ChemPubSoc Europe

DOI: 10.1002/ejic.201600048

EurJIC European Journal of Inorganic Chemistry

Full Paper

Metallomacrocycles

Hydrophobic-Driven, Metallomacrocyclic Assembly – Towards Quantitative Construction

Ting-Zheng Xie,[a][‡] Jing-Yi Li,[a][‡] Zaihong Guo,[b] James M. Ludlow III,[a] Xiaocun Lu,[a] Charles N. Moorefield,[a] Chrys Wesdemiotis,*[a,b] and George R. Newkome*[a,b]

Abstract: A series of coordination-driven, heteroleptic self-assembled, bowtie-shaped bis-macrocycles were designed and constructed by combining tetrakis(terpyridinyl)thianthrene and bis-terpyridine, 60°-directed, Ru^{2+} dimers. The resulting complexes were characterized by NMR spectroscopy and ESI-MS coupled with travelling wave ion mobility spectrometry (ESI-TWIM-MS) experiments. The desired bis-macrocycles were obtained in quantitative yields through the use of long alkyl-chain substituents, in contrast to the lower yields obtained for smaller alkyl moieties.

Introduction

A primary goal related to single-step molecular-construction procedures is the quantitative assembly of the desired target. Of course, this has important ramifications in product isolation, purification, and characterization, among other aspects. Therefore, it is advantageous to limit the degrees-of-freedom related to the possible outcomes of the transformation.

This is the goal for terpyridine-based, homoleptic, metal-mediated self-assembly, which is used widely for the construction of supramolecular architectures,[1] such as macrocycles,[2] cages,[3] and polyhedrons.[4] Beyond the simple shape considerations provided by homoleptic complexes, heteroleptic assemblies[5] add to the available molecular design parameters by allowing the incorporation of complementary substituents. Thus, the molecular complexity and practical prospects can be enhanced greatly by this "designer asymmetry." The added flexibility of heteroleptic assemblies broadens the construction outcomes significantly and warrants renewed consideration.

Results and Discussion

Previously, we reported the self-assembly of homoleptic[6] and heteroleptic[7] stable mono- and poly-triangular macrocycles. Furthermore, we have developed several tetrakis- and hexakis-macrocycles[8] with tpy–Ru^{2+}–tpy connectivity (tpy = 2,2′:6′,2″-terpyridine). Herein, we report the self-assembly of bis-triangular (bowtie-shaped) macrocycles through the reactions of dimeric [tpy–$Ar_{60°}$–tpy–Ru^{2+}–tpy–$Ar_{60°}$–tpy] species with Zn^{2+} ions and a new, sulfur-modified tetrakis-terpyridinyl ligand. A dynamic outcome is observed between the target bowtie-shaped bis-macrocycle and a tetrakis-macrocyclic complex, if the dimeric units are substituted with short OMe or $OCH_2C_6H_5$ moieties. However, the use of long, hydrophobic, C_{16} alkyl chains on the outer rim of the dimeric monomer forces the reaction towards quantitative bowtie assembly. This phenomenon is in agreement with a previous study,[7a] in which a core tetrakis-terpyridine possessed short C_6 alkyl substituents as solubilizing groups.

The synthesis of ligand **2** was accomplished through multiple Suzuki couplings with 2,3,7,8-tetrabromothianthrene (obtained from the bromination[9] of commercially available thianthrene) and the key intermediate 4′-(2,2′:6′,2″-terpyridinyl)-phenylboronic acid.[10] The product was purified by flash chromatography (73 %) and characterized by ^1H and ^{13}C NMR spectroscopy. The single set of peaks assigned to the terpyridinyl moieties (e.g., ^1H NMR: δ = 8.74 ppm, s, tpy$H^{3',5'}$) suggests that the four arms of the ligand are in identical chemical and magnetic environments, as expected (Figure 1, c). This tetradentate ligand consists of two 60°-oriented binding sites that form the core of the target triangular macrocycle through combination with two capping dimers and four Zn^{II} ions.[7b]

The mono-Ru^{2+} terpyridinyl dimers were synthesized[7a] from the corresponding 1,2-bis(terpyridinylphenyl)benzene (prepared by a two-fold Suzuki coupling of an aryl dibromide and the terpyridineboronic acid). The ^1H NMR spectra of the dimeric complexes showed two sets of terpyridinyl peaks [δ = 9.01 ppm, s, (complexed)tpy-$H^{3',5'}$; δ = 8.64 ppm, (free)tpy-$H^{3',5'}$; Figure 1], assigned to the different terpyridinyl moieties. Notably, the shorter methoxy and benzyloxy substituents of **1b** and **1c** exhibit two ^1H NMR resonances that correspond to the complexed and uncomplexed environments (Figures S6 and S8); however, the dimer with the hexadecyloxy chains (**1a**) shows a single resonance for the corresponding OCH_2 moieties.

[a] *Department of Polymer Science, The University of Akron, 170 University Cr., Akron, OH 44325-4717, USA*
[b] *Department of Chemistry, The University of Akron, 190 Buchtel Commons, Akron, OH 44325-3601, USA*
E-mail: wesdemiotis@uakron.edu
newkome@uakron.edu
http://www.dendrimers.com
[‡] Jing-Yi Li and Ting-Zheng Xie contributed equally to this work.
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201600048.

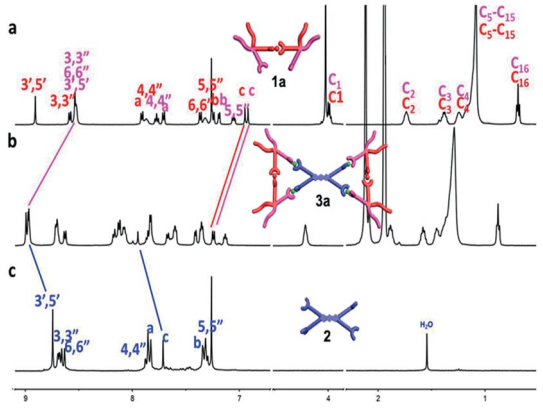
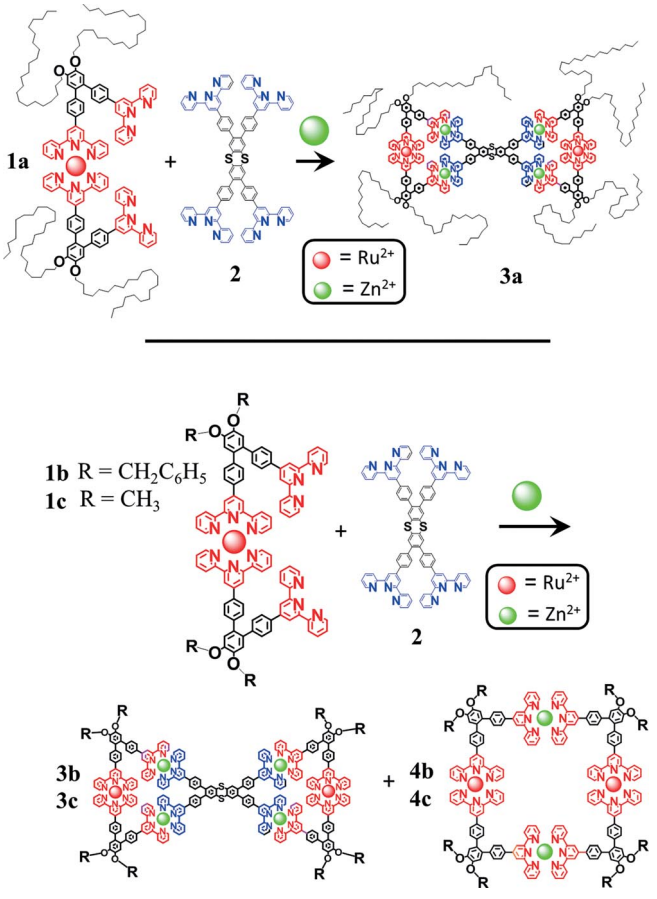


Figure 1. ^{1}H NMR spectra of (a) dimer **1a** with hexadecyloxy groups, (b) bowtie-shaped complex **3a**, and (c) tetrakis-terpyridinyl ligand **2**.

The self-assembly of the bis-triangular macrocycles was achieved by combining the tetrakis-terpyridinyl ligands, Ru^{2+} dimers, and zinc nitrate in a 1:2:4 ratio in a mixture of $CHCl_3$ and MeOH (1:1 v/v). The addition of saturated aqueous NH_4PF_6 solution (to exchange the NO_3^- ions for PF_6^- ions) produced a deep red precipitate, which was collected by filtration to give hexadecyloxy (**3a**, 98 %), benzyloxy (**3b**, 80 %), and methoxy (**3c**, 50 %) bowtie complexes (Scheme 1). Characterization was accomplished through 1D and 2D NMR spectroscopy as well as ESI-MS coupled with travelling wave ion mobility spectrometry (ESI-TWIM-MS), a variant of ion mobility spectrometry[14] whereby the ions are separated on the basis of their unique charge and shape. The hydrophobic effect of the hexadecyloxy chains in polar solvents forced the self-assembly toward the formation of aggregates with less particles and greater charges. By utilizing the hydrophobic effect, chemists have developed tailored vesicles[11] and membranes,[12] but it is rare to construct single molecules.[13]

The ^{1}H NMR spectrum of **3a** shows a peak pattern that suggests the formation of a discrete, symmetrical product (Figure 1). The D_{2h} symmetry of this bis-macrocyclic complex arises from the arrangement of the two simple triangles and gives rise to three peak patterns corresponding to the three different coordinated terpyridine moieties. All of the peaks were assigned on the basis of ^{1}H–^{1}H COSY and NOESY NMR spectra. As expected, the two sets of terpyridine peaks for the dimeric portion show downfield shifts (e.g., Figure 1, pink lines, δ = 8.64 to 8.97 ppm, tpy$H^{3',5'}$) as do the resonances of the tetra-armed ligand (e.g., Figure 1, blue lines, δ = 8.74 to 8.96 ppm, tpy$H^{3',5'}$) owing to the coordination effect. Also noticeable are the single downfield resonances attributed to the protons of the aryl thianthrene rings (ArH^c) and the protons of the dimeric unit (Ar$H^{a,b}$; $\Delta\delta$ = 0.24 and 0.20 ppm downfield). The alkyloxy chains for **3a**, like those of **1a**, display only one resonance for the OCH_2 moieties.

