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Self-Assembly of Shape-Persistent Hexagonal Macrocycles with Trimeric Bis(terpyridine)–Fe^{II} Connectivity

Sinan Li,[a] Charles N. Moorefield,[b] Pingshan Wang,[a] Carol D. Shreiner,[a] and George R. Newkome*[a,b,c]

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A novel family of bis(terpyridinyl) ligands was designed and constructed by facile Pd-catalyzed coupling reactions. Subsequent terpyridine–transition-metal complexation facilitated self-assembly resulting in a hexagonal, trimeric series of metallomacrocycles. An enhanced solubility of a macrocycle and its bis(terpyridine) precursor possessing elongated, alkyl-branched phenylacetylene spacers was achieved by the incorporation of dodecyloxy moieties. The characterization of the metallomacrocycles included ^{1}H, ^{13}C NMR, and UV spectroscopy and mass spectrometry, as well as electrochemistry.

Introduction

The construction of shape-persistent supramolecular architectures has been of considerable interest in view of the design and assembly of single molecule nanodevices.[1] Such rigid scaffolds are composed of macroscopic rings with nanoregime interiors, thus playing an important role in the design of macromolecular architectures based on their unique shape and structural characteristics when compared to their open-end chain or hyperbranched analogues.[2] The growing interests in shape-persistent metallomacrocycles afford new opportunities to develop versatile synthetic methodologies.[3–6] Apart from classic covalent macrocycles, Stang[7] and Lehn[8] prompted the design and construction of self-assembling monomeric precursors with transition metals to form shape-persistent macrocycles possessing unique electronic and photonic properties. Most shape-persistent macrocycles possess polygon-based motifs, in particular, regular convex polygons, such as: tri-, tetra-, penta-, and hexagons. From a geometric viewpoint, these regular polygons can be dissected into fragments with similar shape and size, which can then be used as building blocks for reconstruction. For example, a regular triangle consists of three exact monomers, each possessing a corner ("vertex") with two lines ("arms") forming a 60° angle; whereas, a regular hexagon can be constructed using six building blocks – each possessing two arms with 120° bond angle. In that most self-assembled metallomacrocycles utilize metal corners to instill the appropriate bond angle with organic sides;[9–12] similarly, most shape-persistent macrocycles are derived from organic coroners as well as sides.[13–15] As well, many macromolecular polygons are equiangular, not equilateral, but still geometrically symmetric.[4,7,16]

Our strategy for macrocycle self-assembly has been based on organic corners using bis(terpyridinyl) monomers possessing an angle between 60–180° with respect to the two ligating termini.[17] On the basis of our previous work, triangle- (60°),[17] pentagon- (105°),[18] and hexagon-like (120°)[19–21] macrocycles were readily formed and in high overall yields. Although the simple terpyridine was first synthesized by Morgan and Burstall in 1932,[22] the use of terpyridine as a key component to the self-assembly of complex molecules has been demonstrated throughout the past decade.[23,24] The chemistry of terpyridine–metal complexes is a particularly powerful tool for the construction of supramolecular architectures, because these ligands are capable of forming stable complexes with numerous metal ions; thus opening opportunities to incorporate the properties of the imbedded metal centers into a rigid predesigned environment.[23] The use of different metals in the formation of the bis(terpyridine) connection unit permits the tuning of the construct's properties and stability; the assembly of a molecular construct and its subsequent disassembly demonstrates that some of the terpyridine–metal complexes are totally reversible under specific condition.[25]

Herein, we report the design and construction of a series of new bis(terpyridinyl) monomers by Pd-catalyzed coupling reactions, where the overall angle between the two bidentate arms of the bis(terpyridine)s is ca. 60°. Subsequent complexation between these bis(terpyridine) ligands and

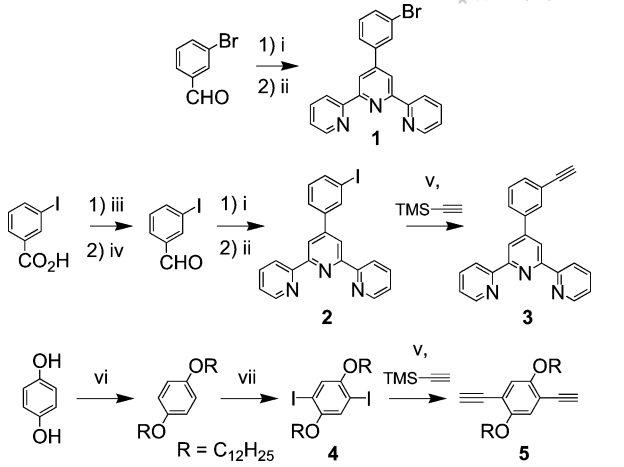
[a] Department of Polymer Science, The University of Akron, Akron, OH 44325-3909, USA
Fax: +1-330-972-2413
E-mail: newkome@uakron.edu
[b] Maurice Morton Institute of Polymer Science, Akron, OH 44325-3909, USA
[c] Department of Chemistry, The University of Akron, Akron, OH 44325-3909, USA

transition metal, Fe^{II}, produces trimeric metallomacrocycles possessing non-regular, hexagonal motifs. The steady-state absorption and electrochemical properties of these shape-persistent metallomacrocycles are characterized and described.

Results and Discussion

It is well-known that shape-persistent macrocycles can be produced through substituted aromatic, including heterocyclic, compounds. Geometrically, bis-substituted compounds with aromatic moieties as the connectors prefer to assemble into exclusive cyclic compounds as long as the vertex angle between the two substituent "arms" is in the 60–150° range. In view of the chemical diversity associated with the particular terpyridine–metal–terpyridine linkages, the choice of metal center determines the product's stability, physical as well as chemical properties. The most bis(terpyridines) have been constructed on the basis of a single aromatic moiety branching corner. For example, two terpyridines attached to the aryl *ortho*-positions forming the 60° angle lead to triangular structures. The *meta*-aryl arrangement with respect to the directed terpyridines prefers to arrange or assemble into hexagon-like architectures; however, the construction of shape-persistent macrocycles with extended size is still limited because of the poor ligand solubility and characterization of the resultant complicated structures. We subsequently undertook the construction of a series of ligands to allow the systematic study of hexagons possessing elongated sides based on ligands with vertices possessing 120° corners. Employing a simple scheme opened routes to the construction of a series of related, laterally extended metallomacrocycles.

