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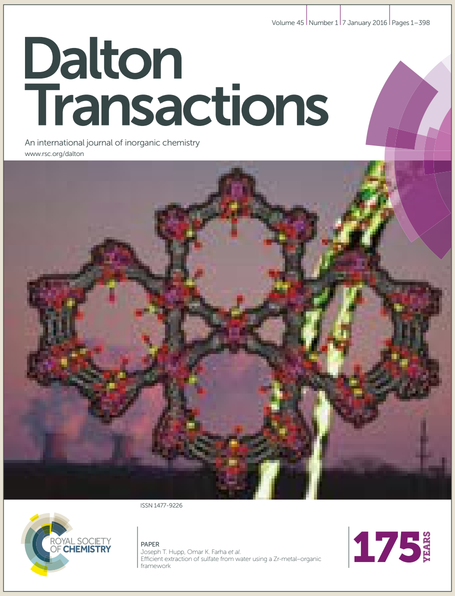

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COMMUNICATION

Diversity of Metal-Organic Macrocycles Assembled from Carbazole Based Ligands with Different Length

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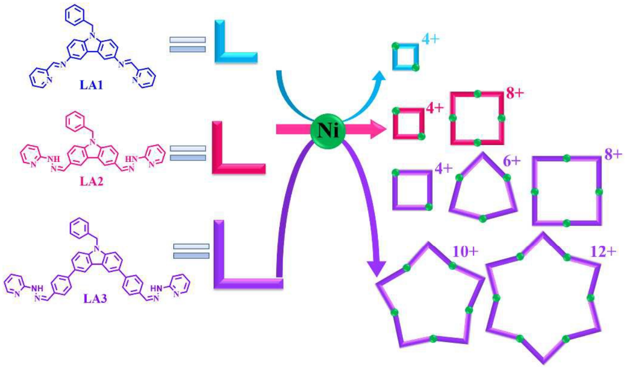
A series of carbazole based ligands with different length were assembled with nickle ions to construct metal-organic macrocycles. High-resolution mass spectrometry and ion mobility-mass spectrometry have been used to analyse the resulted M_nL_n assembly coexisted in solution. Combining with the structural analysis of their solid confirmation, it was revealed that the diversity of the metal-organic macrocycles was increased with the flexity of the ligands.

Coordination driven supramolecular assemblies have attracted considerable attention of chemists due to their high symmetry and rich physical/chemical properties.[1] In particularly, the dynamic and reversible features of metal-ligand interaction usually endow disassembly and reassembly processes of the coordination assemblies, resulting in the interconversions between different self-assembled architectures under external stimuli.[2] By taking advantage of the relatively rigid yet dynamic nature of coordination bonds, these coordination-driven assembled architectures could provide an ideal platform for studying supramolecular transformations,[3] which is the important process occurred in biological systems, such as the allosteric regulation.[4]

Among these architectures, metal-organic macrocycles with M_nL_n formula, constructed from metal ions and organic ligands with two individual chelating sites represent a typical class of supramolecules with remarkable feature on structural diversity.[5] Usually, in such two dimensional systems, more than one species could be in equilibrium in solution (n= 2, 3, 4, 5, 6…) if there is no clear thermodynamic preference for one species over the others.[6] Illustrating the coordination driven constitutional dynamic libraries of such oligomers in solution would be helpful to study the structurally dependent properties and applications of the resultant assemblies.[7] Herein, by introducing planar carbazole moiety as main framework, a series of ligands (**LA1**-**3**) having two predisposed NN bidentate chelators were designed to assembly with the nickel ions, resulting in macrocycles (Ni-**LA1**, Ni-**LA2** and Ni-**LA3**; **Scheme 1**). The rigid carbazole moiety and the bidentate coordination sites could enhance the possibility of the resulted structures to be fixed in a two-dimensional discrete one.[8] And the increase of the length and rotation ability on the ligands would cause the more possible species coexisting in the dynamic libraries.



Scheme 1. Procedure for the synthesis of the metal-organic macrocycles based on Ni-**LA**.