The ^{1}H NMR spectra for **3a** and **3b** appear similar and have three separate tpy-$H^{3',5'}$ singlets (**3a**: δ = 8.99, 8.97, 8.97 ppm; **3b**: δ = 8.99, 8.98, 8.96 ppm). Two singlets are assigned to the outer vertex Ar*H* protons of **3a** (δ = 7.25, 7.23 ppm), whereas similar proton resonances for **3b** appear further downfield. Analogously, the ^{1}H NMR of **3c** (Figure 2, c) shows a more complicated pattern of resonances, which were assigned to bis-triangle **3c** (δ = 9.00, 8.98, 8.97 ppm, tpy$H^{3',5'}$; δ = 7.26, 7.25 ppm, PhH^c) and tetramer **4c** (δ = 9.00, 8.97 ppm, tpy$H^{3',5}$; δ = 7.21, 7.20 ppm, PhH^c). Two-dimensional COSY and NOESY NMR spectra were used to confirm all assignments and verify the resulting bowtie–tetramer mixture.



Scheme 1. Synthesis of the alkylated bowtie complexes **3a**–**3c**. Dimer **1a** with the long $C_{16}H_{33}$ chain produced the desired product **3a** quantitatively, whereas shorter substituents resulted in mixtures.

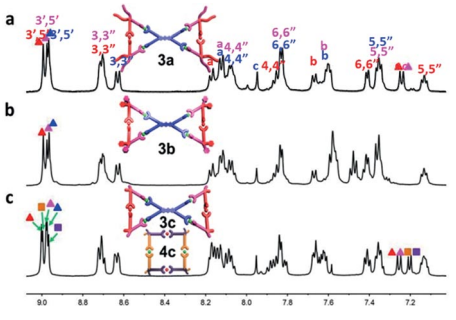


Figure 2. Partial ^{1}H NMR spectra of (a) **3a** with hexadecyloxy chains, (b) **3b** with benzyloxy groups, and (c) **3c** and **4c** with methoxy groups. The triangles indicate the resonances of the bowtie, and the squares indicate those of the tetramer. The different colors indicate the corresponding moieties in the structure.

The ESI-MS spectrum of the bis-triangle **3a** with 12 PF_6^- ions further supports the structure, and dominant peaks at *m*/*z* = 550.3, 613.6, 689.2, 781.9, 897.7, 1046.9, and 1245.3 correspond

to the charge states from 12+ to 6+, respectively. These *m/z* values from the experimental mass spectrum are consistent with the calculated values. In contrast, the ESI-MS spectra of the corresponding self-assembled benzyloxy- or methoxy-substituted **3b** and **3c**, respectively, exhibit more complicated mass spectra comprising two sets of peaks: one set for the formation of the bis-macrocycles and another set indicating the presence of the substituted tetramers formed through the self-coupling of the Ru^{2+} dimers with the Zn^{2+} ions. Evidence for the resulting mixtures is discernible in both the NMR and MS data.

Additional supportive evidence for the structure of **3a** was provided by ESI-TWIM-MS experiments. The TWIM-MS spectrum of **3a** (Figure 3) exhibits a single band of signals, indicative of a single species with charge states of 11+ to 5+; this is consistent with the NMR spectroscopy results. In contrast, the 2D TWIM-MS spectra of **3b** and **3c** (Figure 3) both show two sets of peaks, which are attributed to the bowtie and tetramer with different sizes and shapes.

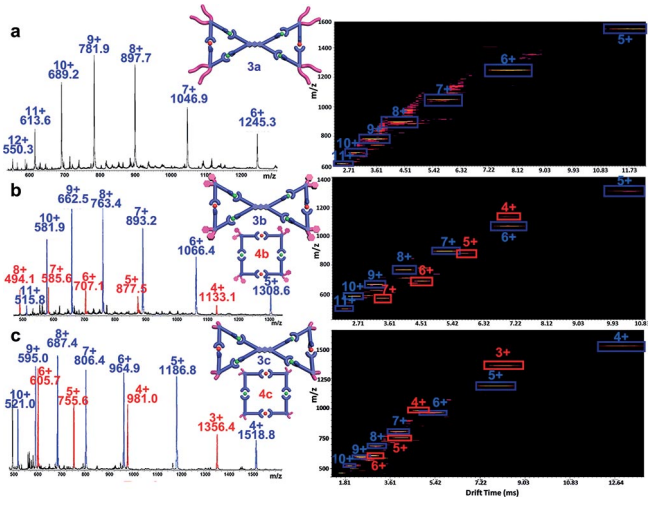


Figure 3. The ESI-MS and TWIM-MS spectra of the bowtie reactions for **3a**–**3c**; the blue and red peaks and boxes correspond to the desired and unanticipated products, respectively.

Self-assembly with Zn^{2+} ions proceeds through reversible equilibria that lead to the thermodynamically most stable product(s). Our results indicate that long hydrophobic chains destabilize the tetramer, in which such chains are closer to each other than in the bowtie, and thereby shift the equilibrium **3** ⇌ **4** + **2** quantitatively to the side of the bowtie (**3**).

The stabilities of the bowtie complexes were probed separately through gradient tandem MS (gMS^2).[15] For each complex, the 6+ charge ions [corresponding to *m/z* = 1245.33 (**3a**), 1066.38 (**3b**), and 964.85 (**3c**)] were isolated and subjected to collisionally activated dissociation (CAD) before ion mobility separation at nominal collision energies ranging from 10 to 70 eV. Notably, **3a** with hexadecyloxy chains is more stable than the related methoxy and benzyloxy derivatives. For **3b** and **3c**, the 6+ ions were completely absent when the collision energy reached 48 and 44 eV, respectively. However, for **3a**, an increased collision energy of 63 eV was required for the complete disappearance of the 6+ ion (*m/z* = 1245.33). This indicates that the bowtie complex **3a** possesses the highest stability of the three complexes (Figure S23). The gMS^2 disappearance energies reflect the intrinsic stabilities of the complexes, which may be affected by solvation. However, as all of the bowtie structures carry the same number of metal ions and counteranions, a polar solvent (which will interact most strongly with these ionic sites) is not expected to change the intrinsic stability order.

The computer-generated, energy-minimized modeling of **3a** reveals the rigid, shape-persistent, and highly symmetric bowtie-shaped structure with D_{2h} symmetry. The longest distance between two carbon atoms located at the vertices near the alkyl chains is ca. 9.3 nm, and the distance between two Ru ions in two outer rims of the triangles is ca. 4.7 nm. The same-side corner-to-corner distances are ca. 6.1 nm.

Further proof of the structures was provided by the collision cross-sections (CCSs) determined from the drift times measured in the TWIM-MS experiments. The CCSs for selected nanobowtie ion charge states are shown in Table 1. The average values observed for the charges from 9+ to 6+ (**3a**: 1183.7 Å^2 **3b**: 1099.9 Å^2 to **3c**: 938.2 Å^2) indicate a degree of flexibility for the bowtie-shaped species with the disulfur moieties. Expectedly, the largest CCS corresponds to the structure with the largest corner substituents (i.e., $OC_{16}H_{33}$ for **3a**).

Table 1. Experimentally determined CCS [Å^2] versus charge for the substituted bowties **3a**–**3c**.

Charged species (*z*)	**3a**	**3b**	**3c**
9+	1123.2	1041.5	873.4
8+	1173.4	1083.5	925.7
7+	1200.6	1135.0	961.6
6+	1237.7	1139.8	991.9
Average	1183.7	1099.9	938.2

The UV/Vis absorption spectra for the tetradentate ligand **2** exhibited intense ligand-centered (LC) π–π* transitions from the terpyridine moieties at λ = 292 nm (Figure 4). For the dimer with hexadecyloxy chains, the bands at λ = 286 and 312 nm could be assigned to the π–π* transitions of the terpyridinyl units, and the peak at λ = 494 nm corresponds to a metal-to-ligand charge transfer (MLCT). Upon the formation of **3a**, the coordination with Zn^{II} ions increased the intensity of the band

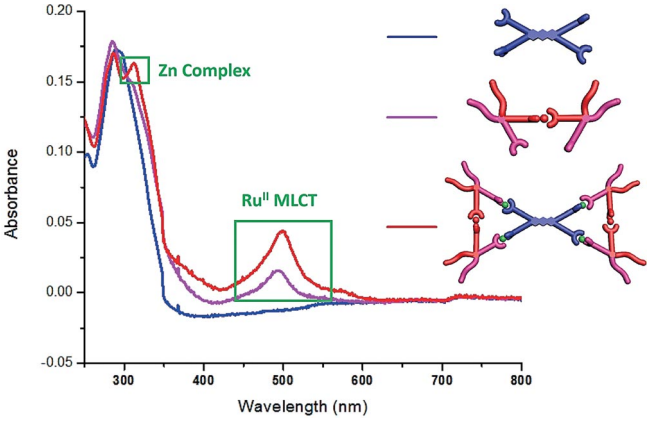


Figure 4. Comparison of the UV/Vis absorption spectra of dimer **1a**, ligand **2**, and complex **3a**.

at λ = 312 nm band, whereas the MLCT peak at λ = 496 nm exhibited a redshift compared with that of the uncomplexed Ru^{II} dimer.

