

CrystEngComm

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



COMMUNICATION

pH-Dependent supramolecular self-assemblies of copper(II) (fluorene-9,9-diyl)dipropionic acid complexes[†]

Fu Feng,^{a,b} Nan-Nan Song,^b Wei-Bing Hu,^b Hai-Yang Tu,^a Xiang-Gao Meng^{*a} and Ai-Dong Zhang^{*a}Received 00th January 2015,
Accepted 00th January 2015

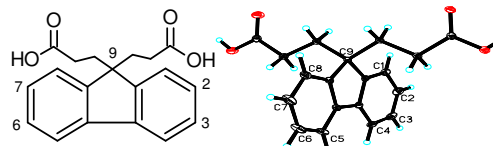
DOI: 10.1039/x0xx00000x

www.rsc.org/

Four cupric complexes 1-4 with a newly designed ligand (fluorene-9,9-diyl)dipropionic acid were obtained under different pH conditions. These complexes exhibit pH-dependent supramolecular self-assembly morphologies as 0D, 1D and 2D architectures, among which 1D water channels are formed by triple winding helical chain with opposite chiral configurations in 3.

In the past decade, metal–organic frameworks (MOFs) have attracted great interest due to their potential applications in gas storage, magnetism, catalysis, sensing and drug delivery.¹ It is well known that the specific function and/or property of a MOF material is definitively determined by its intriguing micro-structure.² The assembly of functional compounds into various MOF structures are significantly dependent upon the reaction conditions, such as the pH medium,³ temperature,⁴ solvent,⁵ pressure⁶ and geometric requirements of metal centers and ligands, among which organic ligands play an important role through their versatile coordination modes.⁷ Aliphatic and semi-rigid carboxylic ligands, serving as a type of flexible bridge-linker favorable for constructing novel structures, have been widely used in building MOFs.⁸ Fluorene derivatives, as a notable class of fluorescent molecules, have been often used in the synthesis of luminescent materials due to their larger delocalized π system.⁹ With aim to construct functional compounds based fluorene derivatives, the chemical decorations at the 1-, 2- or 2,7- site of fluorene ring have been reported recently.^{9a,10} However, fluorene MOFs are sparsely reported and the structure diversity is only restricted to the fluorene derivatives with carboxyl group directly attached to aromatic ring. In this context, a new functional fluorene derivative decorated at the 9-site with two propanoxyl groups, namely (fluorene-9,9-diyl)dipropionic acid (H_2L) (Scheme 1), is designed and its complexation with cupric ion under

different conditions and the resultant MOF morphologies are investigated in the present work. The choice of the ligand H_2L mainly rests with the considerations that the ligand may provide the following merits in complexation with metal ion: 1) flexibility of the propanoic moiety; 2) opposite extending direction of the two carboxyl groups; 3) side chain stacking effect due to the existence of the large π conjugated fluorene ring. On the basis of these merits bestowed to the ligand H_2L , it is expected to discover intriguing MOF structures and unique chemical and physical properties.



Scheme 1 Schematic illustration (left) and molecular structure (right) of the ligand (fluorene-9,9-diyl)dipropionic acid (H_2L).

The reaction of the ligand H_2L with cupric ion was performed in a similar reactive medium but with different pH ranging from 4.0 to 8.0 (Comment S1) and four Cu(II) complexes, namely, $[Cu_2(HL)_4(Py)_4] \cdot 2H_2O$ (1), $[Cu(L)(H_2O)_2]_n \cdot 2nH_2O \cdot nEtOH$ (2), $[Cu(L)(Py)_3]_n \cdot 3.23nH_2O$ (3), $[Cu(L)(Py)]_{2n} \cdot nPy$ (4) were obtained. All the complexes were characterized by X-ray diffraction (Comment S2, S3 and Table S1), and the results indicate that these complexes form distinctly different MOF morphologies under different pH in which discrete dinuclear (0D) Cu(II) complex (1), 2D coordination layer polymer (2), 1D helical chain in (3) and 1D straight chain in (4), respectively, were able to be clearly assigned.

