Functional Nanohybrids Constructed via Complexation of Multiwalled Carbon Nanotubes with Novel Hexameric Metallomacrocyles

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A new family of hexameric metallomacrocycles employing a functionalized bis(terpyridine) building block was prepared by both self-assembly and stepwise procedures capitalizing on terpyridine−metal-(II)−terpyridine connectivity. Their structural composition was established by NMR, UV/vis, and mass techniques. Treatment of the hexameric Ru(II) macrocycle with carboxylate-functionalized, multiwalled carbon nanotubes (MWNTs) followed by dialysis led to cation-exchange-induced complexation and generated a nanohybrid adduct that was evidenced by both transmission electron microscopy imaging with energy dispersive X-ray spectroscopy and Raman spectroscopy.

I. Introduction

In recent years, there has been an increasing interest in the coordination of relatively simple ligands to afford di- and polynuclear complexes that exhibit high order, structural complexity,[1,2] in both solution and the solid state. Although contemporary supramolecular chemistry has its roots in classical covalent macrocycles,[3] metal-mediated and architecturally directed self-assembly has now been widely used to construct novel, ordered nanoscale arrays, such as grids,[4,5] helicates,[6] cubes,[7] cylinders,[8] and cages.[9]

In general, the majority of metallocycles that have been created so far are based on structures possessing heteroorganic sides with metal corners; this mode of construction has been elegantly exploited by Stang[2,10,11] and Atwood,[12] and has been the topic of numerous reviews.[13−17] Recently,

a different series of metallomacrocycles has been reported based on bis(terpyridinyl)aryl monomers possessing a critical, preset coordination angle of 120° with respect to the two metal-ligating moieties. This facilitates the assembly of six building blocks with six connecting metals in the ubiquitous benzenoid architecture.[18−20]

Herein, we report the design and preparation of new extended members of a "modular building block set"[21] that are capable of forming stable, irreversible, "higher order" architectures. Incorporation of linear triple bonds in the building block between the central connective aromatic ring and the two terpyridine ligands generates relatively rigid yet simple scaffolding that can be employed for the preparation of novel carbon-rich nanoscale architectures possessing tunable chemical, physical, electronic, and optical properties. Subsequent treatment of carboxylate-modified, multiwalled carbon nanotubes (MWNTs) with these metallohexamers afforded ionically hybridized carbon nanotubes that can be envisioned as components in devices such as single-electron transistors,[22,23] molecular diodes,[24−26] memory elements,[27] logic gates,[28,29] and nanoscale low-ohmic metallic contacts.[30]

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II. Experimental Section

Chemicals were commercially purchased and used without further purification. Thin-layer chromatography (TLC) was conducted on flexible sheets (Baker-flex) precoated with Al_2O_3 (IB-F) or SiO_2 (IB2-F) and visualized by UV light. Column chromatography was conducted using neutral/basic Al_2O_3, Brockman Activity I (60–325 mesh), or SiO_2 (60–200 mesh) from Fisher Scientific. Melting points were determined on an Electrothermal 9100 heater and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 300 NMR spectrometer using $CDCl_3$, as the solvent, except where noted. Mass spectra were obtained on a Bruker Esquire electrospray ion trap mass spectrometer (ESI-MS). UV/vis absorption spectra were obtained on Hewlett-Packard UV/vis spectrophotometer. Raman spectra were measured in backscattering geometry with Jobin Yvon T64000 triple monochromator; an argon laser with a wavelength of 514.7 nm and power of 20 mW as excitation source. Transmission electron microscopy (TEM) images were obtained by using scanning transmission electron microscopy (FEI; Tacnai 12) at an acceleration voltage of 120 kV. Energy dispersive X-ray spectroscopy (EDXS) analyses were conducted on an EDAX, EDAMIII apparatus. Samples for TEM were prepared by drop-casting the solution of acid-treatment MWNT, which is treated with aqueous NaOH, dispersed in MeCN onto a carbon film-coated grid, then air-dried, and washed several times with MeCN to remove any residual unreacted hexamers.

1,3-Bis(hydroxymethyl)-5-*tert*-butylbenzene (1).[31] To a solution of 5-*tert*-butylisophthalic acid (10.0 g, 45.0 mmol) in dry tetrahydrofuran (THF; 60 mL) at 0 °C was added dropwise a $BH_3\cdot$THF solution (270 mL, 270 mmol) over 30 min. After 1 h, the stirred solution was warmed to 25 °C for 24 h. Excess of a saturated aqueous $NaHCO_3$ solution was carefully added; the mixture was extracted with $CHCl_3$ and then dried ($MgSO_4$). The combined extract was concentrated in vacuo to give a residue, which was column chromatographed (SiO_2), eluting with a mixture of hexane: EtOAc (1:4; v/v) to afford (8.3 g, 95%) **1**, as a white solid: mp 74–75 °C; ^1H NMR δ 7.29 (s, 4,6-Ar*H*, 2H), 7.16 (s, 2-Ar*H*, 1H), 4.64 (s, C*H_2*OH, 4H), 2.40 (s, CH_2O*H*, 2H), 1.32 [s, C(C*H_3*)_3, 9H]; ^{13}C NMR δ 152.10, 141.09, 123.57, 123.12, 65.62, 34.94, 31.56; ESI-MS *m/z* 216.9 [M + Na^+] (calcd *m/z* = 217.2).

