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COMMUNICATION

Stable, trinuclear Zn(II)- and Cd(II)-metallocycles: TWIM-MS, photophysical properties, and nanofiber formation†

Anthony Schultz,[a] Yan Cao,[b] Mingjun Huang,[b] Stephen Z. D. Cheng,[b] Xiaopeng Li,[a] Charles N. Moorefield,[c] Chrys Wesdemiotis*[a,b] and George R. Newkome*[a,b,c]

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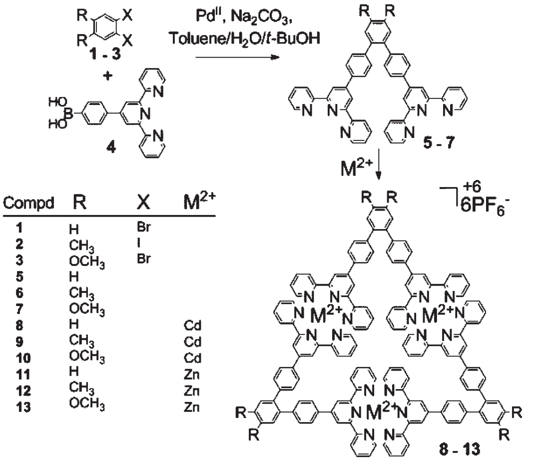
A series of trimeric, Zn(II)- and Cd(II)-metallocycles is reported. Structural characterization of the highly stable triangles was supported by traveling-wave ion mobility-mass spectrometry (TWIM-MS) and gradient tandem mass spectrometry (gMS^2). Their unique photophysical properties and self-assembly to form nanofibers are also described.

Self-assembly of predesigned architectures has attracted much attention in recent years.[1–6] Crystal engineering,[7–9] as practiced with non-covalent structural control, provides insight into the use of supramolecular synthons for the generation of highly ordered structures. With few exceptions, ionic interactions provide a superb pathway to ordered, stable assemblies, and networks. Whereas, complex polyionic interactions have played critical roles in the development of novel materials that include rotaxanes,[10] porphyrins,[11] and dendrimers;[12] with one exception,[13] there has been limited reports in the area of nanofiber formation. Nanofibers prepared by traditional methods have found application in gene delivery,[14] photonics and electronics,[15] and offer new avenues to functional materials. We herein report the creation and characterization of nanoscale fibers, based on the polyionic-mediated assembly of metallomacrocycles, constructed from bis(2,2′:6′,2″-terpyridinyl) ligands possessing a 60° orientation.



Compd	R	X	M^{2+}
1	H	Br	
2	CH$_3$	I	
3	OCH$_3$	Br	
5	H		
6	CH$_3$		
7	OCH$_3$		
8	H		Cd
9	CH$_3$		Cd
10	OCH$_3$		Cd
11	H		Zn
12	CH$_3$		Zn
13	OCH$_3$		Zn

Scheme 1 Metallocycle synthesis.

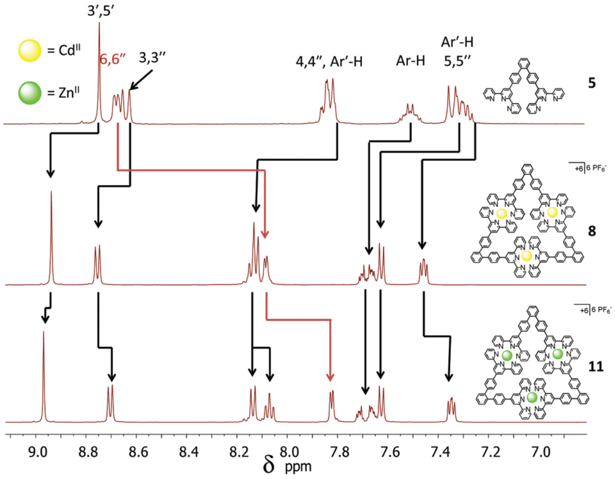


Fig. 1 Stacked ^{1}H NMR spectra for terpyridine ligand **5**, with cadmium and zinc complexes **8** and **11**.