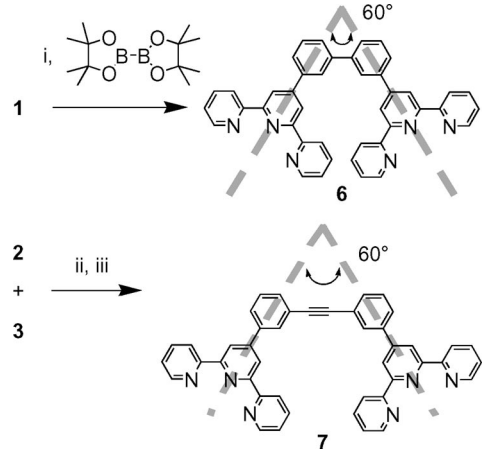
Scheme 1 shows the routes to the basic subunits **1**–**5**, which were synthesized according to standard procedures that led to the requisite bis(terpyridine) building blocks used for trimetallic hexagon construction. The 4′-(3-bromophenyl)-2,2′:6′,2′′-terpyridine (**1**) was obtained from the commercially available 3-bromobenzaldehyde.[26] The starting aldehyde was treated with 2.1 equiv. of 2-acetylpyridine at 25 °C under basic conditions for 12 h, followed by addition of excess NH_4OAc in HOAc. After being heated at reflux for 8 h, the desired monoterpyridine **1** was isolated in 50% yield. Reduction of the commercially available 3-iodobenzoic acid by BH_3·THF[27,28] gave the corresponding alcohol, which was subsequently oxidized using PCC to afford 3-iodobenzaldehyde,[29] which was then treated under the same conditions as the bromoaldehyde to give 4′-(3-iodophenyl)-2,2′:6′,2′′-terpyridine (**2**) in 31% yield. The structure of **2** showed a distinct 6,6′′-tpy*H* (^{1}H NMR) peak at δ = 8.74 ppm and a (Ar)*C*-I (^{13}C NMR) peak at δ = 95.05 ppm and was further confirmed by a mass peak (ESI-MS) at *m*/*z* = 435.8 for $[M + H]^+$. A Pd-catalyzed coupling of **2** with $Me_3SiC{\equiv}CH$ followed by deprotection with KF gave the desired ethynyl-substituted terpyridine **3**; the structure was supported by the appearance of a signal for C≡C*H* (^{1}H NMR) at δ = 3.16 ppm and a mass peak (ESI-MS) at *m*/*z* = 334.0 $[M + H]^+$.



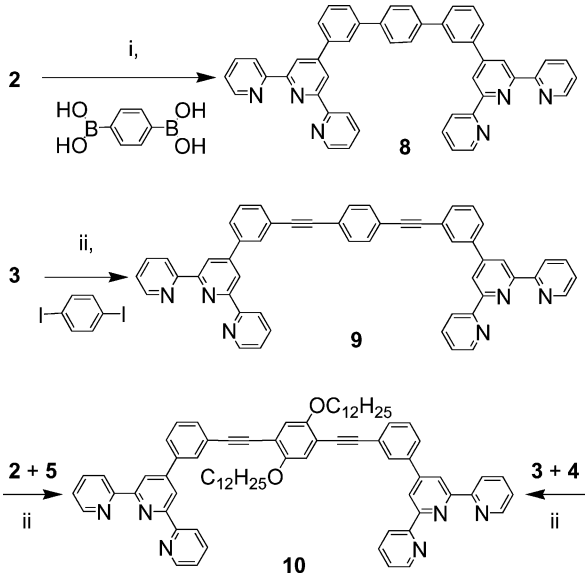
Scheme 1. (i) 2-Acetylpyridine, (ii) NH_4OAc, HOAc; (iii) BH_3·THF; (iv) PCC; (v) $Pd(PPh_3)_2Cl_2$, CuI, DIPA, THF; (vi) KI, K_2CO_3, 1-chlorododecane, MeCN; (vii) HOAc, H_2SO_4, I_2, KIO_3, H_2O.

The benzene extender units **4** and **5** were prepared by published procedures,[30–32] and their structures were confirmed by NMR characterization. It has been reported that 4′-(4-pinacolatoboronphenyl)-2,2′:6′,2′′-terpyridine was prepared (42%) by Miyaura's method[33–37] employing a $[Pd(dppf)_2Cl_2]$-catalyzed coupling of 4′-(4-bromophenyl)-2,2′:6′,2′′-terpyridine with bis(pinacolato)diboron. The pinacolate ester has been typically used to perform Suzuki coupling reactions[34,38–40] with aryl halides by forming a (Ar)C–C(Ar) bond. Terpyridine **1** was treated with bis(pinacolato)diboron to make 4′-(3-pinacolatoboronphenyl)-2,2′:6′,2′′-terpyridine; however, instead of the pinacolate ester-functionalized monoterpyridine, bis(terpyridine) **6** (Scheme 2) was produced with a 32% yield. This transformation was attributed to a simultaneous Suzuki coupling reaction between the generated pinacolate ester functionalized monoterpyridine and the bromo-substituted monoterpyridine. Its structure was confirmed by mass peaks (ESI-MS) at *m*/*z* = 617.3 $[M + H]^+$ and *m*/*z* = 639.2 $[M + Na]^+$. The solubility of **6** is very poor and is only slightly soluble in $CHCl_3$ or DMF, which can be attributed to the strong intermolecular packing. Besides the broad ^{1}H NMR peaks, caused by the poor solubility, the ^{13}C NMR spectrum could not be obtained due to its rapid precipitation in the NMR tube. After mixing **6** and 1 equiv. of $FeCl_2$ in DMF at 50 °C for 48 h, a purple solution was obtained. The crude product **11** was chromatographed on SiO_2 [H_2O/KNO_3(concd.)/MeCN 1:1:10]. NH_4PF_6 was used to exchange the counterions of **11**, which improved its solubility in MeCN. The generation of the bulky orthogonal bis(terpyridine)–iron(II) complex removed the undesirable planar structural intermolecular interactions of the ligand. Comparing the NMR spectra of **6**, the structure of **11** was supported by observing a downfield shift in the ^{1}H NMR of singlet corresponding to the 3′,5′-tpy*H* from 8.82 to 9.37 ppm, and an upfield shift of the 6,6′′-tpy*H* from 8.73 to 7.22 ppm, which also confirmed the symmetry of the macrocycle **11**. The trimeric motif was established by the

ESI-MS signals for multiple-charged entities derived from the loss of both PF_6^- and PF_5[41] (m/z = 1298.4 $[M - 2PF_6]^{2+}$, 817.6 $[M - 3PF_6]^{3+}$, and 691.2 $[M - 3PF_6 - 3PF_5]^{3+}$).



Scheme 2. (i) $Pd(dppf)Cl_2$, KOAc, DMSO; (ii) 2-acetylpyridine, base, (iii) HOAc, NH_4OAc.