1,3-Bis(formyl)-5-*tert*-butylbenzene (2).[32] 1,3-Bis(hydroxymethyl)-5-*tert*-butylbenzene (3.0 g, 16 mmol) was added to a stirred mixture of pyridinium chlorochromate (10.0 g, 46.3 mmol) in anhydrous CH_2Cl_2 (200 mL) at 0 °C; the solution was then warmed to 25 °C for 24 h. The mixture was filtered through a Celite pad and then concentrated in vacuo to give a crude product, which was

column chromatographed (SiO_2), eluting with a mixture of hexane: EtOAc (1:1; v/v) to give (2.7 g, 92%) **2**, as a white solid: mp 62–63 °C; ^1H NMR δ 10.12 (s, C*H*O, 2H), 8.19 (s, 2,4,6-Ar*H*, 3H), 1.42 [s, C(C*H_3*)_3, 9H]; ^{13}C NMR δ 191.69, 153.93, 137.22, 131.86, 129.26, 35.36, 31.32; ESI-MS *m/z* 212.9 [M + Na^+] (calcd *m/z* = 213.2).

1,3-Bis(2,2-dibromoethenyl)-5-*tert*-butylbenzene (3). A stirred suspension of zinc (2.8 g, 43 mmol), $(C_6H_5)_3$P (11.2 g, 42.6 mmol), and CBr_4 (14.1 g, 42.6 mmol) in anhydrous CH_2Cl_2 (100 mL) was initially created at −20 °C and then maintained with stirring at 25 °C for 30 h. 1,3-Bis(formyl)-5-*tert*-butylbenzene (2.7 g, 14 mmol) was added to this suspension; stirring was continued for 2 h. The reaction mixture was poured into pentane (150 mL) and the insoluble material was filtered. The filtrate was poured into excess hexane and filtered (Celite) to afford a filtrate, which was evaporated in vacuo to gave (3.7 g, 52%) **3**, as a colorless oil: ^1H NMR δ 7.59 (s, 2-Ar*H*, 1H), 7.50 (s, 4,6-Ar*H*, 2H), 1.34 [s, C(C*H_3*)_3, 9H]; ^{13}C NMR δ 151.77, 136.96, 135.37, 126.14, 125.27, 90.24, 35.06, 31.42; HRMS *m/z* 524.7678 [M + Na^+] (calcd *m/z* = 524.7686).

1,3-Bis(diethynyl)-5-*tert*-butylbenzene (4).[33] To a stirred solution of **3** (6.5 g, 13 mmol) in anhydrous THF (200 mL), was added in KO*t*-Bu (5.0 g, 52 mmol) at −76 °C over 1 h. The mixture was stirred for an additional 5 h at −76 °C and then quenched with excess H_2O. The mixture was extracted with $CHCl_3$, dried ($MgSO_4$), and concentrated in vacuo to give a residue, which was flash column chromatographed (SiO_2) eluting with a hexane:EtOAc (1:1; v/v) mixture to afford (3.9 g, 89%) a yellow oil.

An *n*-BuLi solution (5.1 mL; 2.5 M in hexane, 13 mmol) was added dropwise to this crude oil (3.9 g, 11 mmol) in anhydrous Et_2O (100 mL) at 0 °C over 30 min. After further stirring for 30 min at 0 °C, the solution was cooled to −10 °C and carefully quenched with H_2O (5 mL). The mixture was poured into ice-cold water (200 mL) and extracted with Et_2O. The combined organic extract was washed with brine, dried ($MgSO_4$), and concentrated in vacuo to give a residue, which was column chromatographed (SiO_2), eluting with hexane to afford (1.9 g, 91%) **4**, as a colorless oil: ^1H NMR δ 7.54 (s, 2,6-Ar*H*, 2H), 7.50 (s, 4-Ar*H*, 1H), 3.10 (s, C*H*, 2H), 1.33 [s, C(C*H_3*)_3, 9H]; ^{13}C NMR δ 151.72, 132.95, 129.88, 122.27, 83.37, 77.54, 34.75, 31.17; ESI-MS *m/z* 205.2 [M + Na^+] (calcd *m/z* = 205.3).

