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## COMMUNICATION

# Crystal engineering through charge-assisted hydrogen bonds, multiple C–H···O bonds and $\pi$ – $\pi$ stacking: from (H<sub>2</sub>bipy)[Cu(ox)<sub>2</sub>] to (H<sub>2</sub>bipy)[NaH(ox)<sub>2</sub>] and (H<sub>2</sub>bipy)[H<sub>2</sub>(ox)<sub>2</sub>] (H<sub>2</sub>bipy = 4,4'-bipyridin-1,1'-dium; ox = oxalate)<sup>†</sup>

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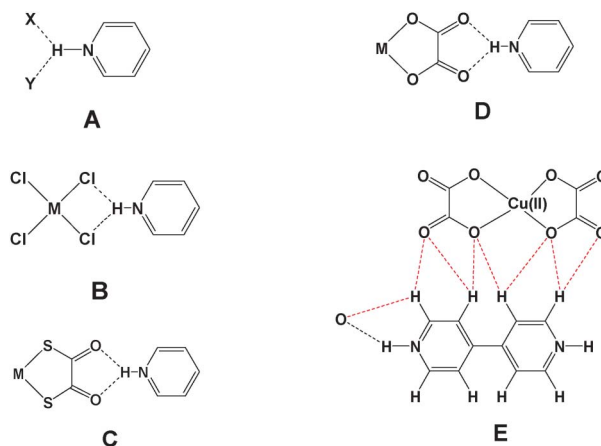
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The title compounds were assembled through charge-assisted hydrogen bonds, multiple C–H···O bonds and  $\pi$ – $\pi$  stacking, and structurally characterized. The compounds, with dramatic differences in the cations of their tectons, are isostructural and featured 1D ribbons of alternating anions and cations. The 1D ribbons are aligned edge-to-edge to generate 2D sheets through arrays of C–H···O bonds. The 2D sheets then stack directly upon each other, resulting in alternating homogeneous columns of bipyridinium cations and oxalate anions in the structure.

Crystal engineering is the science of understanding the principles of intermolecular interactions, such as metal–ligand coordination bonds, hydrogen-bonds and  $\pi$ -stacking *etc.* and using these principles to design and synthesise functional solid-state materials from neutral or ionic molecular-based building blocks. Many efforts have been devoted to this field for decades,<sup>1–5</sup> since the pioneering studies by Schmidt and Desiraju on organic crystals<sup>3,4</sup> and Hoskins and Robson on coordination polymers were published,<sup>5</sup> fuelled by the intriguing architectures and structural diversity of the materials and by their potential applications in material sciences<sup>6,10</sup> and biological/medical sciences.<sup>7</sup> However, since intermolecular interactions are much weaker and less directional than covalent bonds, crystal engineering more often leads to unpredictable products when compared to classic organic synthesis.<sup>2–7</sup> In general, crystallization is governed by both strong and weak intermolecular interactions, where basic structural units are linked together through relatively strong interactions or robust supramolecular synthons, such as strong hydrogen bonds (X–H···Y (X, Y = O or N)) and metal–ligand coordination bonds, while the 3D arrangement of the structural motifs is determined by weaker and less well-defined interactions, such as halogen bonds,  $\pi$ – $\pi$  stacking, CH···O interactions, *etc.* Thus, the rational design

and synthesis of a functional material/crystal relies on our knowledge of both the strong and weak intermolecular interactions of the system.<sup>2,3,8</sup>



The di-cation, 4,4'-bipyridin-1,1'-dium (H<sub>2</sub>bipy<sup>2+</sup>), has been widely used in crystal engineering due to its rich chemistry: the geometry of the two pyridinium rings (planar or twisted),<sup>9</sup> the formation of strong hydrogen-bonds from the two N–Hs and the ability for  $\pi$ – $\pi$  stacking ( $\pi$ ···H–C) as well as C–H···X (X = N, O, F, Cl, Br and S) interactions. Structures of H<sub>2</sub>bipy<sup>2+</sup> salts with organic anions,<sup>10,11</sup> simple inorganic anions,<sup>12</sup> polyoxometalates<sup>13</sup> and metal complex anions<sup>14,15</sup> have been reported. The robust synthon **A** (X or Y = N, O, Cl and Br) was found to be present in most of these salts, while their crystal structures vary from 1D chains to 2D or 3D hydrogen-bonded networks, depending on the dimensions, geometry as well as the nature or the stereochemical preference of the anions. Orpen and his colleagues designed and synthesized a series of [H<sub>2</sub>bipy]<sup>2+</sup> salts with a variety of metal complex anions by altering the metal center and/or the ligands attached to the metals.<sup>14</sup> They found that the square planar complex anion, [MCl<sub>4</sub>]<sup>2–</sup> (M = Pd and Pt) and its mimics, [M(dto)<sub>2</sub>]<sup>2–</sup> (M = Ni, Pt and Cu; dto = 1,2-dithiooxalate) can be used as tectons to couple with [H<sub>2</sub>bipy]<sup>2+</sup> and form linear ribbons through synthon **B** or **C**. We obtained (H<sub>2</sub>bipy)[Cu(ox)<sub>2</sub>] (ox = oxalate) (**1**) by accident<sup>16</sup> and found that it can be considered as a

