Synthesis of a water-soluble hexameric metallomacrocycle and its oxidized single-wall carbon nanotube composite[†]

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Polycationic water-soluble metallomacrocycles possessing 12 positive charges that facilitate ionic coordination with the carboxylate moieties of Oxi-SWNTs form a nanotube composite *en route* to tailored electronic properties. The multiple ionic pair interactions between the positively charged metallohexamers and carboxylate modified SWNT are evidenced by TEM and AFM images.

Introduction

Transition metal-bisterpyridine complexes, specifically with Ru(II), have been widely utilized in electron transfer and photoluminescence research and utilitarian applications.¹ Crystalline [tpy₂Ru^{II}] (tpy = 2,2':6',2"-terpyridine)² upon electrochemical reduction to crystalline [tpy₂Ru⁰] has been demonstrated³ to undergo a facile reversible, stable, two-electron transfer. The incorporation of this simple monomeric unit into stable hexametallomacrocycles [(tpy)₆Ru^{II}₆]^{4,5} has been achieved *via* the self-assembly of the ditopic ligand *meta*-bis(terpyridinyl)benzene and [Ru(DMSO)₄Cl₂]. As a result of the light absorbing properties of these stable hexamers, they have been utilized as components in photovoltaic devices,^{6,7} demonstrated to possess photoactive⁸ and electronic properties, and employed as polyelectrolytes^{9,10} by taking advantage of their donor–acceptor and electrostatic interactions.

Carbon nanotubes^{11–14} and their corresponding oxidized single-wall carbon nanotubes (Oxi-SWNT, where 'Oxi' is an abbreviation for oxidized) with their extended π -electron conjugation are often utilized as electron acceptors. The Oxi-SWNTs^{15,16} have been further modified with a wide variety of useful functional groups by chemical and physical methods.^{17,18} Organic or organic/inorganic composites, as well as biomaterials, have been attached to the ends and sidewalls of the Oxi-SWNTs by covalent modification in efforts to enhance their physical and optoelectronic properties.¹⁹ Recently, the combination of SWNTs with photoactive electron donors,²⁰ e.g. porphyrins,²¹ has been developed for their potential application as solar energy conversion devices (*ca.* 4.2% monochromatic conversion efficiency)²² capitalizing on their electron-acceptor properties. We herein report the preparation of a water-soluble metallomacrocycle possessing 12 positive charges that facilitate ionic coordination with the negatively charged carboxylate moieties of Oxi-SWNTs thereby forming a nanotube composite with unique electronic properties.

Experimental

General information

TEM characterization. An FEI TECNAI 12 transmission electron microscope (TEM) with an accelerating voltage of 120 kV was used to study the size, distribution, and structure of the carbon nanotubes and the composite. Samples for analysis were prepared by adding a droplet of either dilute solution or suspension to the surface of carbon coated, 400 mesh Cu or Ni grids (available from SPI Supplies), followed by drying at 25 °C for 48 h.

AFM characterization. Droplets of dilute solutions or suspensions of the commercial Oxi-SWNTs, **2**, [(Oxi-SWNT)_n**2**_m] or the disassembled composite, were placed on the surface of freshly cleaved mica. After drying at 25 °C for 6 h, the samples were characterized by atomic force microscopy (AFM) using a Digital Instruments Nanoscope IIIa scanning probe microscope equipped with a Multi 75, Force Modulation Etched Silicon Probe (model MPP-21100) and operating in tapping mode.

UV characterization. UV-Vis spectra were recorded on an Ocean Optics, Inc. Chem2000 UV-Vis spectrophotometer.

Cyclic voltammetry. Cyclic voltammograms were recorded on a BAS C3-Voltammetry Cell Stand with an Epsilon potentiostat at 20 °C. A three-electrode configuration was used with a glassy carbon working electrode, a platinum auxiliary electrode, and an Ag/AgCl reference electrode with a scan rate of 100 mV s⁻¹. The analyte concentration was 1 mg sample per 10 mL of water. A pH 7 buffer solution (Alfa Aesar) was used as the supporting electrolyte and solvent. Depositing a drop of the analyte solution onto the electrode surface and drying with an infrared lamp formed the film of the sample. The solvent was purged with argon for 10 minutes

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prior to the experiment and kept under a blanket of argon throughout the experiment.

