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Clover leaf-shaped supramolecules assembled using a predesigned metallo-organic ligand†

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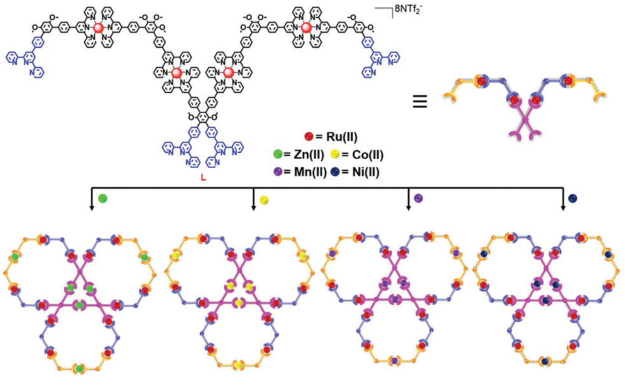
Inspired by the clover plant in nature, clover leaf-shaped supramolecular structures with three hexagons fused to create a triangular core were designed and self-assembled using a combination of Ru–Zn, Ru–Co, Ru–Mn or Ru–Ni metal ions. These results lay the foundation for further applications of heterometallic multinuclear metallo-supramolecules.

An important subfield of supramolecular chemistry, coordination-driven self-assembly has emerged in many synthetic systems that have dynamic characteristics over the past few decades.[1,2] These metallo-supramolecular structures, that have increasing complexity and diversity, play an increasingly significant role in catalysis,[3] sensing,[4] drug delivery and release,[5] gas storage,[6] and smart materials[7] due to their specific sizes and shapes. Of the diverse library of organic building blocks that exist, 2,2′:6′,2″-terpyridine (tpy) has been extensively used as a tridentate motif because of its excellent complexation ability toward different metal ions.[8] In addition to the common one-step self-assembly methodology that utilizes organic ligands and metal ions, the kinetically inert <tpy-Ru^{2+}-tpy> connectivity allows for an alternative step-wise self-assembly approach for constructing supramolecular structures with increased complexity.[9] Usually, a stable Ru(II)-organic ligand is synthesized and subsequently self-assembles with other metal ions with weak coordination, such as Zn(II), Cd(II) and Fe(II), to form heterometallic metallo-supramolecules.[10] However, the lack of other suitable metal ions has created great obstacles for the diversity of tpy-based metallo-supramolecules.[11] In most of these cases, Zn(II), Cd(II) and Fe(II) only serve as the connectors in the final supramolecular structures.[12] The question this raises is whether we are able to use other metal ions to serve as connectors and to introduce potentially new functionality to the supramolecule on account of the redox properties, magnetic properties, and photo-activities of the ions.[13] Recently, Ni(II), Co(II), Mn(II), and Cu(II) were used in a self-assembly process with tpy.[14] However, this was still limited to the self-assembly of a single-type of metal ion with organic building blocks. Perhaps due to the challenges of the design and characterization of complex metal–organic building blocks, few cases have expanded the scope of this method to metal–organic ligands.[15,16]

Herein, we report the design and synthesis of four clover leaf-shaped bimetallic supramolecular structures (Scheme 1). The structures were obtained through the coordination of tetratopic metal–organic ligand **L**, which contains Ru(II), with 4 different transition metals, Zn(II), Co(II), Mn(II), and Ni(II). As



Scheme 1 Self-assembly of clover leaf-shaped supramolecular structures obtained through the coordination of **L** with four different metal ions.

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designed, these complexes exhibit distinctive redox properties. The key metal–organic ligand **L**, which has four uncomplexed terpyridinyl units, was obtained *via* a 4-fold Suzuki coupling reaction of 4-(2,2′:6′,2″-terpyridyl)-phenylboronic acid with a precursor, **5** (Scheme S1, ESI†). **L** and Zn(NTf_2)$_2$ were self-assembled in MeCN/MeOH at a stoichiometric ratio of 1 : 2. The assembly was stirred at 60 °C for 8 h followed by addition of excess LiNTf$_2$. The resulting solid was washed with water and MeOH. The reddish supramolecular metal complex **Zn$_6$L$_3$** was obtained in a relatively high yield (98%). Subsequently, self-assembly with other metals was undertaken using some common metal salts, *i.e.*, $CoCl_2·6H_2O$, $MnClO_4·6H_2O$ and $NiSO_4·7H_2O$ (Scheme S2, ESI†). As a result, a series of bi-metallic clover leaf-shaped supramolecules with high symmetry were obtained. The structures were characterized using 1D and 2D NMR spectroscopy, electrospray ionization-mass spectrometry (ESI-MS), traveling wave ion mobility-mass spectrometry (TWIM-MS),[17] gradient tandem-mass spectrometry (gMS^2),[18] transmission electron microscopy (TEM), and cyclic voltammetry (CV).