Complex 1, obtained in a reaction medium at pH 4.0, exhibits a neutral dinuclear copper(II) unit with four pendent arms from four HL^- anion penetrating into different directions. Its asymmetric unit contains one Cu(II) ion, two mono-deprotonated HL^- anions, two coordinated pyridine molecules and one free H_2O molecule (Fig. 1a). The Cu(II) center adopts a slightly distorted square-pyramidal geometry ($\tau=0.038$)¹¹ with a basal plane defined by a $\{N_2O_2\}$ donor

^aKey Laboratory of Pesticide and Chemical Biology, Ministry of Education, and School of Chemistry, Central China Normal University, Wuhan 430079, China. E-mail: mengxianggao@mail.ccnu.edu.cn; adzhang@mail.ccnu.edu.cn.

^bCollege of Chemistry and Environmental Engineering, Hubei Institute for Nationalities, Enshi, Hubei 445000, China.

[†] Electronic Supplementary Information (ESI) available: CCDC 1414834–1414838. For crystallographic data of H_2L and 1–4 in CIF format and other supporting electronic materials, See DOI: 10.1039/x0xx00000x.

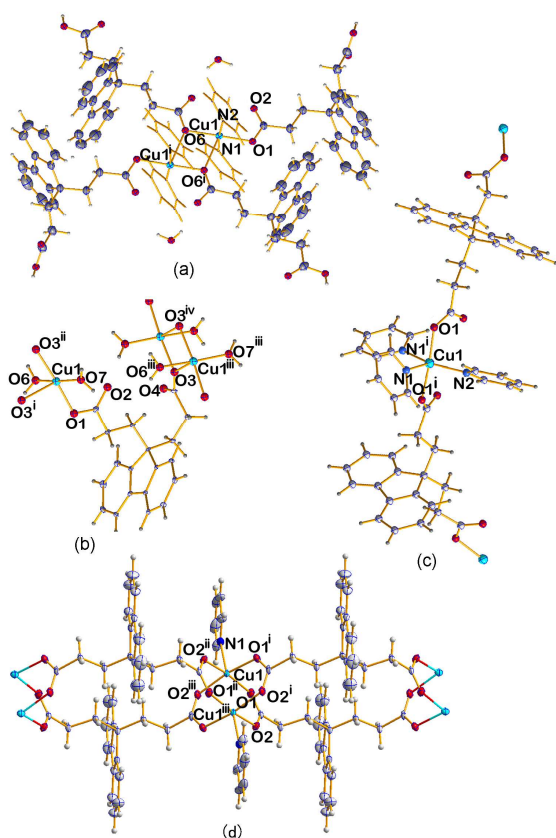


Fig. 1 The molecular structures of complexes 1-4 showing the coordination environments around the Cu(II) center, (a) for 1, (b) for 2, (c) for 3 and (d) for 4, respectively. Symmetry codes: For 1, $i = 1-x, 1-y, 1-z$; For 2, $i = 0.5-x, 0.5+y, z$; $ii = 0.5+x, 0.5-y, z$; $iii = 0.5-x, y-0.5, z$; $iv = -x, -y, -z$; For 3, $i = 1/2-x, y, -z$; For 4, $i = x, 1-y, z$; $ii = 2-x, 1-y, -z$; $iii = 2-x, y, -z$.

set and the axial position is occupied by the η^2 -O6 atom. The Cu-O_{axial} bond is longer by about 0.4 Å than those Cu-N/O_{basal} bonds (Table S2). The cis- and trans- angles around Cu(II) center range from 76.17(3)° to 177.74(3)°. In the dinuclear unit, the Cu...Cu distance of 3.478(2) Å is comparable to some analogs.¹² In the crystal packing, the dinuclear Cu(II) unit and water molecules are linked into a 2D H-bonded layer by four O-H...O hydrogen bonds (Fig. S1 and Table S3). Firstly, two of these four mono-deprotonated propionate groups in (1) at (x, y, z) are hydrogen-bonded, via O3 atom, to two neighbour HL⁻ ligands at (1+x, y, z) and (-x, 1-y, -z) with O2 atom as acceptors, forming a linear chain along the [011] direction ($d_{O3...O2} = 2.604(3)$ Å) (Fig. S2). Then, the rest two HL⁻ anions, via carboxylic O8 atom, are hydrogen-bonded to the water O9 atom which is anchored to the [011] chain by a combination of O9...O4/O5 hydrogen bonds, resulting in the entire 2D H-bonded layer structure parallel to the [11-1] plane. It is worth mentioning that four types of hydrogen-bonding ring motifs are observed in the 2D H-bonded layers, i.e. $R_2^2(20)$, $R_3^3(14)$, $R_4^4(24)$ and $R_4^4(44)$ ¹³ (Fig. S3). When the neutral dinuclear Cu(II) unit and water molecules are regarded as 8-connected and 3-connected nodes, respectively, the