Conclusions

A series of bowtie-shaped, supramolecules was prepared through the heteroleptic self-assembly of Ru^{2+}-coordinated terpyridinyl dimers and a new tetrakis-terpyridinyl ligand. Unequivocal characterization was accomplished by 1D and 2D NMR spectroscopy experiments, ESI-MS, gMS^2, and ESI-TWIM-MS analyses. The variation of the substituent groups revealed that precise control of the self-assembly processes can be achieved by enhancing the solubility of the ultimate product(s). In turn, this provides insight into the future use of tailored self-assembly protocols for the formation of supramacromolecules as reagents for new and more readily accessed macromolecular and nanoscale materials.

Experimental Section

4,5-Dibromobenzene-1,2-diol (S1): Prepared by a literature procedure.[7e]

1,2-Dibromo-4,5-bis(hexadecyloxy)benzene (S2a): A mixture of 4,5-dibromobenzene-1,2-diol (**S1**, 2.60 g, 8.0 mmol), 1-bromohexadecane (14.8 g, 25 mmol), toluene (100 mL), NaOH (2.0 g, 50 mmol) in water (50 mL) and nBu$_4$NBr (5 mmol) was heated under reflux for 6 h. The mixture was then cooled to 25 °C, and the organic phase was collected and concentrated in vacuo to afford **S2a** as a white solid (6.8 g, 53 %); m.p. 92 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 7.03 (s, 2 H, PhH), 4.11 (dd, 4 H, $J_{C1\text{-}C2}$ = 12 Hz, 2 × CH_2), 1.88 (dd, 4 H, $J_{C1\text{-}C2}$ = 12 Hz, $J_{C2\text{-}C3}$ = 2 Hz, 2 × CH_2), 1.52 (dd, $J_{C2\text{-}C3}$ = 2 Hz, $J_{C3\text{-}C4}$ = 2 Hz, 4 H, 2 × CH_2), 1.35–1.25 (m, 22 H, 11 × CH_2), 0.86 (t, 6 H, J = 2 Hz, 2 × CH_3) ppm. ^{13}C NMR (500 MHz, $CDCl_3$, 300 K): δ = 149.20, 118.19, 114.81, 69.78, 32.09, 29.87, 29.85, 29.83, 29.77, 29.75, 29.70, 29.60, 29.53, 29.50, 29.21, 26.08, 22.85, 14.28 ppm. MALDI-TOF MS: m/z = 715.52 [$C_{38}H_{68}Br_2O_2$ + H]$^+$ (calcd. 715.36).

4′,4′′′′-[4′,5′-Bis(hexadecyloxy)(1,1′:2′,1′′-terphenyl)-4,4′′-diyl]di-2,2′:6′,2′′-terpyridine (S3a): Compound **S2a** (1.08 g, 15.0 mmol), 4′-boronatophenyl-2,2′:6′,2′′-terpyridine[10] (1.59 g, 45 mmol), Na_2CO_3 (9.54 g, 90 mmol), and a solvent mixture of toluene (300 mL), H_2O (180 mL), and EtOH (120 mL) was added to a 1 L flask. The system was subjected to freeze–pump–thaw cycles (3 ×) and back-filled with nitrogen; then, $PdCl_2(PPh_3)_2$ (61.76 mg, 1.2 mmol) was added. The resultant suspension was heated under reflux for 48 h under nitrogen and then cooled to 25 °C, and the aqueous layer was extracted with $CHCl_3$ (3 × 50 mL). The combined organic phase was dried ($MgSO_4$) and concentrated in vacuo to give a residue, which was recrystallized with hexane and $CHCl_3$ and dried with suction filtration to give **S3a** as a lavender solid (1.09 g, 62 %); m.p. 47–48 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 8.74 (s, 2 H, tpy$H^{3',5'}$), 8.68 (d, $J_{3,3''\text{-}4,4''}$ = 4 Hz, 2 H, tpy$H^{3,3''}$), 8.64 (d, $J_{6,6''\text{-}5,5''}$ = 6.5 Hz, 2 H, tpy$H^{6,6''}$), 7.85 (dd, $J_{4,4''\text{-}3,3''}$ = 4 Hz, $J_{4,4''\text{-}5,5''}$ = 2.5 Hz, 2 H, tpy$H^{4,4''}$), 7.81 (d, $J_{a\text{-}b}$ = 2.5 Hz, 2 H, PhH^a), 7.32 (m, $J_{b\text{-}a}$ = 2 Hz, $J_{5,5''\text{-}4,4''}$ = 2.5 Hz, $J_{5,5''\text{-}6,6''}$ = 6.5 Hz, 4 H, tpy$H^{5,5''}$, PhH^b), 7.03 (s, 1 H, PhH^c), 4.11 (t, 4 H, $J_{C1\text{-}C2}$ = 12 Hz, 2 × CH_2), 1.88 (tt, 4 H, $J_{C2\text{-}C1}$ = 12 Hz, $J_{C2\text{-}C3}$ = 2 Hz, 2 × CH_2), 1.52 (tt, $J_{C3\text{-}C2}$ = 2 Hz, $J_{C3\text{-}C4}$ = 0.6 Hz, 4 H, 2 × CH_2), 1.39 (tt, $J_{C4\text{-}C3}$ = $J_{C4\text{-}C5}$ = 0.6 Hz, 4 H, 2 × CH_2), 1.35–1.25 (m, 22 H, 11 × CH_2), 0.86 (t, 6 H, J = 2 Hz, 2 × CH_3) ppm. ^{13}C NMR (500 MHz, $CDCl_3$, 300 K): δ = 156.49, 156.02, 149.96, 149.24, 148.87, 142.48, 136.91, 136.38, 132.74, 130.63, 127.13, 123.84, 121.45, 118.92, 116.36, 69.74, 32.09, 29.89, 29.88, 29.84, 29.83, 29.63, 29.53, 26.25, 22.85, 14.28 ppm. MALDI-TOF MS: m/z = 1107.41 [$C_{80}H_{30}N_6O_2$ + H]$^+$ (calcd. 1107.24)

[Ru(S3a)$_2$Cl$_2$] (1a): To a 1 L round-bottomed flask was added **S3a** (1.17 mg, 1.0 mmol), $RuCl_2(DMSO)_4$ (162 mg, 333 μmol; DMSO = dimethyl sulfoxide), and $CHCl_3$/MeOH (700 mL, 1:1), and then the mixture was heated under reflux for 48 h. The reaction mixture was cooled to 25 °C and concentrated in vacuo to give a red powder, which was purified by column chromatography (Al_2O_3) with a solution of $CHCl_3$/MeOH (40:1) as the eluent to give uncomplexed **S3a** initially and then **1a** as a red powder (435 mg, 35 %); m.p. >300 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 9.01 (s, 4 H, tpy$H^{complex\ 3',5'}$), 8.69 (d, $J_{3,3''\text{-}4,4''}$ = 6.5 Hz, 4 H, tpy$H^{complex\ 3,3''}$), 8.64–8.63 (m, $J_{3,3''\text{-}4,4''}$ = 4 Hz, $J_{6,6''\text{-}5,5''}$ = 1 Hz, 12 H, tpy$H^{free\ 3',5'}$, tpy$H^{free\ 3,3''}$, tpy$H^{free\ 6,6''}$), 8.02–7.97 (m, $J_{3,3''\text{-}4,4''}$ = 6.5 Hz, $J_{4,4''\text{-}5,5''}$ = 5.0 Hz, $J_{a\text{-}b}$ = 4.5 Hz, 8 H, Ph$H^{complex\ a}$, tpy$H^{complex\ 4,4''}$), 7.88 (dd, $J_{3,3''\text{-}4,4''}$ = 5.0 Hz, $J_{4,4''\text{-}5,5''}$ = 4.0 Hz, 4 H, tpy$H^{free\ 4,4''}$), 7.81 (d, $J_{a\text{-}b}$ = 3.5 Hz, 4 H, Ph$H^{free\ a}$), 7.47–7.36 (m, $J_{4,4''\text{-}5,5''}$ = 5.0 Hz, 8 H, tpy$H^{complex\ 6,6''}$, tpy$H^{complex\ 5,5''}$), 7.34 (d, $J_{a\text{-}b}$ = 4.5 Hz, 4 H, Ph$H^{complex\ b}$), 7.30 (d, $J_{a\text{-}b}$ = 3.5 Hz, 4 H, Ph$H^{free\ b}$), 7.16 (dd, $J_{4,4''\text{-}5,5''}$ = 5.0 Hz, $J_{5,5''\text{-}6,6''}$ = 8.0 Hz, 4 H, tpy$H^{free\ 5,5''}$), 7.05 (s, 2 H, Ph$H^{complex\ c}$), 7.02 (s, 2 H, Ph$H^{free\ c}$), 4.13 (t, 8 H, $J_{C1\text{-}C2}$ = 12 Hz, 2 × CH_2), 1.84 (tt, 8 H, $J_{C2\text{-}C1}$ = 12 Hz, $J_{C2\text{-}C3}$ = 2 Hz, 2 × CH_2), 1.52 (tt, $J_{C3\text{-}C2}$ = 2 Hz, $J_{C3\text{-}C4}$ = 0.6 Hz, 4 H, 2 × CH_2), 1.33 (tt, $J_{C4\text{-}C3}$ = 0.6 Hz, $J_{C4\text{-}C5}$ = 1 Hz, 4 H, 2 × CH_2), 1.19 (m, 22 H, 11 × CH_2), 0.79 (t, 6 H, J = 2 Hz, 2 × CH_3) ppm. ^{13}C NMR (500 MHz, $CDCl_3$, 300 K): δ = 158.31, 155.22, 151.89, 151.43, 149.27, 144.95, 138.56, 134.08, 132.59, 132.39, 131.60, 131.07, 128.07, 127.53, 123.54, 122.25, 119.16, 116.35, 115.89, 112.35, 32.09, 29.90, 29.66, 26.32, 22.85, 14.27 ppm. ESI-MS: m/z = 2376.5 [M – NO_3^-]$^+$ (calcd. 2376.4).

