Emissive lead(II) benzenedicarboxylate metal-organic frameworks

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Abstract. Two known Pb(II) metal-organic frameworks (MOFs), pseudo-supramolecular isomeric pairs synthesized namely, $[\text{Pb}_3(\text{BDC})_3(\text{DMF})_{3.5}]$ (**1**) and $[\text{Pb}(\text{BDC})(\text{H}_2\text{O})]$ (**2**) (where BDC = benzenedicarboxylate) were synthesized and reexamined their structures to determine the topology of the networks. In that **1** displayed a 3D (10,3)-*b* linked network with having the **ths** topology whereas **2** shows a (6,3) 2D layers interconnected to a 3D framework structure. Remarkably, the desolvation of both **1** and **2** cause structural transformation to a known 3D network structure of $[\text{Pb}(\text{BDC})]_n$ (**3**) as established by X-ray powder diffraction patterns. Photoluminescence studies in the solid-state at room temperature of **1–3** compounds exhibit interesting luminescence close to white light region due to ligand-to-metal charge-transfer (LMCT).

Keywords. Metal-organic frameworks (MOFs); lead (II); structural transformation; photoluminescence; white light emission.

1. Introduction

White-light emitting (WLE) materials have generated substantial attention in recent years owing to their application in lightings and displays.¹ Conventionally, white light is created *via* exciting multiphosphors using UV LED,² mixing blue LED with yellow phosphor,³ and blending multi-LED. However, this method may cause problems due to color aging.⁴ Such problems can be solved by developing direct WLE from single-component materials. WLE of single-component material is unusual but identified in polymers,⁵ organic molecules,⁶ ceramics,⁷ hybrid inorganic materials,⁸ and nanomaterials.⁹ Luminescent Metal-organic frameworks (L-MOFs) have been established as emissive solid-state materials which could deliver boundless prospects for constructing single-component WLE.¹⁰ The luminescence can be generated from both organic ligands and metal centers through ligand-metal/metal-ligand charge transfer (LMCT/MLCT).^{11,12} Presently, majority of the investigations are concentrated on

lanthanides L-MOFs¹³ or d-block transition metal L-MOFs.¹⁴

Despite its toxicity, lead(II) compounds have shown promising applications in organic light-emitting diodes, electroluminescence, fluorescent sensors, and photovoltaic conversion.¹⁵ Lead(II) has the capability to express interesting and rare topologies of various framework and structures owing to its flexible coordination geometries (2 to 10) with huge ionic radius (1.20 Å).¹⁶ The outer electronic configuration with 6s² lone pair has stimulated enormous attention in photophysics, photochemistry and coordination chemistry due to their exceptional coordination priority and electronic intrinsic properties.¹⁷ Lead(II) MOFs have also shown interesting photophysical properties like luminescence^{17,18} and birefringence.¹⁹

In this report, we studied two known pseudo-supramolecular isomeric MOFs $[\text{Pb}_3(\text{BDC})_3(\text{DMF})_{3.5}]$ ^{16a} (**1**) and $[\text{Pb}(\text{BDC})(\text{H}_2\text{O})]$ ²⁰ (**2**). Both compounds have been synthesized *via* modified procedure from the reported methods. Compound **1** was synthesized from the reac-

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tion of H_2BDC with $\text{Pb}(\text{NO}_3)_2$ in DMF (DMF = dimethylformamide), while the reaction of H_2BDC with $\text{Pb}(\text{NO}_3)_2$ in DMF/ H_2O afforded **2**. The topological structures of both compounds were studied. **1** forms four Pb(II) hexa-coordinated geometry linked by linear trinuclear cluster and that results in a 3D non-interpenetrated net with (10,3)-*b* linked with having the **ths** topology. However, **2** exhibits hexa-nuclear rings and these rings form a (6,3) connected layers. These layers are linked further through bridging BDC ligands that make 3D non-interpenetrated MOF net with a novel topology. Interestingly, compounds **1** and **2** undergo $3\text{D} \rightarrow 3\text{D}$ structural transformation *via* desolvation to the desolvated form known in the literature,²¹ $[\text{Pb}(\text{BDC})]_n$ (**3**) was confirmed by X-ray powder diffraction analysis. Photoluminescence studies in the solid-state at room temperature exhibit very interesting emission close to the white light region, probably due to the charge-transfer from ligand-to-metal (LMCT).