2D H-bonded layer can be topologically simplified into a 2-nodal 3,8-connected network with a Schläfli symbol of $(3.4^2)_2.(3^4.4^6.5^6.6^8.7^3.8)^{14}$ (Fig. S4). Finally, these adjacent 2D H-bonded layers are linked into a 3D network by weak intermolecular $\pi\cdots\pi$ interactions between pyridine ring and fluorene ring ($d_{\pi\cdots\pi} = 3.957(2)$ Å).

Contrasted to the 0D morphology of complex 1, compound 2 is assembled into a 2D coordination polymer in the orthorhombic *Pbca* space group at pH 5.5. H₂L ligand is di-protonated with the asymmetric unit consisting of one Cu(II) cation, one L²⁻ anion, two coordinated water, two free water and one ethanol molecules (Fig. 1b). The Cu(II) center adopts a distorted square-pyramidal coordination polyhedron constructed from a {O₅} donor set ($\tau = 0.07$). The basal plane consists of each two oxygen atoms of two L²⁻ anions and two water oxygen atoms. The Cu-O_{axial} bond (2.352(4) Å) is longer by ca. 0.37 Å than the mean Cu-O_{basal} bond (1.986(6) Å) due to a steric requirement. The O-Cu-O angles range from 76.44(14)° to 175.95(17)°. As for the L²⁻ ligand, it adopts a seriously bended μ_3 -bridging mode, shaping into a 2D layer polymer in which each L²⁻ anion is coordinated to three Cu(II) center and vice versa. The Cu...Cu distance of 3.439(2) Å is bridged by μ_2 -O3 atom. In the crystal packing, there are extensive hydrogen bonds further consolidating the 2D layer structure (Table S3). Adjacent layers are only interacted by rather weak C-H... π interactions. In a separated 2D layer, if both L²⁻ and Cu(II) have been regarded as three-connected nodes, the 2D layer can be rationally simplified into a Shubnikov plane net with a Schläfli symbol $(4.8^2)^{13}$ (Fig. S5 and S6).

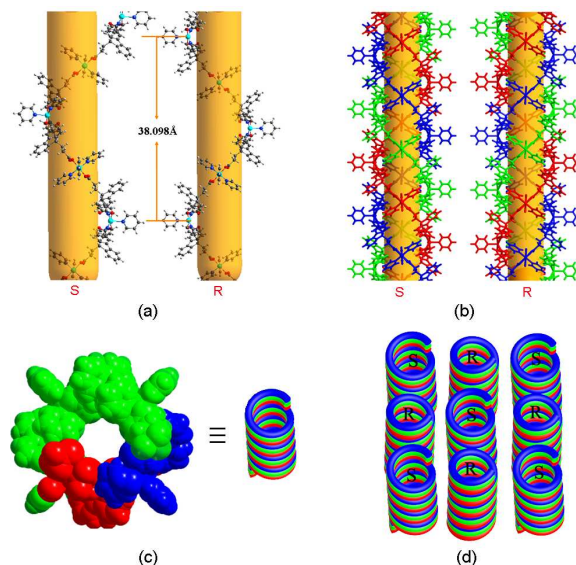


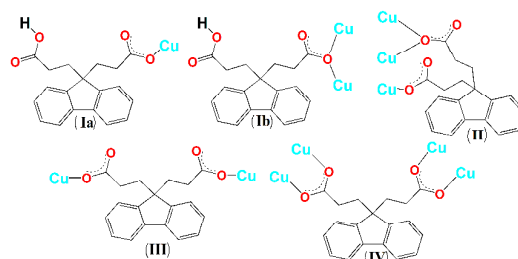
Fig. 2 (a) Each a single-helical chain winding in S and R chiral configurations with a pitch of 38.098 Å; (b) Side views of winded triple-chain helices with the left-handed helix denoted as S and the right-handed helix as R. (c) Space filling mode of the triple-chain helix showing the formation of the 1D water channel; (d) Schematic representation of the spatial arrangements of the triple-chain helices.