Scheme 3. (i) $Pd(PPh_3)_4$, K_2CO_3, toluene; (ii) $Pd(PPh_3)_2Cl_2$, CuI, DIPA, THF.

The alkyne-extended bis(terpyridine) **7** was prepared by the palladium-catalyzed Sonogashira coupling[42] between **2** and **3**. The solubility of **7** is much better than that of **6**, in that **7** readily dissolves in $CHCl_3$, THF, and DMF. The ^{13}C NMR spectrum of **7** revealed one distinct peak at δ = 89.87 ppm, which is assigned to the symmetric acetylene carbon; its mass signal at m/z = 617.3 $[M + H]^+$ further confirmed the product. Bis(terpyridine) **7** was dissolved in MeOH with the Fe^{II} salt giving rise to complex **12** (86% yield), as a purple solid. The ^1H NMR spectrum of **12** exhibited a downfield shift of the 3′,5′-tpy*H*s as a singlet (δ = 9.21 ppm, $\Delta\delta$ = +0.43) and an upfield shift of the doublet (δ = 7.20 ppm, $\Delta\delta$ = –1.47) assigned to the 6,6′′-tpy*H*s, which also revealed the symmetric and cyclic structure of **12**. The mass spectrum showed signals of multiple-charged entities at $[M - 5PF_6]^{5+}$ and $[M - 6PF_6]^{6+}$ charge states.

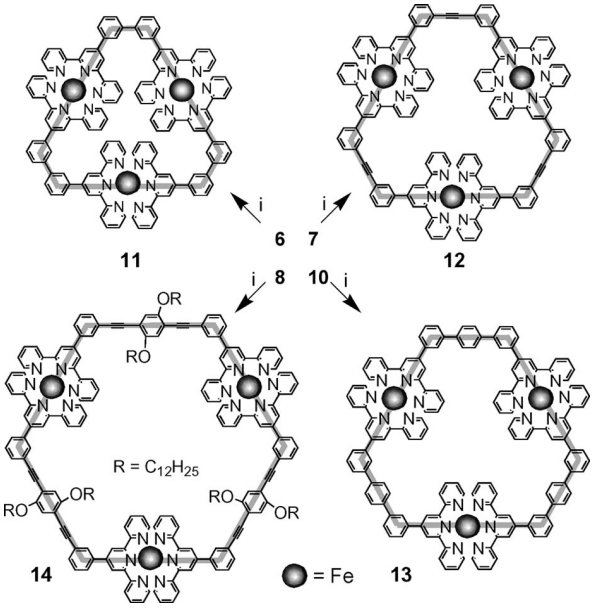
To further increase the size of the trimeric macrocycles, an additional phenyl moiety was introduced into the bis(terpyridine) building blocks. The commercial 1,4-benzenediboronic acid was used to perform the Suzuki coupling with 2.2 equiv. of **2** in order to give bis(terpyridine) **8** (Scheme 3).

The additional phenyl group enhanced the packing ability of the molecules making **8** less soluble than **6** in comparable solvents. Bisligand **8** dissolves marginally in DMSO or DMF, and its ^1H NMR peaks, although supporting the desired structure, are very broad. The corresponding ^{13}C NMR and mass spectra failed due to its poor solubility; however, after complexation with Fe^{II} in DMF, the desired trimeric complex **13** showed enhanced solubility relative to the starting material. Distinct ^1H NMR peaks were observed and assigned to the 3′,5′-tpy*H*s (δ = 9.29 ppm, $\Delta\delta$ = +0.48), 6,6′′-tpy*H*s (δ = 7.25 ppm, $\Delta\delta$ = –1.65), and the 2,3,5,6-Ar_{center}*H*s (8.00–7.89 ppm, $\Delta\delta$ ca. +0.23). The ESI-MS spectrum displayed definitive signals for multiple-charged entities ranging from the +3 to +6 charge states derived from the loss of both PF_6^- and PF_5.[41]

1,4-Diiodobenzene was treated with **3** via Sonogashira coupling conditions in order to enlarge the size of the potential macrocycle complex; however, the crude desired yellow solid, bis(terpyridine) **9**, was insoluble in almost all common solvents, such as: toluene, $CHCl_3$, THF, DMF, DMSO, to mention but a few. To solve the problem, bis(terpyridine) **10** was designed and synthesized from 1,4-diiodo-2,5-bis(dodecyloxy)benzene **4**, which was prepared by a literature procedure.[32] To a mixture of iodine (2 equiv.) and KIO_4 (1 equiv.) in $HOAc/H_2SO_4/H_2O$ (27:1:4), 1,4-bis(dodecyloxy)benzene (2.5 equiv.) was added to give (60%) **4**, as a white solid. The 1,4-diethynyl-2,5-bis(dodecyloxy)benzene **5**[28] was synthesized employing a Sonogashira coupling of **4** and trimethylsilylacetylene, followed by deprotection with KF.

Two types of palladium-catalyzed coupling reactions were employed to prepare a more soluble bis(terpyridine) ligand **10** possessing two alkoxy ($C_{12}H_{25}O$) groups attached at the 2 and 5 positions of the central benzene ring (Ar_{center}). In Method A, a mixture of **2** (2.08 equiv.), **5** (1 equiv.), $Pd(PPh_3)_4$ (0.04 equiv.), and CuI (0.08 equiv.) in THF was heated at reflux under basic conditions for 12 h to give (70%) the desired compound **10**. In Method B, **3** (2.1 equiv.) and **4** (1 equiv.) were treated with $Pd(PPh_3)_4$ (0.04 equiv.) and CuI (0.08 equiv.) in THF. After addition of Et_3N, the mixture was heated at reflux for 12 h, and bis(terpyridine) **10** was isolated (68%) as a white solid. The structure of **10** was confirmed by the appearance of ^1H NMR peaks for the 3′,5′-tpy*H*s (δ = 8.78 ppm), 6,6′′-tpy*H*s (δ = 8.77 ppm), and Ar_{center}–OCH_2s (δ = 4.13 ppm) as well as the ESI-MS signals at m/z = 1109.6 $[M + H]^+$ and 1132.6 $[M + Na]^+$. Ligand **10** was then treated with $FeCl_2$ in MeOH to prepare the corresponding trimetallic hexagonal macrocycle **14**, which was isolated (72%) as a purple solid (Scheme 4). The structure was supported by an anticipated downfield shift in the ^1H NMR from 8.78 to 9.22 ppm of

the 3′,5′-tpy*H*s combined with an upfield shift of the 6,6′′-tpy*H*s (δ = 7.21 ppm, $\Delta\delta$ = –1.55). The mass spectrum of this trimeric motif showed definitive signals for the multiple-charged entities ranging from the +2 to +6 charge states derived from the loss of both PF_6^- and PF_5.



