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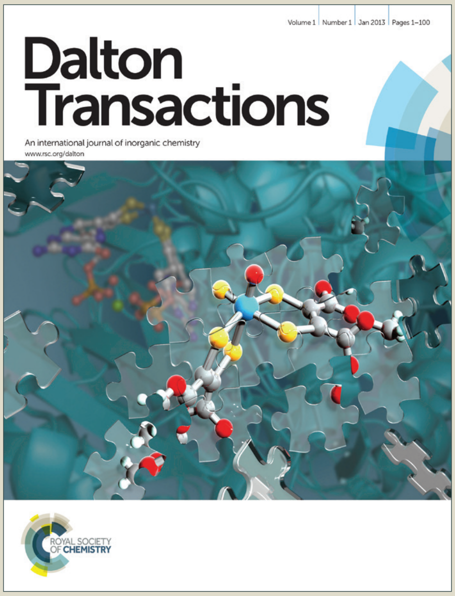

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COMMUNICATION

Macrocyclic Cu(II)-organophosphonate building block with room temperature magnetic ordering

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Engineering the copper coordination sphere with organoimine ligands and tuning organophosphonate protonation states produced [{Cu(2,2′-bpy)}$_2$(HO$_3$P(CH$_2$)$_8$PO$_3$H$_2$)$_4$] (1) and [{Cu(terpy)}$_2$(2,7-FDA-H$_2$)$_2$] · (2,7-FDA-H$_4$)(2H$_2$O) (2) (2,7-FDA-H$_4$ = 2,7-fluorenonediphosphonic acid) macrocyclic copper-organophosphonate building blocks. 1 exhibits high temperature magnetic ordering while 2 is paramagnetic. The structures were characterized by single crystal X-ray diffraction.

The predesigned synthesis of two and three dimensional inorganic/organic hybrid molecules is near absent and there is a need for new methodologies to tailor porosities, catalytic and magnetic properties of organic/inorganic hybrid molecules.[1-6] Hypothetically, tuning the catalytic and magnetic properties could be achieved via controlling the metal coordination sites with organoimine chelators while engineering the metal oxidation states with organophosphonates through pH modulations. One approach for the designed synthesis could be the use of well-defined macrocyclic building blocks. Metallo-macrocycles are known to have catalytic properties.[7] They can store small molecules by forming well-defined flexible porous sites[8] optimizing the selectivity in gas uptake[9] and macrocyclic building blocks are rare.[10-12] They could form an alternative approach for widely explored carboxylate and heterocyclic donors in MOF synthesis.[13,14] Here we present a new synthetic route and the crystal structures of two novel metallo-macrocyclic building blocks based on a Cu(II) ion and organophosphonates [{Cu(2,2′-bpy)}$_2$(HO$_3$P(CH$_2$)$_8$PO$_3$H$_2$)$_4$] (**1**) and [{Cu(terpy)}$_2$(2,7-FDA-H$_2$)$_2$] · (2,7-FDA-H$_4$)(2H$_2$O) (**2**) (2,7-FDA-H$_4$ = 2,7-fluorenonediphosphonic acid). [{Cu(2,2′-bpy)}$_2$(HO$_3$P(CH$_2$)$_8$PO$_3$H$_2$)$_4$] is a novel metallo-macrocyclic building block with long flanking octylphosphonate arms that are available for metal coordination. It can sustain magnetic ordering at 400 K and exhibits superparamagnetic effect due to the fact that the ferromagnetically coupled Cu(II) ions occupy a very small volume in the crystal structure, where aliphatic 1,8-octanediphosphonate units are packed in a similar pattern seen in phospholipid bilayers.