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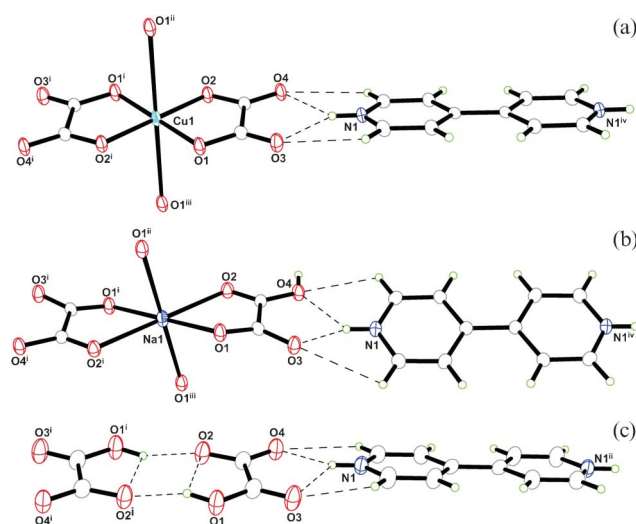
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member of the  $(\text{H}_2\text{bipy})[\text{PtCl}_4]$  family but with synthon **D** for the ribbons. Further analysis of the structure shows that, in addition to the typical  $\pi$ - $\pi$  stacking, the crystal structure has a unique C-H $\cdots$ O bond network (synthon **E** (highlighted in red)). Thus, each  $\text{H}_2\text{bipy}^{2+}$  forms a total of sixteen ( $2 \times 8 = 16$ ) C-H $\cdots$ O bonds (see Fig. 2(a)) with its two neighbouring  $[\text{Cu}(\text{ox})_2]^{2-}$  anions. This means that the  $\text{H}_2\text{bipy}^{2+}$  cations and the  $[\text{Cu}(\text{ox})_2]^{2-}$  anions could be strongly bonded, given that the theoretical and experimental data indicate that the bond energy for a C-H $\cdots$ O bond (1.9 to 3.2 kJ mol $^{-1}$  in the diether dimer) is about a tenth of that for O-H $\cdots$ O or N-H $\cdots$ O.<sup>17</sup> A search of the Cambridge Structural Database (CSD)<sup>18</sup> shows that exactly the same structure was also obtained by accident by Zhang *et al.* through the hydrothermal reaction of sodium 2-hydroxyphosphonocarboxylate with  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  and 4,4'-bipyridine in EtOH-water (1 : 1),<sup>19</sup> which confirms the good stability of the structure. At the same time, we found that, unlike the tectons in Orpen's work, which are 4-coordinated, planar and discrete, the  $[\text{Cu}(\text{ox})_2]^{2-}$  di-anion in the structure is coordinated not only in a square planar position by two chelating  $\text{ox}^{2-}$ , but also axially by two oxygen atoms from its neighbouring  $[\text{Cu}(\text{ox})_2]^{2-}$  units. We argue that the tolerance for the replacement of 4-coordinated square planar tectons by 6-coordinated distorted octahedral ones while maintaining a similar crystal structure is a strong indication of the high stability of the frameworks, including the local structure and their packing. To this end, we seek to examine the stability of the structure further by replacing the cation of the tecton with less geometrically-preferred cations, such as  $\text{Na}^+$  and even  $\text{H}^+$ . We thus synthesized  $(\text{H}_2\text{bipy})[\text{NaH}(\text{ox})_2]$  (**2**) and  $(\text{H}_2\text{bipy})[\text{H}_2(\text{ox})_2]$  (**3**) and examined their structures.<sup>16</sup> The results show that the structures of **1**, **2** and **3** are isostructural with the equivalent  $\cdots\text{dioxalate}^{2-}\cdots\text{bipyH}_2^{2+}\cdots$  ribbons, the similar ribbon-ribbon interaction patterns, as well as being very close to the unit cell parameters. ‡ The structures of **1** and **3** are so similar that the structure of **3** can be simply refined using the INS. file (a file for the SHELXTL program<sup>20</sup>) from **1** with the Cu(II) atom removed.

