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Supramolecular Chemistry

One Ligand in Dual Roles: Self-Assembly of a Bis-Rhomboidal-Shaped, Three-Dimensional Molecular Wheel

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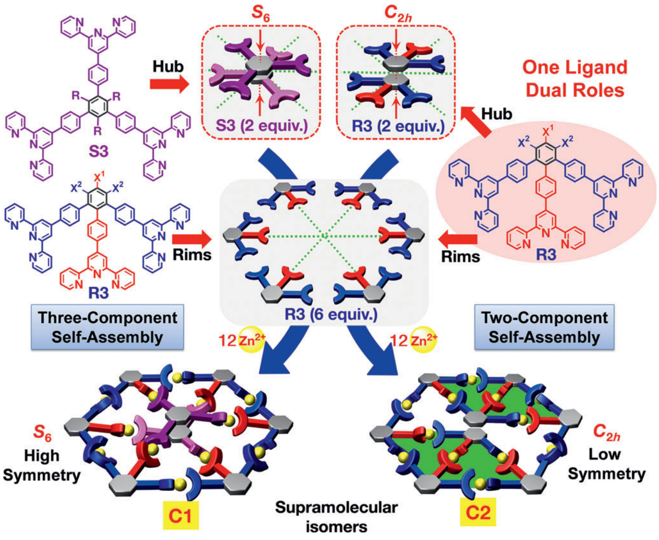
Abstract: A facile high yield, self-assembly process that leads to a terpyridine-based, three-dimensional, bis-rhomboidal-shaped, molecular wheel is reported. The desired coordination-driven supramolecular wheel involves eight structurally distorted tristerpyridine (tpy) ligands possessing a 60° angle between the adjacent tpy units and twelve Zn^{2+} ions. The tpy ligand plays dual roles in the self-assembly process: two are staggered at 180° to create the internal hub, while six produce the external rim. The wheel can be readily generated by mixing the tpy ligand and Zn^{2+} in a stoichiometric ratio of 2:3; full characterization is provided by ESI-MS, NMR spectroscopy, and TEM imaging.

Supramolecular assemblies play key roles in natural processes, such as metabolism and gene expression;[1] whereas, many three-dimensional abiological metallosupramolecular architectures, such as a cage or prism,[2] have been widely reported[3] and then utilized in nanotechnology, chemical sensing, molecular electronics, catalysis and biomedicine.[4]

Three-dimensional polyhedron structures can be constructed by either locating the metal ions at the vertices with the requisite organic ligands at the edges[2a,c–e,g,j,5] or employing multitopic organic ligands as the vertices with ligand–metal–ligand linkages delineating the edges.[2b,k,6] Only few such 3D supramolecular assemblies[2b,h,k,7] have been reported employing terpyridine-based connectivity. Herein, a novel, two-component supramolecular bis-rhomboidal architecture is reported that is derived from single, highly distortable, hexasubstituted, aryl ligands.

A hexagonal-shaped, 3D-spoked wheel contains two structural components: the central hub and the outer rims. Hence, the original synthetic route[8] involved a three-component system (Scheme 1): two tritopic ligands to form the central hub (two tris-terpyridine **S3** in **C1**), six tritopic ligands forming the rims (six tris-terpyridine **R3** in **C1**) and twelve metal ions as the linkage. Due to the highly deformed nature of **R3**, it was questioned if it could also be used as a substitute central core; thus, complex **C2** involves eight **R3** ligands and twelve ions in an 8:12 ratio, in which this single ligand serves dual roles. Six **R3** ligands are used to construct the rim and two others serve as the internal hub. As a result, this **C2** assembly can be envisioned as being derived from two, stable, independent rhomboidal moieties,[9] as depicted in Scheme 1 with the green shadow.

Initially the trimethoxy-functionalized tris-terpyridine ligand **R3a**[10] ($X^1=X^2=OMe$, Scheme 1) was used. The Zn^{2+}-based wheel **C2a** was prepared by mixing a precise stoichiometric ratio (2:3) of ligand **R3a** and $Zn(NO_3)_2{\cdot}6H_2O$ in MeOH stirring at 75 °C for 3 h. After cooling to 25 °C, an excess of NH_4PF_6 was added to give a light-yellow precipitate, which was thoroughly



Scheme 1. Pictorial assembly of the supramolecular 3D wheels **C1** and **C2**.