2. Experimental

2.1 Methods and materials

All the chemicals were purchased from commercial sources and used as received. All solvents used were of reagent grade. The yields of **1–2** are reported with respect to the metal salts. The ^1H NMR spectra were recorded in a Bruker ACF 300 FT-NMR spectrometer with TMS as an internal reference. FT-IR spectra were recorded from KBr pellets (FTS 165 Bio-Rad FT-IR). Thermogravimetric analysis for metal complexes was run on a TA Instrument SDT 2960 TGA Thermal Analyzer. Samples were heated at a constant rate of $5\text{ }^\circ\text{C min}^{-1}$ from room temperature to $600\text{ }^\circ\text{C}$ and the samples held in a continuous flow nitrogen atmosphere. Photoluminescence spectra of the solid samples were recorded on a Horiba Fluorolog-3 spectrometer. All the spectra were recorded with 2 nm spectral slit width.

2.2 Synthesis

2.2a Synthesis of $[\text{Pb}_3(\text{BDC})_3(\text{DMF})_{3.5}](\text{I})$: A mixture of $\text{Pb}(\text{NO}_3)_2$ (0.05 mmol, 0.017 g) and H_2BDC (0.05 mmol, 0.008 g) in 1.5 mL DMF was heated in a sealed vial at $115\text{ }^\circ\text{C}$. Colorless rod-like crystals were formed after two days, decanted and air dried. [Yield: 19.1 mg, 84%] Elemental analysis: Calculated for $\text{Pb}_3\text{C}_{34.5}\text{N}_{3.5}\text{O}_{15.5}\text{H}_{36.5}$ (1369.69): C, 30.0; H, 2.7; N, 3.6%. Found: C, 29.59; H, 2.34; N, 3.2%. IR ν/cm^{-1} : 1645s, 1546s, 1374s, 1103m, 832m, 746m, 521m. Thermal gravimetric analysis (DMF weight loss%) Calculated 18.6% Found 17.7%.

2.2b Synthesis of $[\text{Pb}(\text{BDC})(\text{H}_2\text{O})](\text{2})$: A mixture of $\text{Pb}(\text{NO}_3)_2$ (0.05 mmol, 0.017 g) and H_2BDC (0.05 mmol,

0.008 g) in 2 mL DMF/ H_2O (3:1) was heated in a sealed vial at $85\text{ }^\circ\text{C}$. Colorless block-like crystals were formed after two days, decanted and air dried. [Yield: 14.5 mg, 75%] Elemental analysis: Calculated for $\text{PbC}_8\text{O}_5\text{H}_6$ (389.33): C, 24.68; H, 1.55%. Found: C, 24.91; H, 1.59%. IR ν/cm^{-1} : 1636w, 1528s, 1358s, 1012m, 816m, 746m, 517m. Thermal gravimetric analysis (H_2O weight loss %) Calculated 4.6%; Found 4.2%.

3. Results and Discussion

3.1 Synthesis

Pb(II) MOFs **1–2** have been synthesized using the modified procedure reported previously.^{16a,20} Both compounds were isolated from the solvothermal method in different reaction conditions. The difference in the temperature and water addition in the solvothermal conditions generated **1** and **2** with two different connectivities between Pb(II) and BDC ligands in the three-dimensional structure. Apart from these two forms, a third form without any solvent, $[\text{Pb}(\text{BDC})]_n$ (**3**) had been reported in 2009.²¹ The influence of water on the crystallization conditions certainly altered the final topology of the structures.²²

3.2 Crystal structures of compounds **1** & **2**

Although Batten and co-workers reported the crystal structure of **1** in 2007, the detailed crystal description was not given.^{16a} The single crystal X-ray diffraction studies reveal that **1** crystallizes in monoclinic system with $C2/c$ space group. The asymmetric units contain one unit of $[\text{Pb}_3(\text{BDC})_3(\text{DMF})_{3.5}]$. There are three crystallographically independent Pb(II) atoms (Figure 1). All the Pb(II) centers display highly-distorted *hemi-directed* six-coordinate geometry. The distorted Pb(II) environment is caused by the stereochemically active lone pair. Of the six pairs of carboxylate oxygen atoms in the asymmetric unit, two pairs (O1 & O2; O11 & O12) are exclusively chelating and the O4, O5, O8 and O9 oxygen atoms in the rest of the carboxylate ligands are involved in both chelation and bridging (μ_2 - η^1 : $\eta^{1,2}$) mode. Pb1 has seven-coordinate geometry with two chelating carboxylates, two DMF molecules and a bridging oxygen atom, O8. The O4 atom also bridges the nearby Pb3 atom. Pb3 has six-coordinate geometry with two chelating carboxylates, one DMF molecule and a bridging oxygen atom. The Pb...Pb are separated by 4.366 Å. The two six-coordinate Pb3 atoms are bridged by an O9 oxygen atom, in addition to two chelating carboxylate oxygen atoms and one DMF molecule