With the reaction environment being near to the neutral condition (pH 6.5), compound 3 was obtained which has 1D helical morphology with some fascinating structural features. The crystal exhibits high-symmetric tetragonal $I4_1/acd$ space group with the asymmetric unit consisting of half a Cu(II) cation, half one of deprotonated L^{2-} dianion, one and a half coordinated pyridine molecules (Fig. 1c). The Cu(II) ion is coordinated by two oxygen atoms from two separate L^{2-} anions and three pyridine nitrogen atoms, furnishing a distorted square-pyramidal polyhedron ($\tau=0.34$). In the assembly of compound 3, the L^{2-} ligand adopts a μ_2 -bridging mode which is distinctly different from that of both 1 and 2. By using a four-fold axial symmetry, the helical chain runs along the crystallographic c axis with a larger helical pitch of 38.098 Å (Fig. 2a). It is interesting that three such 1D helix polymeric chains wind each other around one same 4-fold axis, leading to the formation of a triple helix column (Fig. 2b) in which a water channel is formed (Fig. 2c). In each column, the three 1D polymers have the same type of chirality. However, its adjacent column consists of triple helices of the opposite chirality, which lead to the loss of the chirality of the whole assembly system of compound 3 (Fig. 2d and Fig. S7). To the best of our knowledge, this is the first example that water channels are composed of such chirality-opposite triple-helix structures in a supramolecular system.

When the pH was further adjusted to 8.0, a 1D linear chain polymer (4) was obtained, which has a crystal structure in the monoclinic space group $C2/m$. In 4, its asymmetric unit contains half a Cu(II) ions, half a L^{2-} anions, half a coordinated pyridine and one-fourth free pyridine (Fig. 1d). The building block is based on a $\{Cu_2(OOC)_4\}$ "paddlewheel" unit. Cu(II) center adopts a square pyramid polyhedron ($\tau=0$) by a $\{O_4N\}$ donor set. The basal plane consists of two pairs of carboxylate O1/O2 atoms and the apical site is occupied by pyridine N1 with Cu(II) lying above away from the basal plane by only 0.204 Å. The Cu1-N1 (2.141(4) Å) is ca. 0.17 Å longer than the mean Cu1-O1/O2 bonds (1.974(4) Å). In comparison with 1-3, L^{2-} anion in 4 is coordinated in a μ_4 -bridge mode, shaping into a nearly four-Cu(II) rectangle arrangement with Cu...Cu side lengths of 2.6267(4) and 11.062(4) Å, leading to the formation of 1D [100] chain polymer (Fig. S8). These adjacent 1D chains are further joined together by weak π - π packing interaction between pyridines, forming the 2D supramolecular structure ($d_{\pi\cdots\pi}=3.455(3)$ Å and 3.811(3) Å).

From the results mentioned above, it can be concluded that pH value plays a crucial role for the self-assembly of complexes 1-4. With the pH variation from 4.0 for 1, 5.5 for 2, 6.5 for 3, to 8.0 for 4, the coordination mode and conformation of ligand H_2L (Scheme 2) are greatly affected. At the weaker acidic condition for the formation of 1-3, H_2L can be mono- and di- deprotonated and each carboxylate group is prone to adopting the μ_1 - or μ_2 -bridge mode using only one oxygen atom. However, the μ_2 -bridge in 4 is accomplished by two carboxylic oxygen atoms. The conformations of the aliphatic chains of H_2L are also apparently affected by the pH medium, as reflected by the diverse torsion angles of propionate

group in the morphologies of 1-4 (Table S4). For instance, the two pairs of propionate groups protrude into two trans-directions in 1, giving an extended spatial arrangement. On the contrary, these two propionate groups in 2 point to the cis-directions, resulting in a distinct 2D coordination polymer. In one word, the moderately acidic medium facilitates the formation of the discrete Cu(II) compound 1; The weakly acidic and basic environment is in favor of the self-assembly of the coordination polymers 2-4. When the pH exceeded 9.0, only some amorphous cyan solid powders were obtained which are not suitable for X-ray determination.