Three ligands (**5–7**; Scheme 1) possessing 60° directionality were synthesized by Suzuki coupling[16] with known aryl halides **1–3** and 4-terpyridinylphenylboronic acid (**4**) by refluxing in a 3 : 3 : 1 toluene : water : *t*-butanol mixture for 48 hours. The previously unsynthesized ligands were readily purified by either column chromatography or simple recrystallization from the reaction mixture to give the bisterpyridines in good yields. These ligands can be identified by their easily assignable ^{1}H NMR spectra (Fig. 1), as well as by ESI-MS (ESI†). When these ligands were mixed stoichiometrically with Zn(BF$_4$)$_2$ as well as Cd(NO$_3$)$_2$ followed by precipitation with NH$_4$PF$_6$, a series of six triangular metallomacrocycles (**8–13**) was generated in 80–92% yield.

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[a] *Department of Chemistry, The University of Akron, Akron, OH 44325-4717, USA*
[b] *Department of Polymer Science, The University of Akron, Akron, OH 44325-4717, USA*
[c] *The Maurice Morton Institute for Polymer Science, The University of Akron, Akron, OH 44325-4717, USA. E-mail: newkome@uakron.edu, wesdemiotis@uakron.edu; Fax: +1 330-972-2368; Tel: +1 330-972-8595*

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The triangles exhibited ^1H NMR spectra indicative of their equilateral symmetry that facilitates easy structure elucidation. Characteristic upfield shifts (Fig. 1) for the terpyridinyl 6,6″ protons from ~8.7 ppm for the free ligand to ~8.1 and ~7.8 ppm for the cadmium and zinc triangles, respectively, are indicative of <M^{2+}> (where, < = terpyridine) octahedral complex formation. The ^{13}C–^1H and ^1H–^1H COSY NMR spectra (see ESI†) of the products are also consistent with the triangular structures.

Electrospray ionization mass spectrometry (ESI-MS) coupled with traveling-wave ion mobility-mass spectrometry (TWIM-MS),[17–19] a variant of ion mobility mass spectrometry,[20,21] was employed to aid in the characterization of these triangular architectures. A typical ESI mass spectrum for the triangles is shown in Fig. 2A, which exhibits the charge state distribution observed for the methoxy-substituted, Cd-based triangle **10**, ranging from Z = 2+ to 6+, as well as the theoretical and experimental isotope patterns for the 4+ charge state. Analysis by ESI-TWIM-MS ensured that there were no superimposed isomers or conformers within the sample as corroborated by the single, regular step-like spectrum (Fig. 2B) and only minor fragments at low drift times; hence, the intact triangle was the primary species observed. Subsequently, the triangle stability for **10** was examined using gradient tandem mass spectrometry[17] (gMS^2, Fig. 2C) by selecting the 4+ charge state (m/z = 722) and subjecting it to collisionally activated dissociation prior to ion mobility separation at collision energies ranging from 6 to 32 V. At an ion trap voltage 32 V, the 4+ complex completely disappears, corresponding to a center-of-mass collision energy (E_{cm}) of 1.75 eV.