Figure 1. Coordination environment around Pb(II) atoms and connectivity of **1**.

around them. This connectivity generates roughly a two-dimensional sheet structure. These sheets are further mended through Pb2-O4-Pb3 bonds to produce three-dimensional architecture. The overall structure is made up of (10,3)-*b* network with **ths** topology as shown in Figure 2. The topology analysis of the network was conducted using TOPOS²³ by considering the Pb1 and carbon atom of the carboxylate anions as the point of extension or nodes in the structure. The connectivity of these nodes forms shortest circuits comprising of ten nodes, where each node is inter-connected to three other nodal units. Several porous MOFs have been reported with (10,3) network topologies.^{24,25} The most symmetrical of these is the cubic (10,3)-*a* net or **srs** net.^{22b} Other (10,3) nets include (10,3)-*b* (**ths**), (10,3)-*c* (**bto**), (10,3)-*d* (**utp**) nets. The most common (10,3)-*a* and (10,3)-*b* and others are less common. Compound **1** has (10,3)-*b* connected net with **ths** topology. This net is characterized by crosslinked zig-zag chains formed from the Pb(II) centers which acts as the 3-connected nodes. Large cavities were found to be present in **1** after removal of occluded and coordinated solvent. The total effective void volume occupied by coordinated DMF molecules is 42.2% per unit cell as calculated using PLATON.²⁶

Compound **2** crystallizes in monoclinic space group $P2_1/c$ as reported earlier.²⁰ There is a slight change in the crystallographic parameters especially along *c*-axis, probably due to coordinated water, from the reported dehydrated form, $[\text{Pb}(\text{BDC})]_n$ which crystallized in

Figure 2. (a) Perspective view of the 3D structure of **1**. (b) Perspective view of the (10,3) network topology in **1**.

Figure 3. (a) Connectivity and coordination environment at Pb(II) in **2**. (b) A portion of the three-dimensional structure in **2**.

orthorhombic space group *Pbca*.²¹ The asymmetric unit in **2** contains one formula unit of [Pb(BDC)(H₂O)]. The coordination environment of Pb1 as shown in the Figure 3a has highly-distorted *hemi-directed* seven-coordinate geometry. Pb1 is coordinated to five oxygen atoms from BDC ligands and two oxygen atoms from the coordinated water molecules. Of the two carboxylate groups, one with O4 and O5 atoms has $\mu_2 - \eta^1 : \eta^{1,2}$ bonding mode while in the second carboxylate group, O2 was bridging two Pb(II). The coordination geometry at Pb(II) can be described as highly distorted capped pentagonal pyramid with stereochemically active lone pair probably opposite to O4 atom. Very interestingly,

a pair of adjacent BDC ligands oriented in parallel is bridging two Pb(II) as shown in Figure 3b. The BDC ligand is planar (best plane rms, 0.0867 Å). The strain is relieved by slightly slip stacked such that the C6 atom is closer to the centroid of the other BDC ring by 3.327 Å. The aqua ligand is bridging the adjacent Pb(II) atoms forming a zigzag PbO chain roughly along *b*-axis. The adjacent chains are cross-linked to each other and form a 2D layer like with (6,3) topology (Figure 4a). Infinite (6,3) sheets are further connected by BDC ligands to form 3D non-interpenetrated framework as shown in Figure 4b. Calculation using PLATON²⁶ shows that there is no effective void volume in **2** unlike in **1**.

Figure 4. (a) A fragment of Pb(II) hexanuclear rings in **2** which subsequently form the honeycomb 2D (6,3) connected topology. (b) Perspective view of the packing structure of compound **2**.