Fig. 1 shows the ^{1}H NMR spectra of (a) ligand **L**, (b) **Zn$_6$L$_3$** and (c) **Co$_6$L$_3$**. Three sets of distinctive signals appear at 9.11, 8.86 and 8.73 ppm, split in a 4 : 1 : 1 ratio, in the aromatic region of the spectrum of **L**. These are assigned to the three sets of tpyH$^{3′,5′}$ protons of the Ru-based tpy moieties (A–D, E, and F tpy-phenyl peaks). In addition, the characteristic tpyH$^{6,6″}$ protons exhibited two sets of peaks, proving the formation of a highly symmetric structure (Fig. 1a). The other assignments were confirmed with the aid of 2D COSY and NOESY NMR spectroscopy (Fig. S16 and S17, ESI†). Shown in Fig. 1b, the signals of all the coordinated tpy moieties merged into broad peaks caused by their large planar structures. Compared with the signals of the free tpy groups of **L**, the proton signals attributed to E-tpyH$^{3′,5′}$ and F-tpyH$^{3′,5′}$ were shifted downfield, from 8.86 and 8.73 ppm to 9.12 ppm. Meanwhile, an expected upfield shift of the tpyH$^{6,6″}$ proton signals from 8.9 and 8.7 ppm to 7.82 ppm can be observed due to the electronic shielding effect that arises after coordination with the metals. The remaining signals of the **Zn$_6$L$_3$** spectrum were confirmed using 2D COSY and NOESY NMR spectroscopy (Fig. S20 and S21, ESI†). In order to acquire more evidence of the structure, diffusion-ordered NMR spectroscopy (DOSY) was used to measure the size of **Zn$_6$L$_3$**. The DOSY spectrum (Fig. S22, ESI†) of **Zn$_6$L$_3$** shows that the protons are found in a narrow band at $\log D = -9.88$, which also demonstrates the formation of a discrete structure. The diffusion coefficient D was calculated to be 1.32×10^{-10} m^2 s^{-1}, from which the hydrodynamic radius, according to the Stokes–Einstein equation, is 2.42 nm for **Zn$_6$L$_3$** (D = 4.84 nm). This result is consistent with the modelling data (4.67 nm). The paramagnetic nature of Co(II) is well-known, therefore, the Co(II) complexes were hard to characterize using ^{1}H NMR. Nevertheless, we obtained the ^{1}H NMR spectrum of **Co$_6$L$_3$** (Fig. S23–25, ESI†) which spreads out over a wide range from 3 to 100 ppm (Fig. 1c). Although the 2D COSY and 2D NOESY spectra of the tpy protons could not be obtained because of fast relaxation, the ^{1}H NMR signals from the tpy protons of **Co$_6$L$_3$** could be assigned based on their characteristic chemical shifts and literature reports.[14,19] Compared with Co(II), Mn(II) and Ni(II) exhibit stronger paramagnetic behaviour with shorter relaxation times, thus resulting in unsatisfactory ^{1}H NMR spectra.[20]

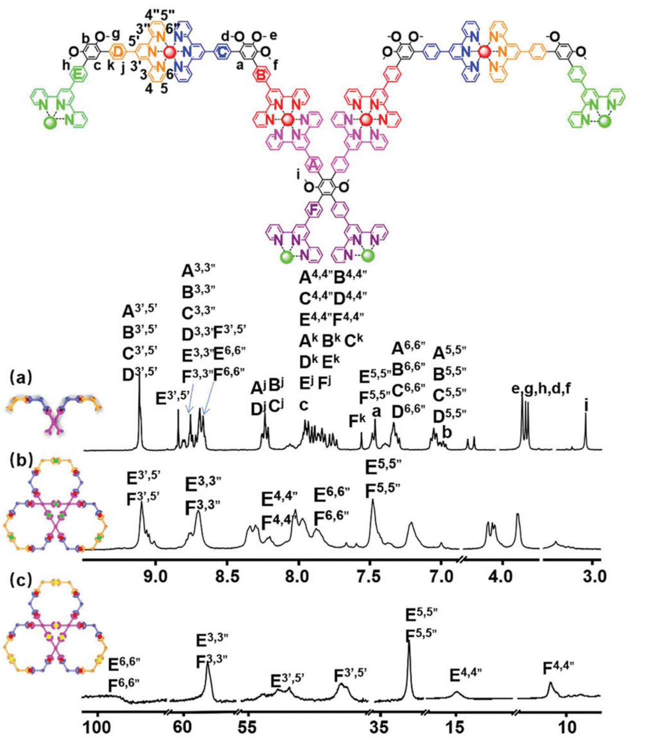

Fig. 1 The ^{1}H NMR spectra of (a) **L**, (b) **Zn$_6$L$_3$** and (c) **Co$_6$L$_3$** (500 MHz, CDCN$_3$, 300 K).

