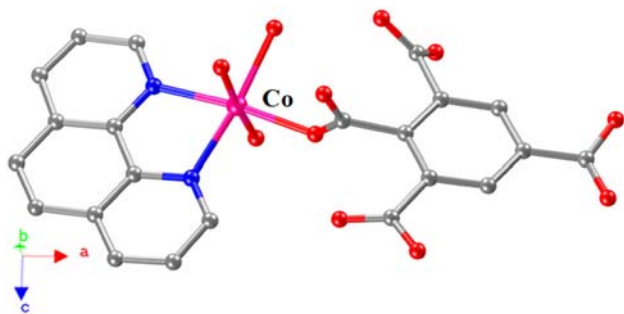


Figure 1. Structure of compound **1** (*b* axis). All hydrogen atoms are omitted for clarity.

bond lengths vary from $2.097(4)$ – $2.127(4)$ Å. The packing structure of compound **1** is displayed in Figure S5 (see Supplementary Information). Moreover, the 0D discrete molecules are further constructed into three-dimensional supramolecular framework via hydrogen bonding interactions (Figure S6 in SI).

3.2b Crystal structure of 2: Single-crystal X-ray structural analysis reveals that compound **2** crystallizes in the monoclinic system with *P2₁/c* space group. The asymmetric unit of **2** consists of two crystallographically independent cobalt(II) ions, one $btec^{4-}$ ligand, two 2,2'-bipy ligands, one coordinated water molecule and one free water molecule (Figure S7 in SI).: As shown in Figure 2, the Co ion in compound **2** adopts a distorted octahedral coordination geometry but has two different coordination environments: Co1 ion is coordinated by two nitrogen atoms from the chelating 2,2'-bipy ligand, four carboxylate oxygen atoms from two different $btec^{4-}$ ligands, while Co2 ion is coordinated by two nitrogen atoms from the chelating 2,2'-bipy ligand, three carboxylate oxygen atoms from two different $btec^{4-}$ ligands and one oxygen atom from coordinated water molecule. H_4btec ligand in compound **2** is fully deprotonated, which is in agreement with the IR data in which no strong absorption peaks around 1720 cm^{-1} for $-COOH$ are observed. Each $btec^{4-}$ ligand bridges seven Co^{2+} ion with the μ_7 -coordination mode. The Co–N bond length is in the range of $2.090(6)$ – $2.124(6)$ Å, while the Co–O bond lengths vary from $2.003(6)$ – $2.260(6)$ Å.

Viewed from Figure 3a, four Co atoms bridged by μ_2 -carboxylate groups from four different $btec^{4-}$ ligands form 4-membered rings. Such rings are then extended to

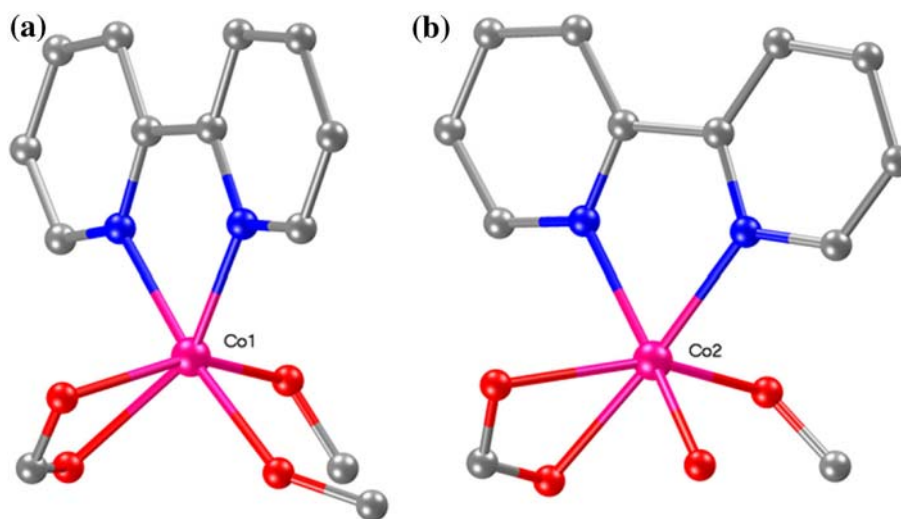


Figure 2. (a) Coordination environment of Co1 ion in compound **2**. (b) Coordination environment of Co2 ion in compound **2**. All hydrogen atoms are omitted for clarity.