1,2-Bis(benzyloxy)-4,5-bis[*p*-(4′-terpyridinyl)phenyl]benzene (S3b): To a three-necked 1 L round-bottomed flask, 1,2-bis(benzyloxy)-4,5-dibromobenzene (1.50 g, 3.35 mmol), 4′-(4-boronatophenyl)- 2,2′:6′,2′′-terpyridine[10] (3.55 g, 10.1 mmol), Na_2CO_3 (7.10 g, 67.0 mmol), and a mixture of water (120 mL), toluene (200 mL), and EtOH (180 mL) were added. The system was subjected to freeze–pump–thaw cycles (3 ×) and back-filled with N_2; then, $PdCl_2(PPh_3)_2$ (280 mg, 400 μmol) was added. The resultant suspension was heated under reflux for 48 h under N_2. The mixture was cooled to 25 °C, and the aqueous layer was extracted with $CHCl_3$ (3 × 50 mL). The combined organic phase was dried ($MgSO_4$) and concentrated in vacuo to give a residue, which was purified by flash column chromatography (Al_2O_3) with $CHCl_3$ as the eluent to give **S3b** as a white solid (1.95 g, 64 %); m.p. 219–221 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 8.74 (s, 2 H, tpy$H^{3',5'}$), 8.69 (d, $J_{3,3''\text{-}4,4''}$ = 8 Hz, 2 H, tpy$H^{3,3''}$), 8.65 (d, $J_{6,6''\text{-}5,5''}$ = 6 Hz, 2 H, tpy$H^{6,6''}$), 7.86 (dd, $J_{4,4''\text{-}3,3''}$ = $J_{5,5''\text{-}4,4''}$ = 8 Hz, 2 H, tpy$H^{4,4''}$), 7.81 (d, $J_{a\text{-}b}$ = 7.5 Hz, 2 H, PhH^a), 7.53 (d, $J_{e\text{-}f}$ = 7.5 Hz, 2 H, PhH^e), 7.42 (dd, $J_{f\text{-}e}$ = $J_{f\text{-}g}$ = 7.5 Hz, 2 H, PhH^f), 7.36 (t, $J_{g\text{-}f}$ = 7.5 Hz, 1 H, PhH^g), 7.30 (dd, $J_{5,5''\text{-}6,6''}$ = 8 Hz, $J_{5,5''\text{-}4,4''}$ = 5 Hz, 2 H, tpy$H^{5,5''}$), 7.26 (d, $J_{b\text{-}a}$ = 7.5 Hz, 2 H, PhH^b), 7.11 (s, 1 H, PhH^c), 5.28 (s, 1 H, PhH^d) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ = 156.46, 156.00, 150.01, 149.21, 148.72, 142.29, 137.44, 137.11, 136.52, 133.43, 130.65, 128.79, 128.14, 127.70, 127.23, 123.94, 121.59, 119.06, 117.72, 71.82 ppm. MALDI-TOF MS: m/z = 905.38 [$C_{62}H_{44}N_6O_2$+H]$^+$ (calcd. 905.36).

[Ru(S3b)$_2$Cl$_2$] (1b): To a 1 L round-bottomed flask were added **S3b** (905 mg, 1.0 mmol), $RuCl_2(DMSO)_4$ (162 mg, 333 μmol), and a solvent mixture of $CHCl_3$/MeOH (1:1, 700 mL), and the mixture was heated under reflux for 48 h. The reaction was concentrated in vacuo to give a red powder, which was purified by column chroma-

tography (Al_2O_3) with a mixture of $CHCl_3$/MeOH (35:1) as the eluent to afford **1b** as a red powder (325 mg, 34 %) after the removal of uncomplexed **S3b**; m.p. >300 °C. ^{1}H NMR (500 MHz, $CD_3OD/CDCl_3$ 1:1, 300 K): δ = 9.34 (s, 4 H, tpy$H^{complex\ 3',5'}$), 9.11 (d, $J_{3,3''\text{-}4,4''}$ = 6.0 Hz, 4 H, tpy$H^{complex\ 3,3''}$), 8.73 (s, 4 H, tpy$H^{free\ 3',5'}$), 8.67–8.64 (m, $J_{3,3''\text{-}4,4''}$ = 4.0 Hz, $J_{6,6''\text{-}5',5''}$ = 7.5 Hz, 8 H, tpy$H^{free\ 3,3''}$, tpy$H^{free\ 6,6''}$), 8.32 (d, $J_{a\text{-}b}$ = 4.5 Hz, 4 H, Ph$H^{complex\ a}$), 7.91–7.88 [m, $J_{3,3''\text{-}4,4''(complex)}$ = 6.0 Hz, $J_{4,4''\text{-}5,5''(complex)}$ = 2.5 Hz, $J_{3,3''\text{-}4,4''(free)}$ = 4.0 Hz, $J_{4,4''\text{-}5,5''(free)}$ = 3.5 Hz, 8 H, tpy$H^{free\ 4,4''}$, tpy$H^{complex\ 4,4''}$], 7.80 (d, $J_{a\text{-}b}$ = 2.5 Hz, Ph$H^{free\ a}$), 7.55–7.46 [m, $J_{f\text{-}e(complex)}$ = 0.6 Hz, $J_{f\text{-}g(complex)}$ = 1.0 Hz, $J_{f\text{-}e(free)}$ = 0.4 Hz, $J_{f\text{-}g(free)}$ = 0.8 Hz, 8 H, Ph$H^{complex\ f}$, Ph$H^{free\ f}$], 7.45 (d, $J_{b\text{-}a}$ = 4.5 Hz, 4 H, Ph$H^{complex\ b}$), 7.42 [m, $J_{5,5''\text{-}4,4''}$ = 2.5 Hz, $J_{5,5''\text{-}6,6''}$ = 0.6 Hz, $J_{f\text{-}g(complex)}$ = 1.0 Hz, $J_{f\text{-}g(free)}$ = 0.8 Hz, 8 H, tpy$H^{complex\ 5,5''}$, Ph$H^{complex\ g}$, Ph$H^{free\ g}$], 7.36–7.34 [m, $J_{b\text{-}a}$ = 2.5 Hz, $J_{f\text{-}e(complex)}$ = 0.6 Hz, $J_{f\text{-}e(free)}$ = 0.4 Hz, 12 H, Ph$H^{free\ b}$, Ph$H^{complex\ e}$, Ph$H^{free\ e}$], 7.30 (d, $J_{5,5''\text{-}6,6''}$ = 0.6 Hz, 4 H, tpy$H^{complex\ 6,6''}$), 7.22 (s, 2 H, Ph$H^{complex\ c}$), 7.18 (dd, $J_{5,5''\text{-}6,6''}$ = 7.5 Hz, $J_{5,5''\text{-}4,4''}$ = 3.5 Hz, 4 H, tpy$H^{free\ 5,5''}$), 7.13 (s, 2 H, Ph$H^{free\ c}$), 5.31 (s, 2 H, Ph$H^{complex\ d}$), 5.29 (s, 2 H, Ph$H^{free\ d}$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$/MeOD 2:1 v/v, 300 K): δ = 158.41, 155.67, 152.14, 150.67, 149.30, 149.05, 148.66, 144.41, 142.94, 138.94, 137.39, 137.31, 136.32, 134.48, 133.83, 133.22, 133.04, 131.69, 131.20, 128.95, 128.43, 127.99, 127.97, 127.81, 127.33, 125.50, 124.97, 122.72, 121.80, 120.58, 119.43, 117.99, 117.88, 72.26, 72.07 ppm. ESI-MS: *m/z* = 2055.57 $[M - PF_6]^+$ (calcd. 2055.57).

3,4-Bis(4-terpyridyl-*p*-phenyl)-*o*-dimethoxybenzene (S3c):[6b] M.p. 267.3–268.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 8.75 (s, 2 H, tpy$H^{3',5'}$), 8.69 (d, $J_{6,6''\text{-}5,5''}$ = 7 Hz, 2 H, tpy$H^{6,6''}$), 8.65 (d, $J_{3,3''\text{-}4,4''}$ = 8 Hz, 2 H, tpy$H^{3,3''}$), 7.85 (m, 4 H, tpy$H^{4,4''}$, PhH^a), 7.33 (m, 4 H, tpy$H^{5,5''}$, PhH^b), 7.03 (s, 1 H, PhH^c), 4.01 (s, 1 H, PhH^d) ppm. ^{13}C NMR (300 MHz, $CDCl_3$, 300 K): δ = 56.2, 113.6, 118.7, 123.7, 127.0, 130.5, 136.3, 142.2, 148.5, 149.1, 155.8, 156.2 ppm. ESI-MS: *m/z* = 753.3 $[M + H]^+$ (calcd. 753.9).