1,3-Bis(2,2′:6′,2″-terpyridin-4-ylethynyl)-5-*tert*-butylbenzene (6). 1,3-Bis(diethynyl)-5-*tert*-butylbenzene (800 mg, 4 mmol) and 4′-[(trifluoromethyl)sulfonyloxy]-2,2′:6′,6″-terpyridine[34] (3.9 g, 11 mmol) were coupled by a Pd-catalyzed coupling procedure using tetrakis(triphenylphosphine)palladium(0) (500 mg, 0.4 mmol), diisopropylamine (40 mL), and toluene (50 mL) at 80 °C. After 3 days, the solvent was removed in vacuo to give a residue, which was column chromatographed (Al_2O_3) eluting with $CHCl_3$ to afford (990 mg, 35%) pure **6**, as an off-white solid: mp 269–270 °C; ^1H NMR δ 8.76 (d, *J* = 5.7 Hz, 6,6″-tpy*H*, 4H), 8.65 (d, *J* = 7.8 Hz, 3,3″-tpy*H*, 4H), 8.62 (s, 3′,5′-tpy*H*, 4H), 7.92 (dd, *J* = 7.8, 6.6 Hz, 4,4″-tpy*H*, 4H), 7.65 (s, 4,6-Ar*H*, 2H), 7.61 (s, 2-Ar*H*, 1H), 7.38 (dd, *J* = 6.6, 5.7 Hz, 5,5″-tpy*H*, 4H), 1.41 (s, C(C*H_3*)_3, 9H); ^{13}C NMR δ 155.68, 155.61, 152.21, 149.28, 137.35, 133.52, 132.30, 130.25, 124.30, 123.24, 122.81, 121.57, 93.60, 87.80, 35.06, 31.43; HRMS *m/z* 645.2769 [M + H^+] (calcd *m/z* = 645.2766).

[(6)₆Fe₆ (PF₆)₁₂] (7). A MeOH solution of 1 equiv of $FeCl_2\cdot4H_2O$ (59 mg, 0.29 mmol) was added to a stirred solution of 1,3-bis-(2,2′:6′,2″-terpyridin-4-ylethynyl)-5-*tert*-butylbenzene (210 mg, 0.29 mmol) in MeOH (150 mL). After 24 h at 25 °C, the resultant deep

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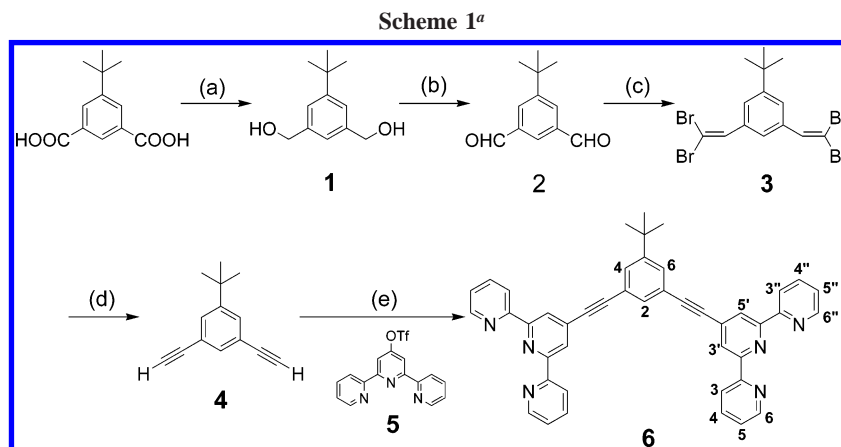(30) Hornbaker, D. J.; Kahng, S.-J.; Misra, S.; Smith, B. W.; Johnson, A. T.; Mele, E. J.; Luzzi, D. E.; Yazdani, A. *Science* **2002**, *295*, 828–831.
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Scheme 1[a]

[a] Reagents and conditions: (a) BH$_3$·THF, THF; (b) PCC, CH$_2$Cl$_2$, 25 °C; (c) Zn, Ph$_3$P, CBr$_4$, CH$_2$Cl$_2$, 25 °C; (d) (i) *t*-BuOK, THF, −76 °C, (ii) *n*-BuLi, Et$_2$O, 0 °C, H$_2$O; (e) Pd(Ph$_3$P)$_4$, ^{i}Pr$_2$NH/toluene.

