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Introducing Seven Transition Metal Ions into Terpyridine-Based Supramolecules: Self-Assembly and Dynamic Ligand Exchange Study

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KEYWORDS: self-assembly, supramolecular chemistry, terpyridine, dynamic ligand exchange

ABSTRACT: In coordination-driven self-assembly, 2,2':6',2"-terpyridine (tpy) has gained extensive attention in constructing supramolecular architectures on the basis of <tpy-M-tpy> connectivity. In direct self-assembly of large discrete structures, however, the metal ions were mainly limited to Cd(II), Zn(II) and Fe(II) ions. Herein, we significantly broaden the spectrum of metal ions with seven divalent transition metal ions M(II) (M=Mn, Fe, Co, Ni, Cu, Zn, Cd) to assemble a series of supramolecular fractals. In particular, Mn(II), Co(II), Ni(II), Cu(II) were reported for the first time to form such large and discrete structures with<tpy-M-tpy> connectivity. In addition, the structural stabilities of those supramolecules in gas phase and the kinetics of the ligand exchange process in solution were investigated using mass spectrometry. Such a fundamental study gave the relative order of structural stability in gas phase and revealed the inertness of coordination in solution depending on the metal ions. Those results would guide the future study in tpy-based supramolecular chemistry in terms of self-assembly, characterization, property and application.

Introduction

With the goal of understanding the organizing principle of nature for constructing macromolecules and supramolecular complexes in biosystems, supramolecular chemistry has gradually developed a myriad of synthetic systems with dynamic features through self-assembly in the past few decades.[1] In particular, the active research interest in the field of coordination-driven self-assembly has witnessed a wide array of well-defined metallo-supramolecular architectures.[2] With a large structural diversity of organic building blocks and accessibility to different metal ions, metallo-supramolecules have been assembled with different topologies, such as one-dimensional (1D) helicates,[3] two-dimensional (2D) complexes (e.g., polygons,[4] fractals,[5] knots and links[6]), and three-dimensional (3D) cages (e.g., Platonic solids,[7] Archimedean solids,[8] Goldberg polyhedrons[9], and prisms[10]). Those metallo-supramolecules with increasing complexity and diversity have also given rise to further explorations of their fascinating physical and chemical properties, leading to the applications in host–guest chemistry,[11] catalysis,[12] sensing,[13] gas storage,[14] drug delivery and antimicrobial materials,[15] etc.

Among the diverse library of organic donor building blocks, e.g., pyridine,[16] bipyridine,[17] phenantroline,[18] terpyridine,[19] pyridine-diamide,[20] and carboxylic acids,[21] 2,2':6',2"-terpyridine (tpy) has been extensively used as a tridentate motif because of its excellent complexing ability towards different metal ions, i.e., main group, transition metals and lanthanide cations.[22] As such, many supramolecular architectures with <tpy-M-tpy> connectivity have been demonstrated for both discrete structures such as macrocycles[23], cages,[24] and infinite structures including supramolecular polymers[25] and networks.[26] The metal ions adopted to construct large discrete structures through direct self-assembly, however, were mainly limited to three metal ions with highly reversible coordination, viz., Cd(II), Zn(II) and Fe(II).[27] Very few cases have expanded the scope to Ru(II) and Os(II) with simple geometry and low complexity either by tedious post-assembly separation or under harsh reaction condition with low yields.[28] Perhaps, the lack of other metal ions in tpy-based supramolecular chemistry is due to the variable self-assembly conditions, and challenging characterization.[2b] Herein, we present a series of hexameric supramolecules with fractal characteristics[5c,5e] assembled by two tetratopic tpy ligands with seven different divalent transition metal ions M(II) (M=Mn, Fe, Co, Ni, Cu, Zn, Cd) under mild conditions after many trials (Figure 1a). Those supramolecular fractals have significantly broadened the spectrum of metal ions used in self-assembly of discrete supramolecular architectures with increasing diversity. Furthermore, the introduction of different types of metal ions is expected to advance the future study in metal-dependent functions and applications.

Compared to the conventional synthetic chemistry which deals with covalent bonds, one of the basic features inherent in supramolecular chemistry is its dynamic capability which can organize the molecular components into a supramolecular entity by virtue of non-covalent interactions. The dynamic nature allows the supramolecular species to reversibly dissociate and associate to ultimately generate the highly complex architectures.[29] Therefore, studying the self-assembly dynamics not only enhances the understanding of the processes but also facilitates the design and construction of supramolecular architectures with desired functionality. However, it remains a formidable challenge to characterize