$[Ru(S3c)_2Cl_2]$: To a 1 L round-bottomed flask were added **S3c** (750 mg, 1.0 mmol), $RuCl_2(DMSO)_4$ (162 mg, 333 μmol), and a solvent mixture of $CHCl_3$/MeOH (1:1, 700 mL), and then the mixture was heated under reflux for 48 h. The reaction was concentrated in vacuo to give a red powder, which was purified by column chromatography (Al_2O_3) with $CHCl_3$/MeOH (35:1) as the eluent to afford **1c** as a red powder (168 mg, 29 %) upon the removal of uncomplexed **S3c**; m.p. >300 °C. ^{1}H NMR (500 MHz, $CD_3OD/CDCl_3$ 1:1, 300 K): δ = 9.36 (s, 4 H, tpy$H^{complex\ 3',5'}$), 9.14 (d, $J_{3,3''\text{-}4,4''}$ = 6.5 Hz, 4 H, tpy$H^{complex\ 3,3''}$), 8.71 (s, 4 H, tpy$H^{free\ 3',5'}$), 8.62 (m, $J_{3,3''\text{-}4,4''}$ = 4 Hz, $J_{6,6''\text{-}5,5''}$ = 1 Hz, 8 H, tpy$H^{free\ 3,3''}$, tpy$H^{free\ 6,6''}$), 8.32 (d, $J_{a\text{-}b}$ = 5 Hz, 4 H, Ph$H^{complex\ a}$),7.84 [dd, $J_{3,3''\text{-}4,4''(free)}$ = 4 Hz, $J_{4,4''\text{-}5,5''(free)}$ = 3.5 Hz, $J_{3,3''\text{-}4,4''(complex)}$ = 5 Hz, $J_{4,4''\text{-}5,5''(complex)}$ = 3.5 Hz, 8 H, tpy$H^{free\ 4,4''}$, tpy$H^{complex\ 4,4''}$], 7.78 (d, $J_{a\text{-}b}$ = 2.5 Hz, 4 H, Ph$H^{free\ a}$), 7.48 (d, $J_{6,6''\text{-}5',5''}$ = 1 Hz, 4 H, tpy$H^{complex\ 6,6''}$), 7.33–7.29 [m, $J_{b\text{-}a(complex)}$ = 5 Hz, $J_{b\text{-}a(free)}$ = 2.5 Hz, $J_{5,5''\text{-}4,4''(complex)}$ = 3.5 Hz, $J_{5,5''\text{-}6,6''(complex)}$ = 1 Hz, 12 H, Ph-$H^{complex\ b}$, Ph$H^{free\ b}$, tpy$H^{complex\ 5,5''}$], 7.12 [dd, $J_{5,5''\text{-}4,4''(free)}$ = 3.5 Hz, $J_{5,5''\text{-}6,6''(free)}$ = 1 Hz, 4 H, tpy$H^{free\ 5,5''}$], 7.07 (s, 1 H, Ph$H^{complex\ c}$), 6.98 (s, 1 H, Ph$H^{free\ c}$), 3.98 (s, 1 H, Ph$H^{complex\ d}$), 3.95 (s, 1 H, Ph$H^{free\ d}$) ppm. ^{13}C NMR (300 MHz, $CD_3OD/CDCl_3$ 1:1, 300 K): δ = 173.4, 157.8, 155.9, 155.0, 151.7, 149.5, 149.0, 148.7, 148.6, 148.5, 143.9, 142.3, 138.3, 137.1, 136.1, 166.9, 132.4, 131.9, 131.3, 130.6, 127.9, 127.5, 126.9, 125.1, 124.0, 121.4, 118.4, 116.6, 113.7, 56.2, 56.1 ppm. MALDI-MS: *m/z* = 1668.01 $[M - NO_3]^+$ (calcd. 1668.01).

2,3,7,8-Tetrabromothianthrene (S5): To thianthrene (6.48 g, 30 mmol) in a flask, bromine (38.4 g, 24 mmol) was added, and an immediate reaction (take care) occurred with the evolution of HBr gas. Then, glacial acetic acid (20 mL) was added to the black solid to give a red suspension, which was stirred and then heated under reflux for 24 h. The mixture was extracted with a dilute solution of sodium thiosulfate to remove any excess bromine. The crude product was washed with water and dried in vacuo to give a faint yellow solid, which was further rinsed with acetone and EtOH and dried to afford **1** as a white solid (7.42 g, 46 %); m.p. 252–268 °C (ref.[9] 247–264 °C). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 7.23 (s, 4 H, Ph*H*) ppm. ^{13}C NMR (300 MHz, $CDCl_3$, 300 K): δ = 138.91, 132.44, 125.27 ppm. MALDI-TOF MS: *m/z* = 528.46 $[C_{12}H_4Br_4S_2+H]^+$ (calcd. 528.65).

2,3,7,8-Tetrakis[4-(2,2′:6′,2″-terpyridin-4′-yl)phenyl]thianthrene (2): Compound **1** (1.06 g, 2.00 mmol), **2**[10] (4.24 g, 12.00 mmol), Na_2CO_3 (5.30 g, 50 mmol), and a solvent mixture of toluene (250 mL), H_2O (150 mL), and EtOH (100 mL) were added to a 1 L flask. The system was subjected to freeze–pump–thaw cycles (3 ×) and back-filled with argon, and $PdCl_2(PPh_3)_2$ (246 mg, 350 μmol) was added. The resultant mixture was heated under reflux under argon. The reaction mixture was cooled to 25 °C, and the aqueous layer was extracted with $CHCl_3$ (3 × 200 mL). The combined organic phase was dried ($MgSO_4$) and then concentrated in vacuo to give a whitish yellow residue, which was purified by flash column chromatography (Al_2O_3) with a mixture of hexane, EtOAc, and $CHCl_3$ (3:1:1 v/v/v) as the eluent to give **3** as an off-white solid (2.14 g, 74 %); m.p. 225 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 8.74 (s, 2 H, tpy$H^{3',5'}$), 8.69 (d, $J_{3,3''\text{-}4,4''}$ = 4 Hz, 2 H, tpy$H^{3,3''}$), 8.65 (d, $J_{6,6''\text{-}5,5''}$ = 6 Hz, 2 H, tpy$H^{6,6''}$), 7.87 (dd, $J_{4,4''\text{-}3,3''}$ = $J_{5,5''\text{-}4,4''}$ = 4 Hz, 2 H, tpy$H^{4,4''}$), 7.84 (d, $J_{a\text{-}b}$ = 3 Hz, 2 H, PhH^a), 7.71 (s, 1 H, PhH^c), 7.34 (d, $J_{b\text{-}a}$ = 3 Hz, 2 H, PhH^b), 7.32 (dd, $J_{5,5''\text{-}6,6''}$ = 6 Hz, $J_{5,5''\text{-}4,4''}$ = 4 Hz, 2 H, tpy$H^{5,5''}$) ppm. ^{13}C NMR (300 MHz, $CDCl_3$, 300 K): δ = 156.27, 155.93, 149.78, 149.15, 139.98, 137.16, 137.10, 135.02, 130.90, 130.40, 127.38, 123.93, 121.51, 119.03 ppm. MALDI-TOF MS: *m/z* = 1446.74 $[C_{96}H_{60}N_{12}S_2+H]^+$ (calcd. 1446.45).