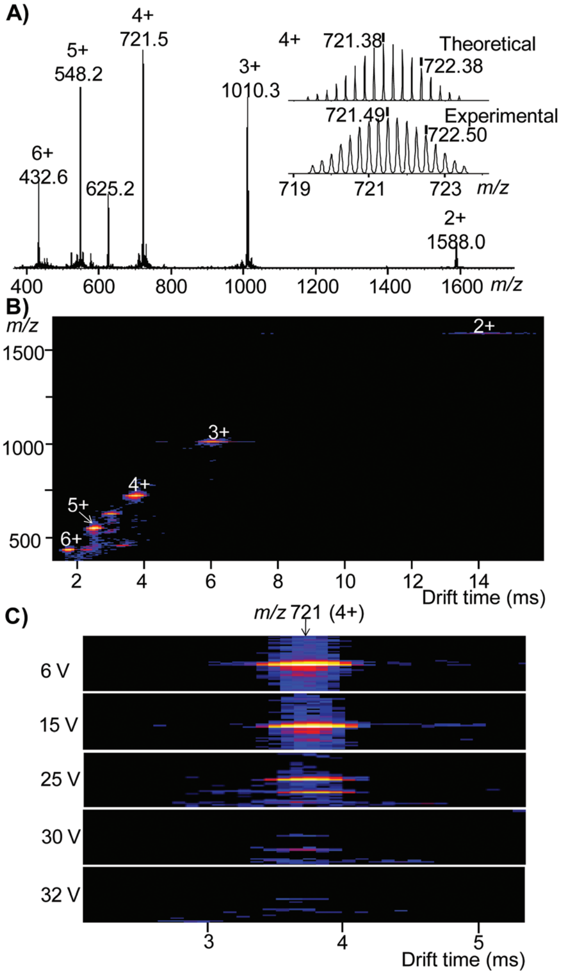

Fig. 2 ESI mass spectrum of triangle **10** (A), TWIM-MS plot of **10** (B), and gMS^2 plot of m/z 721.5 (4+ charge state) from **10**.

All triangles **8–13** displayed similar spectra (see ESI†). In contrast, previous studies on 4+ ions of hexacadmium macrocycles exhibited a E_{cm} value of 0.75 eV.[22] Notably, a MALDI mass spectrum was also obtained for the triangle **8** (Fig. S17†); this technique is typically useful for the characterization of the more stable bisterpyridine–Ru^{2+} complexes.[23] Terpyridine-based Cd^{2+} and Zn^{2+} complexes have been observed to be much weaker than the Ru^{2+} counterparts resulting in inconclusive spectra.[24] Note that for the first time intact terpyridine-based supramolecular macrocycles with Cd^{2+} were observed in MALDI. This suggests that the triangular rigid geometry could be playing an important role in self-assembly and stability.

The UV-visible and photoluminescence (PL) spectra of the free ligands **5–7** and the corresponding Cd- and Zn-based triangles were recorded. A bathochromic shift is observed in the UV absorptions (Fig. 3A) of the ligands **5–7** that is attributed to the increasing electron-donating capability of the peripheral groups (*i.e.*, H-, Me-, and MeO-) of the corner benzene rings. While, UV absorption in the metallocycles **8–13** shows little difference, due presumably to the d_{10} metals inhibition of the MLCT bands.

However, the PL spectra of the H- and Me-modified trigonal complexes **8**, **9**, **11**, and **12** exhibit a significant bathochromic shift from 467 to 499 nm (Cd-based) and 474 to 510 nm (Zn-based), respectively. For both triangles **10** and **13** possessing a methoxy substituent, nearly complete quenching of the photoluminescence is observed.

Attempts to investigate the utility of the macrocycles to self-assemble into ordered arrays resulted in the formation of composite nanofibers. Pairing the hexavalent positively charged

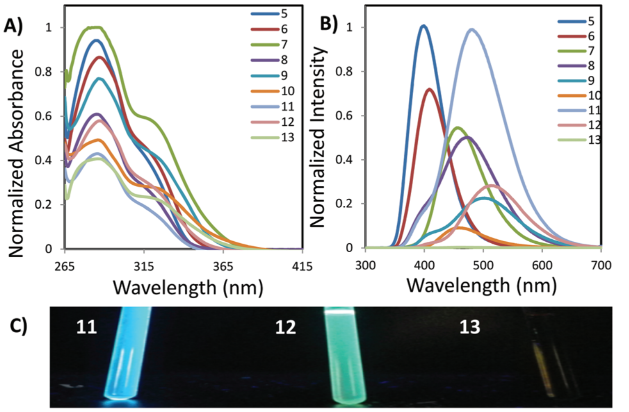

Fig. 3 UV-vis (A) and photoluminescence (B) spectra of the H-, methyl-, and methoxy-substituted bisterpyridines **5–7** and triangles **8–13** were obtained using spectrophotometric grade DMF, along with a photograph (C) of the luminescence properties of **11–13**. Excitation wavelength was 285 nm for ligands was 315 nm for complexes. Data was collected at a concentration of 5.0×10^{-5} M for ligands and 5.0×10^{-6} M for complexes, respectively.