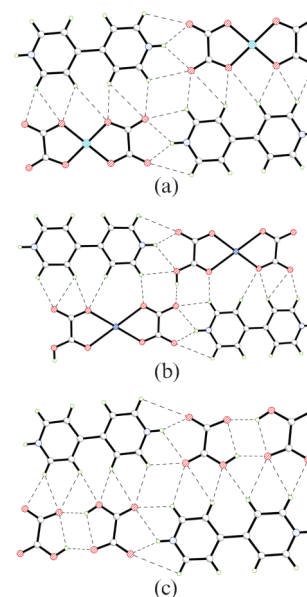
The structure of **1** is shown in Fig. 1(a). The asymmetric unit contains half a  $\text{Cu}^{2+}$ , half a  $\text{H}_2\text{bipy}^{2+}$  and an  $\text{ox}^{2-}$ . The  $\text{Cu}^{2+}$  is located at a crystallographic inversion centre and is coordinated by six oxygen atoms from 4 oxalates in a tetragonally elongated octahedral model, with O(1), O(2), O(1 $^i$ ) and O(2 $^i$ ) in the equatorial plane (Cu-O(eq.) = 1.92–1.93 Å), while O(1 $^{ii}$ ) and O(2 $^{ii}$ ) are in the axial positions (Cu-O(ax.) = 2.88 Å), which is comparable to other reports on  $[\text{Cu}(\text{ox})_2]^{2-}$ .<sup>21</sup> The di-cation,  $\text{H}_2\text{bipy}^{2+}$ , is also found at a crystallographic inversion center and is perfectly planar. Each  $\text{H}_2\text{bipy}^{2+}$  is hydrogen-bonded to two metal centres through synthon **D** to form a linear and close-to-planar  $\cdots\text{cation}\cdots\text{anion}\cdots$  ribbon. The ribbons are then joined together edge-to-edge to form sheets which are parallel to the plane (1–2 1) through the array of C-H $\cdots$ O bonds, synthon **E** (Fig. 2(a)). The edge-to-edge alignment is so precise that each C-H is bifurcatedly bonded and each  $\text{H}_2\text{bipy}^{2+}$  forms a total of 16 C-H $\cdots$ O bonds with average CH $\cdots$ O distances of 2.66 Å (ranging from 2.39 to 3.05 Å),<sup>17</sup> in addition to the 4 N-H $\cdots$ O bonds. The sheets then interact face-to-face through the Cu-O (axial) bonds (Cu-O = 2.884(2) Å) and the slipped  $\pi$ - $\pi$  stacking of  $\text{H}_2\text{bipy}^{2+}$ , with centroid-centroid contacts between the  $\text{Hpy}^+$  groups of about 3.67 Å, a ring-normal ring distance of about 3.42 Å, an angle between the normal ring and the centroid vector of about 22° and



**Fig. 1** (a) Structures of **1** (symmetry code: i)  $1 - x, 1 - y, 1 - z$ ; ii)  $1 + x, y, z$ ; iii)  $-x, 1 - y, 1 - z$  and iv)  $-2 - x, -1 - y, -z$ ). (b) Structure of **2** (symmetry code: i)  $1 - x, -y, -z$ ; ii)  $-x, -y, -z$ ; iii)  $1 + x, y, z$  and iv)  $-x, 2 - y, 1 - z$ ) and **3** (symmetry code: i)  $1 - x, 1 - y, 1 - z$  and ii)  $-2 - x, -1 - y, -z$ ).

a displacement shift of 1.40 Å from the face-to-face alignment of the rings, which is consistent with Janiak's observation from the CSD.<sup>22</sup> Thus, the packing of the ribbons for **1** is totally different from that of  $(\text{H}_2\text{bipy})[\text{PtCl}_4]$ , where the ribbons edge-to-edge alignment is offset while the face-to-face arrangement is perfectly overlapped. It results in alternating homogeneous columns of bipyridinium cations and oxalate anions in the structure (Fig. 3), which may ultimately give rise to unexpected bulk properties, such as electronic or magnetic communication between metal ions.<sup>23</sup>