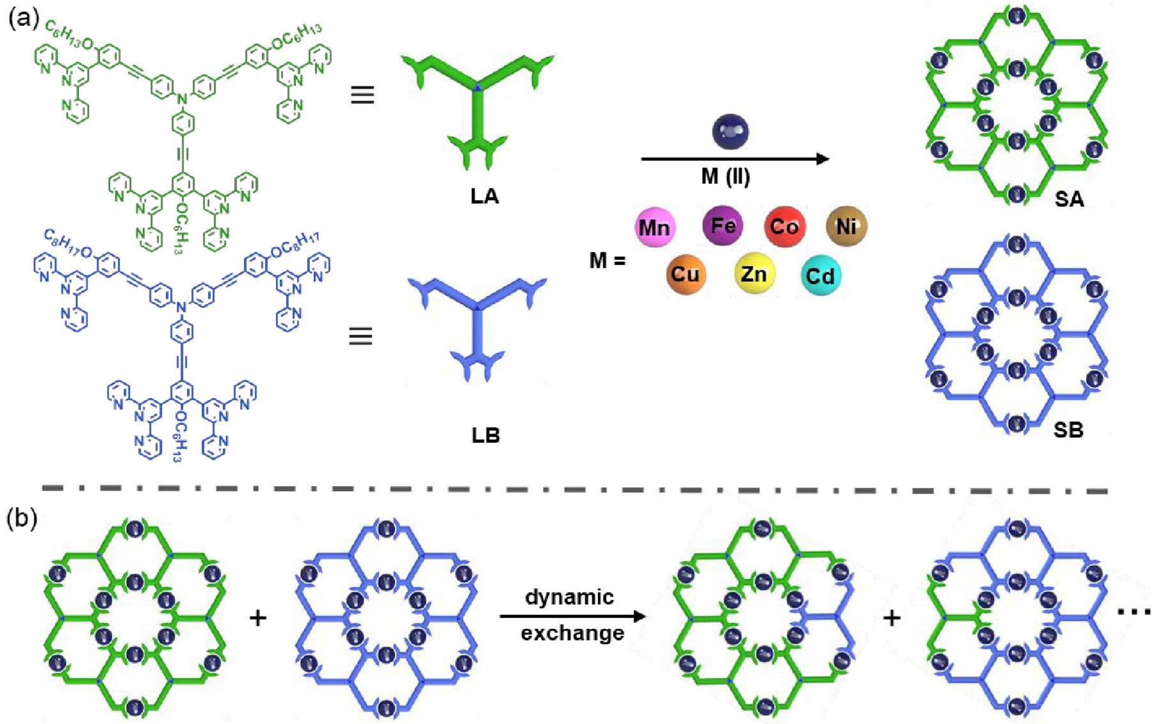

Figure 1. (a) Self-assembly of hexameric fractals through **LA** and **LB** with seven different transition metal ions; (b) Dynamic ligand exchange study between two fractals with the same metal ion.

the dynamic process with multiple possible intermediates and processes involved at different concentration, temperature, time, etc. To date, only a few examples have been reported with the aid of NMR,[30] mass spectrometry (MS)[31], fluorescence-resonance energy transfer (FRET),[32] and other methods.[33] In this report, we studied the kinetics of the dynamic ligand exchange process of assembled hexameric fractals using mass spectrometry (Figure 1b).The results revealed the inertness of coordination or how fast the self-assembly proceeded in solution depending on the metal ions. This fundamental study would guide the future study in tpy-based supramolecular chemistry in terms of characterization, property and application explorations.

Results and Discussion.

Self-assembly with different metal ions. In an effort to explore the possibility of construction of metallo-supramolecules with different <tpy-M-tpy> connectivity, the tetratopic ligand **LA** [5e] was first utilized to conduct the self-assembly with a series of divalent transition metal ions M(II). The other tetratopic ligand **LB** with the same rigid scaffold, but different side alkyl chains, was synthesized for dynamic ligand exchange study. **LB** was obtained in a moderate yield in a similar manner to **LA** through two steps of Sonogashira coupling reactions between tris(4-iodophenyl)amine and tpy motifs (Scheme S1). Because of the intrinsic bond angles controlled by triphenylamine and appropriate molecular rigidity, **LA** and **LB** were anticipated to form giant hexameric fractals through self-assembly.[5c,5e]

The self-assembly was first carried out with Zn(II) and Cd(II), which were widely used for construction of discrete structures based on the labile <tpy-M-tpy> connectivity. When **LA** or **LB** was mixed with $Zn(NO_3)_2·6H_2O$ or $Cd(NO_3)_2·4H_2O$ at a stoichiometric ratio of 1:2 in $CHCl_3$/MeOH (v/v 1:3) at 50 °C for 8h, the fractal structures were readily obtained as expected in high yields after counterion exchange and washing. Further study showed that Co(II), Ni(II), Cu(II) would also favor the formation of discrete structures rather than polymers by using common metal ions, i.e., $CoCl_2·6H_2O$, $NiSO_4·7H_2O$ and $CuCl_2$. Note that the self-assemblies for those three metals were performed in a sealed vessel at 80 °C to avoid the evaporation of $CHCl_3$ and MeOH. $MnClO_4$ was found capable of forming the same geometric structure in $CHCl_3$/MeCN (v/v 1:3) at 50 °C as well. Following the successful results of those metal ions, Fe(II) was similarly examined for the self-assembly. To our surprise, none of the conditions turned out to work for the Fe(II) including the reported method by using ethylene glycol at 190 °C.[27c,27d] Numerous efforts were made to construct the structure with <tpy-Fe-tpy> connectivity, and finally the goal was achieved by performing the self-assembly in DMF/CF_3CH_2OH (v/v 1:3) in a sealed vessel at 120 °C, followed by treatment with precipitation in saturated NH_4PF_6 solution. According to previous study, CF_3CH_2OH is able to weaken the nitrogen ligand-metal interaction because of its strong H-bond donating ability.[34] We reasoned that the coordination of tpy-Fe(II) could be weakened and became more labile, leading to the thermodynamically controlled product with designed structure instead of mixtures.[22b]