On the other hand, unambiguous describing the structure of coexistent species in solution presents a huge challenge. Irrefutable evidence for the precise configuration and conformation of complex architectures is difficult to obtain solely from NMR spectroscopic methods due to their related higher symmetries and the presence of paramagnetic ions. In recent years the use of electrospray ionisation mass spectrometry (ESI-MS) has allowed analysis of the intact biological non-covalent assemblies as well as metal-organic supramolecular self-assemblies.[9] Mass spectrometry based methods can provide detailed information of the stoichiometry and structure of metal-organic macrocycles by the use of collisional activation. Ion mobility-mass spectrometry (IM-MS) is increasingly utilised for structural analysis of ions following ESI-MS.[10] In traveling wave ion

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mobility-mass spectrometry (TWIMS), ions are allowed to separate with an inert buffer gas under the stacked ring ion guides in which an radio frequency voltage is applied across consecutive electrodes and used to stop the radial spread of ions.[11] In this work, we adopt IM-MS to analyse the diversity of the metal-organic macrocycles self-assembled from ligands with different lengths in solution.

Ligand **LA1** was obtained by a Schiff-base reaction of 9-benzyl-3,6-diaminecarbazole with 2-pyridine-carboxaldehyde. The ESI mass spectrum of **LA1** (2.0 mM) with 1 equiv of $Ni(ClO_4)_2 \cdot 6H_2O$ mixed in CH_3CN/CH_3OH (v/v, 9:1) solution exhibited a series of multi-charge peaks at *m/z* 262.07, 382.40, 623.08 and 1345.11 that corresponded to $[Ni_2(\mathbf{LA1})_2]^{4+}$, $[Ni_2(\mathbf{LA1})_2(ClO_4^-)]^{3+}$, $[Ni_2(\mathbf{LA1})_2(ClO_4^-)_2]^{2+}$ and $[Ni_2(\mathbf{LA1})_2(ClO_4^-)_3]^{+}$, respectively. A comparison of experimentally obtained peaks with those obtained via the simulation, based on natural isotopic abundance, revealed that only the $Ni_2(\mathbf{LA1})_2$ species existed in solution (Fig. S10, S11). Diffusing diethyl ether into the solution led to the formation of red needle-like crystals of complex Ni-**LA1** in a yield of about 50%. As shown in Fig. 1b, single crystal X-ray structural analysis of Ni-**LA1** confirmed the formation of a M_2L_2 metal-organic macrocycle structure.[12] Each nickel atom was hexa-coordinated to two ligands and two CH_3CN molecules. The two ligands were completely symmetrical about the Ni-Ni axis, and the angle from the centre of pyridine to carbazole N atom was 75.12°. It seems that the bidentate coordination moiety directly linked to the central carbazole part make the ligand **LA1** have a strong rigidity, so that ligand **LA1** could not flexibly twist too much to form structures with varying extensibility. As the related rigid conformation of ligand **LA1** and hexa-coordination of nickel atom, the binuclear macrocyclic Ni-**LA1[22]** species was the only favoured in solution.

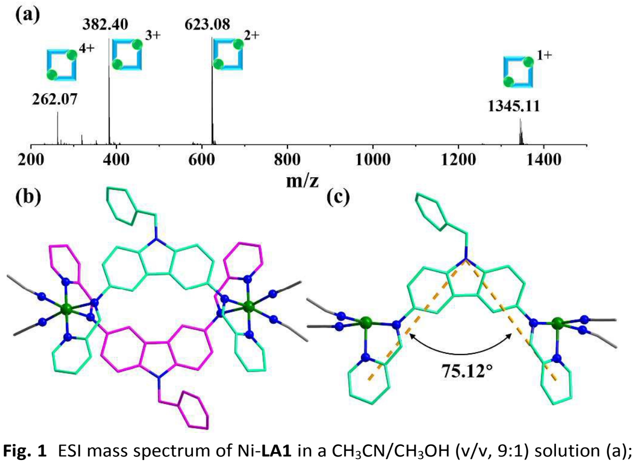

Fig. 1 ESI mass spectrum of Ni-**LA1** in a CH_3CN/CH_3OH (v/v, 9:1) solution (a); the structures of the metal-organic macrocycle Ni-**LA1** (b) and one of the ligands in Ni-**LA1**(c). The Ni and N atoms are drawn in green and blue, respectively. For the structures representing each symbol, see Scheme 1.