Studies on the structures of Na-ox complexes showed that each Na(I) tends to chelate to three  $\text{ox}^{2-}$  anions to give a distorted octahedral coordination geometry and no planar  $[\text{Na}(\text{ox})_2]^{3-}$  or  $[\text{NaH}(\text{ox})_2]^-$  species have been reported so far.<sup>24</sup> However, our



**Fig. 2** The hydrogen bond networks of **1** (a), **2** (b) and **3** (c).

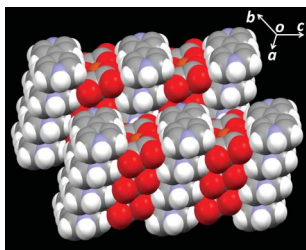


Fig. 3 The unit cell packing of **1**.

structural analysis of **2** reveals a very similar structure to **1**, where Na(I) is coordinated to two  $\text{ox}^{2-}$  inside the tecton,  $[\text{NaH}(\text{ox})_2]^{2-}$ , in a planar manner and with another two oxygen atoms situated axially from two neighbouring tectons (Fig. 1(b)). The coordination geometry of Na(I) is slightly distorted octahedral with  $\text{Na}-\text{O}(\text{eq.}) = 2.35\text{--}2.36 \text{ \AA}$  and  $\text{Na}-\text{O}(\text{ax.}) = 2.58 \text{ \AA}$ . The tectons,  $[\text{NaH}(\text{ox})_2]^{2-}$ , are somewhat off planar due to the formation of the two  $\text{Na}-\text{O}(\text{ax.})$  bonds but the di-cations,  $[\text{H}_2\text{bipy}]^{2+}$ , are still perfectly planar. Through synthon **D**, linear and close-to-planar  $\cdots\text{cation}\cdots\text{anion}\cdots$  ribbons are formed, similar to **1**. The ribbons lay edge-to-edge to give rise to ribbon sheets running in the (202) direction. The alignment of the ribbons of **2** is shown in Fig. 2(b). Compared to the “precise alignment” in **1**, fewer  $\text{C}-\text{H}\cdots\text{O}$  bonds are observed between the ribbons in **2**. This is a result of the presence of the extra  $\text{H}^+$  and the longer “metal– $\text{O}(\text{eq.})$ ” distances of **2**. Firstly, the stronger  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds (compared to the  $\text{C}-\text{H}\cdots\text{O}$  bonds) from the extra  $\text{H}^+$  shift the ribbons in a way to make the two neighbouring  $\text{ox}^{2-}$  anions from the adjacent ribbons become closer, which prevents the uncoordinated oxygen atoms from forming quadruple  $\text{C}-\text{H}\cdots\text{O}$  bonds like they do in **1**. Secondly, the longer  $\text{Na}-\text{O}(\text{eq.})$  distances result in longer distances between the two  $\text{ox}^{2-}$  anions inside the tecton,  $[\text{NaH}(\text{ox})_2]^{2-}$ , which means that only the H atoms at the 3 or 3' position of the  $\text{H}_2\text{bipy}^{2+}$  cations can form bifurcated  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds. The face-to-face alignment of the ribbon sheets is again offset, which is very similar to that in **1**, with a centroid–centroid contact between the  $\text{Hpy}^+$  groups of about  $3.64 \text{ \AA}$ , a ring–normal ring distance of about  $3.30 \text{ \AA}$ , an angle between the normal ring and the centroid vector of about  $22^\circ$  and a displacement shift of  $1.40 \text{ \AA}$  from the face-to-face alignment of the rings.