Other transition metal ions (i.e., Cr(II), Hg(II), Ir(III), Ru(II)), main group metal ions (i.e., Mg(II), Ca(II), Ga(III), Pb(II)) and lanthanides (i.e., La(III), Sm(III), Eu(III), Tb(III)) were all investigated and none of them could form a discrete

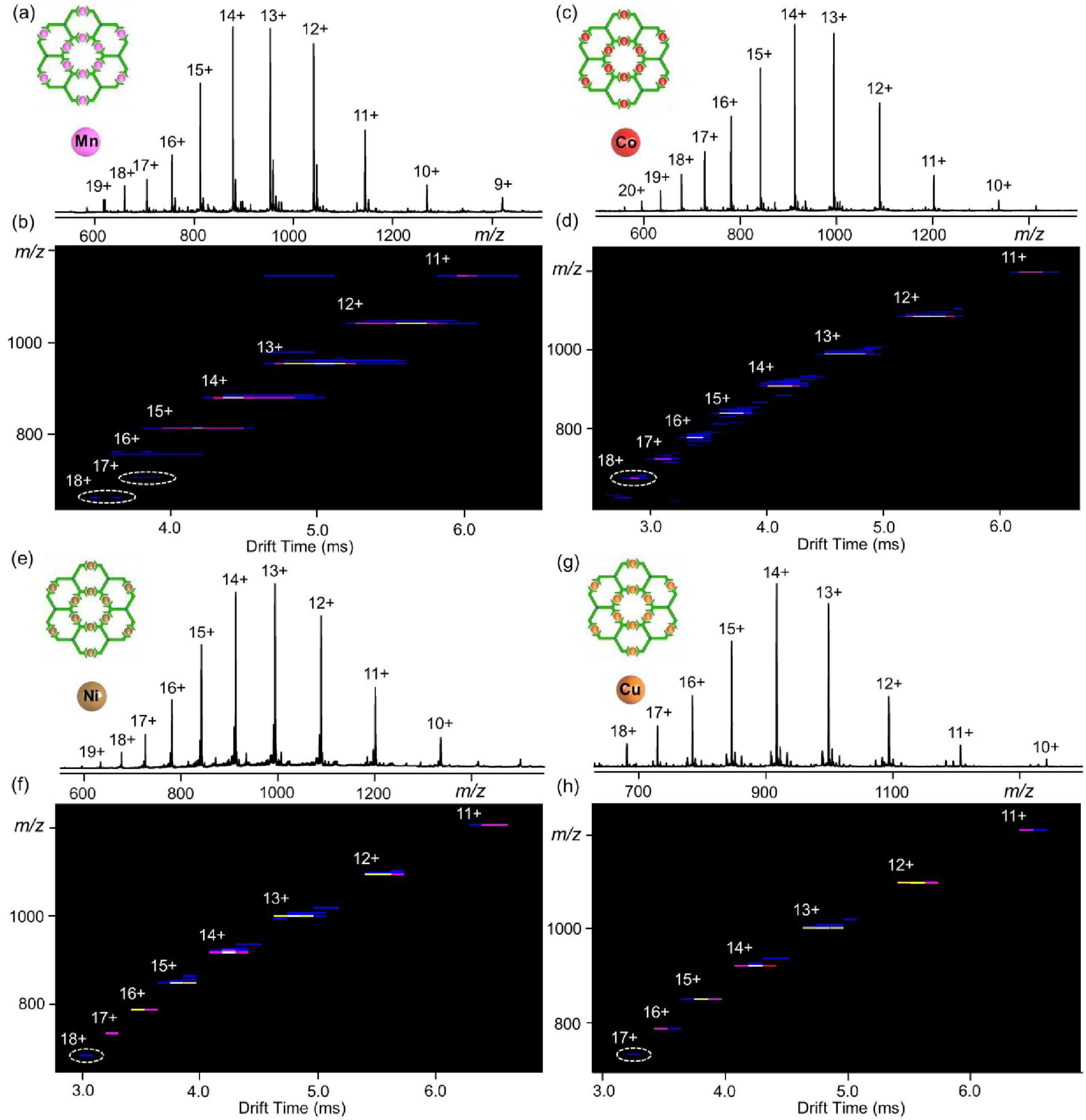

Figure 2. ESI-MS of (a) **SA-Mn**, (c) **SA-Co**, (e) **SA-Ni**, (g) **SA-Cu** and TWIM-MS plot (*m/z* vs. drift time) of (b) **SA-Mn**, (d) **SA-Co**, (f) **SA-Ni**, (h) **SA-Cu**.

structure according to ESI-MS. The unsuccessful trials might be attributed to either the unmatchable lability and reversibility of <tpy-M-tpy> connectivity that was hard to maintain an exclusive thermodynamic-favored structure, or the chelating effect of the ligand with solvents and counterions that might prevent the formation of discrete structures. Thus, seven transition metals were found capable of self-assembling into hexameric fractal structures, so far, by using the tetratopic ligands **LA/LB** we designed. Among them, Mn(II), Co(II), Ni(II), Cu(II) were reported for the first time to form such giant supramolecules with precisely-controlled shapes and sizes in the field of tpy-based coordination-driven self-assembly, and thus, substantially enriched the library of discrete metallo-supramolecules with different metal ions.