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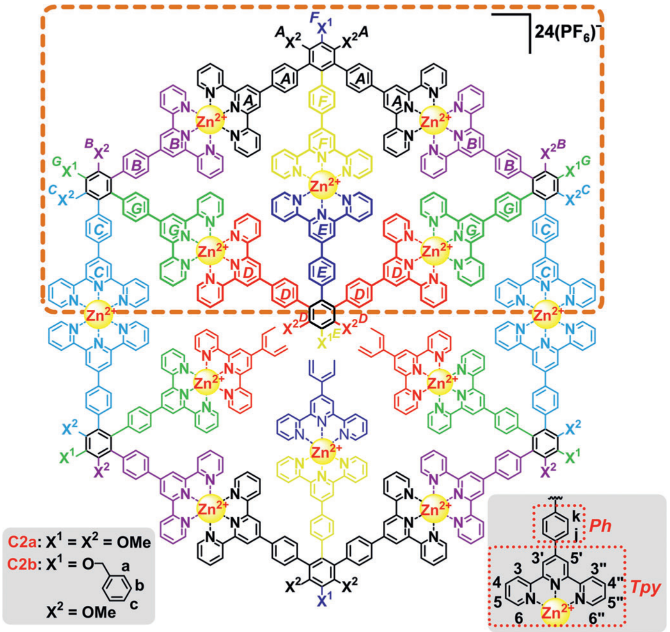

Figure 1. Structure of the supramolecular 3D bis-rhomboidal-shaped wheel **C2** with the illustration of different tpy units denoted by different color and letter assignments A to G [dotted square denotes the smallest subunit (rhomboid)].

washed with water. The desired wheel **C2a** (Figure 1) was isolated (>91%), as a light-yellow powder with PF_6^-, as the counterion, after drying in vacuo at 50 °C without further purification.

The bis-rhomboidal-shaped **C2a** was characterized by NMR spectroscopy and ESI-MS coupled with traveling-wave ion mobility (TWIM) mass spectrometry (MS).[10,11] With ESI-MS (Figure 2A), a series of peaks with charge states from 6+ to 15+ was observed, derived by the loss of a different number of PF_6^- units. The precise molecular weight of 12 985.7 Da was exhibited and is consistent with the formation of **C2a**. Isotope patterns of each charge state agreed well with the corresponding simulated isotope patterns. ESI-TWIM-MS (Figure 2B) further confirmed the structural assignment. Each charge state showed a narrow drift time distribution indicating that no other structural conformers or isomers were present.

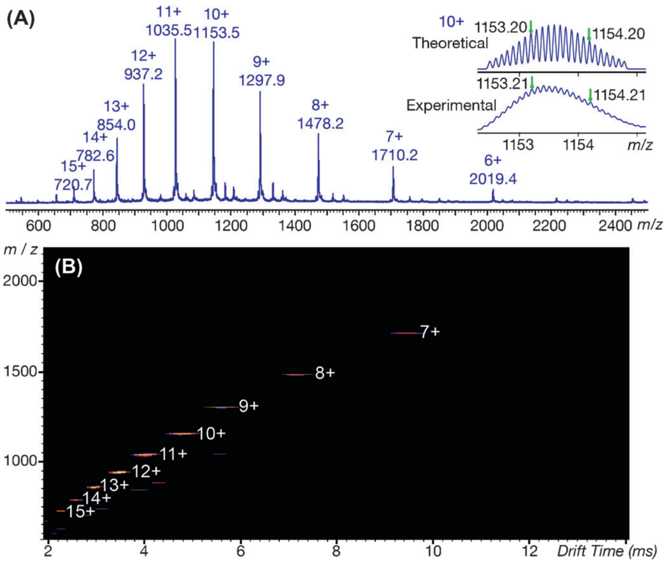

Figure 2. A) ESI-MS of **C2a**. B) 2D ESI-TWIM-MS plot (*m/z* vs. drift time) for **C2a** with the charge states of the intact assemblies marked.