Experimental procedures

General procedure for synthesis of 1. A mixture of di(terpyridinyl)phenol²³ (200 mg, 36 mmol), 18-crown-6 ether (95 mg, 36 mmol) and K₂CO₃ (49.6 mg, 36 mmol) in DMF (60 mL) was stirred at 25 °C for 30 min, then the 3,4,5tris[(tetraethylene glycol)-functionalized](chloromethyl)benzene²⁴ (40 mmol) was added. The resultant suspension was stirred at 80 °C for 10 h under N₂. The solvent was removed in vacuo to give a pale yellow oily residue, which was column chromatographed (Al₂O₃) eluting with CHCl₃- CH_3OH (1 : 10 v/v) to give (90%) the alkylated product, as a colorless oil. ¹H NMR (CDCl₃) δ 8.77 (s, 4H, Ar $H^{3',5'}$), 8.71 (d, 4H, PyH^{3,3"}), 8.66 (d, 4H, PyH^{6,6"}), 7.93 (s, 1H, ArH⁴), 7.84 (t, 4H, PyH^{4,4"}), 7.55 (s, 2H, ArH^{2,6}), 7.32 (t, 4H, PyH^{5,5"}), 6.77 (s, 2H, BnH), 5.16 (s, 2H, OCH₂Ar), 4.20 (t, 4H, OCH₂), 4.16 (t, 2H, OCH₂), 3.84 (t, 4H, OCH₂), 3.79 (t, 2H, OCH₂), 3.71-3.46 (m, 36H, OCH₂), 3.34 (s, 3H, CH₃), 3.31 (s, 6H, CH_3). ¹³C NMR (CDCl₃) δ 159.2, 156.2, 156.1, 152.9, 150.1, 149.2, 141.1, 136.9, 132.1, 123.9, 121.5, 119.3, 114.5, 107.3, 72.4, 72.0, 71.9, 70.9, 70.7, 70.6, 70.56, 70.53, 69.8, 69.0, 59.0; ESI-MS (m/z, %): 1266.0 (M⁺ + H, 100%), 1287.9 (M⁺ + Na) and $1373.9 (M^+ + Ag)$.

Synthesis of Ru-hexamer 2. To a solution of ligand 1 (80 mg) dissolved in MeOH (20 mL) was slowly added dropwise a mixture of $Ru(DMSO)_4Cl_2^{25}$ (one equiv.) in MeOH (100 mL) at 25 °C. The resultant red solution was refluxed for 12 h then filtered through a celite layer, and concentrated *in vacuo* to give a deep red residue. After column chromatography (SiO₂, CH₃Cl–CH₃OH 10 : 1), the counterions were exchanged by

adding NH₄PF₆ to give (45%) red hexamer **2**; mp >300 °C; ¹H NMR (CD₃CN) δ 9.24 (s, 4H, Ar $H^{3',5'}$), 8.81 (d, 4H, Py $H^{3,3'}$), 8.64 (s, 1H, Ar H^2), 8.01 (s, 2H, Ar $H^{4,6}$), 8.04 (t, 4H, Py $H^{4,4''}$), 7.55 (d, 4H, Py $H^{6,6''}$), 7.28 (s, 4H, Py $H^{5,5''}$), 7.02 (s, 2H, BnH), 5.53 (s, 2H, OC H_2 Ar), 4.23 (t, 4H, OC H_2), 4.15 (t, 4H, OC H_2), 3.71–3.46 (m, 40H, OCH₂), 3.26 (s, 3H, CH₃), 3.31 (s, 6H, CH₃); ¹³C NMR (CDCl₃) δ 161.6, 159.3, 156.7, 154.1, 153.6, 148.5, 140.8, 139.3, 133.6, 128.8, 125.9, 123.9, 121.6, 117.2, 108.4, 73.4, 72.7, 71.5, 71.3, 71.2, 71.1, 70.5, 70.0, 59.0; ESI-MS: m/z: 1276.4 (M – 7PF₆)⁷⁺, 1098.1 (M – 8PF₆)⁸⁺, 958.3 (M – 9PF₆)⁹⁺, 849.7 (M – 10PF₆)¹⁰⁺, 758.1 (M – 11PF₆)¹¹⁺, 683.8 (M – 12PF₆)¹²⁺.