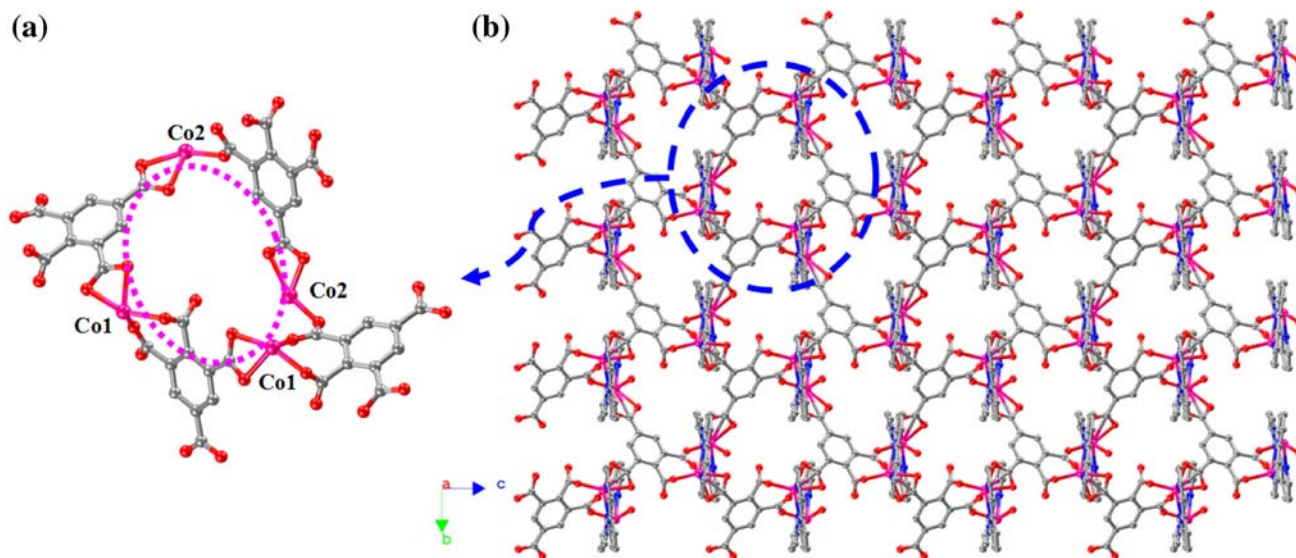


Figure 3. Packing structure of compound **2** (*a* axis). All hydrogen atoms are omitted for clarity.

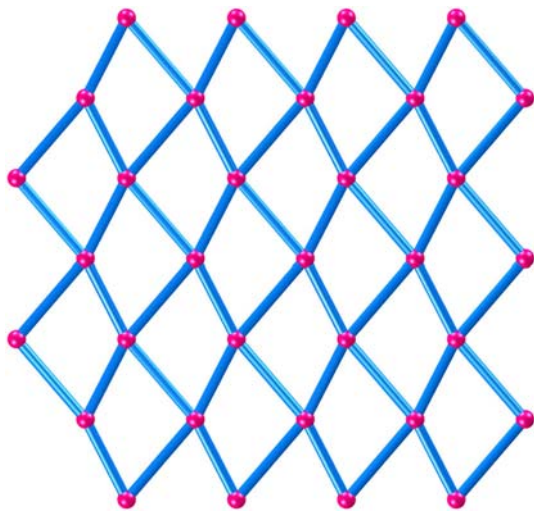


Figure 4. Topological structure of compound **2**.

a 2D network structure through the 4-connected btec^{4-} ligands (Figure 3b). The network analysis based on TOPOS program reveals that compound **2** has a point symbol of (4,4), which indicates a **sql** topology geometry (Figure 4).