Scheme 4. Self-assembly of the trimetallic hexamers. (i) $FeCl_2$, MeOH.

The UV/Vis absorption spectra, which were recorded for the macrocycles of trimeric terpyridine–Fe^{II} complexes in dilute MeCN solution, exhibited the expected absorption transition peaks. All of the complexes exhibited two ligand-centered π–π* transitions of the terpyridine moieties at approximately λ_{max} = 285 and 320 nm. They also exhibited the typical metal–ligand charge-transfer (MLCT) transition[23] ($\lambda_{max} \approx 567$ nm), which has been described as the promotion of an electron from metal-centered d-orbitals to an unfilled ligand-centered π* orbital (Figure 1).

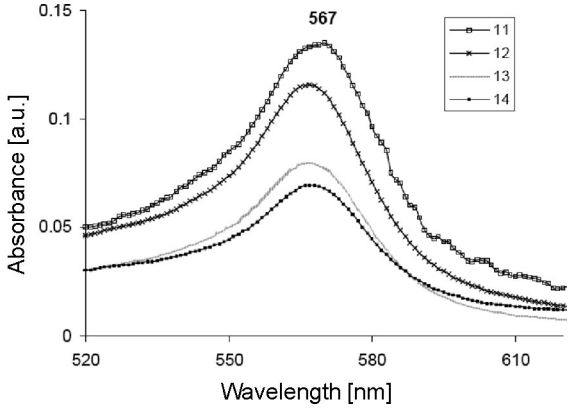


Figure 1. UV absorption data for complexes **11**–**14**.

The electrochemical response of the terpyridine–Fe^{II} macrocycles were characterized by cyclic voltammetry (CV). Experiments were conducted in dry MeCN solutions using 0.1 M Bu_4NPF_6 as the supporting electrolyte at 25 °C. The metallomacrocycles **11**–**14** were dissolved in the MeCN/Bu_4NPF_6 to give 1.0 mM solutions and each exhibited a reversible, metal-based, oxidation for the Fe^{III}/Fe^{II} couple between 1.06 and 1.12 V (vs. Ag/AgCl reference electrode), see Table 1. The observation of a single oxidation potential for each multi-metal macrocycle suggests each metal center functions independently of the other two as expected with the ligand *meta*-connectivity; reduction waves were irreversible.

Table 1. Reduction and oxidation potentials of complexes **11**–**14**.[a]

	$E_{Red/Ox}$ of **11**[b]	$E_{Red/Ox}$ of **12**	$E_{Red/Ox}$ of **13**	$E_{Red/Ox}$ of **14**
E_{pc}[c]	–1.29/1.06	–1.23/1.12	–1.25/1.09	–1.21/1.14
E_{pa}[d]	–1.04/1.13	–1.09/1.20	–1.12/1.15	–1.10/1.18
$E_{1/2}$	1.10	1.16	1.12	1.16

[a] Reduction waves were irreversible. [b] *E* is the potential in volts. [c] pa is the potential of the anodic peak. [d] pc is the potential of the cathodic peak.

Conclusions

The self-assembly of different organic building blocks gave rise to a family of shape-persistent metallomacrocycles possessing variable distances between the vertices. Circumvention of the insolubility properties utilized a traditional approach by attaching alkyl groups to disrupt the packing of these rigid and planar aromatic monomers and products. The minor changes in the physical properties, such as the MLCT absorption and oxidation/reduction potentials, may start to give insight into intermolecular interactions and stacking in the solid state.

Experimental Section

General Information: The ^1H and ^{13}C NMR spectra were recorded by using a Mercury 300 MHz (75 MHz) and with $CDCl_3$ as solvent, except where noted. Mass spectra were obtained with a Bruker Esquire Electrospray Ion Trap mass spectrometer (ESI-MS). UV/Vis absorption (Hewlett–Packard 8452A diode array spectrophotometer), cyclic voltammetry (CHI 440 Electrochemical Workstation), and X-ray photoelectron spectroscopy (monochromatic Mg-K_α radiation at 250 W, 93.90 eV) measurements were also utilized in the characterizations.

Materials: 3-Bromobenzaldehyde, 3-iodobenzoic acid, 1,4-diiodobenzene, 1,4-benzenediboronic acid, *p*-hydroquinone, 2-acetylpyridine, trimethylsilylacetylene, palladium catalysts [$Pd(PPh_3)_4$, $Pd(PPh_3)_2Cl_2$, and $Pd(dppf)Cl_2$], 1-chlorododecane, ammonium acetate (NH_4OAc), BH_3·THF, pyridinium chlorochromate (PCC), $FeCl_2$, CuI, and ammonium hexafluorophosphate (NH_4PF_6 were purchased from either Aldrich or Acros and were used without further purification). **1**,[26] **4**,[31] and **5**[30] were prepared by following the literature procedure, and the structures were characterized and confirmed. Column chromatography was performed by using SiO_2 (60–200 mesh) or basic Al_2O_3, Brockman Activity I (60–325 mesh).

General Procedure for the Sonogashira Coupling Reaction (GP1): A solution of the halo-substituted benzene or 4′-aryl-2,2′:6′,2′′-terpyridine (1 equiv.) was degassed five times with argon. Then, palladium catalyst [0.04 equiv., $Pd(PPh_3)_4$ or $Pd(PPh_3)_2Cl_2$], base

[Et_3N or $(Me_2CH)_2NH$], and CuI (0.08 equiv.) in anhydrous THF, and the appropriate ethynyl-substituted compound (1 equiv. ethynyl per halide) were added. This mixture was degassed three additional times and heated at reflux for 12 h, after which the solvent was removed in vacuo to give a residue, which was passed through a column (SiO_2 or Al_2O_3) to give the pure product.