Organodiphosphonic acids (H$_2$O$_3$P-R-PO$_3$H$_2$) provides pH dependent modes of negative charges between the values of 0 and -4.[8,15,16] Metal oxidation state is one of the key parameters defining the magnetic properties,[1] which can be tuned by organodiphosphonate protonation. Likewise, blocking the copper coordination sites with organoimine chelators defines the total number phosphonate coordination on the copper center.[17] Based on this strategy, various modes of metal-oxidation states and coordination possibilities can be produced leading to interesting properties.[18] The distorted square pyramidal Cu(II) center in **1** was produced by blocking the two coordination sites of the square pyramidal copper with 2,2′-biypridine ligand to leave three possible sites for organophosphonate coordination. The thick plates of turquoise crystals of **1** (0.35-0.21-0.08 mm) were obtained after hydrothermal reactions as seen in Fig. 1 inset. The crystal structure in Fig. 1 reveals that three phosphonate units occupy the three

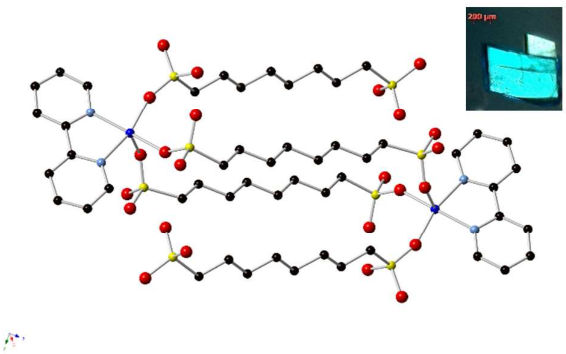

Figure 1. The crystal structure of [{Cu(2,2′-bpy)}$_2$(HO$_3$P(CH$_2$)$_8$PO$_3$H$_2$)$_4$] (**1**).

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Electronic Supplementary Information (ESI) available: The synthesis, ICP-MS, TGA and crystallographic information is available. CCDC 1050581 CCDC 1052685. See DOI: 10.1039/x0xx00000x empty $[\{Cu(2,2'\text{-}bpy)\}]^{2+}$ coordination sites with a single oxygen arm providing -2 charge in total. $[\{Cu(2,2'\text{-}bpy)\}_2(HO_3P(CH_2)_8PO_3H_2)_4]$ has two distinctive 1,8-octanediphosphonate units coordinated to two Cu(II) centers. The first $(H_2O_3P(CH_2)_8PO_3H)^-$ couple provides a total of -2 negative charge to form the 16 carbon aliphatic $[\{Cu(2,2'\text{-}bpy)\}_2(HO_3P(CH_2)_8PO_3H)_2]^{2+}$ metallo-macrocycle by coordinating to the square pyramidal $[\{Cu(2,2'\text{-}bpy)\}_2]^{4+}$ from the apical position and the basal plane. The second distinctive $(HO_3P(CH_2)_8PO_3H_2)^-$ unit has a fully protonated flanking phosphonate end. The other half-protonated side provide a total of -2 negative charge by coordinating to the basal plane of the square pyramidal $[\{Cu(2,2'\text{-}bpy)\}]^{2+}$ as shown in Fig. 1. The total of -4 negative charge provided by 1,8-octanediphosphonate units is balanced by two Cu^{2+} ions. Single crystal X-ray diffraction data does not show hydronium peaks in the crystal structure ruling out the presence of additional positive charges. The crystal structure indicates perfect segregation of hydrophobic and hydrophilic components. In addition to copper binding, hydrophilic phosphonate hats were hold together by a network of hydrogen bonds. The presence of strong hydrophobic organizations of octyl groups was another important driving force organizing the phosphonate groups together. The overall crystal structure is reminiscent of phospholipid bilayers. To the best of our knowledge, **1** has the largest organic units among the other metal-organic molecules that show high temperature ferromagnetic ordering.

In accordance with the single crystal X-ray diffraction data, the thermo-gravimetric analysis (TGA) has shown that the molecule displays no weight loss up to ca. 210°C indicating the absence of water molecules. **1** starts to decompose at ca. 210°C and the decomposition continues until ca. 500°C. In addition to the thermal stability, **1** is partially soluble in methanol, acetonitrile, DMSO and fully soluble 5 % Na_2CO_3 and acetic acid producing a blue solution. The visual solubility of **1** in various solvents at room temperature indicates that the two flanking octylphosphonate arms could be further used as a bridging ligand to construct novel MOFs with well-defined macrocyclic centers.