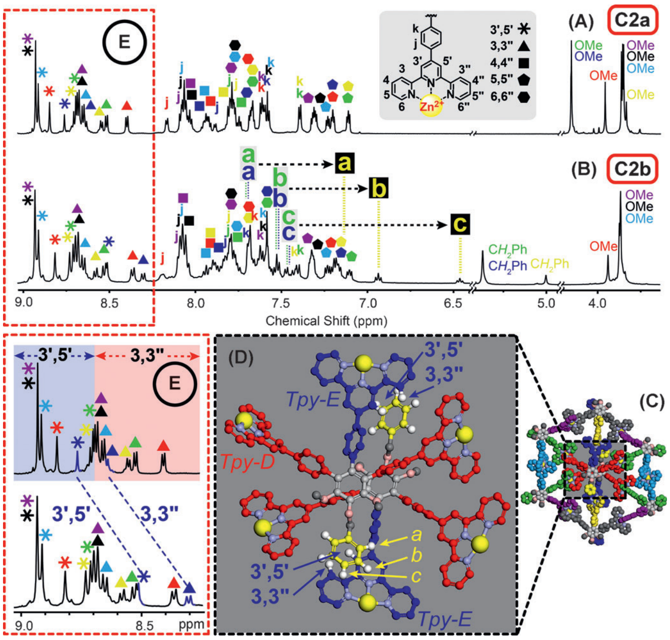

Figure 3. ^{1}H NMR spectra (CD_3CN, 750 MHz) of A) wheel **C2a** and B) wheel **C2b** (an enlarged NMR (Figure **S12**) with full assignments is included in the Supporting Information); the upfield chemical shift of the protons from OBn^E (a, b and c in yellow) was denoted as dotted black arrow. C) Representative energy-minimized structure of **C2b**. D) Representative energy-minimized structure of staggered two tpy units located in the molecular hub of **C2b**. E) Enlarged 3′,5′ and 3,3″ regions of the NMR spectra (the blue dotted lines illustrates the upfield chemical shift of protons 3′,5′ and 3,3″ in **C2b**).

Wheel **C2a** was also characterized by ^{1}H NMR spectroscopy (Figure 3), which showed a complex spectrum comprised of seven different tpy units with an expected integration ratio of 2:2:2:2:2:1:1; this was consistent with the assignment (Figure 1; each tpy unit is denoted with different color and assigned with letters from A to G). The aromatic region of the ^{1}H NMR was complicated due to the overlapping peaks from the similar, yet different structural environments of the tpy moieties. Assignment of the peaks was based on the analysis of 2D COSY and 2D NOESY NMR spectra (Supporting Information). All of the 6,6″ protons from the tpy units were significantly shifted upfield due to the electron-shielding effects, which is typical of the inherent pseudo-octahedral arrangement in the ⟨tpy-Zn^{II}-tpy⟩ connectivity.[12] Complex **C2a** exhibited two singlets and two multiplets between 3.5 and 4.5 ppm that were assigned to the OMe markers. The two singlets at 3.99 and 3.86 ppm with an integration ratio of 2:1 were assigned to H$^{OMe\text{–}D}$ and H$^{OMe\text{–}E}$ from the adjacent OMe groups, respectively. The multiplet centered at 4.17 ppm was attributed to the overlapped peaks of H^{OMe-G} and H^{OMe-F} and the multiplet centered at 3.89 ppm was assigned to the remaining OMe groups (H^{OMe-A}, H^{OMe-B} and H^{OMe-C}).

ESI-MS and NMR spectroscopy confirmed the bis-rhomboidal architecture **C2a** with clear information about constitution and the manner of connectivity. To explore the complicated internally stacked hub region, the central methoxy moiety was replaced with an aryl group, so that the imposed neighboring ring current could be used to assign the adjacent protons and to afford structural insight to the inner core region. Thus, ligand **R3b**,[8] (X^1 = OBn, X^2 = OMe, Scheme 1) possessing a benzyloxy group, was utilized to construct the related bis-rhomboidal-shaped **C2b** (Figure 1), which was prepared by mixing **R3b** and $Zn(NO_3)_2\cdot 6H_2O$ in a stoichiometric ratio (2:3) under identical conditions (75 °C in MeOH) as used above. After the counterion exchanged from NO_3^- to PF_6^-, the desired wheel **C2b** was isolated with 90% yield.

The ESI mass spectrum of **C2b** (Figure 4A) also showed a series of peaks with charge states from 6+ to 15+. The precise molecular weight of 13594.3 Da deduced by ESI-MS confirmed the desired structure. The narrow drift time distribution in the bands in the ESI-TWIM-MS plot (Figure 4B) further demonstrated that there were no other structural conformers or isomers present.