In addition, ESI-MS coupled with TWIM-MS was applied to validate the proposed structures. Fig. 2a shows a series of peaks with continuous charges from 11+ to 21+ for **Zn$_6$L$_3$** due to the successive loss of the NTf_2^- counterion. After deconvolution, the obtained molecular weight of 25 007 Da agreed well with the proposed molecular composition $[(C_{234}H_{210}N_{36}O_{12})_3Ru_{12}Zn_6(NTF_2^-)_{36}]$. The experimental isotope pattern of each charged state is consistent with the simulated isotopic distribution (Fig. S6, ESI†). TWIM-MS showed a series of charged states with a narrow drift time distribution ranging from 11+ to 20+, excluding the formation of other isomers or conformers (Fig. 2b). Moreover, the molecular weights of **Co$_6$L$_3$**, **Mn$_6$L$_3$** and **Ni$_6$L$_3$** were also confirmed to correspond with their proposed molecular compositions (Fig. 2c, e and Fig. S4, ESI†). Similarly, the complexes with Co(II), Mn(II) and Ni(II) have comparable drift times in the same charge states (Fig. 2d, f and Fig. S5, ESI†), indicating that these complexes have similar shapes.

In order to examine the stability of the supramolecular complex, gMS^2 experiments were performed on the 17+ ions at *m*/*z* 1190.4 *via* collision-induced dissociation with collision energies ranging from 4 to 28 V (Fig. 3c). There was no obvious

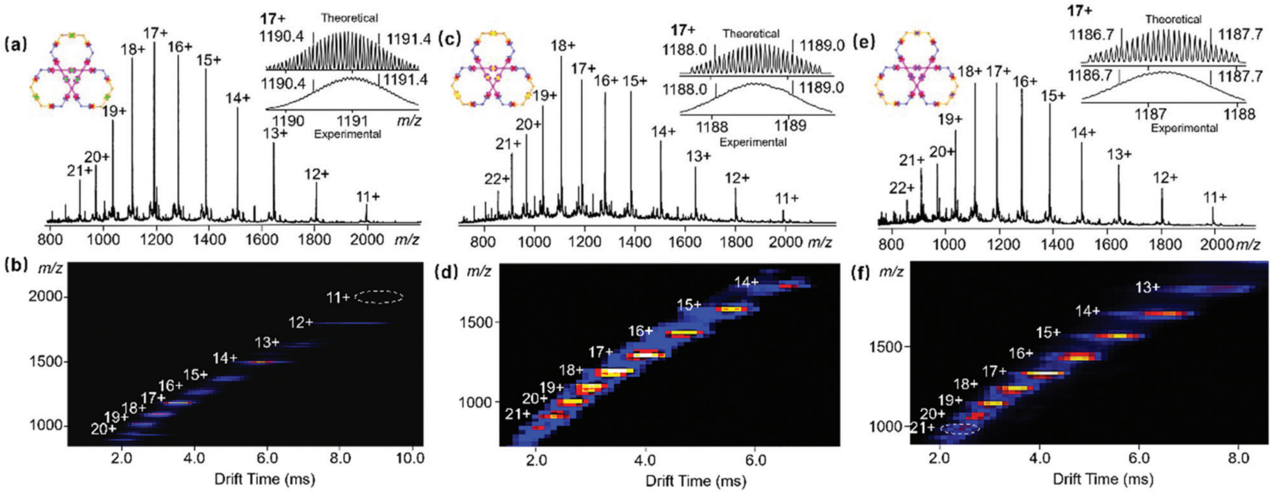

Fig. 2 ESI-MS of (a) $\mathbf{Zn_6L_3}$, (c) $\mathbf{Co_6L_3}$ and (e) $\mathbf{Mn_6L_3}$; TWIM-MS plots (*m/z vs.* drift time) of (b) $\mathbf{Zn_6L_3}$, (d) $\mathbf{Co_6L_3}$ and (f) $\mathbf{Mn_6L_3}$.