3.2c Crystal structure of 3: The crystallographic analysis reveals that compound **3** crystallizes in the monoclinic system with $C2$ space group. The asymmetric unit consists of three crystallographically independent cobalt(II) ions, one $\text{H}_2\text{btec}^{2-}$, two 4,4'-bipy ligands, six coordinated water molecules, two OH^- ions and two free water molecules (Figure S8 in SI).: As in compound **3**, the Co ions have two different coordination environments: Co1 ion shows a distorted octahedral

geometry [CoN_2O_4], which is surrounded by two nitrogen atoms from 4,4'-bipy ligand, four carboxylate oxygen atoms from coordinated water molecules, while Co2 ion is coordinated by two nitrogen atoms from 4,4'-bipy ligand, two carboxylate oxygen atoms from two different $\text{H}_2\text{btec}^{2-}$ ligands and two oxygen atoms from coordinated water molecules. As displayed in Figure 5, the 4,4'-bipy ligand in compound **3** also has two different modes: two pyridine rings in ligand 4,4'-bipy(A) are located in a plane, while another two pyridine rings of 4,4'-bipy(B) have a torsion angle. The Co–N bond length falls in the range of 2.106(5)–2.155(6) Å, while the Co–O bond lengths vary from 2.075(4)–2.184(3) Å.

In compound **3**, Co1 and Co2 ions are bridged by 4,4'-bipy(A) 4,4'-bipy(B) ligands, respectively, to form the one-dimensional Co-bipy chains. These 1D chains are further connected with each other to form a 2D network structure through the μ_2 -bridged $\text{H}_2\text{btec}^{2-}$ ligand (Figure 6). From the topological point of view, each Co atom can be defined as a 4-connected node, while the bridging $\text{H}_2\text{btec}^{2-}$ and 4,4'-bipy ligands can act as the edges. The network analysis reveals that the net of compound **3** also represents a (4, 4)-connected **sql** topology (Figure 7).

3.3 Thermogravimetric analysis

Thermal properties of all three compounds were evaluated by thermogravimetric analysis from 25°C to 800°C under the nitrogen atmosphere with a heating rate of $10^\circ\text{C} \cdot \text{min}^{-1}$. TGA measurements reveal that compound **3** is unstable in N_2 atmosphere with the increase

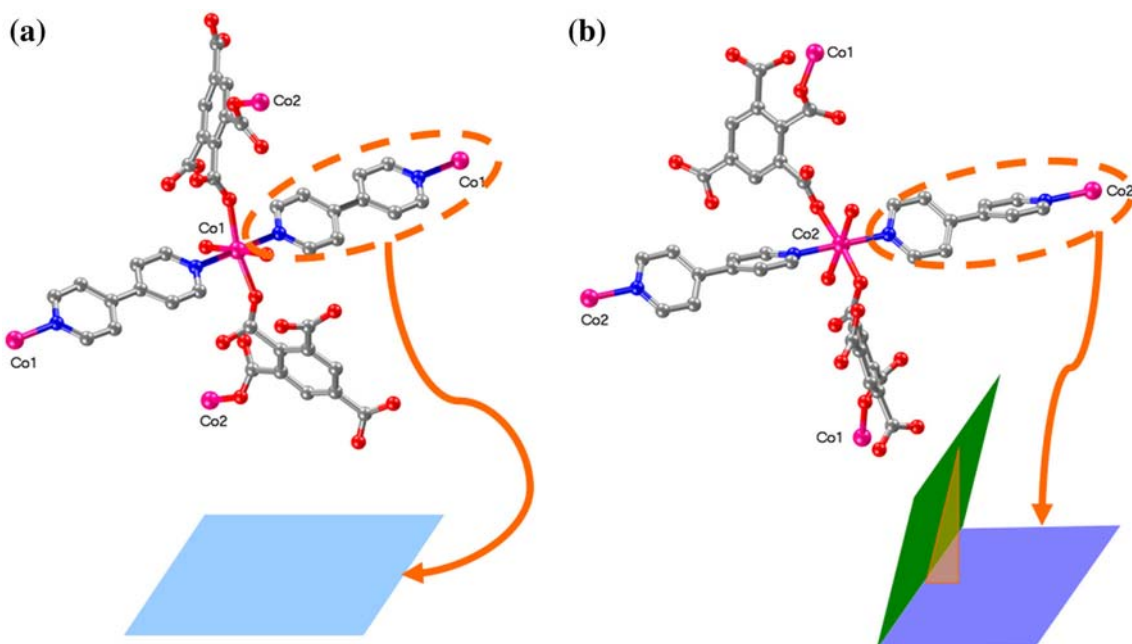


Figure 5. (a) Coordination environment of Co1 ion in compound **3**. (b) Coordination environment of Co2 ion in compound **3**. All hydrogen atoms are omitted for clarity.