purple solution was filtered (Celite); a slight excess of methanolic ammonium hexafluorophosphate was added in order to precipitate the complex, which was column chromatographed (SiO$_2$) eluting with a H$_2$O:CH$_3$CN:saturated aqueous KNO$_3$ (1:10:1; v/v/v) mixture to afford (1.2 g, ~70%) **7**, as a purple solid: mp > 400 °C; ^{1}H NMR (CD$_3$CN) δ 9.13 (s, 3′,5′-tpy*H*, 4H), 8.56 (d, *J* = 7.8 Hz, 3,3″-tpy*H*, 4H), 8.11 (s, 4,6-Ar*H*, 2H), 7.97 (m, 2-Ar*H*, 4,4″-tpy*H*, 4H), 7.22 (d, *J* = 6.0 Hz, 6,6″-tpy*H*, 4H), 7.15 (dd, *J* = 6.6, 6.0 Hz, 5,5″-tpy*H*, 4H), 1.56 [s, C(C*H*$_3$)$_3$, 9H]; ^{13}C NMR (CD$_3$CN) δ 161.34, 158.42, 154.32, 140.13, 138.44, 133.32, 132.30, 128.75, 126.29, 125.66, 125.17, 123.26, 97.82, 87.98, 35.90, 31.37; UV/vis (CH$_3$CN) λ_{max} (ϵ) = 285 (2.75 × 10^5 dm^3 mol^{-1} cm^{-1}), 338 (3.55 × 10^5), 584 nm (1.74 × 10^5); HRMS *m/z* = 1134.7947 [M^{12+} + PF$_6^-$ + 7F$^-$]$^{4+}$ (calcd *m/z* = 1134.7950), 1055.1956 [M^{12+} + 7PF$_6^-$]$^{5+}$ (calcd. *m/z* = 1055.1952).

[(RuCl$_3$)$_2$(6)] (8). The bis (ligand) **6** (41 mg, 58 μmol) was added to a solution of RuCl$_3$·3H$_2$O (26 mg, 0.13 mmol) in MeOH (40 mL), and then the suspension was refluxed for 12 h. After the mixture was cooled, the resultant dark red solid was filtered, washed with MeOH and CHCl$_3$, and dried in vacuo to give (52 mg, ~80%) the bis[Ru(III)] adduct **8**, as a dark brown solid. This material was used in the next step without further purification.

[(6)$_3$(Ru)$_2$(Cl)$_4$] (9). The bis (ligand) **6** (66 mg, 93 μmol) was added to a suspension of bis[Ru(III)] adduct **8** (52 mg, 46 μmol) in MeOH (50 mL), and then *N*-ethylmorpholine (3 drops) was added; the mixture was refluxed for 24 h. After cooling, the resulting deep red solution was filtered through Celite, followed by the addition of a slight excess of methanolic ammonium hexafluorophosphate to precipitate the complex, which was subsequentially column chromatographed (Al$_2$O$_3$) eluting with a H$_2$O:CH$_3$CN: saturated aqueous KNO$_3$ (1:10:1; v/v/v) mixture to give (51 mg, ~47%) trimer **9**, as a dark red solid: mp > 400 °C; ^{1}H NMR (CD$_3$-CN; PF$_6^-$ counterion) δ 8.94 (s, 3′,5′-tpy*H* coordinated of center ligand, 4H), 8.92 (s, 3′,5′-tpy*H* coordinated of side ligand, 4H), 8.86 (d, *J* = 5.7 Hz, 6,6″-tpy*H* free ligand, 4H), 8.77 (d, *J* = 7.5 Hz, 3,3″-tpy*H* free ligand, 4H), 8.68 (s, 3′,5′-tpy*H* free ligand, 4H), 8.56 (dd, *J* = 7.2, 6.3 Hz, 3,3″-tpy*H* coordinated of center and side ligand, 8H), 8.38 (dd, *J* = 7.5, 6.6 Hz, 4,4″-tpy*H* free ligand, 4H), 8.01−7.92 (m, 4,4″-tpy*H* coordinated center and side ligand, 2-Ar*H*, 4,6-Ar*H* coordinated and free ligand, 17H), 7.81 (dd, *J* = 6.6, 5.7 Hz, 5,5″-tpy*H* free ligand, 4H), 7.45 (d, *J* = 5.7 Hz, 6,6″-tpy*H* coordinated of center and side ligand, 8H), 7.23 (dd, *J* = 5.7, 5.7 Hz, 5,5″-tpy*H* coordinated of center and side ligand, 8H), 1.52 [s, C(C*H*$_3$)$_3$ center ligand, 9H], 1.47 [s, C(C*H*$_3$)$_3$ side ligand, 18H]; HRMS *m/z* = 556.1948 [M^{4+}] (calcd *m/z* = 556.1851).