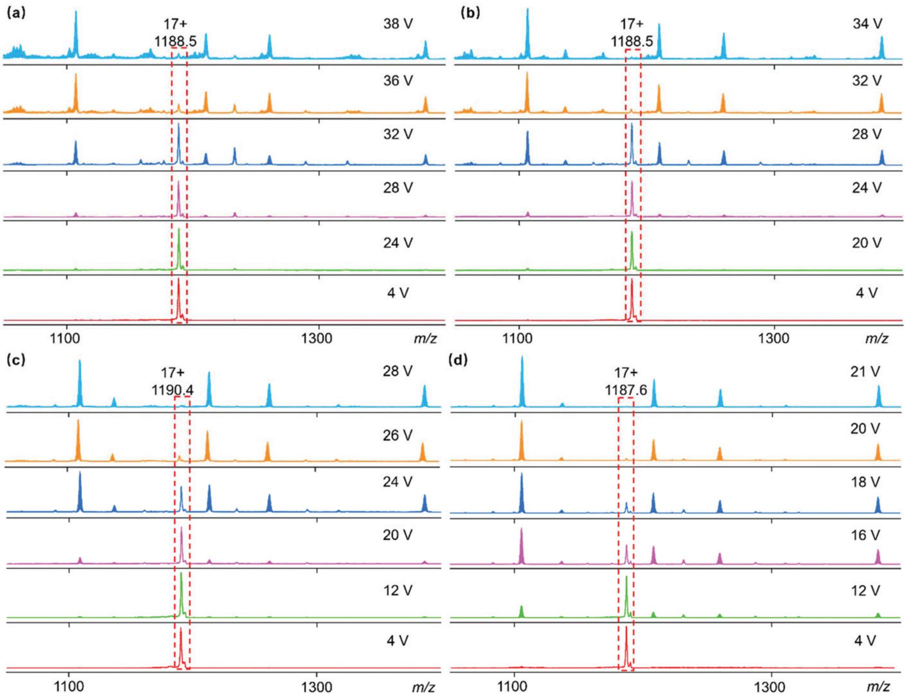

Fig. 3 gMS^2 of (a) $\mathbf{Ni_6L_3}$ at *m/z* 1188.5 with different collision energies, (b) $\mathbf{Co_6L_3}$ at *m/z* 1188.5 with different collision energies, (c) $\mathbf{Zn_6L_3}$ at *m/z* 1190.4 with different collision energies and (d) $\mathbf{Mn_6L_3}$ at *m/z* 1187.6 with different collision energies.

fragmentation peak observed below 20 V and when the voltage reached 28 V the complex ions completely dissociated. The stability of $\mathbf{Co_6L_3}$, $\mathbf{Mn_6L_3}$ and $\mathbf{Ni_6L_3}$ was examined under the same test conditions. The 17+ ions of $\mathbf{Ni_6L_3}$ dissociated at 38 V, while $\mathbf{Co_6L_3}$ and $\mathbf{Mn_6L_3}$ became fragments at 34 V and 21 V, respectively. The stabilities of these supermolecules in the gas phase were estimated and were found to depend on the metal ions with a relative order of Ni > Co > Zn > Mn. This is similar to the relative order of stabilities observed for previously reported simple complexes.[21,22]

Furthermore, TEM also provided evidence for the formation of the clover-type bimetallic supramolecular structure. As shown in Fig. 4b, a reasonable measured diameter of 4.90 nm could be observed from the TEM image. This is similar to the size simulated from molecular modelling (4.67 nm) (Fig. 4b and Fig. S26–S28, ESI†). Finally, CV was used to characterize the electrical properties of the supramolecules, and a three-electrode working system consisting of a 3 mm glassy carbon electrode (WE), platinum wire electrode (CE) and Ag/AgCl electrode (RE) was used for testing. Due to the oxidation of the

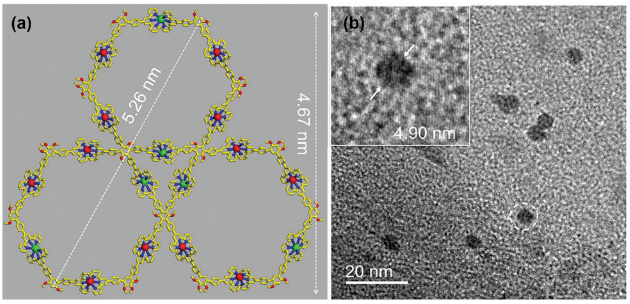

Fig. 4 (a) Representative energy-minimized structure obtained from molecular modelling of **Zn_6L_3**, (b) TEM images of **Zn_6L_3**.