3.3 Structural transformation via desolvation

The single crystal structure of the $[\text{Pb}(\text{BDC})]_n$ (**3**) also has been reported in the literature.²¹ Hence, it prompted us to investigate the desolvation of **1** and **2** to find out whether they are converted to form **3**. The thermogravimetric studies show that all the coordinated DMF molecules were lost from **1**, in the temperature zone 150–250 °C (Weight loss observed, 17.7% and calculated, 18.7%) while the aqua ligand was lost in the temperature region 115–150 °C (Weight loss observed, 4.2% and calculated, 4.6%) for **2** (Figure S8 in Supplementary Information). Since both solids were thermally stable after the solvent loss until *ca* 380 °C, the PXRD patterns were recorded after heating both the solids at 350 °C for 2 h. A comparison of the PXRD patterns of these desolvated solids with the simulated PXRD patterns of the known compound revealed that desolvated **1** has probably transformed to **3** whereas dehydrated **2** is completely converted to **3** (Figure S6 and S7 in Supplementary Information). This

is not a single-crystal-to-single-crystal conversion and has been termed as crystal-to-crystal transformation. Crystal-to-crystal transformation in the solid-state has been observed before.²⁷

3.4 Photoluminescence studies

Due to their potential applications in photochemistry, chemical sensors, and electroluminescent displays, L-MOFs are quite attractive for the development of WLE materials. For this reason, the solid-state photoluminescence property of **1** and **2** was investigated. Solid-state luminescence emission under UV light for **1–3** are shown in Figure 5. It is known that metal-free BDC ligand showed emission at 375 nm, which can be attributed to $\pi \rightarrow \pi^*$ transition.²⁸ Contrarily, compound **1** exhibits emission maximum at 512 nm upon excitation at 332 nm as shown in Figure 6. The emission peak of **1** is red-shifted by about 130 nm compared to that of ligand probably due to the coordination of the ligand with Pb(II). Compound **2** exhibits emission maximum located at 526 nm upon excitation at 329 nm as shown in Figure 6. The emission peak of **2** is red-shifted by about 150 nm compared to that of the ligand. Compound

Figure 5. Photographs show the emission of powder samples of (a) **1** (b) **2** and (c) **3**, under UV light.

Figure 6. Solid-state luminescent emission spectra of compound **1–3** ($\lambda_{\text{ex}} = 332$ nm, $\lambda_{\text{ex}} = 329$ nm and $\lambda_{\text{ex}} = 320$ nm for **1**, **2** and **3**, respectively) at room temperature.

Figure 7. The CIE chromaticity diagram for **1–3** ($\lambda_{\text{ex}} = 332$ nm, $\lambda_{\text{ex}} = 329$ nm and $\lambda_{\text{ex}} = 320$ nm for **1**, **2** and **3**, respectively).

3 exhibits emission maximum located at 511 nm upon excitation at 320 nm as shown in Figure 6. The emission peak of **3** is red-shifted by about 136 nm compared to that of the ligand. The difference in the PL obtained for **3** compared to **1–2** is attributed to the removal of solvent molecules. Particularly, the peak obtained at around 545 nm in **3** is probably due to vibrational structure. The emissions of the compounds **1–3** are attributed to the ligand-to-metal charge transfer (LMCT) between the delocalized π -bond of carboxylate groups and p orbitals of Pb(II) centers.²⁹ The color of the emission has been quantified with the Commission Internationale de l'Eclairage (CIE) chromaticity diagram in Figure 7. The chromaticity coordinates for **1** is (0.25, 0.42) when irradiated by 332 nm light. The coordinates for **2** is (0.21, 0.44) when irradiated by 329 nm light and the coordinates for **3** is (0.24, 0.38) when irradiated by 329 nm light. These are located in the gamut, both falling close to the white gamut of the CIE-1931 color space chromaticity diagram.³⁰ The compound **3** shows emission which is very close to the white light region as shown in the chromaticity diagram.

4. Conclusions

Two pseudo-supramolecular isomers pairs were isolated from Pb(II) ion and the BDC ligand by varying the experimental conditions. Compound **1** exhibits a non-interpenetrated 3D network with (10,3)-*b* linked with having the **ths** topology. However, compound **2** shows a (6,3) network in which 2D layers are subsequently interconnected through the ligands to

form a non-interpenetrated network topology. Interestingly, compound **1** and **2** undergo 3D→3D structural transformation *via* desolvation to a solvent-less form, [Pb(BDC)]_n (**3**) as confirmed by consecutive thermal and X-ray powder pattern analysis. It is important to monitor such structural transformation using powder diffraction patterns in the case of disintegration of single crystal. Solid-state emission of **1–3** was recorded at room temperature. Interestingly, all the compounds display single-component close to white light emission due to ligand-to-metal charge-transfer (LMCT). These studies also open up more opportunities to attain better perception of the fundamental aspects that effect crystal structural transformation and help develop better single-component WLE materials.