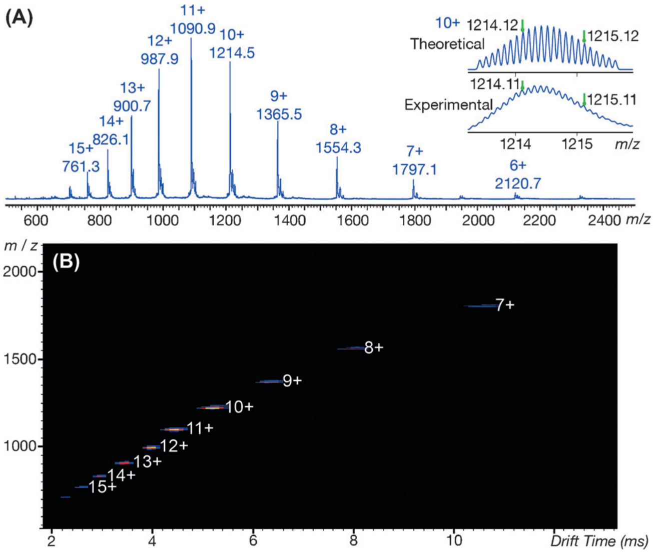

Figure 4. A) ESI-MS of **C2b**. B) 2D ESI-TWIM-MS plot (*m/z* vs. drift time) for **C2b**. The charge states of intact assemblies are marked.

Complex **C2b** was further characterized by ^{1}H NMR spectroscopy (Figure 3) and the seven different tpy units with an identical integration ratio as for **C2a** were assigned with the aid of 2D COSY and NOESY obtained through high-resolution NMR spectroscopy (750 MHz, Figure 5). Complex **C2b** showed two singlets at 5.36 and 5.00 ppm with an integration of 3:1, which were assigned to the CH$_2$ from benzyloxy groups (δ = 5.36 ppm, CH$_2^{Bn-G}$ and CH$_2^{Bn-F}$; δ = 5.00 ppm, CH$_2^{Bn-E}$). The remaining OMe markers exhibited as one singlet and one multiplet, which were assigned to H^{OMe-D} and the overlapped peaks of H^{OMe-A}, H^{OMe-B}, and H^{OMe-C}, respectively. The protons Ph-H^k from the adjacent tpy units show space correlation in 2D NOESY spectra (Figure 5) due to the hindered steric condition, for example, correlation between Ph^F-H^k and Ph^A-H^k, Ph^B-H^k and Ph^G-H^k as well as Ph^G-H^k and Ph^C-H^k.

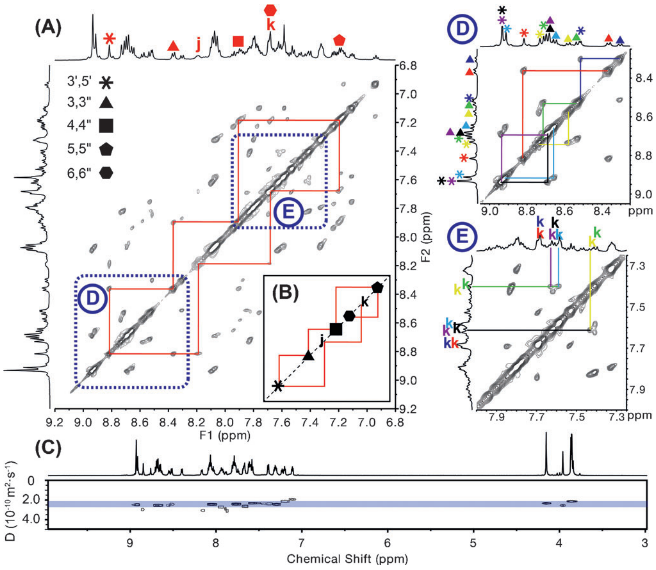

Figure 5. A) 2D NOESY NMR spectra (750 MHz, CD$_3$CN) and D) and E) two enlarged regions of complex **C2b**. B) Typical NOESY pattern of ⟨tpy-Zn^{II}-tpy⟩. C) 2D DOSY NMR spectrum of wheel **C2a** in CD$_3$CN.

The molecular dynamics simulation showed that the benzyloxy group OBn^E from one hub of the molecular wheel **C2b** was located very close to the tpy^E of the other molecular hub (Figure 3D), causing tpy^E-H$^{3,3''}$ and tpy^E-H$^{3',5'}$ to be shifted upfield compared to **C2a** [$\Delta\delta$: −0.35 ppm for tpy^E-H$^{3,3''}$ (Figure 3E, blue triangle sign) and −0.28 ppm for tpy^E-H$^{3',5'}$ (Figure 3E, blue star sign)]. Meanwhile, tpy^E also impacted this OBn^E through its highly electron-shielding environment (Figure 3E), causing the chemical shift of its protons to move dramatically upfield compared to the other rim-based benzyloxy groups [Figure 3B, $\Delta\delta$: −0.51 ppm for OBn^E-H^a (label a in yellow), −0.56 ppm for OBn^E-H^b (label b in yellow), and −0.92 ppm for OBn^E-H^c (label c in yellow)].