Scheme 2 The different coordination modes of carboxyl group in the complexes 1-4, (Ia), (Ib) for 1, (II) for 2, (III) for 3 and (IV) for 4, respectively.

In order to check the phase purity of complexes 1-4, their powder X-ray diffraction patterns (PXRD) were recorded at room temperature. As shown in Fig. S9–12, the diffraction peaks of both experimental and simulated patterns match well in key positions, demonstrating the phase purities of complexes 1-4.

Given that complex 3 possesses a highly-opened framework, gas adsorption measurement for N_2 was carried out over the thermally activated sample. N_2 gas adsorption measurement at 77 K revealed that complex 3 is capable to possess permanent pores (Fig. S13) and exhibits a type I isotherm. The calculated surface areas as estimated from the first step adsorption by applying Brunauer-Emmett-Teller (BET) and Langmuir methods are $238.4 \text{ m}^2 \text{ g}^{-1}$ and $312.5 \text{ m}^2 \text{ g}^{-1}$, respectively. The pore volume $0.032 \text{ cm}^3 \text{ g}^{-1}$ estimated from the desorption curve is smaller than the free volume $0.113 \text{ cm}^3 \text{ g}^{-1}$ (1827.4 Å^3 /per unit cell) estimated by using PLATON.¹⁵ The difference is probably due to the incomplete removal of guest molecules or structural deformation during the thermal activation prior to N_2 adsorption measurement, which is often observed in coordination polymers.¹⁶

Thermal analyses for compounds 1–4 were performed from room temperature to 1000°C under a N_2 atmosphere (Fig. S14). For 1, it showed a two-step weight loss over the whole temperature range. The first weight loss of 2.25% between 50 and 100°C is assigned to the release of guest water (*calcd.* 2.11%). The second weight loss of 87.19% is observed in a narrow temperature range 150 – 350°C , corresponding to the decomposition of organic ligands (*calcd.* 88.58%). For 2, it underwent a three-step degradation process with the first weight loss of 9.82% between 40 – 80°C , which is attributed to the loss of one guest ethanol per formula unit (*calcd.*

9.39%). The second weight loss of 14.35% was observed in 85–120 °C, corresponding to the release of water (calcd 14.69%). The third weight loss of 66.17% in the temperature range 150–1000 °C corresponds to releasing L^{2-} (calcd 66.58%). Compound 3 gave a steady weight loss of 9.21% from 80 to 120 °C, which should be attributed to the release of guest molecules in the 1D water channels (calcd 8.72%, based on $[Cu(L)(Py)_3]_n \cdot 3.23nH_2O$). Then, a successive step with weight loss of 78.25% in the temperature range 180–1000 °C corresponds to the elimination of coordinated pyridine and L^{2-} ligand (calcd 79.16%). Compound 4 began to lose the free pyridine from 80 to 130 °C. The coordinated pyridine and L^{2-} ligands were gradually lost at temperature from 180 till 550 °C, the observed weight loss of 83.01% is in agreement with the expected value of 83.69%.

It is known that fluorene-containing complexes have good optical properties and high luminescent efficiencies.^{9b,17} Thus the solid-state photoluminescent properties of 1–4 were investigated and the results are shown in Fig. 3. It can be easily found that all these emissions of compounds 1–4 are quenched due to the metal coordination. However, some differences exist between them because of their different supramolecular assembly. For instance, complex 1 has an emission at 435 nm (λ_{ex} = 316 nm), while 2, 3 and 4 display a stronger emission at 438 nm (λ_{ex} = 321 nm), 441 nm (λ_{ex} = 325 nm), 443 nm (λ_{ex} = 327 nm), respectively. The free H_2L ligand has a stronger emission at 429 nm (λ_{ex} = 311 nm). In contrast to the free H_2L , the photoluminescences at longer wavelength in complexes 1–4 can be attributed to the π – π^* electron transfer in the H_2L ligand (LLCT), resulting in red-shifts by 6 nm, 9 nm, 12 nm and 14 nm, respectively.^{9a}

In summary, a series of Cu(II) complexes based on the ligand (fluorene-9,9-diyl)dipropionic acid have been obtained via controlling the reaction medium pH from 4.0 to 8.0 during the synthesis. Due to the flexibility of the aliphatic chains and the π – π ability of the fluorene ring, these four complexes exhibit distinctly different morphologies as discrete (0D), 1D, and 2D coordination self-assemblies. Analyses of the thermal stability and fluorescence spectra give a clue of developing new sensing materials by using these fluorescent complexes.