Ligand **LA2** was obtained by reaction of 9-benzyl-3,6-dicarbaldehydecarbazole with 2-hydrazinylpyridine. Compared with **LA1, LA2** could be simply seen as inserting one carbon atom between the bidentate coordination and the central carbazole moieties. The ESI mass spectrum (Fig. 2) of Ni-**LA2** solution exhibited a number of intense peaks at *m/z* 904.45, 503.09 and 402.42. The peaks were assigned to the species of $[Ni_4(\mathbf{LA2})_4(ClO_4^-)_5]^{3+}$, $[Ni_4(\mathbf{LA2})_4(ClO_4^-)_3]^{5+}$ and $[Ni_2(\mathbf{LA2})_2(ClO_4^-)]^{3+}$, respectively, suggesting the coexistence of the $Ni_4(\mathbf{LA2})_4$ and $Ni_2(\mathbf{LA2})_2$ species in solution. Interestingly, the characteristic peaks of Ni-**LA2[44]** at *m/z* 1406.15 and 653.10 were not exactly the same as its isotopic pattern. Those peaks, assigned as fully assembled $[Ni_4(\mathbf{LA2})_4(ClO_4^-)_6]^{2+}/[Ni_2(\mathbf{LA2})_2(ClO_4^-)_3]^{+}$ and $[Ni_4(\mathbf{LA2})_4(ClO_4^-)_4]^{4+}/[Ni_2(\mathbf{LA2})_2(ClO_4^-)_2]^{2+}$, had a minor additional feature presented at longer times in IM mass spectrua (for example *m/z* 1406, approximately 3.39 and 6.93 bins, respectively). In both, these minor peaks could be unambiguously assigned to the species of Ni-**LA2** with different formula. From the IM mass spectrum, it could be seen that the macrocycle of M_4L_4 existed in solution as the major structure of Ni-**LA2** at *m/z* 1406. However, some charge states of Ni-**LA2[44]** (*m/z* 904.45 for $[Ni_4(\mathbf{LA2})_4(ClO_4^-)_5]^{3+}$, *m/z* 503.09 for $[Ni_4(\mathbf{LA2})_4(ClO_4^-)_3]^{5+}$) were unique to the fully assembled complex, and it was not possible to have Ni-**LA2[22]** species at these corresponding *m/z* values since a fraction of the counterion would be required.

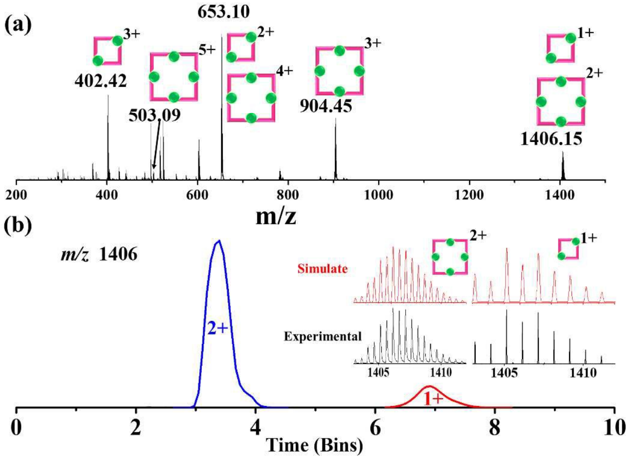

Fig. 2 ESI mass spectrum of Ni-**LA2** with peaks of interest assigned in a CH_3CN solution (a); drift time distribution for the *m/z* 1406.1537 corresponding to the 2+ charge state of Ni-**LA2[44]** and the 1+ charge state of Ni-**LA2[22]** by ion mobility-mass spectrometry (b).