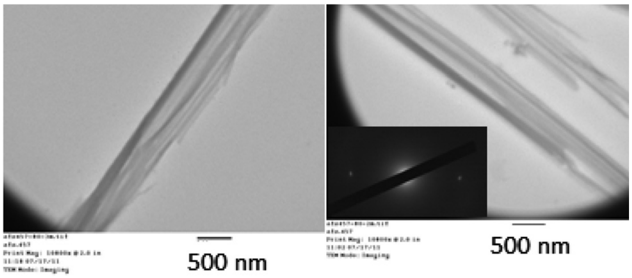

Fig. 4 TEM images of fibers formed from triangles **13** (left), and **12** (right) with benzenehexacarboxylate (inset: SAXD diffraction pattern from trimer **12**).

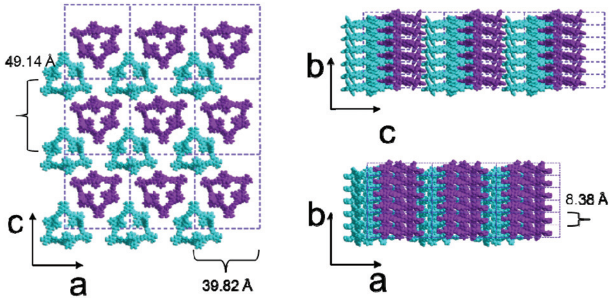

Fig. 5 Proposed packing model of triangle **12** in the fiber based on powder and selected area X-ray diffraction (counterions omitted).

metallotriangles with benzenehexacarboxylate afforded ion-paired nanofibers as observed by transmission electron microscopy (Fig. 4, TEM). The linear, hair-like fibers were obtained using a mixed solvent system prepared from dilute solutions (~1 mM) of metallocycle in MeCN and sodium hexabenzoate in water. Fiber formation was observed to begin at the solvent interface 24 hours after layering and was complete in 6 days, filtered, then washed with water and MeCN. The filtrate was analysed by ^{1}H, ^{31}P, and ^{19}F NMR spectroscopies and revealed the presence of PF_6^-, consistent with counterion exchange, and the absence of terpyridine resonances. The fibers of **12** were slightly soluble in MeOH, and possessed signals from terpyridine cyclics, however, there was no phosphorus based on the ^{31}P NMR spectrum (see ESI†). From fibers that were drop cast onto a carbon-coated copper TEM grids, large bundled structures were observed (~300 nm in diameter), composed of smaller organized fibers with diameters of 20 nm closely corresponding to the triangular side length, as determined by molecular modeling. Selected area X-ray diffraction (SAXD) of the Zn-based triangle **12** gave a *d*-spacing value of 0.589 nm. Notably, control experiments with sodium hexabenzoate and $Cd(NO_3)_2$ or $Zn(OTf)_2$ gave no fiber growth under identical conditions.

Powder XRD (X-ray diffraction) data obtained from microcrystalline regions within the fibers supports the SAXD data and provides insight into the long range order in the fibers; orthorhombic unit cell dimensions of 39.82, 8.38, and 49.14 Å for a, b, and c, respectively, were found. Based on these data, a packing model for the triangles in the fiber was derived from molecular modeling (Fig. 5). The counterions have been omitted from this model, and further studies are on-going to determine the exact location of the hexacarboxylate. A tabulated summary of the SAXD for the microcrystals (see ESI†) gives all unit cell and theoretical data.

In conclusion, new bisterpyridine ligands possessing a 60° interior angle with respect to the ligating moieties have been synthesized and their facile self-assembly with cadmium and zinc afforded high yields of the corresponding metallotriangles. TWIM-MS and gMS^{2} show the triangular motif to be unexpectedly stable and the PL properties can be engineered to generate good candidates for electronic applications, such as in LEDs. The potential to self-assemble offers avenues to higher ordered supramacromolecular materials.

Acknowledgements

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