The DOSY NMR spectrum of complex **C2a** revealed that only one species was present in solution with a diffusion coefficient of 2.5×10^{-10} m^2 s^{-1} (Figure 5C). Transmission electron microscopy (TEM) images were also acquired (Figure 6) by cast-

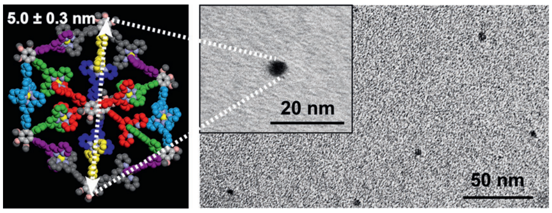

Figure 6. Left: Computer-generated, energy-minimized structure of **C2a**. Right: TEM images of **C2a** on carbon-coated Cu grid.

ing a dilute (ca. 10^{-6} M) solution of **C2 a/b** in CH_3CN on carbon-coated Cu grids (400 mesh). The average diameters for both structures are (5.0 ± 0.3) nm, which is totally consistent with the optimized molecular model.

The collision cross sections (CCSs)[11e,13] of the complex ions in different charge states were also derived from the corresponding drift times in the TWIM-MS plots. The CCSs varied only slightly with charge state (Table 1) for both **C2 a** ((1549.7 ± 29.0) $Å^2$) and **C2 b** ((1647.2 ± 43.1) $Å^2$), consistent with their structural rigidity. Theoretical CCSs were also calculated based on 300 candidate structures (from molecular dynamics simulations) of each complex, using the projection approximation (PA), trajectory (TJ), and exact hard sphere scattering (EHSS) methods.[14] The TJ model provides a more realistic CCS prediction, as it considers both long-range interactions and momentum transfer between the ions and the gas in the ion mobility region.[14] Given the size of the supramolecular wheels **C2 a** and **C2 b**, the agreement between measured and predicted (TJ model) CCSs is satisfactory (better than 10 %). The CCSs simulated by the TJ model and the corresponding experimental CCSs differ by 6.0 % for **C2 a** and 6.5 % for **C2 b**, indicating consistent trends between the experimental and theoretical CCS values for both bis-rhomboidal-shaped wheels **C2 a/b**.

Table 1. Experimental and theoretical collision cross sections (CCSs) of supramolecular wheel **C2 a/b**.

Charge state	Drift time [ms]	Collision cross-sections [$Å^2$] Exptl	 Exptl av	 Calcd av
wheel **C2 a**				
6+	5.23	1519.1	(1549.7±29.0)	(1334.5±32.3) (PA[a])
7+	3.79	1579.8		(1350.6±30.7) (PA[b])
8+	2.71	1568.2		(1692.8±37.1) (EHSS)
9+	2.08	1531.5		(1648.8±41.0) (TJ)
wheel **C2 b**				
6+	5.96	1586.3	(1647.2±43.1)	(1515.0±36.4) (PA[a])
7+	4.24	1647.1		(1448.6±34.6) (PA[b])
8+	3.16	1679.1		(1812.0±41.0) (EHSS)
9+	2.44	1676.2		(1762.4±47.6) (TJ)

[a] PA value obtained using DriftScope 2.1. [b] PA value obtained using MOBCAL.

Gradient tandem MS (gMS^2) experiments[15] were also performed on both assemblies **C2 a** and **C2 b** with charge state of 11+ to examine the complex's stability (Supporting Information). The maximum center-of-mass collision energies, at which intact complexes were still observed for **C2 a** and **C2 b** were 1.27 and 1.28 eV, respectively, suggesting very similar binding energetics.

To summarize, two 3D supramolecular bis-rhomboidal-shaped wheel architectures **C2 a** and **C2 b** were assembled in near quantitative yield capitalizing on the inherent molecular distortion associated with the hexasubstituted starting core ligands (two 180°-staggered tris-terpyridine). Both wheels were fully characterized by NMR spectroscopy, ESI-MS, and TEM imaging and the calculated CCSs (collision cross sections) agreed well with the theoretically simulated values. The central two **R3** ligands in **C2** exhibit C_{2h} symmetry compared to the two staggered tritopic ligands **S3** (S_6) in **C1** due to the geometric constraints. This localized distortion affects the symmetry of the overall complex; thus, **C2** shows reduced symmetry (C_{2h}) compared to the highly-symmetric **C1** (S_6). This type of self-assembly utilizing such highly distorted ligands offers an interesting high yield avenue to novel 3D nanoconstructs; further investigation is ongoing.

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Keywords: NMR spectroscopy · self-assembly · supramolecular chemistry · terpyridine · travelling-wave ion mobility

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