4′-(3-Iodophenyl)-2,2′:6′,2′′-terpyridine (2): To a solution of 3-iodobenzoic acid (4 g, 16 mmol) in THF (50 mL) was added BH_3·THF solution (2 equiv., 1.0 M). After stirring for 20 h at 25 °C, 3-iodobenzyl alcohol[27,29] (3.5 g, 93%) was generated and then oxidized with PCC to give 3-iodobenzaldehyde[33] (3.03 g, 87%) as a yellowish solid. Aqueous NaOH (2.1 equiv., 1.0 M) was added dropwise to a stirred solution of 3-iodobenzaldehyde (1 equiv.) and 2-acetylpyridine (2.1 equiv.) in EtOH (95%). After stirring for 12 h at 25 °C, the solvent was evaporated in vacuo to give a dark red, solid intermediate to which excess NH_4OAc and HOAc were added. This resultant mixture was heated at reflux for 8 h, after which the excess HOAc was removed in vacuo. The remaining brown residue was partitioned between $CHCl_3$ (300 mL) and H_2O (300 mL). The organic layer was washed twice with H_2O, dried ($MgSO_4$), and concentrated in vacuo to give the crude product, which was chromatographed on Al_2O_3 (EtOAc/hexane, 1:1). The 4′-(3-iodophenyl)-2,2′:6′,2′′-terpyridine (**2**) was isolated (31%) as a white solid: ^{1}H NMR: δ = 8.74 (d, J = 5 Hz, 2 H, 6,6′′-tpy*H*), 8.73–8.66 (m, 4 H, 3′,5′-tpy*H* and 3,3′′-tpy*H*), 8.23 (s, 1 H, 2-Ar*H*), 7.92–7.84 (m, 3 H, 6-Ar*H* and 4,4′′-tpy*H*), 7.90 (d, J = 8 Hz, 1 H, 4-Ar*H*), 7.39 (t, J = 7 Hz, 2 H, 5,5′′-tpy*H*), 7.26 (d, J = 7 Hz, 2 H, 5-Ar*H*) ppm. ^{13}C NMR: δ = 156.23 ($C_{tpy}^{2'}$), 156.17 (C_{tpy}^{2}), 149.34 (C_{tpy}^{6}), 148.99 ($C_{tpy}^{4'}$), 140.91 (C_{Ar}^{3}), 138.12 (C_{Ar}^{6}), 137.13 (C_{tpy}^{4}), 136.27 (C_{Ar}^{2}), 130.77 (C_{Ar}^{5}), 126.88 (C_{Ar}^{4}), 124.17 (C_{tpy}^{3}), 121.59 (C_{tpy}^{5}), 118.96 ($C_{tpy}^{3'}$), 95.05 (C_{Ar}^{1}) ppm. ESI-MS: calcd. for $C_{21}H_{13}IN_3$ [M] 435.02; found for $[M + H]^+$ 435.8.

4′-(3-Ethynylphenyl)-2,2′:6′,2′′-terpyridine (3): Following general procedure **GP1**, terpyridine **2** (1 g, 2.3 mmol), diisopropylamine (16 mL), $[Pd(PPh_3)_2Cl_2]$ (64.4 mg, 90 μmol), and CuI (34.9 mg, 180 μmol) were dissolved in anhydrous THF (50 mL). After degassing five times with N_2, TMS-acetylene (450 mg, excess) was added. The mixture was degassed another three times, followed by heating at reflux for 12 h. After removal of the solvent in vacuo, the residue was chromatographed on Al_2O_3 ($CHCl_3$). The collected solid was mixed with KF (400 g, excess) in THF/MeOH (50 mL/50 mL). After being stirred for 12 h at 25 °C, the solvent was evaporated in vacuo. The residue was partitioned between $CHCl_3$ and H_2O and washed (H_2O) two times. The organic layer was then dried, concentrated in vacuo, and chromatographed on Al_2O_3 ($CHCl_3$) to afford **3** (547 mg, 71%) as a white solid. ^{1}H NMR: δ = 8.76–8.74 (d, 4 H, 6,6′′-tpy*H* and 3′,5′-tpy*H*), 8.70 (d, J = 8 Hz, 2 H, 3,3′′-tpy*H*), 8.06 (s, 1 H, 2-Ar*H*), 7.93–7.88 (m, 3 H, 6-Ar*H* and 4,4′′-tpy*H*), 7.90 (d, J = 8 Hz, 1 H, 4-Ar*H*), 7.51 (t, J = 8 Hz, 2 H, 5-Ar*H*), 7.40 (t, J = 7 Hz, 2 H, 5,5′′-tpy*H*), 3.16 (s, 1 H, C≡C*H*) ppm. ^{13}C NMR: δ = 156.01 ($C_{tpy}^{2'}$), 155.97 (C_{tpy}^{2}), 149.61 ($C_{tpy}^{4'}$), 149.09 (C_{tpy}^{6}), 138.87 (C_{Ar}^{3}), 137.42 (C_{tpy}^{4}), 132.79 (C_{Ar}^{6}), 131.18 (C_{Ar}^{2}), 129.23 (C_{Ar}^{5}), 128.03 (C_{Ar}^{4}), 124.21 (C_{tpy}^{3}), 123.13 (C_{Ar}^{1}), 121.74 (C_{tpy}^{5}), 119.22 ($C_{tpy}^{3'}$), 83.47 (*C*≡CH), 78.03 (*C*H≡C) ppm. ESI-MS: calcd. for $C_{23}H_{15}N_3$ [M] 333.13; found for $[M + H]^+$ 334.0.

Bis(terpyridine) 6: A mixture of bis(pinacolato)diboron (344 mg, 1.35 mmol), $[Pd(dppf)Cl_2]$ (32 mg, 39 μmol), and KOAc (379 mg, 3.86 mmol) in DMSO (5 mL) was degassed five times with argon. Then, terpyridine **1** (500 mg, 1.29 mmol) was added to it. The resulting mixture was degassed three additional times and then heated at reflux for 8 h. After being cooled to 25 °C, the mixture was diluted with toluene (50 mL) and washed twice with water (50 mL) to remove excess DMSO. The organic layer was evaporated in vacuo to give a residue, which was chromatographed (Al_2O_3) by eluting with $CHCl_3$ to give pure **6** (128 mg, 32%) as a white solid. ^{1}H NMR: δ = 8.82 (s, 4 H, 3′,5′-tpy*H*), 8.73 (br.m, 8 H, 6,6′′-tpy*H* and 3,3′′-tpy*H*), 8.18 (s, 2 H, 2-Ar*H*), 7.92–7.89 (br.m, 6 *H*, 4,4′′-tpy*H* and 6-Ar*H*), 7.78 (br.d, 2 H, 4-Ar*H*), 7.67 (br.t, 2 H, 5-Ar*H*), 7.36 (br.t, 4 H, 5,5′′-tpy*H*) ppm. ESI-MS: calcd. for $C_{42}H_{28}N_6$ [M] 616.2; found for $[M + H]^+$ 617.3 and for $[M + Na]^+$ 639.2. $C_{42}H_{28}N_6$ (616.72): calcd. C 81.80, H 4.58, N 13.63; found C 81.63, H 4.55, N 13.29.