The success of replacing  $\text{Cu}^{2+}$  with  $\text{Na}^+$  while keeping the crystal structure unchanged encouraged us to further substitute the  $\text{Na}^+$  ion with the smallest cation,  $\text{H}^+$ , although a study from Cowan *et al.* indicated bipy and  $\text{H}_2\text{ox}$  can form an adduct,  $[\text{bipy}\cdot\text{H}_2\text{ox}]$ , whereby the bipy and  $\text{H}_2\text{ox}$  molecules join together through  $\text{O}-\text{H}\cdots\text{N}$  bonds to form a totally different ribbon,  $\cdots\text{bipy}\cdots\text{H}_2\text{ox}\cdots$  ribbons.<sup>25</sup> By mixing bipy and  $\text{H}_2\text{ox}$  in 1 : 2 ethanol–water (1 : 1), colourless prism-shaped crystals of **3** were obtained at room temperature after evaporation. In the meantime, while we were still working on this paper, the same compound was reported to have been obtained by accident *via* the reaction of oxalatotantalate(V) with 4,4'-bipyridine in dilute hydrochloric acid at room temperature,<sup>26</sup> which again confirms the stability of the structure. As we anticipated, with the same synthon **D**, **3** has almost exactly the same crystal structure as **1**, from the unit cell parameters to the hydrogen bonding networks and packing of the ribbons, and even very close atomic coordinates for the corresponding C, N and O atoms, although no metal– $\text{O}(\text{eq.})$  or

metal– $\text{O}(\text{ax.})$  interaction is present in the compound (Fig. 2(c)). The new tecton,  $[(\text{Hox})_2]^{2-}$ , is completely planar with the two  $\text{ox}^{2-}$  anions linked together distinctively by the two intramolecularly and intermolecularly bonded  $\text{H}^+$  ions. Through synthon **D**, linear and close-to-planar  $\cdots\text{cation}\cdots\text{anion}\cdots$  ribbons are formed, similar to **1** and **2**. The ribbons interact in an edge-to-edge manner to give rise to ribbon sheets with the same array of  $\text{C}-\text{H}\cdots\text{O}$  bonds as in **1**, running in the (1–2 1) direction, and in a face-to-face manner with the  $\text{H}_2\text{bipy}$ -rings from the adjacent ribbons, slipped stacked in a very similar fashion to **1** and **2**: the centroid–centroid contact between the  $\text{Hpy}^+$  groups is about  $3.71 \text{ \AA}$ , the ring–normal ring distance is about  $3.40 \text{ \AA}$ , the angle between the normal ring and the centroid vector is about  $22^\circ$ , and a displacement shift of  $1.40 \text{ \AA}$  from the face-to-face alignment of the rings is seen.

Thus, three isostructures with dramatically different cations on their tectons were assembled. While the successful change of the tecton from  $[\text{Cu}(\text{ox})_2]^{2-}$  to  $[\text{NaH}(\text{ox})_2]^{2-}$  or  $[\text{H}_2(\text{ox})_2]^{2-}$  is an indication of the high stability of the structure, the absence of the metal– $\text{O}(\text{axial})$  bonds in **3** confirms that the stability is mainly from charge-assisted hydrogen bonds (synthon **D**), the multiple  $\text{C}-\text{H}\cdots\text{O}$  bonds (synthon **E**) and the  $\pi$ – $\pi$  stacking amongst the face-to-face packed  $\text{bipyH}_2^{2+}$  cations. Studies on the construction of novel monometallic and bimetallic isostructures (involving d- and f- metals) and their physical properties are in progress.