Fortunately, single crystals of both these two kinds of macrocycles were obtained. Through diffusing diethyl ether into the CH_3CN/CH_3OH (v/v, 9:1) solution of Ni-**LA2**, the formation of yellow needle-like crystals and a farthing thimbleful amount of square-shaped crystals were observed in a total yield of about 65%. These two kinds crystals could be separated manually and were determined respectively. Single crystal X-ray structural analysis revealed that the large amount needle-like crystal was the Ni-**LA2[44]** and the square-shaped one was Ni-**LA2[22]** (Fig. 3), respectively.[13,14] In both of the structures, the nickel atoms coordinated to six atoms similar to the octahedral configuration in Ni-**LA1**, except for the difference that water as a solvent molecule was involved in the coordination with Ni atoms. In the structure of Ni-**LA2[44]**,

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Ni(1) coordinated with two ligands, one CH_3CN molecule and one H_2O molecule. And the five coordination sites of Ni(2) were occupied by four N atoms from the ligands and one CH_3CN molecule, while the remaining one was occupied by H_2O or CH_3CN in part probability. In the structure of Ni-**LA2[22]**, Ni(1) coordinated with two ligands and two CH_3CN molecules while the coordination of Ni(2) was the same like that in Ni-**LA2[44]**. The complex of Ni-**LA2[44]** consisted of four ligands and four nickel ions that connected together alternately. Each ligand bound to the central Ni ion through the pyridine N atom and hydrazine N atom, and 9-benzylcarbazole moiety was located in the edge of the macrocycle. The macrocycle of Ni-**LA2[44]** could also be seen as a rectangle with the Ni-Ni distances of 11.53 and 8.26 Å due to π-π stacking interactions between the two adjacent carbazoles with strong and rigid conjugation plane. Since **LA2** had one more C atom than **LA1**, the hydrazinopyridine moiety could rotate more freely around the C-C axis. There were two kinds of **LA2** with different conformations presence in the rectangular macrocycle of Ni-**LA2[44]** with varying length and width. The angles from the centre of pyridine to carbazole N atom in the two kinds of ligands were 123.04° and 67.14°, respectively. The conformation of the former one is more linear than that of **LA1** in Ni-**LA1**, which is helpful to get less tension in the M_4L_4 macrocycle. The rotatable benzyl groups of the two ligands with larger extensibility positioned inside of the macrocycle and provided additional stacking interactions to stabilize the structure. As the similar coordination structure with Ni-**LA2[44]**, the Ni-Ni distance of Ni-**LA2[22]** was 11.28 Å. Due to π-π stacking interactions between the two adjacent carbazoles, two kinds of **LA2** with different extensibility coexisted in the structure of Ni-**LA2[22]** and the angles from the centre of pyridine to carbazole N atom were 109.90° and 41.02°, respectively. Obviously, the higher flexility of **LA2** could endow itself more conformation freedom to fit the low tension in diverse metal ligand assemblies.[15]

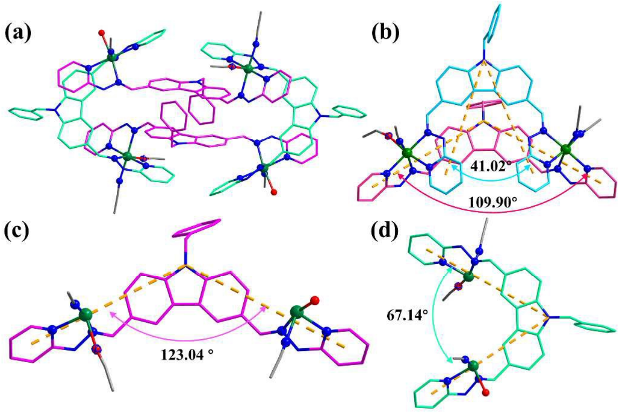

Fig. 3 The structure of the metal-organic macrocycle Ni-**LA2[44]** (a), Ni-**LA2[22]** (b), the larger extensibility ligand of ligand of Ni-**LA2[44]** (c) and the less extensibility ligand of Ni-**LA2[44]** (d). The Ni and N atoms are drawn in green and blue, respectively.