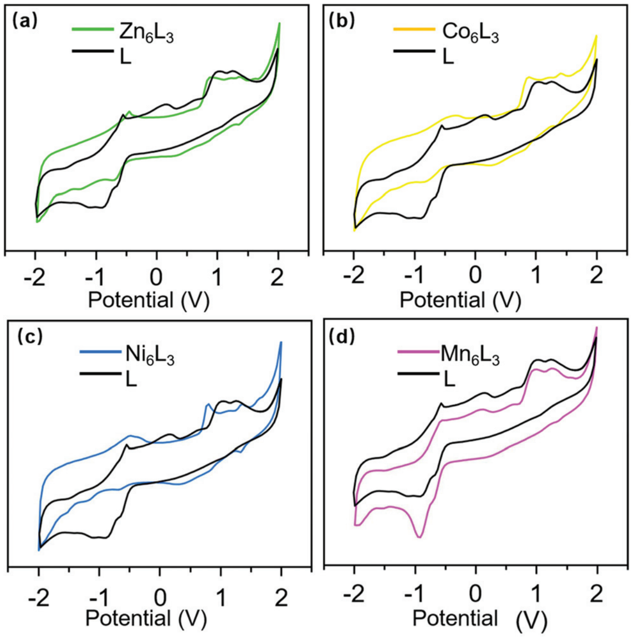

Fig. 5 CV of **L** with (a) **Zn_6L_3**, (b) **Co_6L_3**, (c) **Ni_6L_3**, and (d) **Mn_6L_3** (in a 0.1 M solution of Bu_4NPF_6 in CH_3CN).

Ru(II)/Ru(III) and Ru(III)/Ru(IV) couples,[23] ligand **L** has two oxidation peaks near 1.05 and 1.25 V (Fig. 5). In contrast, the $Ru^{2+/3+}$ and $Ru^{3+/4+}$ oxidation peaks of the supramolecular structure are slightly shifted compared with ligand **L**. Since Zn(II) is already in its highest oxidation state, only the oxidation peaks of Ru can be observed at 0.84 and 1.16 V.[24] In Fig. 5b and c, the irreversible oxidation of Co(II) in **Co_6L_3** can be seen peaking at −0.35 V, while the irreversible oxidation peak of Ni(II) is located at −0.48 V. The supramolecular structure of **Mn_6L_3** gives rise to similar CV curves seen in ligand **L**.[25,26] The photochemical properties of these complexes were also studied using UV-visible spectroscopy and low temperature fluorescence spectroscopy. The absorption spectra of the ligand and all complexes have a characteristic absorption peak near 495 nm, which can be attributed to the metal-to-ligand charge transfer transitions of the tpy-Ru-tpy unit (Fig. S29, ESI†).[27] The emissions from **L** and the supramolecules were detected in CH_3CN solution under 73 K (Fig. S30†). The emission spectra of **Ni_6L_3**, **Mn_6L_3** and **Co_6L_3** overlapped with a major peak at 653 nm while the major peak of **Zn_6L_3** shows a slight shift to 648 nm.[28,29]

In conclusion, four clover leaf-shaped metallo-supramolecular structures were successfully designed and synthesized. This report is the first example where Mn^{2+}, Co^{2+}, Ni^{2+} metal ions are used in a heterometallic multinuclear metallo-supramolecular system. The structures were characterized using 1D and 2D NMR, high-resolution ESI-MS, TWIM-MS, gMS^2, TEM, CV, UV-vis and fluorescence spectroscopy. Moreover, we anticipate that these multinuclear metallo-supramolecules may serve as a model system for further study of the self-assembly behavior and physical properties of 2D materials.

Author contributions

All authors have given approval to the final version of the manuscript. Z.Z., X.L. and P.W. designed the experiments; T.W. and Q.B. completed the synthesis; T.W. and Z.T. carried out the NMR analysis; Q.B. and T.W. did the ESI-MS test and data curation; L.X., Y.G. and M.C. completed the TEM characterization; P.S. performed the low temperature fluorescence measurement; Q.B. and Z.Z. analyzed the experiment data; Q. B. and T.W. wrote the manuscript; Z.Z., X.L., H.W., T.X. and P. W. edited the manuscript. All the authors discussed the results and commented on and proofread the manuscript.

Conflicts of interest

There are no conflicts to declare.

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