Supplementary Information (SI)

Supplementary information associated with this article including X-ray crystallographic analysis, TGA of **1–2**, X-ray powder pattern of **1–3**, FT-IR, emission spectra of **1–3**, excitation spectra of **1–2** are available at www.ias.ac.in/chemsci.

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References

- (a) Waltereit P, Brandt O, Trampert A, Grahn H T, Meninger J, Ramsteiner M, Reiche M and Ploog K H 2000 Nitride semiconductors free of electrostatic fields for efficient white light-emitting diodes *Nature* **406** 865; (b) Jang E, Jun S, Jang H, Lim J, Kim B and Kim Y 2010 White-light-emitting diodes with quantum dot color converters for display backlights *Adv. Mater.* **22** 3076; (c) Li G, Fleetham T and Li J 2014 Efficient and stable white organic light-emitting diodes employing a single emitter *Adv. Mater.* **26** 2931
- Gong X, Wang S, Moses D, Bazan G C and Heeger A J 2005 Multilayer Polymer Light-Emitting Diodes: White-Light Emission with High Efficiency *Adv. Mater.* **17** 2053
- Fan C and Yang C 2014 Yellow/orange emissive heavy-metal complexes as phosphors in monochromatic and white organic light-emitting devices *Chem. Soc. Rev.* **43** 6439
- Yan B P, Cheung C C C, Kui S C F, Xiang H F, Roy V A L, Xu S J and Che C M 2007 Efficient White Organic Light-Emitting Devices Based on Phosphorescent Platinum(II)/Fluorescent Dual-Emitting Layers *Adv. Mater.* **19** 3599
- Wu H B, Zhou G J, Zou J H, Ho C L, Wong W Y, Yang W, Peng J B and Cao Y 2009 Efficient Polymer White-Light-Emitting Devices for Solid-State Lighting *Adv. Mater.* **21** 4181