Characterization of supramolecules. Conventional electrospray ionization-mass spectrometry (ESI-MS) provided strong evidence in determining the composition of $\mathbf{M_{12}L_6}$ with a set of continuous charge states due to the loss of different numbers of counterions for each of the fractal

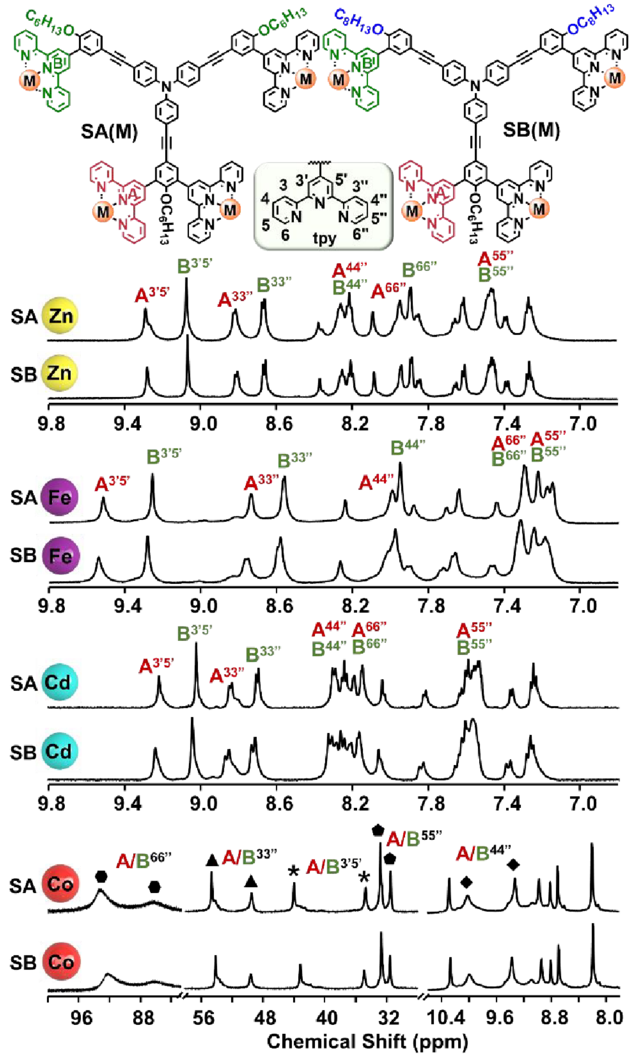

Figure 3. Partial ^{1}H NMR spectra (400 MHz, CD_3CN, 300 K) of **SA/SB-Zn**, **SA/SB-Fe**, **SA/SB-Cd**, **SA/SB-Co** from top to bottom.

structure (Figures 2a, 2c, 2e, 2g, and S2-S8). The experimental molecular weights for **SA**s were obtained as 14766, 14776, 14814, 14811, 14869, 14891, and 15455 Da for Mn, Fe, Co, Ni, Cu, Zn, Cd, respectively. The experimental isotope pattern for each charged state of the supramolecules agreed well with the theoretical one (*i.e.*, 952.3 for **SA-Mn**, 991.7 for **SA-Fe**, 994.5 for **SA-Co,** 994.2 for **SA-Ni**, 998.7 for **SA-Cu,** 1000.4 for **SA-Zn,** 1043.9 for **SA-Cd** at charge state 13+), which strongly supported the formula of the proposed structure $\mathbf{M_{12}L_6}$. Traveling wave ion mobility-mass spectrometry (TWIM-MS)[35] as a powerful tool to differentiate isomers or conformers further confirmed the clean formation of the discrete structures by displaying a narrow distribution of drift time for each charge state in the spectra (Figures 2b, 2d, 2f, 2h, and S2-S8). Moreover, all **SAs** or **SBs** with different metal ions gave comparable drift times at the same charge states (Table S1), suggesting that all those structures possess the same frameworks.

^{1}H NMR was applied to characterize the fractal supramolecules and the results were consistent with the designed structures assembled by Fe(II), Zn(II) and Cd(II). Two sets of characteristic tpy signals were observed in the complexes, indicating the high symmetry of the structure as proposed (Figure 3). Compared with the chemical shift of the free tpy subunits from the ligand **LA/LB** (Figures S43 and S49), all the protons of 3′, 5′ positions in the complexes were shifted downfield; while those protons of 6, 6″ positions were significantly shifted upfield because of either electron deficiency or electron shielding effect after complexation with metal ions.[23-24] The degree of those shifts were slightly different for **SA/SB-Zn**, **SA/SB-Fe** and **SA/SB-Cd** due to the different features of the central metal ions. All the assignments for **SA/SB-Zn** and **SA/SB-Fe** as well as **SA/SB-Cd** were confirmed by detailed 2D COSY (correlation spectroscopy) and 2D NOESY (nuclear Overhauser effect spectroscopy) spectra (Figures S52-S87).