$[Ru_2Zn_4(2)(1a)_4(PF_6)_{12}]$ (3a): To a solution of ligand **2** (2.17 mg, 15.0 μmol) and dimer **1a** (7.56 mg, 30.0 μmol) in a solvent mixture of $CHCl_3$/MeOH (12 mL, 1:1), a solution of $Zn(NO_3)_2{\cdot}6H_2O$ (1.79 mg, 60.0 μmol) in MeOH (6 mL) was added. The mixture was stirred for 1 h, and excess NH_4PF_6 was added to afford a dark red precipitate, which was washed thoroughly with water and MeOH to give the desired **3a** with PF_6^- counterions as a dark red powder (11.75 mg, 95 %); m.p. >300 °C. ^{1}H NMR (500 MHz, CD_3CN, 300 K): δ = 8.99 (s, 8 H, tpy$^A H^{3',5'}$), 8.97 (s, 8 H, tpy$^B H^{3',5'}$), 8.97 (s, 8 H, tpy$^C H^{3',5'}$), 8.70 [d, $J_{3,3''\text{-}4,4''(B)}$ = 6.5 Hz, 16 H, tpy$^B H^{3,3''}$, $J_{3,3''\text{-}4,4''(C)}$ = 4.0 Hz, tpy$^C H^{3,3''}$], 8.63 [d, $J_{3,3''\text{-}4,4''(A)}$ = 6.5 Hz, 8 H, tpy$^A H^{3,3''}$], 8.17 [d, $J_{a\text{-}b(A)}$ = 3.0 Hz, 8 H, Ph$^A H^a$], 8.12 [d, $J_{a\text{-}b(B)}$ = 2.5 Hz, $J_{a\text{-}b(C)}$ = 2.5 Hz, 16 H, Ph$^B H^a$, Ph$^C H^a$], 8.07 [d, 16 H, $J_{3,3''\text{-}4,4''(B)}$ = 6.5 Hz, $J_{4,4''\text{-}5,5''(B)}$ = 3.5 Hz, $J_{3,3''\text{-}4,4''(C)}$ = 4.0 Hz, $J_{4,4''\text{-}5,5''(C)}$ = 2.5 Hz, tpy$^B H^{4,4''}$, tpy$^C H^{4,4''}$], 7.95 (s, 4 H, Ph$^C H^c$), 7.84 [m, $J_{3,3''\text{-}4,4''(A)}$ = 6.5 Hz, $J_{4,4''\text{-}5,5''(A)}$ = 4.5 Hz, $J_{5,5''\text{-}6,6''(B)}$ = 2.5 Hz, $J_{5,5\text{-}6,6''(C)}$ = 1.0 Hz, 24 H, tpy$^A H^{4,4}$, tpy$^B H^{6,6''}$, tpy$^C H^{6,6''}$], 7.61 [m, $J_{a\text{-}b(A)}$ = 3.0 Hz, $J_{a\text{-}b(B)}$ = 2.5 Hz, $J_{a\text{-}b(C)}$ = 2.5 Hz, 24 H, Ph$^A H^b$, Ph$^B H^b$, Ph$^C H^b$], 7.41 [d, $J_{5,5\text{-}6,6''(A)}$ = 3.5 Hz, 8 H, tpy$^A H^{6,6''}$], 7.35 [dd, 16 H, $J_{4,4''\text{-}5,5''(B)}$ = 3.5 Hz, $J_{5,5''\text{-}6,6''(B)}$ = 2.5 Hz, $J_{4,4''\text{-}5,5''(C)}$ = 2.5 Hz, $J_{5,5\text{-}6,6''(C)}$ = 1.0 Hz, tpy$^B H^{5,5''}$, tpy$^C H^{5,5''}$], 7.25 (s, 4 H, Ph$^A H^c$), 7.23 (s, 4 H, Ph$^B H^c$), 7.14 [dd, $J_{4,4''\text{-}5,5''(A)}$ = 4.5 Hz, $J_{5,5\text{-}6,6''(A)}$ = 3.5 Hz, 8 H, tpy$^A H^{5,5''}$], 4.21 (t, 16 H, $J_{C1\text{-}C2}$ = 12 Hz, 8 × CH_2), 1.88 (tt, 16 H, $J_{C2\text{-}C1}$ = 12 Hz, $J_{C2\text{-}C3}$ = 2 Hz, 8 × CH_2), 1.58 (tt, $J_{C3\text{-}C2}$ = 2 Hz, $J_{C3\text{-}C4}$ = 0.6 Hz, 16 H, 8 × CH_2), 1.45 (tt, $J_{C4\text{-}C3}$ = 0.6 Hz, $J_{C4\text{-}C5}$ = 1 Hz, 16 H, 8 × CH_2), 1.42–1.29 (m, 176 H, 88 × CH_2), 0.88 (t, 24 H, *J* = 2 Hz, 8 × CH_3) ppm. ^{13}C NMR (500 MHz, CD_3CN, 300 K): δ = 172.90, 171.07, 166.12, 159.17, 156.26, 150.84, 150.77, 148.95, 148.87, 148.82, 142.18, 142.16, 139.00, 138.13, 132.32, 132.12, 128.95, 128.65, 128.53, 128.50, 128.47, 124.25, 124.20, 122.43, 122.39, 32.64, 30.42, 30.37, 30.12, 30.07, 26.91, 23.38 ppm. ESI-MS: *m/z* = 1245.3 $[M - 6PF_6]^{6+}$ (calcd. 1244.1), 1046.9 $[M - 7PF_6]^{7+}$ (calcd. 1045.7), 897.7 $[M - 8PF_6]^{8+}$ (calcd. 896.9), 781.9 $[M - 9PF_6]^{9+}$ (calcd.

781.1), 689.2 [M – $10PF_6$]$^{10+}$ (calcd. 688.5), 613.6 [M – $11PF_6$]$^{11+}$ (calcd. 612.7), 550.3 [M – $12PF_6$]$^{12+}$ (calcd. 549.6).

[Ru_2Zn_4(2)(1b)$_4$(PF_6)$_{12}$] (3b): To a solution of ligand **2** (3.18 mg, 22.0 μmol) and dimer **1b** (7.38 mg, 44.0 μmol) in a mixture of $CHCl_3$/MeOH (1:1, 12 mL), a solution of $Zn(NO_3)_2$·$6H_2O$ (2.46 mg, 88.0 μmol) in MeOH (6 mL) was added. The reaction mixture was stirred for 1 h, and excess NH_4PF_6 was added to afford a dark red precipitate, which was thoroughly washed with water and MeOH (3 ×) to give the desired **3b** as dark red powder with PF_6^- counterions (8.26 mg, 76 %); m.p. >300 °C. ^{1}H NMR (500 MHz, CD_3CN, 300 K): δ = 8.99 (s, 8 H, tpy^{A}H$^{3',5'}$), 8.98 (s, 8 H, tpy^{B}H$^{3',5'}$), 8.96 (s, 8 H, tpy^{C}H$^{3',5'}$), 8.71–8.70 [m, $J_{3,3''\text{-}4,4''(B)}$ = 6.5 Hz, $J_{3,3''\text{-}4,4''(C)}$ = 4.0 Hz, 16 H, tpy^{B}H$^{3,3''}$, tpy^{C}H$^{3,3''}$], 8.63 [d, $J_{3,3''\text{-}4,4''(A)}$ = 6.5 Hz, 8 H, tpy^{A}H$^{3,3''}$], 8.18–8.07 [m, 40 H, $J_{a\text{-}b(A)}$ = 3.0 Hz, $J_{3,3''\text{-}4,4''(B)}$ = 6.5 Hz, $J_{4,4''\text{-}5,5''(B)}$ = 3.0 Hz, $J_{a\text{-}b(B)}$ = 3.0 Hz, $J_{a\text{-}b(C)}$ = 2.5 Hz, $J_{3,3''\text{-}4,4''(C)}$ = 4.0 Hz, $J_{4,4''\text{-}5,5''(C)}$ = 3.5 Hz, Ph^{A}H^a, tpy^{B}H$^{4,4''}$, tpy^{C}H$^{4,4''}$, Ph^{B}H^a, Ph^{C}H^a, tpy^{C}H$^{4,4''}$], 7.95 (s, 4 H, Ph^{C}H^c), 7.87–7.83 [m, $J_{3,3''\text{-}4,4''(A)}$ = 6.5 Hz, $J_{4,4''\text{-}5,5''(A)}$ = 4.0 Hz, $J_{5,5''\text{-}6,6''(B)}$ = 1.5 Hz, $J_{5,5''\text{-}6,6''(C)}$ = 2.5 Hz, 24 H, tpy^{A}H$^{4,4''}$, tpy^{B}H$^{6,6''}$, tpy^{C}H$^{6,6''}$], 7.66 [d, $J_{a\text{-}b(C)}$ = 2.5 Hz, 4 H, Ph^{C}H^b], 7.59–7.57 [m, $J_{a\text{-}b(A)}$ = 3.0 Hz, $J_{a\text{-}b(B)}$ = 3.0 Hz, $J_{4,4''\text{-}5,5''(B)}$ = 3.0 Hz, $J_{5,5''\text{-}6,6''(B)}$ = 1.5 Hz, 40 H, Ph^{A}H^c, Ph^{B}H^c, Ph^{A}H^b, Ph^{B}H^b, tpy^{B}H$^{5,5''}$], 7.48 [dd, $J_{e\text{-}f(A)}$ = 0.6 Hz, $J_{f\text{-}g(A)}$ = 0.3 Hz, $J_{e\text{-}f(B)}$ = 0.6 Hz, $J_{f\text{-}g(B)}$ = 0.3 Hz, 16 H, Ph^{A}H^f, Ph^{B}H^f], 7.43–7.41 [m, $J_{5,5''\text{-}6,6''(A)}$ = 1.5 Hz, $J_{f\text{-}g(A)}$ = 0.3 Hz, $J_{f\text{-}g(B)}$ = 0.3 Hz, 24 H, tpy^{A}H$^{6,6''}$, Ph^{A}H^g, Ph^{B}H^g], 7.41–7.35 [m, $J_{4,4''\text{-}5,5''(C)}$ = 3.5 Hz, $J_{5,5''\text{-}6,6''(C)}$ = 2.5 Hz, $J_{e\text{-}f(A)}$ = 0.6 Hz, $J_{e\text{-}f(B)}$ = 0.6 Hz, 24 H, tpy^{C}H$^{5,5''}$, Ph^{A}H^e, Ph^{B}H^e], 7.13 [dd, $J_{4,4''\text{-}5,5''(A)}$ = 4.0 Hz, $J_{5,5''\text{-}6,6''(A)}$ = 1.5 Hz, 8 H, tpy^{A}H$^{5,5''}$], 5.36 (s, 8 H, Ph^{A}H^d, Ph^{B}H^d) ppm. ^{13}C NMR (500 MHz, CD_3CN, 300 K): δ = 159.12, 156.57, 156.39, 153.32, 150.79, 150.24, 149.71, 148.92, 148.83, 148.80, 142.14, 138.94, 132.33, 132.21, 132.09, 129.61, 129.14, 128.87, 128.44, 125.33, 124.18, 122.39, 118.26, 72.15, 56.89, 30.40, 14.05 ppm. ESI-MS: *m/z* = 1308.6 [M – $5PF_6$]$^{5+}$ (calcd. 1307.2), 1066.4 [M – $6PF_6$]$^{6+}$ (calcd. 1065.2), 893.2 [M – $7PF_6^-$]$^{7+}$ (calcd. 892.3), 763.4 [M – $8PF_6$]$^{8+}$ (calcd. 762.7), 662.5 [M – $9PF_6$]$^{9+}$ (calcd. 661.8), 581.9 [M – $10PF_6$]$^{10+}$ (calcd. 581.1), 515.8 [M – $11PF_6$]$^{11+}$ (calcd. 515.1).