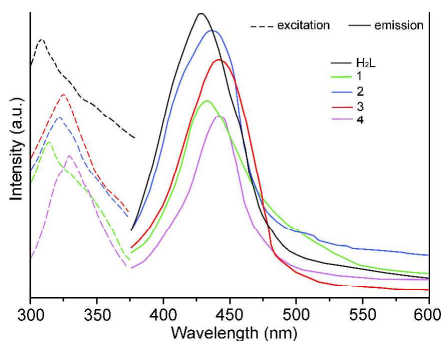


Fig. 3 Solid-state excitation and emission spectra for complexes 1–4 and the powder free H_2L ligand.

Acknowledgement

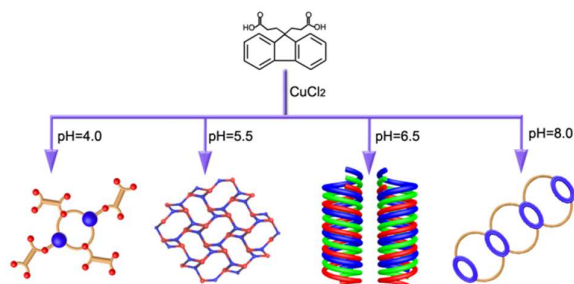
We gratefully acknowledge the financial support by the National Natural Science Foundation of China (21172087 and 21461008), Open Foundation of Key Laboratory of Biologic Resources Protection and Utilization of Hubei Province, Forestry Key Discipline (PKLHB1303 and PKLHB1509).