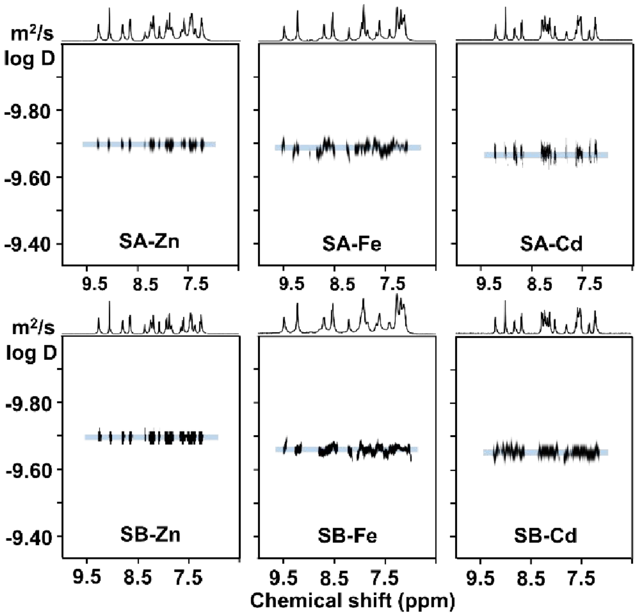

Figure 4. 2D DOSY spectra (400 MHz, CD_3CN, 300 K) of **SA/SB-Zn**, **SA/SB-Fe**, **SA/SB-Cd** from top to bottom.

The NMR characterizations of assemblies with Mn(II), Co(II), Ni(II), and Cu(II), however, were challenging due to the paramagnetic natures of those metals with tpy. Nevertheless, distinct ^{1}H NMR spectra of **SA/SB-Co** with such a high complexity and large molecular weights were still achieved for the first time. Surprisingly, the two sets of tpy signals spread out in a wide range (9 ~ 100 ppm), providing a fingerprint of the complexes. In a sharp contrast to the squeezed aromatic signals in the ^{1}H NMR spectra of Fe(II), Zn(II) and Cd(II) supramolecules, the paramagnetic NMR of **SA/SB-Co** gave more assignable signals due to the dramatic paramagnetic shifts and may facilitate the design and self-assembly more sophisticated structure in the future instead. Although the 2D COSY and 2D NOESY experiments for accessing the protons on the tpys failed because of the rapid T_1 relaxation time, all the tpy signals in the proton NMR were still assigned according to the characteristic chemical shifts of a model Co(II) complex (Figures S88-S101) and literature report.[36] Unfortunately, the ^{1}H NMR spectra for Mn(II), Cu(II) and Ni(II) complexes were unassignable with very broad signals (Figures S102-S106).

Diffusion-ordered NMR spectroscopy (DOSY) were applied to provide dimensional information of those fractals.[27] Except the unsatisfactory results of Mn(II) fractals, the spectra of all others displayed relatively narrow bands of signals with a diffusion coefficient (D, m^2/s) ranging from 1.92×10^{-10} to 2.24×10^{-10}, indicating the discrete architecture with a similar diameter for each fractal (Figure 4, and Figures S107-S112).The calculated hydrodynamic radius from the diffusion coefficient using the modified Stocks-Einstein equation based on the oblate spheroid model[37] is around 3.5 ~ 4.2 nm, which is consistent with the molecular modeling result we reported previously[5e] for the Zn(II) fractal. All the results are summarized in Table S2.

We further investigated the electrochemical properties of these fractals in a three-electrode electrochemical cell with Bu_4NPF_6 (0.001 M) as electrolyte. The oxidations of triphenylamine units were observed at around 0.9 V to 1.2 V in each fractal with broad peak corresponding to successive one electron removal,[38a] and the tpy-ligand-centered redox process occurred at -1.0V to -1.4V according to the literature[5e] (Figure S113). In Fe fractal, both of the Fe(III)/Fe(II) couple ($E_{1/2}$=1.0V, ΔE_p =140 mV) and Fe(II)/Fe(I) couple ($E_{1/2}$ =-1.23V, ΔE_p =120 mV) were observed.[38b] As for Co and Mn, only reduction process was displayed, i.e. Co(II)/Co(I) couple ($E_{1/2}$ = -0.63V, ΔE_p=70 mV) and Mn(II)/Mn(I) couple ($E_{1/2}$=-1.26V, ΔE_p =180 mV).[38c] The oxidation processes of these two metals might be overlapped with the broad peaks of triphenylamine units. Furthermore, irreversible oxidation peaks around 0.07V and 0.57V in Cu fractal indicated the adsorption on the electrode surface.[38d]