[(6)$_6$(Ru$_6$)(PF$_6$)$_{12}$] (10). To a solution of the above precursor **9** (140 mg, 0.59 μmol) in MeOH, Ru(DMSO)$_4$Cl$_2$ (29 mg, 0.59 μmol;

DMSO = dimethyl sulfoxide) was added and the mixture was refluxed for 36 h. After cooling to 25 °C, the resultant deep red solution was filtered through Celite, and then a slight excess of methanolic ammonium hexafluorophosphate was added to precipitate the complex, which was purified by column chromatography (SiO$_2$) eluting with a H$_2$O:CH$_3$CN:saturated aqueous KNO$_3$ (1:10:1; v/v/v) mixture to afford (130 mg, ~35%) hexamer **10**, as a dark red solid: mp > 400 °C; ^{1}H NMR (CD$_3$CN) δ 8.95 (s, 3′,5′-tpy*H*, 4H), 8.57 (d, *J* = 7.8 Hz, 3,3″-tpy*H*, 4H), 8.00 (m, 4-Ar*H*, 2-Ar*H*, 4,4″-tpy*H*, 7H), 7.47 (d, *J* = 6.0 Hz, 6,6″-tpy*H*, 4H), 7.24 (dd, *J* = 6.3, 6.0 Hz, 5,5″-tpy*H*, 4H), 1.52 [s, C(C*H*$_3$)$_3$, 9H]; ^{13}C NMR δ 158.60, 156.44, 154.37, 153.80, 139.49, 133.55, 132.03, 131.21, 128.90, 126.45, 125.79, 123.31, 97.01, 87.88, 35.89, 31.81; UV/vis (CH$_3$CN) λ_{max} 283 (ϵ = 1.66 × 10^5 dm^3 mol^{-1} cm^{-1}), 333 (2.70 × 10^5), 502 nm (1.46 × 10^5); HRMS *m/z* = 2804.3941 [M^{12+} + 7PF$_6^-$ + 3F$^-$]$^{2+}$ (calcd *m/z* = 2804.3946), 1905.2516 [M^{12+} + 8PF$_5^-$ + F$^-$]$^{3+}$ (calcd *m/z* = 1905.2520), 1361.2059 [M^{12+} + 6PF$_6^-$ + 2F$^-$]$^{4+}$ (Calcd. *m/z* = 1361.2064).

Hexamer−MWNT Nanohybrid Complexation. A 250 mL flask charged with 5.0 g of crude MWNT and 100 mL of 60% HNO$_3$ aqueous solution was sonicated in a bath for 30 min. The mixture was then stirred for 24 h under reflux. After cooling to 20 °C, it was diluted with 200 mL of deionized water and filtered. The filtrate was washed with deionized water until the filtrate reached pH 7. The filtered solid was then dried in vacuo for 12 h at 60 °C to give 3.1 g of carboxylic acid−functionalized MWNT (MWNT−COOH). Dried MWNT−COOH (160 mg) and NaOH (excess) were suspended in 30 mL of deionized water and stirred at 25 °C for 12 h. The mixture was then separated by filtration and washed with deionized water. Subsequently, it was dried in vacuo at 25 °C for 6 h to give 150 mg of carboxylate-functionalized MWNT sodium salt (MWNT−CO$_2$Na). The MWNT−CO$_2$Na (ca. 100 mg) was charged in 30 mL of MeCN and sonicated for 30 min. Then 50 mg of ruthenium(II) metallomacrocycle **10** dissolved in 5 mL of anhydrous MeCN was added dropwise at 25 °C and kept with stirring for 48 h. The solid was then separated from the mixture by filtration and washed several times with excess MeCN. The raw product was suspended in excess MeCN followed by dialysis using MWCO = 10,000 membrane. The black solid was collected and dried overnight in vacuo at 25 °C, affording ca. 100 mg of hexamer−MWNT nanohybrid.

III. Results and Discussion

Construction of the desired 120°-based bisligand (Scheme 1) began with initial reduction (BH$_3$·THF) of 5-*tert*-butyl-isophthalic acid to give (95%) the corresponding diol **1**,