Synthesis of the $[(Oxi-SWNT)_n-2_m]$ composite. The oxidized single-wall carbon nanotubes were purchased from Sigma-Aldrich Co. and used without further purification. An aqueous solution of Ru-hexamer 2 (2.5 mg) with five drops of MeCN was added to an aqueous solution of basic, oxidized single-wall carbon nanotubes (8 mg) at 25 °C with agitation to afford a black precipitate. Filtration through a nylon filter, followed by washing with water then MeOH–H₂O (1 : 3) gave (9.1 mg) the black solid nanotube composite.

Disassembly of the composite. 2 mg of the [(Oxi-SWNT)_{*n*}-2_{*m*}] composite was suspended in MeCN–H₂O (6 ml, 1 : 4 v/v) then NH₄PF₆ (1.5 mg) was added; after 5 minutes sonication at 25 °C, the black solid was completely dissolved and the solution became red.

Results and discussion

The water-soluble bis(terpyridinyl) monomer 1 (Scheme 1) was prepared (85%) by alkylation of *meta*-bis(terpyridinyl)phenol^{23,26} with the known tris-3,4,5-(tetraethylene



Scheme 1 Synthesis of hexarutheniomacrocycle 2a, which is represented by cartoon 2b.



Scheme 2 Illustration of multi-ion pair association of Ru-hexamer 2 with Oxi-SWNT.

glycol)-functionalized chloromethylbenzene.²⁴ The structure of monomer 1 was confirmed (¹H and ¹³C NMR) by the singlets at 5.16 and 8.77 ppm assigned to the methylene group and 3',5'-tpyHs, respectively, as well as the ESI-MS peaks at m/z1266.0 $[M + H^+]$ and 1287.9 $[M + Na^+]$. Self-assembly of 1 was achieved by treatment with one equivalent of $[Ru(DMSO)_4Cl_2]^{25}$ in refluxing MeOH for 18 h to give the desired $[(1)_6 Ru_6 (PF_6)_{12}]$ (2), which was column chromatographed (SiO₂) with a CHCl₃-MeOH (10 : 1) mixture. Counterion exchange from Cl⁻ to PF₆⁻ via treatment with an aqueous solution of NH_4PF_6 gave pure red microcrystals. Formation of the macrocycle was confirmed by the diagnostic peaks of 6,6"-tpyH at 7.55 ppm and 3',5'-tpyH at 9.24 ppm (¹H NMR), which exhibited a characteristic low-field shift $(\Delta \delta = + 0.47 \text{ ppm})$ and a high-field shift ($\Delta \delta = -1.16 \text{ ppm}$), respectively, when compared to that of the ligand 1. Multicharged peaks from +7 to +12 were observed in the mass spectrum (ESI-MS) of 2 indicating the loss of either PF_6^- or PF₅ giving further evidence of macrocyclization.

Our preliminary investigation²⁷ concerning nanocomposites derived from $[(bistpy)_6Fe_6(PF_6)_{12}]$ functionalized with dendritic light-absorbing antennae exhibited relatively strong photocurrent responses ranging from ~ 0.5 to 2.5 μA cm⁻² upon exposure to white light (40 mJ cm^{-2}) for the unoptimized devices. In order to evaluate and demonstrate a 'proof-ofconcept' with respect to the capture of photons as well as energy transfer to an accepter species, the water-soluble Ru-hexamer 2 was used. When the deep red solution of 2 (2.5 mg in 2 ml of deionized water) was added to the aqueous solution of Oxi-SWNT (8 mg, pH \approx 9.0) with agitation at 60 °C, a red cotton-like precipitate immediately started to form. After 3 h, the reaction was complete resulting in a notably colorless solution, which lacked either Oxi-SWNT or Ru-hexamer 2, as determined by UV-vis spectroscopy, remained. Further evidence for the formation of the nanocomposite was obtained on this clear aqueous solution, in which a seven peak pattern (${}^{31}P$ NMR) for NaPF₆, the combined by-product, was observed. The physical properties of the nanocomposite $[(Oxi-SWNT)_n(2)_m]$ were tested after filtering through a nylon filter (0.2 μ m), followed by washing initially with copious amounts of water to remove any residual water-soluble components, then with MeOH-H₂O (1 : 3 v/v), and lastly drying in vacuo.

The disassembly of $[(\text{Oxi-SWNT})_n(2)_m]$ was readily induced by its suspension (2 mg) in MeCN/H₂O (3 ml, 1/4 v/v) and adding NH₄PF₆ (1.5 mg), followed by 5 minutes of sonication at 25 °C. The appearance of a red solution with a black suspension supported the dissociation; the UV-vis absorption of regenerated $2 [(1)_6 Ru_6 (PF_6)_{12}]$ was superimposable with the original sample.