To further confirm the relationship between the metal-organic macrocycles and the length of ligands, the longer ligand **LA3** was synthesized by introducing a phenyl group between the carbazole and the coordination moiety. The freely rotatable phenyl group not only enhanced the length of the ligand but also the flexibility of the coordination moiety,[16] so that it might coordinate with Ni atom to form a variety of metal-organic macrocycle structures. The multi-charge characteristic peaks of four species that self-assembled by **LA3** and Ni in a CH_3CN/CH_3OH (v/v, 9:1) solution were observed in ESI mass spectrum (Fig. 4). The peaks at *m/z* 352.99 and 503.63 were assigned to the species of Ni_2(**LA3**)$_2$, the peaks at *m/z* 443.57 and 579.19 were assigned to Ni_3(**LA3**)$_3$, the peaks at *m/z* 624.33 and 1107.18 were assigned to Ni_4(**LA3**)$_4$ and the peaks at *m/z* 1031.86 and 1408.76 were assigned to Ni_5(**LA3**)$_5$, respectively. As the coordination complexes were ionized by removal of one or more ClO_4^-, it was possible for quasi-molecular ion peaks of Ni-**LA3** with same stoichiometric ratio of components to appear at the same m/z value, which not perfectly match their isotopic pattern. Hence, these species also need to be structurally characterized if they are present. As expected, characteristic peaks of $[Ni_2(\mathbf{LA3})_2(ClO_4^-)_2]^{2+}$ and $[Ni_3(\mathbf{LA3})_3(ClO_4^-)_3]^{3+}$ appeared at *m/z* 804, and peaks of $[Ni_3(\mathbf{LA3})_3(ClO_4^-)_4]^{2+}$ and $[Ni_6(\mathbf{LA3})_6(ClO_4^-)_8]^{4+}$ appeared at *m/z* 1258. As shown in the IM mass spectra, the one with high charge had short drift time for the different species of Ni-**LA3** with the same *m/z* value. The introduction of phenyl group increased the length of the ligand and allowed the coordination moiety to rotate properly around the axial direction, which was in favour of the flexible coordination of ligand and metal centre to form a variety of species.

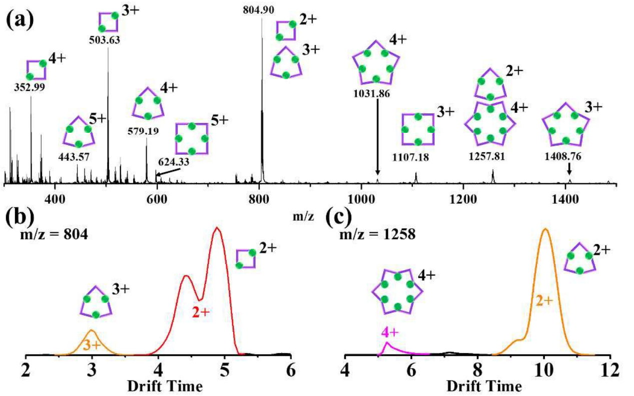

Fig. 4 ESI mass spectrum of Ni-**LA3** in a CH_3CN/CH_3OH (v/v, 9:1) solution (a); drift time distribution for the *m/z* 804 (b) and *m/z* 1258 (c) corresponding to Ni-**LA3**.

Conclusions

In summary, a series of carbazole-based ligands with different lengths were synthesized to coordinate with Ni ions forming metal-organic macrocycles. The high-resolution mass spectrometry coupling with ion mobility-mass spectrometry had been successfully applied as a powerful tool in studying the construction information of metal-organic self-assemblies in solution. The study found that the species coexisted in solution

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became more complex as the increase length of the ligands, which was associated with a more flexible conformation of the ligands.

Conflicts of interest

There are no conflicts to declare.