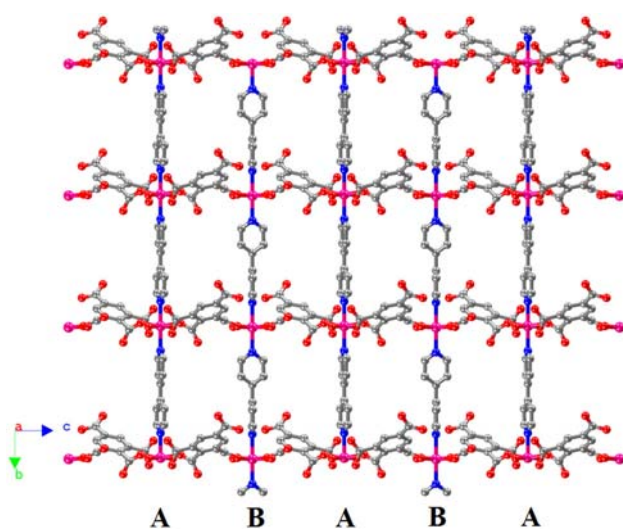


Figure 6. Packing structure of compound **3** (*a* axis).

in temperature. It is worth noting that the structures of compounds **1** and **2** begin to collapse after about 350°C. As shown in the Figure 8, the first weight loss of compound **1** (5.30%) occurs from 50 to 270°C, corresponding to the loss of two water molecules per unit of $[\text{Co}(\text{H}_3\text{btec})(\text{phen})(\text{H}_2\text{O})_2][\text{OH}] \cdot 3\text{H}_2\text{O}$ (calcd.: 6.15%). The second weight loss of 5.91% appears from 270 to 400°C, corresponding to the loss of two water molecules (calcd.: 6.15%). After 400°C, the organic groups start to lose and the structure of compound **1** begins to decompose. As for compound **2**, the first weight loss of 5.20% (calcd.: 5.06%) is observed from

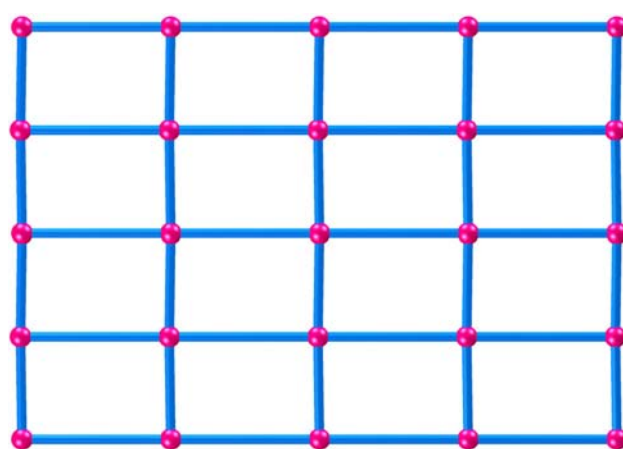


Figure 7. Topological structure of compound **3**.

30 to 295°C, which is in accordance with the loss of two water molecules. As the temperature increases, the 2D network structure of compound **2** begins to collapse after 355°C. The first weight loss of 2.04% for compound **3** is observed from 30 to 175°C, which is corresponding to one water molecule (calcd.: 2.09%). After that, the organic groups start to lose and the structure of compound **3** begins to decompose.

3.4 UV-Vis DRS analysis and photoluminescent properties

The solid state UV-Vis DRS spectra show that the absorption peaks of compounds **1–3** are located at 259,

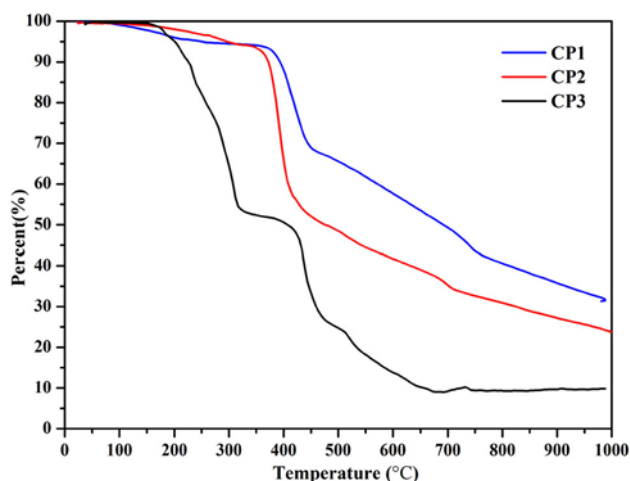


Figure 8. TGA curves of compounds 1–3.