Formation of $[(Oxi-SWNT)_n(2)_m]$ was further demonstrated by transmission electron microscopy (TEM), whereby a dilute sample suspended in H₂O was cast onto a carbon-covered grid (Cu or Ni, 400 mesh). The TEM analysis of [(Oxi- $SWNT_{n}(2)_{m}$ visibly proved the morphologies at different magnifications, as shown in Fig. 1. Comparison of the diameter of commercial Oxi-SWNT (Fig. 1A) with that of $[(Oxi-SWNT)_n(2)_m]$ showed a diameter increase to *ca.* 100 nm, this increase arose from $[(Oxi-SWNT)_n(2)_m]$ being sandwiched together and held in place by electrostatic interactions. Higher magnification (Fig. 1D) gave further information about the surface of the composite by revealing uniform round spots $(4.1 \text{ nm} \pm 0.2 \text{ nm})$ attributed to the Ru-hexamer 2, where the measured dimensions are consistent with the pertinent dimensions of the hexaruthenium ring, which possesses an edge-toedge diameter of 39.5 Å and an internal void region of 17.5 Å as determined by molecular modeling studies.

The atomic force microscopy (AFM) images were derived from one droplet of suspension of $[(Oxi-SWNT)_n(2)_m]$ on a freshly cleaved mica surface and dried under ambient conditions for 6 h (see ESI[†]). In Fig. 2A, the AFM image of starting Oxi-SWNT shows the clean, smooth carbon nanotubes; however, in Fig. 2B, the AFM image of [(Oxi- $SWNT_{n}(2)_{m}$ indicated that the Ru-hexamer 2 was complexed onto the walls/ends of the SWNTs. The diameter of the SWNTs measured 1-1.5 nm (the radius of curvature of the AFM tip was calculated to be 10.5-11 nm),²⁸ and after calibration, the diameter and height of Ru-hexamer 2 were measured at ca. 4-5 nm and 0.6-0.9 nm, respectively, which was similar to the simulated size of the metallohexamer.⁵ Some larger particles were discernible from the sidewall/ends of SWNTs (see ESI[†]) due to some aggregation of Ru-hexamer 2. After the disassociation of $[(Oxi-SWNT)_n(2)_m]$ by adding aqueous NH₄PF₆, the AFM images (see sESI[†]) showed that the surface/ends of Oxi-SWNTs were free of Ru-hexamer 2, which gave further evidence for the ion-pair interactions. Furthermore, height analysis performed using the AFMs revealed average hexamer and CNT heights of 8.7 and 13.5 Å, respectively. This corresponds well with the average measured height of the hexamer/CNT composite of 22.5 Å (see ESI[†] for details).

X-Ray photoelectron spectroscopy (XPS; monochromatic Mg K α radiation at a power of 250 W, 93.90 eV) for bare Oxi-SWNT (Fig. 3A) showed typical graphite-carbon-like peaks²⁹ (C1s) at 285 eV and O1s (from oxidized carbon) at 531 eV. The complexed [(Oxi-SWNT)_n(**2**)_m] (Fig. 3B) revealed new peaks



Fig. 1 TEM images of A) commercial Oxi-SWNT, and the ion-pair association of the $[(Oxi-SWNT)_n(2)_m]$ composite at different magnifications: B) scale bar 1 μ m, C) scale bar 100 nm, D) scale bar 20 nm.



Fig. 2 Typical AFM images of (A) commercially Oxi-SWNTs (scan area: 1.3 μ m × 1.3 μ m, *z* scale: 0–20 nm), and (B) the hybrid [(Oxi-SWNT)_{*n*}(**2**)_{*m*}] structure afforded by multi-ion pair assembly (scan area: 6.4 μ m x 6.4 μ m, *z* scale: 0–50 nm).

attributed to N1s at 398 eV along with other new peaks assigned to Ru ($3d^{3/5}$ at 384 eV and $3d^{5/5}$ at 280 eV) confirming the presence of **2**. The atomic O/C ratio (17.6) of neat Oxi-SWNT was increased to 26.5 after association with **2** affording further evidence for the complexation and the presence of bulky PEG chains. The XPS showed no evidence of either Na⁺

or PF_6^- (Na1s is at 1072 eV and P2p at 130.6 eV), supporting the reaction, SWNT-COONa + [(2)₆Ru₆(PF₆)₁₂] which produced [(Oxi-SWNT)_n2_m]; the by-product, NaPF₆, was easily removed by multiple water washings.