Scheme 2[a]
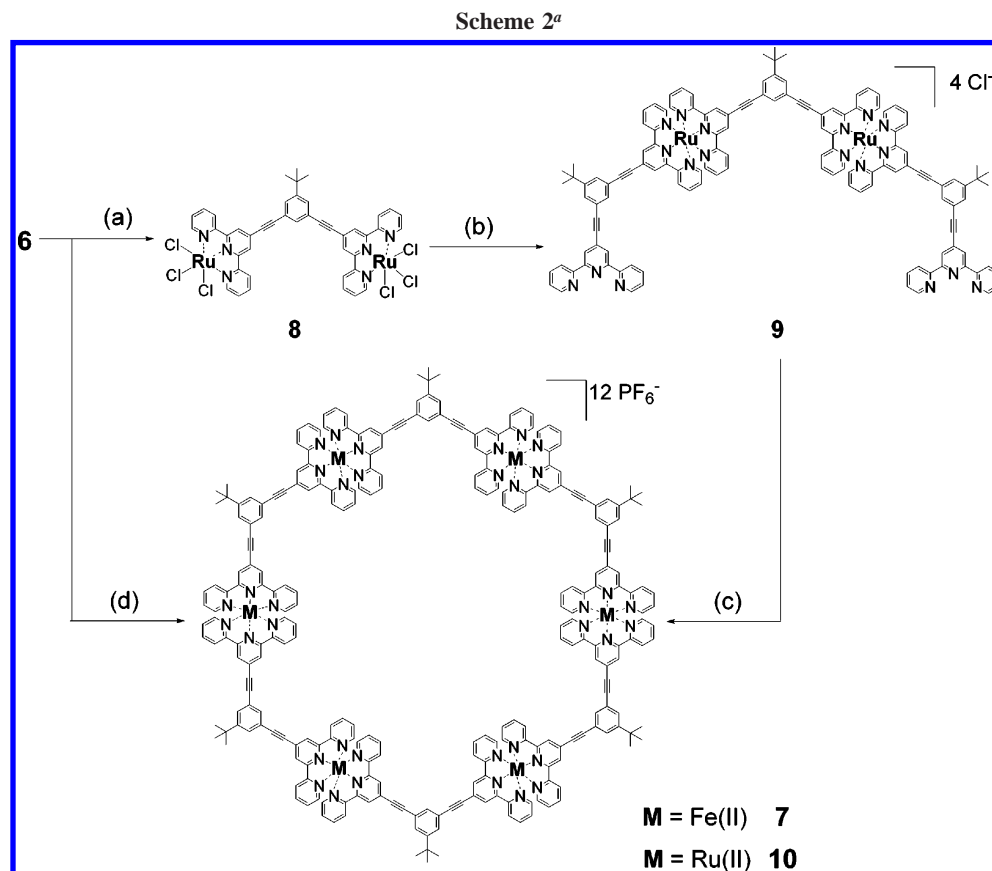
[a] Reagents and conditions: (a) RuCl$_3$·3H$_2$O, MeOH, reflux; (b) 2 equiv of **6**, *N*-ethylmorpholine, MeOH, reflux; (c) (i) Ru(DMSO)$_4$Cl$_2$, MeOH, reflux; (ii) NH$_4$PF$_6$/MeOH; (d) (i) Ru(DMSO)$_4$Cl$_2$ or FeCl$_2$·4H$_2$O, MeOH, reflux; (ii) NH$_4$PF$_6$/MeOH.

which was subsequently oxidized (PCC/CH$_2$Cl$_2$) to afford (92%) dialdehyde **2**. Each transformation was evidenced by the appearance of pivotal absorptions (^{13}C NMR) at 65.62 (*C*H$_2$OH) and 191.69 (*C*HO) ppm, respectively. Wittig-type olefination of aldehyde **2** with a mixture of CBr$_4$, Ph$_3$P, and zinc in CH$_2$Cl$_2$ gave (90%) the tetrabromide **3** that was supported (^{13}C NMR) by the new resonance at 90.24 ppm (C=*C*Br$_2$). Two-stage dehydrobromination of bromide **3** using KO*t*-Bu in THF afforded the dibromo intermediate (not shown), which was subsequently treated, without further purification, with *n*-BuLi in Et$_2$O to give (80%) 1,3-bis-(diethynyl)-5-*tert*-butylbenzene (**4**), as a white solid. Support for the transformation included new peaks (^{13}C NMR) at 83.37 (*C*≡CH) and 77.54 (*C*≡CH) ppm. Reacting this bisalkyne **4** with 2.5 equiv of 4′-trifluoromethanesulfonyl-2,2′:6′,2″-terpyridine[34] (tpy-OTf) by means of a Pd-catalyzed cross-coupling procedure mediated by [(PPh$_3$)$_4$Pd(0)] in diisopropylamine then afforded (35%) the desired angular monomer **6**, as an off-white solid. The successful coupling was evidenced by the appearance of the expected new signals (^{1}H and ^{13}C NMR) attributed to the terpyridinyl moieties and the presence of two similar alkyne peaks (^{13}C NMR) at 93.60 and 87.80 ppm.

Self-assembly of the hexameric iron(II) metallomacrocycle **7** was accomplished by treatment of bis(terpyridine) **6** with 1 equiv of FeCl$_2$·4H$_2$O in MeOH (Scheme 2) to give (70%), after chromatography and counterion exchange (Cl$^-$ to PF$_6^-$), the diamagnetic product, which was characterized (^{1}H NMR) by a resonance at 1.56 ppm [C(C*H*$_3$)$_3$], indicating the

presence of a single homogeneous environment for all such groups; this is in contrast to the broadened or multiple signals realized for either linear or polymeric oligomers. Also obtained were the notable upfield and downfield shifts (^{1}H NMR) of the doublet at 7.22 ppm ($\Delta\delta = -1.54$) for the 6,6″-tpy*H*s and the singlet at 9.13 ppm ($\Delta\delta = 0.51$) for the 3′,5′-tpy*H*s, respectively, when compared to the absorptions for the parent **6**. Other diagnostic signals (^{13}C NMR) included two signals at 97.82 and 87.98 ppm attributed to the dissymmetric acetylenic carbons. COSY and HETCOR spectra of both the starting ligand **6** and self-assembled macrocycle **7** verified the peak assignments, as well as coupling patterns. This hexagonal structure was further established (HRMS) by the observation of signals (m/z = 1134.7947 and 1055.1956) assigned to multiple-charged entities (+4 and +5 charge states) derived from the loss of PF$_5$ and PF$_6^-$, either separately or together.[35] Hexameric metallomacrocycle **7**, initially isolated as the 12 Cl$^-$ salt, was soluble in MeOH and hot H$_2$O; subsequent conversion to the corresponding 12 PF$_6^-$ salt facilitated solubility in MeCN, acetone, DMF, and DMSO.