6. (a) Yang Q Y and Lehn J M 2014 Bright White-Light Emission from a Single Organic Compound in the Solid State *Angew. Chem. Int. Edit.* **53** 4572; (b) Jin X H, Chen C, Ren C X, Cai L X and Zhang J 2014 Bright white-light emission from a novel donor–acceptor organic molecule in the solid state *via* intermolecular charge transfer *Chem. Commun.* **50** 15878
7. Zhang R, Lin H, Yu Y L, Chen D Q, Xu J and Wang Y S 2014 A new-generation color converter for high-power white LED: transparent Ce³⁺:YAG phosphor-in-glass *Laser Photonics Rev.* **8** 158
8. (a) Dohner E R, Hoke E T and Karunadasa H I 2014 Self-Assembly of Broadband White-Light Emitters *J. Am. Chem. Soc.* **136** 1718; (b) Dohner E R, Jaffe A, Bradshaw L R and Karunadasa H I 2014 Intrinsic White-Light Emission from Layered Hybrid Perovskites *J. Am. Chem. Soc.* **136** 13154
9. Kim J H, Ko Y H, Cho J H, Gong S H, Ko S M and Cho Y H 2014 Toward highly radiative white light emitting nanostructures: a new approach to dislocation-eliminated GaN/InGaN core–shell nanostructures with a negligible polarization field *Nanoscale* **26** 14213
10. (a) Heine J and Muller-Buschbaum K 2013 Engineering metal-based luminescence in coordination polymers and metal–organic frameworks *Chem. Soc. Rev.* **42** 9232; (b) Allendorf M D, Bauer C A, Bhakta R K and Houk R J T 2009 Luminescent metal–organic frameworks *Chem. Soc. Rev.* **38** 1330; (c) Haider G, Usman M, Chen T-P, Perumal P, Lu K-L, Chen Y-F 2016 Electrically Driven White Light Emission from Intrinsic Metal–Organic Framework *ACS Nano* **10** 8366; (d) Wu Z-F, Tan B, Deng Z-H, Xie Z-L, Fu J-J, Shen N-N, Huang X-Y 2016 Dual-Emission Luminescence of Magnesium Coordination Polymers Based on Mixed Organic Ligands *Chem. Eur. J.* **22** 1334
11. (a) Chen J, Zhang Q, Zheng F K, Liu Z F, Wang S H, Wu A Q and Guo G C 2015 Intense photo- and tribo-luminescence of three tetrahedral manganese(II) dihalides with chelating bidentate phosphine oxide ligand *Dalton Trans.* **44** 3289; (b) Han Y H, Tian C B, Li Q H, Du S W 2014 Highly chemical and thermally stable luminescent Eu_xTb_{1-x} MOF materials for broad-range pH and temperature sensors *J. Mater. Chem. C* **2** 8065
12. Wei Z, Gu Z Y, Arvapally R K, Chen Y P, McDougald R N, Ivy J F, Yakovenko A A, Feng D M, Omary A and Zhou H C 2014 Rigidifying Fluorescent Linkers by Metal–Organic Framework Formation for Fluorescence Blue Shift and Quantum Yield Enhancement *J. Am. Chem. Soc.* **136** 8269
13. (a) Gao X, Chang S, Liu H and Liu Z 2016 A Promising White-Light-Emitting Material Constructed from Encapsulating Eu³⁺/Tb³⁺ Hybrid Ions into a Robust Microporous Metal–Organic Framework *Eur. J. Inorg. Chem.* **2837**; (b) Li Y-F, Wang D, Liao Z, Kang Y, Ding W-H, Zheng X-J, Jin L-P 2016 Luminescence tuning of the Dy–Zn metal–organic framework and its application in the detection of Fe(III) ions *Mater. J. Chem. C* **4** 4211; (c) Wang X, Yan P, Li Y, An G, Yao X and Li G 2017 Highly Efficient White-Light Emission and UV–Visible/NIR Luminescence Sensing of Lanthanide Metal–Organic Frameworks *Cryst. Growth Des.