Bis(terpyridine) 7: Following procedure **GP1**, to a degassed mixture of terpyridine **2** (131 g, 300 μmol) and terpyridine **3** (100 g, 300 μmol) were added $Pd(PPh_3)_4$ (14 mg, 12 μmol), Et_3N (10 mL), and CuI (4.6 mg, 24 μmol) in anhydrous THF (30 mL). After being degassed three additional times, the mixture was heated at reflux for 12 h. The solution was evaporated in vacuo to give a solid residue, which was chromatographed (Al_2O_3) by eluting with $CHCl_3$ to afford **7** (134 mg, 70%). ^{1}H NMR: δ = 8.78 (s, 4 H, 3′,5′-tpy*H*), 8.77 (d, J = 5 Hz, 4 H, 6,6′′-tpy*H*), 8.71 (d, J = 8 Hz, 4 H, 3,3′′-tpy*H*), 8.15 (s, 2 H, 2-Ar*H*), 7.92–7.87 (m, 6 H, 4,4′′-tpy*H* and 6-Ar*H*), 7.70 (d, J = 8 Hz, 2 H, 4-Ar*H*), 7.57 (t, J = 8 Hz, 2 H, 5-Ar*H*), 7.40 (t, J = 6 Hz, 4 H, 5,5′′-tpy*H*) ppm. ^{13}C NMR: δ = 156.37 ($C_{tpy}^{2'}$), 156.28 (C_{tpy}^{2}), 149.77 ($C_{tpy}^{4'}$), 149.40 (C_{tpy}^{6}), 139.06 (C_{Ar}^{3}), 137.11 (C_{tpy}^{4}), 132.32 (C_{Ar}^{6}), 130.79 (C_{Ar}^{2}), 129.29 (C_{Ar}^{5}), 127.60 (C_{Ar}^{4}), 124.12 (C_{tpy}^{3}), 121.60 (C_{tpy}^{5}), 119.13 ($C_{tpy}^{3'}$), 89.87 (*C*≡*C*) ppm. ESI-MS: calcd. for $C_{44}H_{28}N_6$ [M] 640.2; found for $[M + H]^+$ 641.3. $C_{44}H_{28}N_6$ (640.75): calcd. C 82.48, H 4.40, N 13.12; found C 82.45, H 4.32, N 13.04.

Bis(terpyridine) 8: A mixture of 1,4-benzenediboronic acid (50 mg, 300 μmol), terpyridine **2** (289 mg, 660 μmol), $Pd(PPh_3)_4$ (21 mg, 18 μmol), and 108 mg K_2CO_3 (780 μmol) in toluene/EtOH (v/v: 3:1) was stirred at 100 °C for 16 h. The toluene layer was separated and washed three times with H_2O. After removal of the solvent in vacuo, the residue was chromatographed (Al_2O_3) by eluting with $CHCl_3$ to afford **8** (123 mg, 59%) as a white solid possessing very poor solubility. ^{1}H NMR ([D_6]DMSO): δ = 8.81 (s, 4 H, 3′,5′-tpy*H*), 8.80 (d, J = 5 Hz, 4 H, 6,6′′-tpy*H*), 8.72 (d, J = 8 Hz, 4 H, 3,3′′-tpy*H*), 8.21 (s, 2 H, 2-Ar*H*), 8.09 (t, J = 9 Hz, 4 H, 4,4′′-tpy*H*), 7.98–7.91 (m, 8 H, 2,3,5,6-Ar_{center}*H*, 6-Ar*H*, and 4-Ar*H*), 7.76 (t, J = 8 Hz, 2 H, 5-Ar*H*), 7.56 (t, J = 6 Hz, 4 H, 5,5′′-tpy*H*) ppm. ESI-MS: calcd. for $C_{48}H_{32}N_6$ [M] 692.3; found for $[M + Na]^+$ 715.3.

Bis(terpyridine) 9: Following the procedure **GP1**, terpyridine **2** (280 mg, 640 μmol, 2.1 equiv.) and 1,4-diiodobenzene (101 mg, 310 μmol, 1 equiv.) were used to prepare **9**, which was a yellow insoluble solid that was insoluble in almost every common solvent.

Bis(terpyridine) 10. Route A: Following the procedure **GP1**, to a degassed mixture of terpyridine **2** (314 mg, 720 μmol) and terpyridine **5** (170 mg, 340 μmol) were added $Pd(PPh_3)_4$ (15 mg, 13 μmol) and CuI (5 mg, 26 μmol) in anhydrous THF (40 mL), and Et_3N (10 mL). After being degassed three additional times, the mixture was heated at reflux for 12 h. The solution was evaporated in vacuo to give a solid residue, which was chromatographed (Al_2O_3) by eluting with $CHCl_3$ to afford **10** (263 mg, 70%), identical in all respects to that derived from Route B.

Bis(terpyridine) 10. Route B: To a degassed mixture of terpyridine **3** (150 mg, 450 μmol) and terpyridine **4** (150 mg, 210 μmol) were added $Pd(PPh_3)_4$ (9 mg, 8 μmol) and CuI (3 mg, 16 μmol) in anhydrous THF (20 mL), and Et_3N (10 mL). After being heated at reflux for 12 h, the solution was removed in vacuo to give a residue that was chromatographed (Al_2O_3) by eluting with $CHCl_3$ to give bis(terpyridine) **10** (158 mg, 68%). ^{1}H NMR: δ = 8.78 (s, 4 H, 3′,5′-