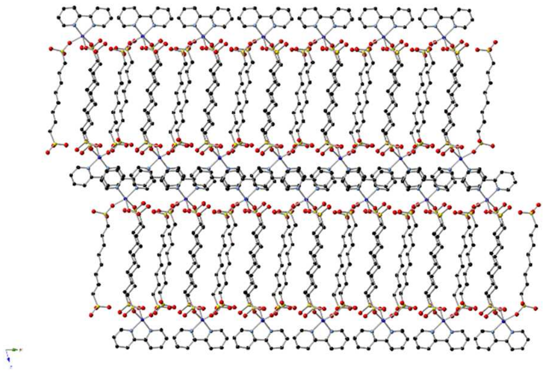

Figure 2. The organization of hydrophobic and hydrophilic units in crystal structure of **1**.

We performed the magnetization measurements using a Quantum Design PPMS vibrating sample magnetometer between 10K-400K. The magnetization curve of **1** is anhysteretic from 10-400K as shown in Fig. 4a contrary to the magnetization of **2**, which is just paramagnetic as shown in Fig. 4b. It is surprising that molecule **1** exhibits almost the same magnetization (~0.157 emu/g) at all temperatures. This value is found by extrapolating the slope of the paramagnetic signal at high field. Normally magnetization increases as the temperature is lowered but in this crystal there is no change in the magnetization as the temperature changes. Presently we do not have a conclusive answer to the source of this magnetization in **1**. Our ICP-MS measurements rules out the possibility of presence of magnetic impurities in the crystal.[19] Possible explanations could be superparamagnetism of very small islands due to dangling bonds from C atoms, [20] giant orbital paramagnetism[21] or defect mediated magnetic interaction. [22]

The hydrothermal methods were proven to be an efficient method to produce the single crystals of **1** and **2** providing the structural detail. In order to better formulate the synthetic route, we have blocked the three coordination sites on square pyramidal copper using a tripodal organoimine ligand to form another Cu(II) macrocycle. As it can be seen in Fig. 3, $[\{Cu(terpy)\}_2(2,7\text{-}FDA\text{-}H_2)_2]\cdot(2,7\text{-}FDA\text{-}H_4)(2H_2O)$ **2** was constructed from 2,2':6':2''-terpyridine (terpy) and 2,7-fluorenonediphosphonic acid (2,7-FDA) units under similar hydrothermal reaction conditions with **1**. As it can be seen in Fig. 4b, **2** is paramagnetic. As we compare the crystal structures of **1** and **2**, it can be seen that 2,2'-bipyridine is influential in determining the structure of the macrocycle by controlling the square pyramidal copper coordination sphere to accept the third phosphonate as a Lewis base, whereas square planar $\{Cu(terpy)\}^{2+}$ has only two sites available for phosphonate coordination. As a result **2** has one uncoordinated and fully protonated 2,7-fluorenonediphosphonic acid in the crystal structure. Hypothetically, the uncoordinated 2,7-fluorenonediphosphonic acid could have also coordinated to the copper center in the presence of dipodal organoimine ligand such as 2,2'-biypyridine. All these information suggest that the organophosphonate protonation states, engineering the metal coordination sites and the hydrophobic organizations were the key and interrelated parameters defining the formation of **1** and **2**.

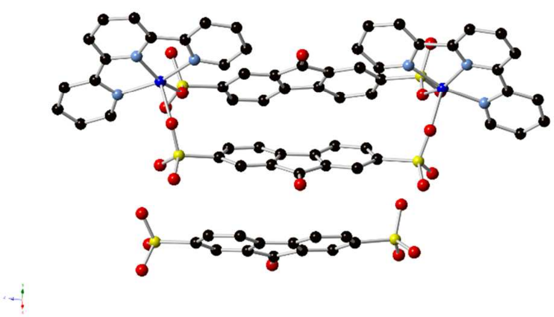

Figure 3. The crystal structure of $[\{Cu(terpy)\}_2(2,7\text{-}FDA\text{-}H_2)_2]\cdot(2,7\text{-}FDA\text{-}H_4)(2H_2O)$ where the third 2,7-fluorenonediphosphonic acid (2,7-FDA-H_4) coordination is blocked by the terpy ligand.