[Ru_2Zn_2(1b)$_4$(PF_6)$_8$] (4b): To a solution of ligand **2** (3.18 mg, 22.0 μmol) and dimer **1b** (7.38 mg, 44.0 μmol) in a solvent mixture of $CHCl_3$/MeOH (1:1, 12 mL), a solution of $Zn(NO_3)_2$·$6H_2O$ (2.46 mg, 88.0 μmol) in MeOH (6 mL) was added. The reaction mixture was stirred for 1 h, and excess NH_4PF_6 was added to afford a dark red precipitate, which was washed thoroughly with water and MeOH (3 ×) to give the desired **4b** as dark red powder with PF_6^- counterions along with bowtie **3b**. The ^{1}H NMR and ESI-MS spectra are shown in parts b of Figures 2 and 3, respectively, and confirm the presence of byproduct **4b** with the known bowtie **3b** in an approximate ratio of 1:4: ESI-MS: *m/z* = 1133.1 [M – $4PF_6$]$^{4+}$ (calcd. 1132.2), 877.5 [M – $5PF_6$]$^{5+}$ (calcd. 876.8), 707.1 [M – $6PF_6$]$^{6+}$ (calcd. 706.5), 585.6 [M – $7PF_6$]$^{7+}$ (calcd. 584.9), 494.1 [M – $8PF_6$]$^{8+}$ (calcd. 493.6).

[Ru_2Zn_4(2)(1c)$_4$(PF_6)$_{12}$] (3c): To a solution of ligand **2** (2.89 mg, 20.0 μmol) and dimer **1c** (7.93 mg, 40.0 μmol) in a mixture of $CHCl_3$/MeOH (1:1, 12 mL), a solution of $Zn(NO_3)_2$·$6H_2O$ (2.23 mg, 80.0 μmol) in MeOH (6 mL) was added. The mixture was stirred for 1 h, and excess NH_4PF_6 was added to afford a dark red precipitate, which was washed thoroughly by water and then MeOH to give the desired **3c** with PF_6^- counterion as a dark red powder (5.16 mg, 48 %); m.p. >300 °C. ^{1}H NMR (500 MHz, CD_3CN, 300 K): δ = 9.00 (s, 8 H, tpy^{A}H$^{3',5'}$), 8.98 (s, 8 H, tpy^{B}H$^{3',5'}$), 8.97 (s, 8 H, tpy^{C}H$^{3',5'}$), 8.71–8.69 [m, $J_{3,3''\text{-}4,4''(B)}$ = 4.0 Hz, $J_{3,3''\text{-}4,4''(C)}$ = 4.0 Hz, 16 H, tpy^{B}H$^{3,3''}$, tpy^{C}H$^{3,3''}$], 8.63 [d, $J_{3,3''\text{-}4,4''(A)}$ = 4.0 Hz, 8 H, tpy^{A}H$^{3,3''}$], 8.18–8.06 [m, 40 H, $J_{a\text{-}b(A)}$ = 4.0 Hz, $J_{a\text{-}b(B)}$ = 2.5 Hz, $J_{a\text{-}b(C)}$ = 2.0 Hz, $J_{3,3''\text{-}4,4''(B)}$ = 4.0 Hz, $J_{4,4''\text{-}5,5''(B)}$ = 3.5 Hz, $J_{3,3''\text{-}4,4''(C)}$ = 4.0 Hz, $J_{4,4''\text{-}5,5''(C)}$ = 2.5 Hz, Ph^{A}H^a, Ph^{B}H^a, Ph^{C}H^a, tpy^{B}H$^{4,4''}$, tpy^{C}H$^{4,4''}$], 7.95 (s, 4 H, Ph^{C}H^c), 7.88–7.80 [m, $J_{3,3''\text{-}4,4''(A)}$ = 4.0 Hz, $J_{4,4''\text{-}5,5''(A)}$ = 4.5 Hz, $J_{5,5''\text{-}6,6''(B)}$ = 1.0 Hz, $J_{5,5''\text{-}6,6''(C)}$ = 1.0 Hz, $J_{a\text{-}b(C)}$ = 4.0 Hz, 24 H, tpy^{A}H$^{4,4''}$, tpy^{B}H$^{6,6''}$, tpy^{C}H$^{6,6''}$, Ph^{C}H^b], 7.68–7.63 [m, $J_{a\text{-}b(B)}$ = 2.5 Hz, $J_{a\text{-}b(A)}$ = 3.0 Hz, 24 H, Ph^{B}H^b, Ph^{A}H^b], 7.41 [dd, $J_{5,5''\text{-}6,6''(A)}$ = 3.5 Hz, 8 H, tpy^{A}H$^{6,6''}$], 7.37–7.35 [m, $J_{4,4''\text{-}5,5''(B)}$ = 3.5 Hz, $J_{5,5''6,6''(B)}$ = 1.0 Hz, $J_{4,4''\text{-}5,5''(C)}$ = 2.5 Hz, $J_{5,5''\text{-}6,6''(C)}$ = 1.0 Hz, 16 H, tpy^{B}H$^{5,5''}$, tpy^{C}H$^{5,5''}$], 7.21 (s, 4 H, Ph^{A}H^c), 7.20 (s, 4 H, Ph^{B}H^c), 7.15 [dd, $J_{4,4''\text{-}5,5''(A)}$ = 4.5 Hz, $J_{5,5''\text{-}6,6''(A)}$ = 3.5 Hz, 8 H, tpy^{A}H$^{5,5''}$], 4.03 (s, 8 H, Ph^{A}H^d), 4.01 (s, 8 H, Ph^{B}H^d) ppm. ^{13}C NMR (500 MHz, CD_3CN, 300 K): 159.18, 156.75, 156.59, 156.40, 153.35, 150.81, 150.77, 150.29, 148.93, 148.88, 148.68, 145.63, 145.46, 144.75, 144.51, 142.15, 138.95, 135.88, 135.73, 135.17, 134.98, 132.88, 132.32, 132.12, 128.68, 128.53, 128.46, 128.35, 125.53, 124.23, 122.42, 122.21, 122.09 ppm. ESI-MS: *m/z* = 1518.8 [M – $4PF_6$]$^{4+}$ (calcd. 1518.2), 1086.8 [M – $5PF_6$]$^{5+}$ (calcd. 1185.6), 964.9 [M – $6PF_6$]$^{6+}$ (calcd. 963.8), 806.4 [M – $7PF_6$]$^{7+}$ (calcd. 805.4), 687.4 [M – $8PF_6$]$^{8+}$ (calcd. 686.6), 595.0 [M – $9PF_6$]$^{9+}$ (calcd. 594.2), 521.0 [M – $10PF_6$]$^{10+}$ (calcd. 520.3).

[Ru_2Zn_2(1c)$_4$(PF_6)$_8$] (4c): To a solution of **2** (2.89 mg, 20.0 μmol) and dimer **1c** (7.93 mg, 40.0 μmol) in a mixture of $CHCl_3$/MeOH (1:1, 12 mL), a solution of $Zn(NO_3)_2$·$6H_2O$ (2.23 mg, 80.0 μmol) in MeOH (6 mL) was added. The mixture was stirred for 1 h, and excess NH_4PF_6 was added to afford a dark red precipitate, which was washed thoroughly with water and MeOH to give the byproduct **4c** with PF_6^- counterions as a dark red powder along with bowtie **3c**. The ^{1}H NMR and ESI-MS spectra are shown in parts c of Figures 2 and 3, respectively, and confirm the presence of byproduct **4c** along with the known bowtie **3c** in an approximate ratio of 2:3. ESI-MS: *m/z* = 1356.4 [M – $3PF_6$]$^{3+}$ (calcd. 1355.2), 981.0 [M – $4PF_6$]$^{4+}$ (calcd. 980.2), 755.6 [M – $5PF_6$]$^{5+}$ (calcd. 755.1), 605.7 [M – $6PF_6$]$^{6+}$ (calcd. 605.1).

Supporting Information (see footnote on the first page of this article): Experimental procedures and characterization data containing COSY and NOESY NMR, ESI-MS, tandem mass, and UV/Vis absorption spectra.

Acknowledgments

The authors gratefully acknowledge funding from the US National Science Foundation (NSF) (grant numbers CHE-1151991 GRN and CHE-1308307 CW).

Keywords: Supramolecular chemistry · Self-assembly · Hydrophobic effect · Nitrogen heterocycles

[1] a) J.-M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, Wiley-VCH, Weinheim, Germany, **1995**; b) R. Chakrabarty, P. S. Mukherjee, P. J. Stang, *Chem. Rev.* **2011**, *111*, 6810–6918; c) T. R. Cook, Y.-R. Zheng, P. J. Stang, *Chem. Rev.* **2013**, *113*, 734–777; d) G. R. Newkome, C. N. Moorefield, *Chem. Soc. Rev.* **2015**, *44*, 3954–3967; e) T. R. Cook, P. J. Stang, *Chem. Rev.* **2015**, *115*, 7001–7045.