tpy*H*), 8.77 (d, *J* = 5 Hz, 4 H, 6,6′′-tpy*H*), 8.72 (d, *J* = 5 Hz, 4 H, 3,3′′-tpy*H*), 8.12 (s, 2 H, 2-Ar*H*), 7.93–7.87 (m, 6 H, 4,4′′-tpy*H* and 6-Ar*H*), 7.66 (d, *J* = 8 Hz, 2 H, 4-Ar*H*), 7.54 (t, *J* = 8 Hz, 2 H, 5-Ar*H*), 7.40 (t, *J* = 6 Hz, 4 H, 5,5′′-tpy*H*), 7.12 (s, 2 H, 3,6-$Ar_{center}H$), 4.13 (t, *J* = 6 Hz, 4 H, $Ar_{center}OCH_2$), 1.93 (m, 4H, $Ar_{center}OCH_2CH_2$), 1.58 [m, 4H, $Ar_{center}O(CH_2)_2CH_2$], 1.40–1.89 [m, 32H, $Ar_{center}O(CH_2)_3(CH_2)_8CH_3$], 0.87 [t, *J* = 7 Hz, 6H, $Ar_{center}O(CH_2)_{11}CH_3$] ppm. ^{13}C NMR: δ = 156.39 ($C_{tpy}^{2'}$), 156.27 (C_{tpy}^{2}), 153.93 ($C_{Ar\text{-}center}^{2}$), 149.78 ($C_{tpy}^{4'}$), 149.37 (C_{tpy}^{6}), 139.00 (C_{Ar}^{3}), 137.09 (C_{tpy}^{4}), 132.21 (C_{Ar}^{6}) 130.68 (C_{Ar}^{2}), 129.19 (C_{Ar}^{5}), 127.42 (C_{Ar}^{4}), 124.55 (C_{Ar}^{1}), 124.10 (C_{tpy}^{3}), 121.58 (C_{tpy}^{5}), 119.09 ($C_{tpy}^{3'}$), 117.29 ($C_{Ar\text{-}center}^{3}$), 114.17 ($C_{Ar\text{-}center}^{1}$), 94.71 (*C*≡C-Ar_{center}), 86.91 (*C*≡C-Ar), 69.92 (*C*H$_2$-O), 32.12 (*C*H$_2$CH$_2$CH$_3$), 29.88 [*C*H$_2$(CH$_2$)$_9$CH$_3$], 29.84 [*C*H$_2$(CH$_2$)$_7$CH$_3$], 29.81 [*C*H$_2$-(CH$_2$)$_6$CH$_3$], 29.64 [*C*H$_2$(CH$_2$)$_5$CH$_3$], 29.58 [*C*H$_2$(CH$_2$)$_4$CH$_3$], 29.56 [*C*H$_2$(CH$_2$)$_3$CH$_3$], 28.30 [*C*H$_2$(CH$_2$)$_2$CH$_3$], 26.34 [*C*H$_2$(CH$_2$)$_8$-CH$_3$], 22.89 (*C*H$_2$CH$_3$), 14.32 (*C*H$_3$) ppm. ESI-MS: calcd. for $C_{76}H_{80}N_6O_2$ [M] 1108.6; found for [M + H]$^+$ 1109.6 and for [M + Na]$^+$ 1132.6. $C_{76}H_{80}N_6O_2$ (1109.51): calcd. C 82.27, H 7.27, N 7.57; found C 82.17, H 7.30, N 7.56.

General Procedure for the Bis(terpyridine)–Fe^{II} Macrocycle Complexes (GP2): $FeCl_2$ (1 equiv.) in MeOH was added to a stirred solution of bis(terpyridine) (1 equiv.) in MeOH or DMF. The color instantly changed to purple, and the mixture was heated at reflux for 24 h under N_2. After the solvent was removed in vacuo, the residue was chromatographed on SiO_2 by eluting with a H_2O/KNO_3(conc.)/MeCN (1:1:10) mixture. After removal of the solvent, the residue was washed with water, redissolved in MeOH, and excess NH_4PF_6 in methanol was added to precipitate the complex. The collected dark purple solid was washed thoroughly with MeOH to afford the desired MeCN-soluble terpyridine-Fe^{II} complex.

[Fe$_3$(6)(PF$_6$)$_6$] (11): A solution of $FeCl_2$ (13 mg, 65 μmol) in MeOH (20 mL) was added dropwise to a stirred solution of **6** (39.9 mg, 65 μmol) in DMF (20 mL). Following the procedure **GP2**, the mixture was stirred for 48 h at 50 °C to afford **11** (35 mg, 62%) as a deep purple solid. ^{1}H NMR (CD_3CN): δ = 9.37 (s, 12 H, 3′,5′-tpyH), 9.08 (s, 6 H, 2-ArH), 8.66 (d, *J* = 6 Hz, 12 H, 3,3′′-tpyH), 8.43 (d, *J* = 9 Hz, 6 H, 6-ArH), 8.33 (d, *J* = 9 Hz, 6 H, 4-ArH), 8.05 (t, *J* = 8 Hz, 6 H, 5-ArH), 7.83 (t, *J* = 6 Hz, 12 H, 4,4′′-tpyH), 7.22 (d, *J* = 6 Hz, 12 H, 6,6′′-tpyH), 7.04 (t, *J* = 6 Hz, 12 H, 5,5′′-tpyH) ppm. ^{13}C NMR (CD_3CN): δ = 161.38 ($C_{tpy}^{2'}$), 159.17 (C_{tpy}^{2}), 154.16 (C_{tpy}^{6}), 151.34 ($C_{tpy}^{4'}$), 141.69 (C_{Ar}^{3}), 139.61 (C_{tpy}^{4}), 139.10 (C_{Ar}^{1}), 131.63 (C_{Ar}^{5}), 131.36 (C_{Ar}^{6}), 129.67 (C_{Ar}^{2}), 128.28 (C_{Ar}^{4}), 127.97 (C_{tpy}^{3}), 124.92 (C_{tpy}^{5}), 123.14 ($C_{tpy}^{3'}$) ppm. ESI-MS: calcd. for $C_{126}H_{84}F_{36}Fe_3N_{18}P_6$ [M] 2886.3; found for [M – 2PF$_6$]$^{2+}$ 1298.4, for [M – 3PF$_6$]$^{3+}$ 817.6, and for [M – 3PF$_6$ – 3PF$_5$]$^{3+}$ 691.2. $C_{48}H_{32}N_6$ (692.82): calcd. C 83.21, H 4.66, N 12.13; found C 82.90, H 4.44, N 11.67.

[Fe$_3$(7)(PF$_6$)$_6$] (12): Following the procedure **GP2**, a mixture of **7** (33 mg, 50 μmol) and $FeCl_2$ (10.2 mg, 50 μmol) in MeOH (20 mL) was heated at reflux for 12 h to afford **12**, (44 mg, 86%) as a deep purple solid. ^{1}H NMR (CD_3CN): δ = 9.21 (s, 12 H, 3′,5′-tpy*H*), 8.64 (d, *J* = 8 Hz, 12 H, 3,3′′-tpy*H*), 8.59 (s, 6 H, 2-Ar*H*), 8.37 (d, *J* = 8 Hz, 6 H, 6-Ar*H*), 8.01 (d, *J* = 8 Hz, 6 H, 4-Ar*H*), 7.94–7.85 (m, 18 H, 4,4′′-tpy*H* and 5-Ar*H*), 7.20 (d, *J* = 5 Hz, 12 H, 6,6′′-tpy*H*), 7.1 (t, *J* = 6 Hz, 12 H, 5,5′′-tpy*H*) ppm. ^{13}C NMR (CD_3CN): δ = 161.82 ($C_{tpy}^{2'}$), 159.34 (C_{tpy}^{2}), 154.46 (C_{tpy}^{6}), 151.09 ($C_{tpy}^{4'}$), 140.17 (C_{Ar}^{3}), 139.08 (C_{tpy}^{4}), 134.55 (C_{Ar}^{6}), 132.82 (C_{Ar}^{2}), 131.69 (C_{Ar}^{5}), 129.72 (C_{Ar}^{4}), 128.77 (C_{tpy}^{3}), 125.65 (C_{Ar}^{1}), 125.37 (C_{tpy}^{5}), 123.25 ($C_{tpy}^{3'}$), 91.07 (*C*≡*C*) ppm. ESI-MS: calcd. for $C_{132}H_{84}F_{36}Fe_3N_{18}P_6$ [M] 2958.3; found for [M – 5PF$_6$]$^{5+}$ 446.7, and for [M – 6PF$_6$]$^{6+}$ 348.1.