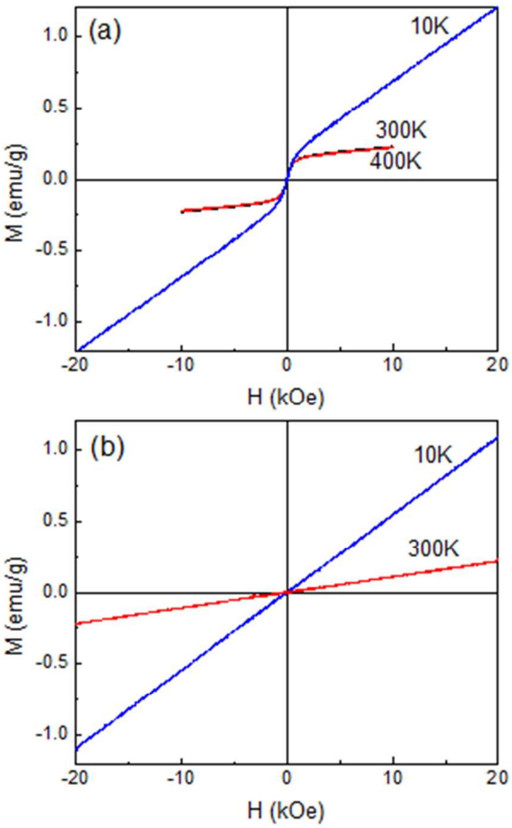

Figure 4. (a) Magnetization measurement of $[\{Cu(2,2'\text{-}bpy)\}_2(HO_3P(CH_2)_8PO_3H_2)_4]$ showing ferromagnetic behavior at 10K, 300K and 400K (b) Magnetization measurement of $[\{Cu(terpy)\}_2(2,7\text{-}FDA\text{-}H_2)_2] \cdot (2,7\text{-}FDA\text{-}H_4)(2H_2O)$ showing paramagnetic behavior at 10K and 300K.

Conclusions

We present the crystal structures of two novel Cu(II) based metal-organic macrocycles. We have shown that engineering the metal coordination center with organoimine chelators and facilitating orgonophosphonates as tunable negative charge donors were influential in defining the ultimate structure of the metal-organic macrocycles. Furthermore, the 18-carbon hydrophobic macrocyclic center makes this Cu(II) molecule a potential platform for many catalytic reactions, especially to functionalize hydrophobic units. The flanking octylphosphonate groups attached to the $[\{Cu(2,2'\text{-}bpy)\}_2(HO_3P(CH_2)_8PO_3H)_2]^{2+}$ macrocycle can further be engineered to form three-dimensional porous metal organic frameworks with predefined macrocyclic cavities. Unfortunately there are no specific models to explain the magnetic behaviour. The long interatomic distances between Cu(II) ions rules out the possibility of known direct or indirect exchange coupling mechanisms to be present. Possible mechanisms include the coupling of magnetic moments on some C atoms due to dangling bonds or defect mediated magnetism as observed in some oxygen deficient dilute magnetic oxides. Further studies are being conducted to understand the mechanism of magnetic coupling observed in **1**.

Acknowledgements

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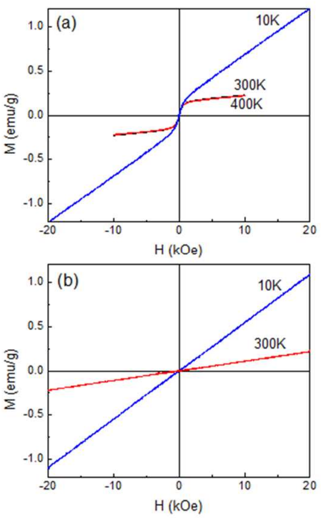
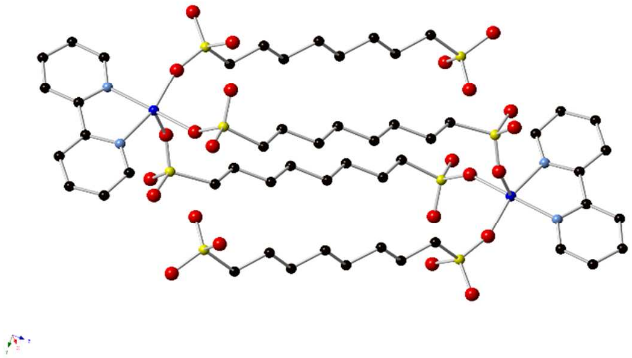
Notes and references