The related diamagnetic, hexameric ruthenium(II) macrocycle, [(**6**)$_6$(Ru)$_6$(PF$_6$)$_{12}$] (**10**, Scheme 2), was prepared by both a single-step and stepwise procedures. The diamagnetic bis-complex **9** was readily prepared by treatment of the paramagnetic precursor **8** with 2 equiv of unmetalated bis-

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Scheme 3[a]
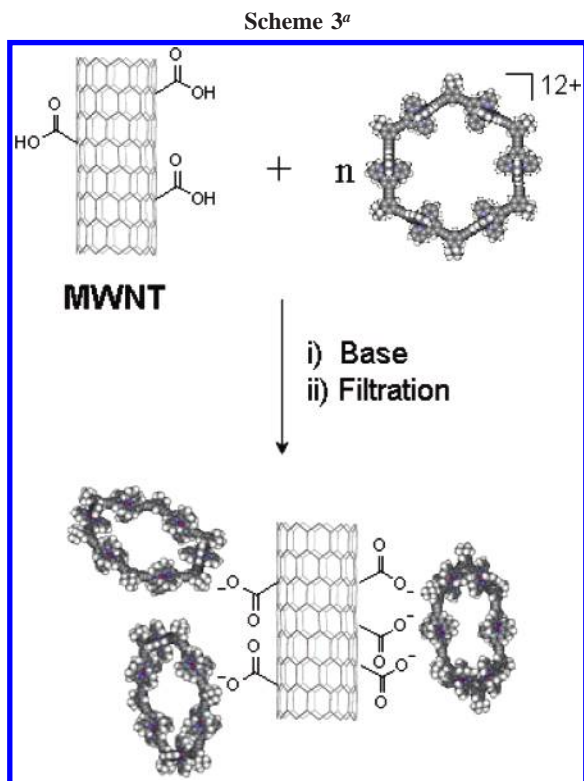
[a] Idealized structure of hexamer/MWNT nanohybrids.

(terpyridine) **6**. The ^{1}H NMR of trimer **9** showed equivalent 3′,5′-tpy*H* peaks (8.94, 8.92, 8.77 ppm; 1:1:1 ratio) as well as two anticipated singlets arising from nonequivalent *tert*-butyl groups (1.52, 1.47 ppm; 1:2 ratio). Treatment of trimer **9** with 1 equiv of $Ru(DMSO)_4Cl_2$ in refluxing MeOH for 36 h gave the desired hexameric complex possessing chloride counterions, which, after chromatography and counterion exchange (Cl^- to PF_6^-), afforded (overall 30%) the pure hexamer **10**. This metallocycle was spectrally identical to the product formed through the self-assembly protocol. The ^{1}H NMR of the hexaruthenium(II) complex **10** revealed a pattern similar to that of the Fe(II)-based metallomacrocycle **7**, except for slight chemical shift difference of the diagnostic doublet (7.47 ppm, $\Delta\delta = -1.29$) of the 6,6″-tpy*H*s and the singlet for the 3′,5′-tpy*H*s (8.95 ppm, $\Delta\delta = 0.33$). The HRMS of macrocycle **10** exhibited signals for the multiple-charged entities ranging from +2 to +4 charge states (m/z = 2804.3940, 1905.2516, and 1361.2059).

To elucidate and support the composition of the hexamers, their UV/vis spectra were measured. The absorption data of **7** and **10** each showed two ligand-centered $\pi-\pi^*$ transitions at ~284 and ~335 nm. The metal−ligand charge-transfer (MLCT) transitions, which were derived from the promotion of an electron from the metal [Fe(II) or Ru(II)]-centered *d*-orbitals to an unfilled ligand-centered π^* orbital,[36] appeared at 584 and 502 nm, respectively.