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12 Crystal data for Ni-**LA1**. $Ni_2C_{70}H_{58}Cl_4N_{14}O_{16}$, Mr= 1610.52, Orthorhombic, space group *P*bcn, a = 16.416(3) Å, b = 31.885(5) Å, c = 15.264(3) Å, *V* = 7989(2) Å^3, Z = 4, μ (MoKα) = 0.675 mm^{-1}, T = 200(2) K, 7012 unique reflections [R_{int} = 0.1265], Final R_1 [with I > 2σ(I)] = 0.0837, wR_2 (all data) = 0.1845. **CCDC NO. 1815437**.

13 Crystal data for Ni-**LA2[22]**. $Ni_4C_{145}H_{138}Cl_8N_{37}O_{34.50}$, Mr= 3469.36, Monoclinic, space group $P2_1/c$, a = 34.426(1) Å, b = 13.971(1) Å, c = 33.542(1) Å, *β* = 96.03(1)°, *V* = 16043.1(5) Å^3, Z = 4, μ(MoKα) = 0.681 mm^{-1}, T = 200(2) K, 28131 unique reflections [R_{int} = 0.0564], Final R_1 [with I > 2σ(I)] = 0.0769, wR_2 (all data) = 0.2319. **CCDC NO. 1815438**.

14 Crystal data for Ni-**LA2[44]**. $Ni_4C_{150}H_{155}Cl_8N_{37}O_{38}$, Mr= 3602.55, Triclinic, space group *P*-1, a = 12.135(1) Å, b = 17.558(1) Å, c = 22.164(2) Å, *α* = 98.47(1)°, *β* = 100.41(1)°, *γ* = 109.07(1)°, *V* = 4280.5(6) Å^3, Z = 1, μ (MoKα) = 0.642 mm^{-1}, T = 150(2) K, 14988 unique reflections [R_{int} = 0.1564], Final R_1 [with I > 2σ(I)] = 0.0898, wR_2 (all data) = 0.2011. **CCDC NO. 1815440**.

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Diversity of Metal-Organic Macrocycles Assembled from Carbazole Based Ligands with Different Length

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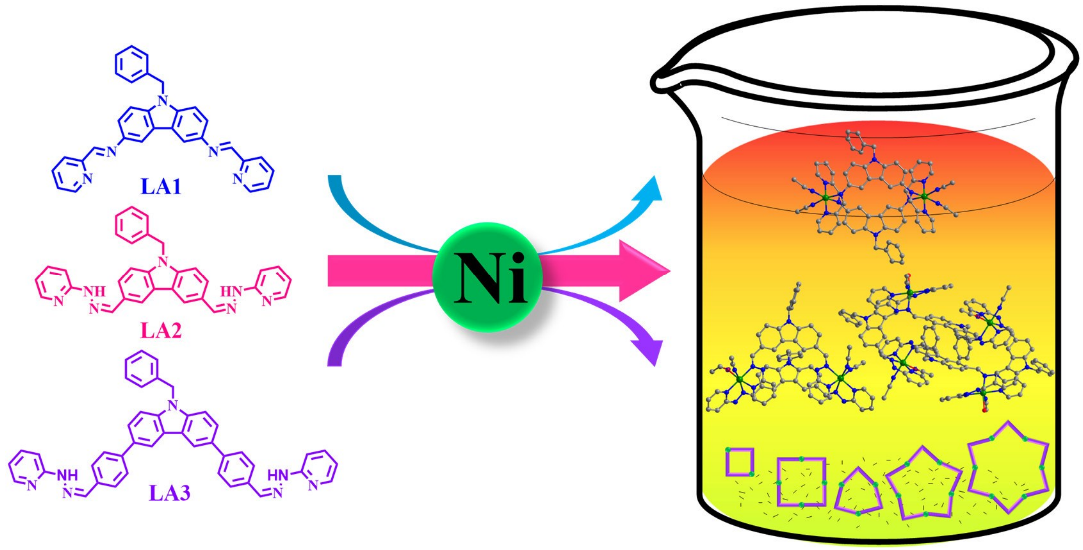

The more species of metal-organic macrocycles coexist in solution due to the increase of the length of the carbazole ligands.