[Fe$_3$(8)(PF$_6$)$_6$] (13): A solution of $FeCl_2$ (6.9 mg, 35 μmol) in MeOH (20 mL) was added dropwise to a solution of **8** (24 mg, 35 μmol) in DMF (20 mL). Following procedure **GP2**, the mixture was stirred for 48 h at 50 °C to afford the deep purple solid **13** (11 mg, 34%), after work-up. ^{1}H NMR (CD_3CN): δ = 9.29 (s, 12 H, 3′,5′-tpy*H*), 8.68 (m, 18 H, 3,3′′-tpy*H* and 2-Ar*H*), 8.35 (d, *J* = 8 Hz, 6 H, 6-Ar*H*), 8.21 (s, 12 H, 2,3,5,6-$Ar_{center}H$), 8.19 (d, *J* = 8 Hz, 6 H, 4-Ar*H*), 8.00–7.89 (m, 18 H, 5-Ar*H* and 4,4′′-tpy*H*), 7.25 (d, *J* = 5 Hz, 12 H, 6,6′′-tpy*H*), 7.13 (t, *J* = 6 Hz, 12 H, 5,5′′-tpy*H*) ppm. ^{13}C NMR (CD_3CN): δ = 161.41 ($C_{tpy}^{2'}$), 159.16 (C_{tpy}^{2}), 154.14 (C_{tpy}^{6}), 151.67 ($C_{tpy}^{4'}$), 142.43 (C_{Ar}^{3}), 140.64 (C_{Ar}^{1}), 139.84 (C_{tpy}^{4}), 138.95 ($C_{Ar\text{-}center}^{1}$), 131.59 (C_{Ar}^{5}), 129.97 (C_{Ar}^{6}), 128.98 ($C_{Ar\text{-}center}^{2}$), 128.42 (C_{tpy}^{3}), 128.26 (C_{Ar}^{2}), 127.76 (C_{Ar}^{4}), 124.99 (C_{tpy}^{5}), 123.19 ($C_{tpy}^{3'}$) ppm. ESI-MS: calcd. for $C_{144}H_{96}F_{36}Fe_3N_{18}P_6$ [M] 3114.4; found for [M – 3PF$_6$]$^{3+}$ 893.5, for [M – 4PF$_6$]$^{4+}$ 633.9, for [M – 5PF$_6$]$^{5+}$ 478.1, for [M – 5PF$_6$ – PF$_5$]$^{5+}$ 452.9, and for [M – 6PF$_6$]$^{6+}$ 374.2.

[Fe$_3$(10)(PF$_6$)$_6$] (14): Following procedure **GP2**, a mixture of **10** (29.6 mg, 27 μmol) and $FeCl_2$ (5.3 mg, 27 μmol) in MeOH (20 mL) was heated at reflux for 12 h to afford the deep purple solid **14** (28 mg, 72%). ^{1}H NMR (CD_3CN): δ = 9.22 (s, 12 H, 3′,5′-tpy*H*), 8.65 (d, *J* = 8 Hz, 12 H, 3,3′′-tpy*H*), 8.45 (s, 6 H, 2-Ar*H*), 8.35 (m, 6 H, 6-Ar*H*), 7.95–7.87 (m, 24 H, 4-Ar*H*, 4,4′′-tpy*H* and 5-Ar*H*), 7.26 (s, 6 H, 3,6-$Ar_{center}H$), 7.21 (d, *J* = 5 Hz, 12 H, 6,6′′-tpy*H*), 7.12 (t, *J* = 6 Hz, 12 H, 5,5′′-tpy*H*), 4.18 (t, *J* = 6 Hz, 12 H, $Ar_{center}OCH_2$) ppm. 1.93 (m, 12H, $Ar_{center}OCH_2CH_2$), 1.70 [m, 12H, $Ar_{center}O(CH_2)_2CH_2$], 1.46–1.06 [m, 96H, $Ar_{center}O(CH_2)_3(CH_2)_8CH_3$], 0.86 [t, *J* = 6 Hz, 18H, $Ar_{center}O(CH_2)_{11}CH_3$]. ^{13}C NMR ($CD_3CN$): δ = 160.68 ($C_{tpy}^{2'}$), 158.18 (C_{tpy}^{2}), 154.11 ($C_{Ar\text{-}center}^{2}$), 153.33 (C_{tpy}^{6}), 150.04 ($C_{tpy}^{4'}$), 139.12 (C_{Ar}^{3}), 137.74 (C_{tpy}^{4}), 133.24 (C_{Ar}^{6}), 131.41 (C_{Ar}^{2}), 130.54 (C_{Ar}^{5}), 128.34 (C_{Ar}^{4}), 127.71 (C_{Ar}^{1}), 124.82 (C_{tpy}^{3}), 124.21 (C_{tpy}^{5}), 122.04 ($C_{tpy}^{3'}$), 115.67 ($C_{Ar\text{-}center}^{3}$), 114.11 ($C_{Ar\text{-}center}^{1}$), 95.48 (*C*≡C-Ar_{center}), 88.43 (*C*≡C-Ar), 70.95 (*C*H$_2$-O), 33.05 (*C*H$_2$CH$_2$CH$_3$), 30.77 [*C*H$_2$(CH$_2$)$_9$CH$_3$], 30.74 [*C*H$_2$(CH$_2$)$_7$CH$_3$], 30.53 [*C*H$_2$(CH$_2$)$_5$CH$_3$], 30.46 [*C*H$_2$-(CH$_2$)$_3$CH$_3$], 27.31 [*C*H$_2$(CH$_2$)$_8$CH$_3$], 23.79 (*C*H$_2$CH$_3$), 14.85 (*C*H$_3$) ppm. ESI-MS: calcd. for $C_{228}H_{240}F_{36}Fe_3N_{18}O_6P_6$ [M] 4363.5; found for [M – 2PF$_6$]$^{2+}$ 2036.8, for [M – 3PF$_6$]$^{3+}$ 1310.2, for [M – 3PF$_6$ –PF$_5$]$^{3+}$ 1267.8, for [M – 3PF$_6$ –3PF$_5$]$^{3+}$ 1183.5, for [M – 4PF$_6$ –2PF$_5$]$^{4+}$ 883.1, for [M – 5PF$_6$ – PF$_5$]$^{5+}$ 702.2, and for [M – 6PF$_6$]$^{6+}$ 582.2.

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