[2] a) G. R. Newkome, T. J. Cho, C. N. Moorefield, G. R. Baker, R. Cush, P. S. Russo, *Angew. Chem. Int. Ed.* **1999**, *38*, 3717–3721; *Angew. Chem.* **1999**, *111*, 3899–3903; b) M. Fujita, J. Yazaki, K. Ogura, *J. Am. Chem. Soc.* **1990**, *112*, 5645–5647; c) B. Hasenknopf, J.-M. Lehn, B. O. Kneisel, G. Baum, D. Fenske, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1838–1840; *Angew. Chem.* **1996**, *108*, 1987–1990; d) G.-H. Ning, T.-Z. Xie, Y.-J. Pan, Y.-Z. Li, S.-Y. Yu, *Dalton Trans.* **2010**, *39*, 3203–3211; e) X. Yu, X. Li, Y. Cao, A. Schultz, J.-L. Wang, C. N. Moorefield, C. Wesdemiotis, S. Z. D. Cheng, G. R. Newkome, *Angew. Chem. Int. Ed.* **2013**, *52*, 7728–7731; *Angew. Chem.* **2013**, *125*, 7882–7885; f) Y. Li, Z. Jiang, J. Yuan, T. Wu, C. N. Moorefield, G. R. Newkome, P. Wang, *Chem. Commun.* **2015**, *51*, 5766–5769.

[3] a) M. Han, D. M. Engelhard, G. H. Clever, *Chem. Soc. Rev.* **2014**, *43*, 1848–1860; b) S. R. Seide, P. J. Stang, *Acc. Chem. Res.* **2002**, *35*, 972–983; c) T.

Schröder, R. Brodbeck, M. C. Letzel, A. Mix, B. Schnatwinkel, M. Tonigold, D. Volkmer, J. Mattay, *Tetrahedron Lett.* **2008**, *49*, 5939–5942; d) T.-Z. Xie, S.-Y. Liao, K. Guo, X. Lu, X. Dong, M. Huang, C. N. Moorefield, S. Z. D. Cheng, X. Liu, C. Wesdemiotis, G. R. Newkome, *J. Am. Chem. Soc.* **2014**, *136*, 8165–8168; e) M. C. Young, L. R. Holloway, A. M. Johnson, R. J. Hooley, *Angew. Chem. Int. Ed.* **2014**, *53*, 9832–9836; *Angew. Chem.* **2014**, *126*, 9990–9994; f) S.-Y. Yu, Q. Jiao, S.-H. Li, H.-P. Huang, Y.-Z. Li, Y.-J. Pan, Y. Sei, K. Yamaguchi, *Org. Lett.* **2007**, *9*, 1379–1382; g) S. Sato, J. Iida, K. Suzuki, M. Kawano, T. Ozeki, M. Fujita, *Science* **2006**, *313*, 1273–1276.

[4] a) D. L. Caulder, C. Brückner, R. E. Powers, S. König, T. N. Parac, J. A. Leary, K. N. Raymond, *J. Am. Chem. Soc.* **2001**, *123*, 8923–8938; b) P. Mal, B. Breiner, K. Rissanen, J. R. Nitschke, *Science* **2009**, *324*, 1697–1699; c) T.-Z. Xie, K. Guo, Z. Guo, L. Wojtas, G.-H. Ning, M. Huang, X. Lu, J.-Y. Li, S.-Y. Liao, Y.-S. Chen, C. N. Moorefield, M. J. Saunders, S. Z. D. Cheng, C. Wesdemiotis, G. R. Newkome, *Angew. Chem. Int. Ed.* **2015**, *54*, 9224–9229; *Angew. Chem.* **2015**, *127*, 9356–9361; d) X. Lu, X. Li, K. Guo, T.-Z. Xie, C. N. Moorefield, C. Wesdemiotis, G. R. Newkome, *J. Am. Chem. Soc.* **2014**, *136*, 18149–18155; e) X. Lu, X. Li, K. Guo, M. Huang, J.-L. Wang, T.-Z. Xie, C. N. Moorefield, S. Z. D. Cheng, C. Wesdemiotis, G. R. Newkome, *Chem. Eur. J.* **2014**, *20*, 13094–13098.

[5] a) S. De, K. Mahata, M. Schmittel, *Chem. Soc. Rev.* **2010**, *39*, 1555–1575; b) J. Fan, M. L. Saha, B. Song, H. Schönherr, M. Schmittel, *J. Am. Chem. Soc.* **2012**, *134*, 150–153; c) N. Mittal, M. L. Saha, M. Schmittel, *Chem. Commun.* **2015**, *51*, 15514–15517; d) M. L. Saha, S. Neogi, M. Schmittel, *Dalton Trans.* **2014**, *43*, 3815–3834; e) M. Schmittel, *Chem. Commun.* **2015**, *51*, 14956–1968; f) A. J. Metherell, M. D. Ward, *Chem. Sci.* **2016**, *7*, 910–915.

[6] a) S.-H. Hwang, C. N. Moorefield, F. R. Fronczek, O. Lukoyanova, L. Echegoyen, G. R. Newkome, *Chem. Commun.* **2005**, 713–715; b) A. Schultz, Y. Cao, M. Huang, S. Z. D. Cheng, X. Li, C. N. Moorefield, C. Wesdemiotis, G. R. Newkome, *Dalton Trans.* **2012**, *41*, 11573–11575.

[7] a) A. Schultz, X. Li, B. Barkakaty, C. N. Moorefield, C. Wesdemiotis, G. R. Newkome, *J. Am. Chem. Soc.* **2012**, *134*, 7672–7675; b) T.-Z. Xie, K. Guo, M. Huang, X. Lu, S.-Y. Liao, R. Sakar, C. N. Moorefield, S. Z. D. Cheng, C. Wesdemiotis, G. R. Newkome, *Chem. Eur. J.* **2014**, *20*, 11291–11294; c) R. Sarkar, K. Guo, C. N. Moorefield, M. J. Saunders, C. Wesdemiotis, G. R. Newkome, *Angew. Chem. Int. Ed.* **2014**, *53*, 12182–12185; *Angew. Chem.* **2014**, *126*, 12378–12381; d) X. Lu, X. Li, J.-L. Wang, C. N. Moorefield, C. Wesdemiotis, G. R. Newkome, *Chem. Commun.* **2012**, *48*, 9873–9875; e) S. De, S. Chaudhuri, S. Mishra, H. Mamtani, A. Bisai, *J. Indian Chem. Soc.* **2013**, *90*, 1871–1884.

[8] a) A. Schultz, P. Li, C. E. McCusker, C. N. Moorefield, F. N. Castellano, C. Wesdemiotis, G. R. Newkome, *Chem. Eur. J.* **2012**, *18*, 11569–11572; b) A. Schultz, X. Li, C. N. Moorefield, C. Wesdemiotis, G. R. Newkome, *Eur. J. Inorg. Chem.* **2013**, 2492–2497.

[9] H. Gilman, D. Swayampati, *J. Org. Chem.* **1958**, *23*, 313–314.

[10] P. Jarozs, K. Lotito, J. Schneider, D. Kumaresan, R. Schmehl, R. Eisenberg, *Inorg. Chem.* **2009**, *48*, 2420–2428.

[11] a) Z. Ge, S. Liu, *Chem. Soc. Rev.* **2013**, *42*, 7289–7325; b) K. Higashiguchi, G. Taira, J. Kitai, T. Hirose, K. Matsuda, *J. Am. Chem. Soc.* **2015**, *137*, 2722–2729.

[12] P. van Rijn, M. Tutus, C. Kathrein, L. Zhu, M. Wessling, U. Schwaneberg, A. Böker, *Chem. Soc. Rev.* **2013**, *42*, 6578–6592.

[13] A. Honciuc, D. K. Schwartz, *J. Am. Chem. Soc.* **2009**, *131*, 5973–5979.

[14] a) S. L. Bernstein, N. F. Dupuis, N. D. Lazo, T. Wyttenbach, M. M. Condron, G. Bitan, D. B. Teplow, J.-E. Shea, B. T. Ruotolo, C. V. Robinson, M. T. Bowers, *Nat. Chem.* **2009**, *1*, 326–331; b) B. T. Ruotolo, J. L. P. Benesch, A. M. Sandercock, S.-J. Hyung, C. V. Robinson, *Nat. Protoc.* **2008**, *3*, 1139–1152; c) C. A. Scarff, J. R. Snelling, M. M. Knust, C. L. Wilkins, J. H. Scrivens, *J. Am. Chem. Soc.* **2012**, *134*, 9193–9198; d) K. Thalassinos, M. Grabenauer, S. E. Slade, G. R. Hilton, M. T. Bowers, J. H. Scrivens, *Anal. Chem.* **2009**, *81*, 248–254; e) E. R. Brocker, S. E. Anderson, B. H. Northrop, P. J. Stang, M. T. Bowers, *J. Am. Chem. Soc.* **2010**, *132*, 13486–13494; f) S. E. Anderson, C. Bleiholder, E. R. Brocker, P. J. Stang, M. T. Bowers, *Int. J. Mass Spectrom.* **2012**, *330–332*, 78–84; g) S. Trimpin, M. Plasencia, D. Isailovic, D. E. Clemmer, *Anal. Chem.* **2007**, *79*, 7965–7974.

[15] X. Li, Y.-T. Chan, G. R. Newkome, C. Wesdemiotis, *Anal. Chem.* **2011**, *83*, 1284–1290.

Received: January 19, 2016
Published Online: March 14, 2016