* **17** 2178; (d) Xu B, Cheng Y, Hu H-M, Bai C, Wang X, Yang M-L, Xue G 2016 Syntheses, crystal structures and luminescence properties of lanthanide-based coordination polymers constructed from a functionalized terpyridyl carboxylate ligand *CrystEngComm* **18** 4613; (e) Yang Y, Chen L, Jiang F, Yu M, Wan X, Zhang B and Hong M 2017 A family of doped lanthanide metal–organic frameworks for wide-range temperature sensing and tunable white light emission *J. Mater. Chem. C* **5** 1981; (f) Zhao Y W, Zhang F-Q, Zhang X-M 2016 Single Component Lanthanide Hybrids Based on Metal–Organic Framework for Near-Ultraviolet White Light LED *ACS Appl. Mater. Interfaces* **8** 24123
14. (a) Wang S H, Zheng F K, Zhang M J, Liu Z F, Chen J, Xiao, Y, Wu A Q, Guo G C and Huang J S 2013 Homochiral zinc(II) coordination compounds based on in-situ-generated chiral amino acid-tetrazole ligands: circular dichroism, excitation light-induced tunable photoluminescence, and energetic performance *Inorg. Chem.* **52** 10096; (b) Wu M F, Liu Z F, Wang S H, Chen J, Xu G, Zheng F K, Guo G C and Huang J S 2011 Structures and photoluminescence of zinc(II) coordination polymers based on *in situ* generated 1*H*-tetrazolate-5-propionic acid ligands *CrystEngComm* **13** 6386; (c) Wu M F, Zheng F K, Wu A Q, Li Y, Wang M S, Zhou W W, Chen F, Guo G C and Huang J S 2010 Hydrothermal syntheses, crystal structures and luminescent properties of zinc(II) coordination polymers constructed by bifunctional tetrazolate-5-carboxylate ligands *CrystEngComm* **12** 260; (d) Xie W, Qin J-S, He W-W, Shao K-Z, Su Z-M, Du D-Y, Li S-L and Lan Y-Q 2017 Encapsulation of an iridium complex in a metal–organic framework to give a composite with efficient white light emission *Inorg. Chem. Front.* **4** 547; (e) Hua C A, Su-Ci M, Kai Z, Cong W C, Wei Z, Jian W A and Jun Q 2017 A New Copper(I) Complex Based on 4-amino-3,5-bis(3-pyridyl)-1,2,4-triazole: Synthesis, Crystal Structure, Theoretical Study, Thermal Behavior and Luminescence *J. Chem. Sci.* **129** 185; (f) Ali F, Nayak P K, Periasamy N and Agarwal N 2017 Synthesis, photophysical, electrochemical and electroluminescence studies of red emitting phosphorescent Ir(III) heteroleptic complexes *J. Chem. Sci.* **129** 1391
15. (a) Vogler A and Nikol H 1992 Photochemistry and photophysics of coordination compounds of the main group metals *Pure Appl. Chem.* **64** 1311; (b) Strasser A and Vogler A 2004 Intraligand phosphorescence of lead(II) β -diketonates under ambient conditions *J. Photochem. Photobiol. A* **165** 115; (c) Roy S, Choubey S, Khan K, Mitra P and Ghosh B K Syntheses, molecular and crystalline architectures, and luminescence behaviour of terephthalate bridged heptacoordinated dinuclear lead(II) complexes containing a pentadentate N-donor Schiff base *J. Chem. Sci.* **125** 715
16. (a) Yang J, Ma J F, Liu Y Y, Ma J C and Batten S R 2007 Organic-Acid Effect on the Structures of a Series of Lead(II) Complexes *Inorg. Chem.* **46** 6542; (b) Fan S R and Zhu L G 2007 Influence of the Reaction Conditions on the Self-assembly of Lead(II) 5-Sulfosalicylate Coordination Polymers with Chelating Amine Ligands *Inorg. Chem.* **46** 6785; (c) Zhao Y H, Xu H B, Fu Y M, Shao K Z, Yang S Y, Su Z M, Hao X R, Zhu D X and Wang E B 2008 A Series of Lead(II)-Organic Frameworks Based