Study of the structural stability in gas phase and dynamic ligand exchange in solution. To evaluate the stability of the supramolecules with different metal ions, gradient tandem mass spectrometry (gMS^2)[39] was employed by applying a graduate increase of collision energy to an isolated charged species of the supramolecules. The results showed that those fractals with different <tpy-M-tpy> connectivity were completely dissociated at different collision energy (Table 1) under gMS^2. For instance, **SA-Cu** was dissociated

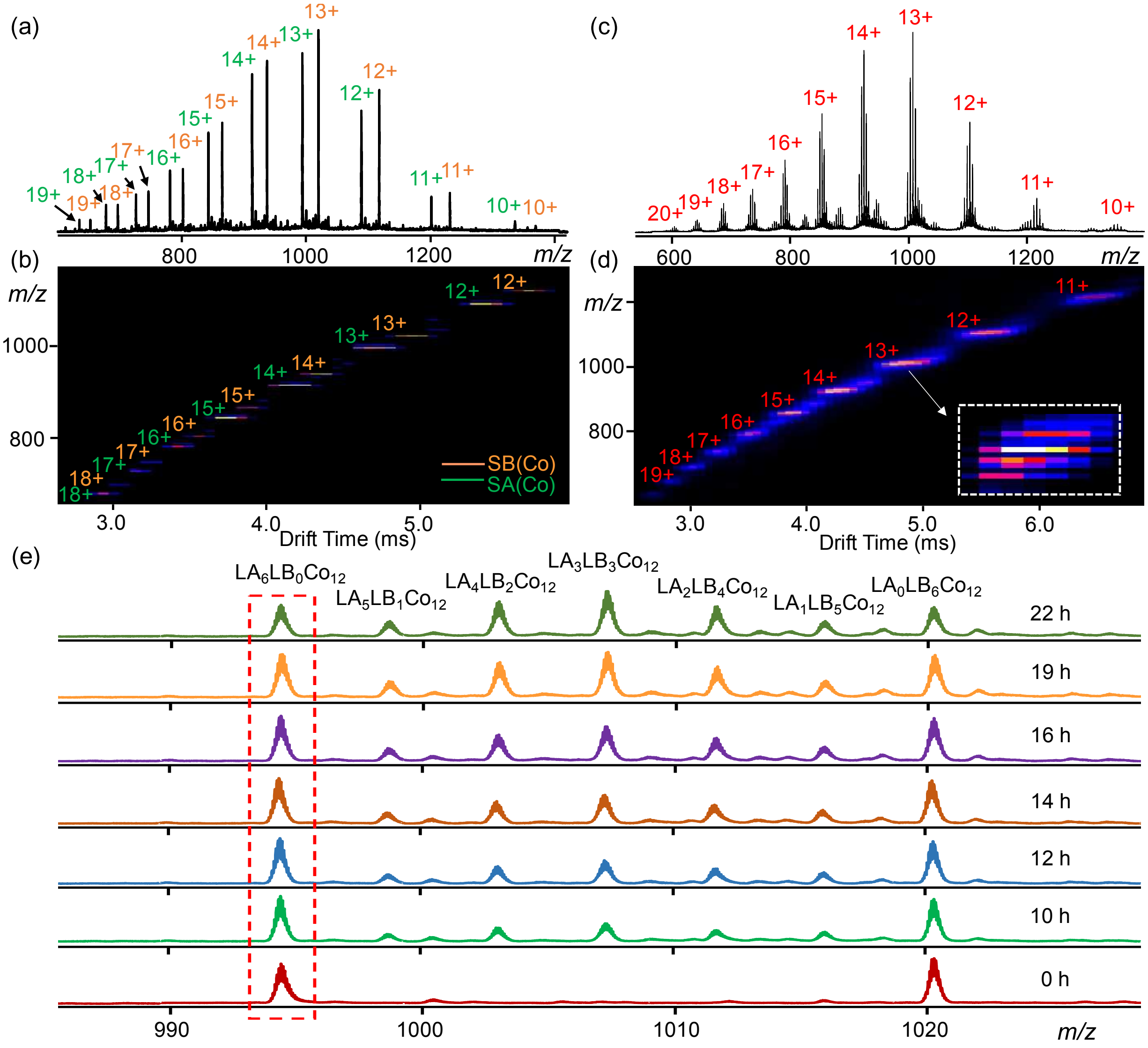

Figure 5. Dynamic ligand exchange study of **SA-Co** and **SB-Co** at 120 °C. ESI-MS spectra of **SA/SB-Co** mixed after (a) 0 h and (c) two days; TWIM-MS plot (*m/z* vs. drift time) of **SA/SB-Co** mixed after (b) 0 h and (d) two days (zoomed-in spectrum of 13+ ions in the inset); (e) the magnified spectra of 13+ ions from the mixture of **SA/SB-Co** at different time spots.