References

- (a) A. H. Chughtai, N. Ahmad, H. A. Younus, A. Laypkov and F. Verpoort, *Chem. Soc. Rev.*, 2015, 10.1039/C4CS00395K; (b) P. Falcaro, R. Ricco, C. M. Doherty, K. Liang, A. J. Hill and M. J. Styles, *Chem. Soc. Rev.*, 2014, **43**, 5513; (c) R. Lee, J. A. K. Howard, M. R. Probert and J. W. Steed, *Chem. Soc. Rev.*, 2014, **43**, 4300; (d) O. Shekhah, J. Liu, R. A. Fischer and C. Woll, *Chem. Soc. Rev.*, 2011, **40**, 1081.
- H. Deng, C. J. Doonan, H. Furukawa; R. B. Ferreira, J. Towne, C. B. Knobler, B. Wang and O. M. Yaghi, *Science*, 2010, **327**, 846.
- (a) T. Li, X. J. Hong, X. Liu, R. Chen, Q. G. Zhan, X. Xu and Y. P. Cai, *CrystEngComm*, 2014, **16**, 3883; (b) S. R. Choudhury, A. D. Jana, C. Y. Chen, A. Dutta, E. Colacio, H. M. Lee, G. Mostafa and S. Mukhopadhyay, *CrystEngComm*, 2008, **10**, 1358.
- C. M. Liu, S. Gao, D. Q. Zhang and D. B. Zhu, *Cryst. Growth Des.*, 2007, **7**, 1312.
- (a) P. Pachfule, R. Das, P. Poddar and R. Banerjee, *Cryst. Growth Des.*, 2011, **11**, 1215; (b) Y. Peng, G. Li, J. Hua, Z. Shi and S. Feng, *CrystEngComm*, 2015, **17**, 3162.
- (a) K. J. Gagnon, C. M. Beavers and A. Clearfield, *J. Am. Chem. Soc.*, 2013, **135**, 1252; (b) E. C. Spencer, R. J. Angel, N. L. Ross, B. E. Hanson and J. A. K. Howard, *J. Am. Chem. Soc.*, 2009, **131**, 4022.
- H. Wu, H. Y. Liu, Y. Y. Liu, J. Yang, B. Liu and J. F. Ma, *Chem. Commun.*, 2011, **47**, 1818.
- (a) T. Ma, M. X. Li, Z. X. Wang, J. C. Zhang, M. Shao and X. He, *Cryst. Growth Des.*, 2014, **14**, 4155; (b) Q. Yue, L. Yan, J. Y. Zhang and E. Q. Gao, *Inorg. Chem.*, 2010, **49**, 8647.
- (a) S. Su, C. Qin, Z. Guo, H. Guo, S. Song, R. Deng, F. Cao, S. Wang, G. Li and H. Zhang, *CrystEngComm*, 2011, **13**, 2935; (b) Y. Li, Z. Wang, X. Li, G. Xie, D. Chen, Y. F. Wang, C. C. Lo, A. Lien, J. Peng, Y. Cao and S. J. Su, *Chem. Mater.*, 2015, **27**, 1100; (c) E. Bindewald, R. Lorenz, O. Huebner, D. Brox, D. P. Herten, E. Kaifer and H. J. Himmel, *Dalton Trans.*, 2015, **44**, 3467; (d) J. Y. Song, S. N. Park, S. J. Lee, Y. K. Kim and S. S. Yoon, *Dyes Pigm.*, 2015, **114**, 40; (e) C. Zhao, L. J. Hua, H. Xie, Y. Jun, Y. G. Ao and L. S. Hua, *Dyes Pigm.*, 2015, **112**, 59; (f) P. K. Clews, R. E. Douthwaite, B. M. Kariuki, T. Moore and M. Taboada, *Cryst. Growth Des.*, 2006, **6**, 1991.
- (a) H. D. Guo, X. M. Guo, S. R. Batten, J. F. Song, S. Y. Song, S. Dang, G. L. Zheng, J. K. Tang and H. J. Zhang, *Cryst. Growth Des.*, 2009, **9**, 1394; (b) P. K. Clews, R. E. Douthwaite, B. M. Kariuki, T. Moore and M. Taboada, *Cryst. Growth Des.*, 2006, **6**, 1991; (c) H. Guo, D. Qiu, X. Guo, S. R. Batten and H. Zhang, *CrystEngComm*, 2009, **11**, 2611.
- A. W. Addison, T. N. Rao, J. Reedijk, J. v. Rijn and G. C. Verschoor, *Dalton Trans.*, 1984, 1349.

12. (a) S. Contaldi, C. Di. Nicola, F. Garau, Y. Y. Karabach, L. M. D. R. S. Martins, M. Monari, L. Pandolfo, C. Pettinari and A. J. L. Pombeiro, *Dalton Trans.*, 2009, 4928; (b) C. Y. Tsai, B. H. Huang, M. W. Hsiao, C. C. Lin and B. T. Ko, *Inorg. Chem.*, 2014, **53**, 5109.
13. J. Bernstein, R. E. Davis, L. Shimoni and N. L. Chang, *Angew. Chem. Int. Ed.*, 1995, **34**, 1555.
14. (a) V. A. Blatov, A. P. Shevchenko and D. M. Proserpio, *Cryst. Growth Des.*, 2014, **14**, 3576; (b) L. Carlucci, G. Ciani, D. M. Proserpio, T. G. Mitina and V. A. Blatov, *Chem. Rev.*, 2014, **114**, 7557.
15. A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, 1999.
16. J. P. S. Mowat, V. R. Seymour, J. M. Griffin, S. P. Thompson, A. M. Z. Slawin, D. Fairen-Jimenez, T. Düren, S. E. Ashbrook and P. A. Wright, *Dalton Trans.*, 2012, **41**, 3937.
17. H. Guo, X. Guo, H. Zou, Y. Qi, R. Chen, L. Zhao and C. Liu, *CrystEngComm*, 2014, **16**, 7459.

Graphical Abstract



Four supramolecular assemblies from 0D, 1D to 2D were obtained by reacting (fluorene-9,9-diyl)dipropionic acid with cupric ion under the different pH medium 4.0~8.0 .