Following acid treatment (60% HNO_3 aqueous solution) of MWNTs to give the partially oxidized carbon nanotubes, ion coordination of hexamer **10** to nanotube carboxylate binding sites was effected by cation exchange to afford
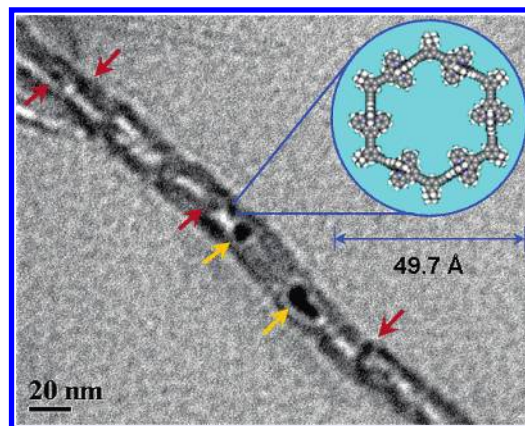
Figure 1. Computer-generated space-filling representation (inset) and TEM photograph of Ru(II)-based hexamer **10** immobilized on a carboxylate-modified MWNT surface. Red arrows indicate single hexamers, and yellow arrows show the agglomerates of several hexamers.
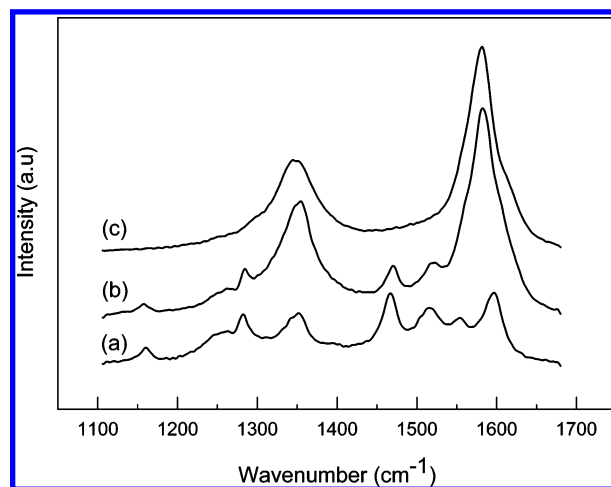
Figure 2. Raman spectra of (a) hexamer **10**, (b) the hexamer/MWNT nanohybrid, and (c) the oxidized MWNT.

(Scheme 3) a new type of surface-bound nanohybrid complex. Binding sites on the modified surface of the MWNTs were detected (TEM) by the presence of the electron dense Ru(II)−hexamer **10** (Figure 1). MWNT coating by hexamer **10** is, of course, not uniform due to random metallohexamer surface−carboxylate association. Computer-aided structure simulation revealed a macrocyclic external diameter of 49.7 Å for hexamer **10**; this calculated size agrees well with the observed ca. 5 nm electron dense spots visible on the MWNT's surface, as shown in the TEM microphotograph. EDXS spectra revealed a distinct peak at 2.6 keV corresponding to ruthenium-based surface absorption, thereby further confirming the construction of the hexamer−MWNT composite.

Raman spectra for pure hexamer **10**, acid-treated MWNT, and the hexamer/MWNT hybrid are shown in Figure 2. A *D*-mode at ~1348 cm^{-1}, which has been attributed to the breakdown of translational symmetry produced by its micro-crystalline structure,[37] as well as a *G*-mode located at the 1580 cm^{-1} related to the tangential shear mode (E_{2g})[38] additionally confirm the composite structures. Figure 2c also shows the as a shoulder, at 1615 cm^{-1} (calculated by using Lorentzian multipeak analysis method), which has a coun-

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terpart in the disordered sp carbons. The frequency of the D^*-mode in graphite corresponds to the mid-zone maximum in the phonon density of states in the optical branch[39,40] and as structural disorder tends to introduce structure in the Raman spectrum near positions of maxima in the one-phonon density of states of the ordered (parent) material; the D^*-mode is therefore another anticipated signature for surface−wall disorder, functionalization, or wall defects, after processing. Introducing defects along the MWNT's surface in a controlled manner, using the initial acid treatment followed by Raman spectroscopy to examine the vibrational response facilitated an understanding of changes along the MWNT surface.[41] Consequently, peak changes, when the hexamer is introduced to the MWNT's surface, were observed as a decrease in the D^*-mode peak. Upon introduction, a sub-

stantial shift (ca. 3 cm^{-1}) in the E_{2g}-mode as well as a shift of the hexamer's peaks, which appeared near the G-mode and D-mode of the oxidized MWNT, was realized.

IV. Conclusion

A pair of hexameric metallomacrocycles have been assembled on the basis of terpyridine−metal(II)−terpyridine connectivity. The complexation of these hexagonal nanoarchitectures was characterized by means of ^1H and ^{13}C NMR, UV/vis spectroscopy, and mass spectrometry and, in the case of Ru(II) metallomacrocycle, by TEM. The complexation of the hexamer to MWNTs was successfully achieved through cation exchange. Use of these rigid metallomacrocycles that can be readily attached to functionalized carbon nanotubes affords access to potential utilitarian nanohybrid structures such as photovoltaic materials[42] field-effect transistors,[43] and electrochemical sensors.[43]

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