- on Pyridyl Carboxylate Acid N-Oxide Derivatives: Syntheses, Structures, and Luminescent Properties *Cryst. Growth Des.* **8** 3566; (d) Yang J, Ma J F, Liu Y Y, Ma J C and Batten S R 2009 A Series of Lead(II) Complexes with $\pi - \pi$ Stackings: Structural Diversities by Varying the Ligands *Cryst. Growth Des.* **9** 1894; (e) Yang J, Li G D, Cao J J, Yue Q, Li G H and Chen J S 2007 Structural Variation from 1D to 3D: Effects of Ligands and Solvents on the Construction of Lead(II)-Organic Coordination Polymers *Chem. Eur. J.* **13** 3248; (f) Wardana F Y, Ng S-W and Wibowo A C 2015 The Lead Coordination Polymers Containing Pyrazine-2,3-Dicarboxylic Acid: Rapid Structural Transformations and Cation Exchange *Cryst. Growth Des.* **15** 5930
17. (a) Deo S H and Godwin A J A 2000 Selective, Ratiometric Fluorescent Sensor for Pb^{2+} *J. Am. Chem. Soc.* **122** 174; (b) Li L, Zhang S, Han L, Sun Z, Luo J and Hong M 2013 A Non-Centrosymmetric Dual-Emissive Metal-Organic Framework with Distinct Nonlinear Optical and Tunable Photoluminescence Properties *Cryst. Growth Des.* **13** 106; (c) Sahu J, Ahmed M and Bharadwaj P K 2013 Structural Diversity and Luminescence Properties of Coordination Polymers Built With a Rigid Linear Dicarboxylate and Zn(II)/Pb(II) Ion *Cryst. Growth Des.* **13** 2618; (d) Huang K-L, Liu X, Li J-K, Ding Y-W, Chen X, Zhang M-X, Xu X-B and Song X-J 2010 Three-Dimensional Metal(II)-Organic Coordination Polymers from Binuclear, Trinuclear, and Polynuclear Clusters Bridged by *p*-Benzenediacrylates: Syntheses, Topologies, Photosensitive Properties, and Hydrogen Uptake *Cryst. Growth Des.* **10** 1508
 18. (a) Zhao Y-H, Xu H-B, Fu Y-M, Shao K-Z, Yang S-Y, Su Z-M, Hao X-R, Zhu D-X and Wang E-B 2008 A Series of Lead(II)-Organic Frameworks Based on Pyridyl Carboxylate Acid N-Oxide Derivatives: Syntheses, Structures, and Luminescent Properties *Cryst. Growth Des.* **8** 3566; (b) Zhao Y-H, Xu H-B, Shao K-Z, Xing Y, Su Z-M and Ma J-F 2007 Syntheses, Characterization, and Luminescent Properties of Three 3D Lead-Organic Frameworks with 1D Channels *Cryst. Growth Des.* **7** 513; (c) Li L, Zhang S, Han L, Sun Z, Luo J and Hong M A 2013 Non-Centrosymmetric Dual-Emissive Metal-Organic Framework with Distinct Nonlinear Optical and Tunable Photoluminescence Properties *Cryst. Growth Des.* **13** 106
 19. (a) Katz M J, Kaluarachi H, Batchelor R J, Bokov A A, Ye Z-G and Leznoff D B 2007 Highly birefringent materials designed using coordination polymer synthetic methodology *Angew. Chem. Int. Edit.* **46** 8804; (b) Katz M J, Aguiar P M, Batchelor R J, Bokov A A, Ye Z-G, Kroeker S and Leznoff D B 2006 Structure and Multinuclear Solid-State NMR of a Highly Birefringent Lead-Gold Cyanide Coordination Polymer *J. Am. Chem. Soc.* **128** 3669
 20. Dale S H, Elsegood M R J and Kainth S 2004 Poly[lead(II)- μ_2 -aqua- μ_4 -terephthalato] *Acta Cryst.* **C60** m76
 21. Zhang P L, Yong H X, Chun G W, Jing L, Xiao Q Z, Mao F G and Shu Y N 2009 A New Coordination Polymer $[Pb(1,4-BDC)]_n$ Containing a Unique μ_6 -Bridging Coordination Mode *Z. Anorg. Allg. Chem.* 1650
 22. (a) Moulton B and Zaworotko M J 2001 From Molecules to Crystal Engineering: Supramolecular Isomerism and Polymorphism in Network Solids *Chem. Rev.* **101** 1629; (b) Batten S R 2001 Topology of interpenetration *CrystEngComm* **3** 67; (c) Biradha K, Sarkar M and Rajput L 2006 Crystal engineering of coordination polymers using 4, 4'-bipyridine as a bond between transition metal atoms *Chem. Commun.* 4169; (d) Nangia A 2010 Supramolecular chemistry and crystal engineering *J. Chem. Sci.* **122** 295
 23. Blatov V A 2006 Multipurpose crystallochemical analysis with the program package TOPOS *IUCr CompComm Newsletter* **7** 4
 24. Batten S R and Robson R 1998 Interpenetrating Nets: Ordered, Periodic Entanglement *Angew. Chem. Int. Edit.* **37** 1461
 25. (a) Ke Y, Collins D J, Sun D and Zhou H-C 2006 (10,3)-a Noninterpenetrated Network Built from a Piedfort Ligand and Pair *Inorg. Chem.* **45** 1897; (b) Kepert C J, Prior T J and Rosseinsky M J A Versatile Family of Interconvertible Microporous Chiral Molecular Frameworks: The First Example of Ligand Control of Network Chirality *J. Am. Chem. Soc.* **2000** 5158; (c) Abrahams B F, Batten S R, Hamit H, Hoskins B F and Robson R A 1996 Wellsian 'three-dimensional' racemate: eight interpenetrating, enantiomorphic (10,3)-a nets, four right- and four left-handed *Chem. Commun.* 1313; (d) Bradshaw D, Claridge J B, Cussen E J, Prior T J and Rosseinsky M J 2005 Design, Chirality, and Flexibility in Nanoporous Molecule-Based Materials *Acc. Chem. Res.* **38** 273; (e) Ma S, Fillinger J A, Ambrogio M W, Zuo J-L and Zhou H-C 2007 Synthesis and Characterizations of a Magnesium Metal-Organic Framework with the (10,3)-a Net Topology *Inorg. Chem. Commun.* **10** 220
 26. Spek A L 2003 PLATON A multipurpose Crystallographic Tool, Utrecht, The Netherlands
 27. (a) Vittal J J 2007 Supramolecular structural transformations involving coordination polymers in the solid-state *Coord. Chem. Rev.* **251** 178; (b) Kuroda R, Higashiguchi K, Hasebe S and Imai Y 2004 Crystal to crystal transformation in the solid state *CrystEngComm* **6** 464
 28. Zheng L-Y, Li K, Zhao S, Liu L, Li B-L and Wu B 2016 Syntheses, structures and properties of eight coordination polymers based on bis(imidazole) and bis-carboxylate ligands *Polyhedron* **104** 1
 29. Santra A and Bharadwaj P K 2014 Solvent-Induced Structural Diversity of Partially Fluorinated, Stable Pb(II) Metal-Organic Frameworks and Their Luminescence Properties *Cryst. Growth Des.* **14** 1476
 30. (a) See http://en.wikipedia.org/wiki/CIE_1931_color_space for more details (accessed on: 20 September, 2017); (b) Silver J and Withnall R 2008 In *Luminescent Materials* A Kitai (Ed.) (Chicester: John Wiley & Sons) p. 75