1 O. Kahn, *Molecular Magnetizm;* VCH, New York, 1993.
2 K. J. Gagnon, H. P. Perry and A. Clearfield, *Chem. Rev.*, 2012, **112**, 1034-1054.
3 E. Pardo, R. Ruiz-Garcia, J. Cano, X. Ottenwaelder, R. Lescouezec, Y. Journaux, F. Lloret and M. Julve, *Dalton Trans.*, 2008, **21**, 2780-2805.
4 M. Ranocchiari and J. A. v. Bokhoven, *Phys. Chem. Chem. Phys.*, 2011, **13**, 6388–6396.
5 D.-Y. Du, J.-S. Qin, S.-L. Li, Z.-M. Su and Y.-Q. Lan, *Chem.Soc.Rev.*, 2014, **43**, 4615--4632.
6 N. Stock and S. Biswas, *Chem. Rev.*, 2012, **112**, 933–969.
7 S. Kal, A. S. Filatov, and P. H. Dinolfo, *Inorg. Chem.*, 2014, **53**, 7137−7145.
8 R. Miyake, C. Kuwata and Y. Masumoto, *Dalton Trans.*, 2015, **44**, 2993–2996.
9 S. Takamizawa and R. Miyake, *Chem. Commun.*, 2009, **27**, 4076-4078.
10 R. Miyake and M. Shionoya, *Chem. Commun.*, 2012, **48**, 7553–7555.
11 R. Miyake and M. Shionoya, *Inorg. Chem.*, 2014, **53**, 5717-5723.
12 M. Abdul-Kadir, L. R. Hanton and C. J. Sumby, *Dalton Trans.*, 2012, **41**, 4497–4505.
13 J. K. Clegg, S. S. Iremonger, M. J. Hayter, P. D. Southon, R. B. Macquart, M. B. Duriska, P. Jensen, P. Turner, K. A. Jolliffe, C. J. Kepert, G. V. Meehan and L. F. Lindoy, *Angew. Chem., Int. Ed.,*, 2010, **49**, 1075-1078.
14 J. K. Clegg, M. J. Hayter, K. A. Jolliffe, L. F. Lindoy, J. C. McMurtrie, G. V. Meehan, S. M. Neville, S. Parsons, P. A. Tasker, P. Turner and F. J. White, *Dalton Trans.*, 2010, **39**, 2804–2815.
15 A. Clearfield and K. D. Demadis, *Metal Phosphonate Chemistry: From Synthesis to Applications;* RSC Publishing, Cambridge, 2012.
16 J. K. Zareba, M. J. Bialek, J. Janczak, J. Zon, A. Dobosz, *Cyrst. Growth Des.*, 2014, **14:11**, 6143-6153.
17 G. Yucesan, M. H. Yu, W. Ouellette, C. J. O'Connor and J. Zubieta, *CrystEngComm*, 2005, **7**, 480–490.
18 D. Sahoo, R. Suriyanarayanan and V. Chandrasekhar, *Dalton Trans.*, 2014, **43**, 10898-10909.
19 Prior to the magnetic analysis, the crystals bigger than 200 µm were hand picked under microscope and washed with aceton over a 40-100 µm fritted pyrex glassware to remove any unseen impurities.
20 Y. W. Ma, Y. H. Lu, J. B. Yi, Y. P. Feng, T. S. Herng, X. Liu, D. Q. Gao, D. S. Xue, J. M. Xue, J. Y. Ouyang and J. Ding, *Nat. Commun.*, 2012, **3:727**, 1-8.
21 A. Hernando, P. Crespo and M. A. Garcia, *Phys. Rev. Lett.*, 2006, **96**, 057206(1-4).

22 J. M. D. Coey, M. Venkatesan and C. B. Fitzgerald, *Nat. Mater.*, 2005, **4**, 173-179.





A novel macrocyclic Cu(II)-organophosphonate building block displaying high temperature magnetic ordering, the structure of [{Cu(2,2'-bpy)}$_2$(HO$_3$P(CH$_2$)$_8$PO$_3$H$_2$)$_4$] (**1**).