at 21 V, which could be converted into a center-of-mass collision energy of 0.06 eV; while **SA-Fe** was completely dissociated at a slightly higher voltage of 22 V, corresponding to a center-of-mass collision energy of 0.06 eV as well. **SA-Zn** and **SA-Co** were decomposed at a moderate collision voltage of 24 V and 26 V, corresponding to a center-of-mass collision energy of 0.06 eV and 0.08 eV, respectively. The collision voltage could be as high as 31 V for **SA-Ni** but as low as 19 V and 18 V for **SA-Cd** and **SA-Mn** with a relevant center-of-mass collision energy of 0.08 eV, 0.06 eV and 0.05 eV, respectively (Figures S25-S31). The decomposition mainly came from the breakage of counterions of PF6$^-$ and <tpy-M- tpy> connectivity after careful analysis of the signals in gMS^2 spectra (Figures S33-S39). According to these results, the structural stabilities of these supramolecules in gas phase was estimated depending on the metal ions with a relative order Ni > Co > Zn > Fe > Cu > Cd > Mn. The relative order of stability indicated the binding strength between the tetratopic ligand and the transition metals in gas phase. Such stabilities might be affected by factors such as the size, coordination number and electronic state of the metal ions cooperatively, thus they are slightly different from the relative order of simple complexes reported.[22a, 40a]

We further performed the oxidation reaction for **SA-Co** using $(NH_4)_2Ce(NO_3)_6$ in order to obtain pure **SA-Co(III)** with enhanced stability according to literature.[41] Using ESI-MS to monitor the reaction, however, all attempts to obtain oxidized fractals with all 12 Co(III) were unsuccessful perhaps due to the poor solubility (Figures S1, S23, and S24). Nevertheless, 13+ charged ions of **SA-Co(III)** complex was then isolated by quadrupole for gMS^2 analysis. It showed a slightly higher stability in gas phase by displaying a total dissociation voltage of 28 V compared with 26 V for **SA-Co** (Figure S32).

In addition to the exploration of structural stability in the gas phase, the kinetic aspects of dynamic ligand exchange process between two supramolecules with the same metal ion were also investigated in solution. In order to assess if ESI-MS could be applied to quantitatively monitor the concentration change, the calibration curve experiment was conducted first to demonstrate the relationship between the concentration and the integration of peak area from the ESI-MS spectrum. Stock solutions (1.0×10^{-4} M in acetonitrile) of **SA** and **SB** were readily mixed in different ratio (v/v) for ESI-MS analysis immediately. A linear relationship between peak area ratio ($A_{SA}/(A_{SA}+A_{SB})$) and concentration ratio ([**SA**]/([**SA**]+[**SB**])) was confirmed and applied as the calibration curve to find the concentration of reactant [**SA**] in the dynamic ligand exchange study (see supporting information for details).

The dynamic ligand exchange study was subsequently performed by mixing the stock solution of **SA** and **SB** in a 1:1 ratio (v/v) in a sealed vessel and stirred at a certain temperature. The process was monitored by time-dependent ESI-MS. For instance, the mixture of **SA-Co** and **SB-Co** was stirred at room temperature over two weeks and the dynamic ligand exchange did not occur at all. When the temperature was increased to 120 ± 1°C, the exchange reaction occurred slowly and new peaks, corresponding to $\mathbf{LA_nLB_{6\text{-}n}Co_{12}}$ (n=1-5), gradually appeared. ESI-MS showed that the system reached an equilibrium after two days (Figures 5a-5d). Moreover, the peak area of **SA-Co** was observed to decrease when the mixing time increased from 10 to 22h (Figure 5e). As a result, the concentration of the reactant (1/[**SA**] - 1/[**SA$_0$**]) was found to be linear with the exchange time (t) after data processing (see supporting information for details).

The linear relationship indicated that the dynamic ligand exchange could be viewed as a second order (simplified) reaction according to the experimental kinetics. As such, the exchange rate constant k_{obs} would be estimated from the slope of the linear curve (*e.g.* $k_{obs} = 3.9 \times 10^{-1}$ M^{-1}s^{-1} for **SA-Co** and **SB-Co** at 120 ± 1 °C). Similarly, the k_{obs} was measured as 60.4 M^{-1}s^{-1} for **SA-Zn** and **SB-Zn** at 70 ± 1 °C). For Cu(II) and Mn(II) fractals, the solution mixture displayed ligand exchange behaviors at room temperature (25 ± 1 °C), and the measured k_{obs} were 17.6 M^{-1}s^{-1} and 19.1 M^{-1}s^{-1}, respectively (Figure 6). The mixture of **SA-Cd** and **SB-Cd** showed a dramatically rapid ligand exchange at 25 ± 1 °C and even at 0 ± 1 °C, which were unable to be monitored by ESI-MS. When the temperature was decreased to -15 ± 1 °C, the exchange process was measured with a k_{obs} as 1.4×10^2 M^{-1}s^{-1} (Figures S134-S135). As for Ni(II) and Fe(II) fractals, the ESI-MS analysis revealed a decomposition after several days at 120 °C and 130 °C before new peaks corresponding to ligand exchange process occurred.