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## References

- † Crystal data for **1**:  $\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}_8\text{Cu}$ ,  $T = 180 \text{ K}$ , triclinic,  $P\bar{1}$ ,  $a = 3.6687(17)$ ,  $b = 9.932(5)$ ,  $c = 10.204(5) \text{ \AA}$ ,  $\alpha = 114.093(4)$ ,  $\beta = 98.647(5)$ ,  $\gamma = 97.244(5)^\circ$ ,  $V = 328.2(3) \text{ \AA}^3$ ,  $Z = 1$ ,  $D_c = 2.012 \text{ g cm}^{-3}$ ,  $M = 397.78$ ,  $\mu(\text{Mo}-\text{K}\alpha) = 1.720 \text{ mm}^{-1}$ . 3055 reflections were collected, 1293 are independent ( $R_{\text{int}} = 0.0183$ ) and 1230 are observed ( $I > 2\sigma(I)$ ). On the basis of all this data and the 115 refined parameters,  $R_1(\text{obs.}) = 0.0262$  and  $wR_2(\text{obs.}) = 0.0687$ , and  $R_1(\text{all}) = 0.0281$  and  $wR_2(\text{all}) = 0.0712$ . Crystal data for **2**:  $\text{C}_{14}\text{H}_{11}\text{N}_2\text{NaO}_8$ ,  $T = 180 \text{ K}$ , triclinic,  $P\bar{1}$ ,  $a = 3.6420(12)$ ,  $b = 9.706(3)$ ,  $c = 10.459(3)$ ,  $\alpha = 109.230(3)$ ,  $\beta = 100.133(3)$ ,  $\gamma = 99.271(3)^\circ$ ,  $V = 333.97(19) \text{ \AA}^3$ ,  $Z = 1$ ,  $D_c = 1.781 \text{ g cm}^{-3}$ ,  $M = 358.24$ ,  $\mu(\text{Mo}-\text{K}\alpha) = 0.175 \text{ mm}^{-1}$ . 3346 reflections were collected, 1310 are independent ( $R_{\text{int}} = 0.0225$ ) and 1097 are observed ( $I > 2\sigma(I)$ ). On the basis of all this data and the 118 refined parameters and 1 restraint,  $R_1(\text{obs.}) = 0.0354$  and  $wR_2(\text{obs.}) = 0.0865$ , and  $R_1(\text{all}) = 0.0438$  and  $wR_2(\text{all}) = 0.0931$ . Crystal data for **3**:  $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_8$ ,  $T = 180 \text{ K}$ , triclinic,  $P\bar{1}$ ,  $a = 3.7117(17)$ ,  $b = 9.871(4)$ ,  $c = 10.440(7)$ ,  $\alpha = 116.081(7)$ ,  $\beta = 97.186(7)$ ,  $\gamma = 97.626(5)^\circ$ ,  $V = 333.2(3) \text{ \AA}^3$ ,  $Z = 1$ ,  $D_c = 1.676 \text{ g cm}^{-3}$ ,  $M = 336.26$ ,  $\mu(\text{Mo}-\text{K}\alpha) = 0.140 \text{ mm}^{-1}$ . 3259 reflections were collected, 1315 are independent ( $R_{\text{int}} = 0.0308$ ) and 934 are observed ( $I > 2\sigma(I)$ ). On the basis of all this data and the 113 refined parameters,  $R_1(\text{obs.}) = 0.0441$  and  $wR_2(\text{obs.}) = 0.1147$ , and  $R_1(\text{all}) = 0.0649$  and  $wR_2(\text{all}) = 0.1267$ .

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  - 16 (a) Preparation of silica gel: The crystals of **1** and **2** were obtained by a gel method. The gel was prepared by adding Na<sub>2</sub>SiO<sub>3</sub>·9H<sub>2</sub>O to a 0.5 mol L<sup>−1</sup> water solution of oxalic acid until pH=5 was reached. The mixture was then transferred to U-tubes or test tubes and the gel was ready after 12 h; (b) Synthesis of (H<sub>2</sub>bipy)[Cu(ox)](**1**): To a U-tube with silica gel, 0.5 mmol CuSO<sub>4</sub>·7H<sub>2</sub>O in 5 mL of water and a mixture of 0.5 mmol of succinic acid and 0.25 mmol of 4,4'-bipyridine in 5 mL water–EtOH(1 : 1) were loaded into the two limbs separately. Blue crystals of **1** appeared on the copper sulfate side within about a week with a yield of about 15%. Elemental analysis calcd(%) for C<sub>14</sub>H<sub>10</sub>N<sub>2</sub>O<sub>8</sub>Cu: C 42.27, H 2.53, N 7.04; found: C 42.60, H 2.58, N 6.98%; (c) Synthesis of (H<sub>2</sub>bipy)[Na(H<sub>0.5</sub>ox)](**2**): To a testtube with silica gel, 0.25 mmol of 4,4'-bipyridine in 5 mL water–EtOH(1 : 1) was added. Colorless crystals of **2** appeared right bellow the water–gel interface in about a week with a yield of about 30%. Elemental analysis calcd(%) for 2 C<sub>14</sub>H<sub>11</sub>N<sub>2</sub>O<sub>8</sub>Na: C 46.94, H 3.09, N 7.82; found: C 47.20, H 2.98, N 7.90%; (d) Synthesis of (H<sub>2</sub>bipy)[(Hox)](**3**): 1.0 mmol of oxalic acid in 5 mL of water–EtOH(1 : 1) and 0.5 mmol of 4,4'-bipyridine in 5 mL water–EtOH(1 : 1) were mixed with stirring at room temperature. After 30 min of stirring, the solution was filtered and the clear solution was allowed to evaporate at room temperature. Colorless crystals of **3** were obtained with a yield of about 70%. Elemental analysis calcd(%) for 3 C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>O<sub>8</sub>: C 50.01, H 3.60, N 8.33; found: C 50.12, H 3.62, N 8.35%.
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