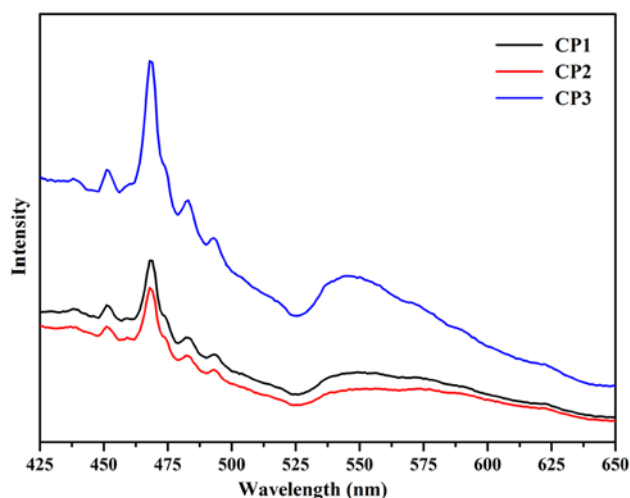


Figure 9. Emission spectra of compounds 1–3. $\lambda_{\text{ex}} = 360$ nm.

287 and 250 nm, respectively (Figure S9 in SI). Besides, there exists a broad absorption peak around 550 nm for compounds 1–3, which is attributed to the transition energy decrease of $\pi - \pi^*$ following the coordination bond formation between Co ion and electron-donating N atom.⁴⁴

Coordination compounds with luminescent properties have attracted much attention due to their potential applications in the areas of chemical sensors and photochemistry.^{4,45,46} Therefore, the luminescent properties of compounds 1–3 were investigated in solid state at room temperature, and the emission spectra are shown in Figure 9. The weak emission of free ligand H_4btec in the energy range of 380–600 nm ($\lambda_{\text{max}} = 394$ nm) upon excitation at 354 nm might be attributed to a $\pi^* - n$ transition in the solid state, similar to those reported for free benzenecarboxylic acids.³⁸ The solid state fluorescence spectra of compounds 1–3 ($\lambda_{\text{ex}} = 360$ nm)

at room temperature show similar properties. As in Figure 9, the fluorescent emission peaks were observed at 459, 468 and 549 nm for 1–3. The maximum emissions occur at 468 nm, which are red-shifted by about 74 nm compared to that of the free H_4btec ligand (394 nm) and may be attributed to a metal-to-ligand charge transfer (MLCT).^{47–49}

4. Conclusions

In summary, three new coordination compounds based on multicarboxylate ligand H_4btec and N-donor auxiliary ligands have been synthesized by hydrothermal method. X-ray crystallographic analysis shows that compound 1 possesses a 0D discrete structure, while compounds 2 and 3 exhibit 2D network structures, which exhibit a **sql** topology with the point symbol of (4,4). Thermal analysis indicates that the main structures of compounds 1 and 2 begin to collapse after 350°C. In addition, the photoluminescent properties of compounds 1–3 were also investigated in the solid state at room temperature.

Supplementary Information (SI)

CCDC 1511552, 1511553, and 1511554 contain the supplementary crystallographic data for the compounds 1–3. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2, 1EZ, UK; Fax: (+44) 1223-336-033, or by e-mail: deposit@ccdc.cam.ac.uk. Crystallographic data for coordination compounds 1–3 (Table S1), ORTEP drawings of compounds 1–3 (Figures S1, S4 and S5), Packing structure of compound 1 (Figure S2), Hydrogen-bonded supramolecular structure of 1 (Figure S3), solid state UV-Vis DRS spectra of compounds 1–3 (Figure S6) and cif/checkcif file are given in Supplementary Information. Supplementary Information is available at www.ias.ac.in/chemsci.

Acknowledgements

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