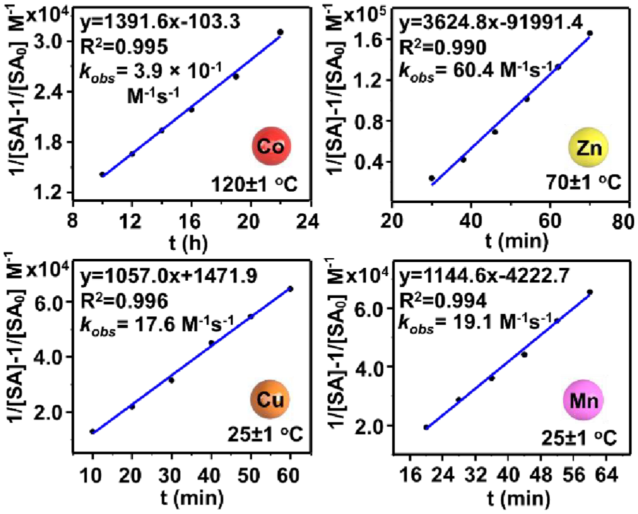

Figure 6. Plot of the concentration of the reactant (1/[**SA**] - 1/[**SA$_0$**]) against reaction time (t) for complexes **SA/SB-Co**, **SA/SB-Zn**, **SA/SB-Cu**, **SA/SB-Mn**.

The preliminary data above demonstrated a substantial difference on the rate of the dynamic ligand exchange process for the supramolecules with different metal ions by showing a distinct k_{obs} at various temperatures (Table S3). In order to compare the k_{obs} under the same temperature, e.g., 25 °C, the k_{obs} constants at another temperature were measured for Co(II), Zn(II) and Cd(II) fractals (i.e., 110 ± 1 °C for Co(II), 60 ± 1 °C for Zn(II) and -25 ± 1 °C for Cd(II)) (Figures S122-S137). The k_{obs} at 25 °C was then roughly calculated using the Arrhenius equation $ln\,(k) = ln\,(A) - E_a/RT$, where A and Ea could be determined by k_{obs} at two other temperatures. Thus, the k_{obs} at 25 °C for five metal ions were obtained either by direct measurement from ESI-MS or through calculation, and the results were summarized in

Table 1. Cd(II) fractals showed the highest exchange rate constant k_{obs} of 2.9 × 10^3 $M^{-1}s^{-1}$, while Co(II) ones displayed a k_{obs} as low as 1.7 × 10^{-9} $M^{-1}s^{-1}$ at 25 °C. The difference between those two was as high as a factor of 10^{12}.

Table 1. Summarized Results of gMS^2 and Exchange Rate Constant k_{obs} at 25 °C

	Mn	Fe	Co	Ni	Cu	Zn	Cd
gMS^2 (V)	18	22	26	31	21	24	19
k_{obs} ($M^{-1}s^{-1}$)	19.1	-	1.7 × 10^{-9}	-	17.6	1.8 × 10^{-2}	2.9 × 10^3

Similar to the relative order of structural stability in gas phase, the structural inertness of metallo-supramolecules in solution was concluded as Fe/Ni ≫ Co ≫ Zn ≫ Cu > Mn > Cd. The results elucidated that the metal ions played an important role for the structural stability in gas phase and kinetics (inertness or lability) in solution. Compared with the structural stability in gas phase which reflected the intrinsic binding strength of the metal-ligand in the complex in a solvent-free environment,[40a] while the dynamic behavior in solution was determined by kinetic liability or reversibility of the metal-ligand interactions which involved multiple processes including dissociation, association, affinitive attachment, etc.[40b,40c] The kinetic study in solution provides us information about how fast the ligand exchange process could be completed and guides us to optimize self-assembly condition in solution for each metal. The thermodynamic stability obtained in gas phase would provide us guidance in selecting a proper method for characterization. Therefore, the stability order of supramolecules in gas with different metal ions could be different from the kinetics (exchange rate) in solution. As such, the method we developed to quantitatively study the experimental kinetics of the complicated dynamic ligand exchange process by ESI-MS along with the relative stability of giant supramolecules depending on the metal ions would advance future study in coordination-driven self-assembly.

Conclusions.

In summary, a series of metallo-supramolecules with fractal features were prepared through coordination-driven self-assembly using two tetratopic tpy ligands with seven different divalent transition metal ions M(II) (M=Mn, Fe, Co, Ni, Cu, Zn, Cd) under mild conditions. Mn(II), Co(II), Ni(II), Cu(II) were reported herein for the first time to form giant and discrete structures in tpy-based supramolecular chemistry. Therefore, this study has largely expanded the spectrum of <tpy-M-tpy> connectivity for the construction of well-defined supramolecular architectures with increasing structural complexity and diversity. In addition, the structural stability of those fractals in the gas phase was investigated by gradient tandem mass spectrometry. The kinetics of the dynamic ligand exchange process between two discrete supramolecules in solution was also approached quantitatively using ESI-MS. It is expected that this fundamental study would advance tpy-based supramolecular chemistry in terms of characterization, property and application explorations.

ASSOCIATED CONTENT

Supporting Information.
Synthetic details, ligands and complexes characterization including ^1H NMR, ^{13}C NMR, 2D COSY, 2D NOESY, ESI-MS, TWIM-MS, details for dynamic ligand exchange are included in supporting information. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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SYNOPSIS TOC

Introducing Seven Transition Metal Ions into Terpyridine-Based Supramolecules: Self-Assembly and Dynamic Ligand Exchange Study

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