IR spectra of Ru-hexamer 2, commercial Oxi-SWNT, and $[(Oxi-SWNT)_n(2)_m]$ showed the stretching vibration v_{P-F} of PF_6^- at 841 cm⁻¹ for the starting Ru-hexamer 2 (Fig. 4, curve C); after ion-pair assembly with Oxi-SWNT (Fig. 4, curve A), the v_{P-F} stretch disappeared (Fig. 4, curve B) and a new broad vibration at *ca.* 1590 cm⁻¹ attributed to the carboxylates of $[(Oxi-SWNT)_n(2)_m]$ was observed. This shift from that observed for the uncomplexed Oxi-SWNTs (1730 cm⁻¹, Fig. 4A) further supports the electrostatic complexation. The stretching vibration v_{C-H} attributed to the PEG chains (2910 cm⁻¹, Fig. 4C) still remained after complexation (see Fig. 4B).

In Fig. 5, comparisons of UV-vis spectra of the starting Oxi-SWNT, complex **2**, and $[(Oxi-SWNT)_n(2)_m]$ exhibited a slight hypsochromic shift (*ca.* 1–2 nm) for the metal–ligand absorbance between **2** and $[(Oxi-SWNT)_n(2)_m]$, which supports



Fig. 3 XPS spectra of (A) commercial Oxi-SWNT, and (B) multi-ion pair association of [(Oxi-SWNT)_n(2)_m].



Fig. 4 FTIR spectra of A) commercial Oxi-SWNT, the peak at 1730 cm⁻¹ is attributed to the surface carboxylic acid groups, B) assembled ion-pair complex, the new vibration at *ca.* 1590 cm⁻¹ is attributed to the carboxylates from Oxi-SWNT, along with the disappearance of v_{P-F} at 841 cm⁻¹, and C) solid Ru-hexamer **2**, the peak at 841 cm⁻¹ indicates the stretching vibration of v_{P-F} from counterion PF_6^- .



Fig. 5 UV-vis absorption spectra in water of (A) commercial Oxi-SWNT; (B) water-soluble Ru-hexamer **2**; (C) complex $[(Oxi-SWNT)_n(2)_m]$.

the electronic association.²⁰ The intensity was suppressed after complexation. A new absorption at ca. 462 nm arose due to the electrostatic interaction between **2** and the Oxi-SWNTs or by the partial aggregation of **2** on the sidewalls or ends of Oxi-SWNT.

The Raman spectrum of Oxi-SWNT (Fig. 6, obtained using a krypton laser with a wavelength of 647 nm at 4 mW power) showed a small disorder mode or sp³ mode (D-band, black line) at *ca.* 1293 cm⁻¹. The frequency of the radial breathing mode (RBM) is inversely proportional to the diameter of the carbon nanotubes, therefore an upshift of the RBM suggests a diameter decrease.³⁰ The commercial Oxi-SWNTs used are bundles with diameters of 4-5 nm; this is partly due to the hydrogen bonding interactions between the oxygenated functionalities (i.e., the carboxylic acid groups) of individual nanotubes.^{31,32}Amidation of Oxi-SWNTs with octadecylamine (ODA) resulted in an upshift of the RBM frequency, which can be attributed to the destruction of hydrogen bonding and nanotube debundling to afford CNTs with smaller diameters (1.3 nm).³³ During our study, hexamer 2 was used to intercalate Oxi-SWNT bundles and ionically coordinate with the carboxylic acid groups thereby further limiting hydrogen bonding. A slight upshift, ca. 2-3 cm⁻¹, of the



Fig. 6 Raman spectra of Oxi-SWNT (black line) and $[(Oxi-SWNT)_n(2)_m]$ (grey line). Insert: the breathing mode fields at *ca*. 165 cm⁻¹.

RBM was observed, which suggested a debundling effect by the hexamer **2**. Notably, the AFM also showed that the height of the bare tubes in the [(Oxi-SWNT)_n**2**_m] composite was in the range of 1–1.5 nm, which is smaller than that of the Oxi-SWNT bundles.

Upon complexation with **2**, the diameter-dependent breathing mode at 165 cm⁻¹ moved slightly by *ca*. 2–3 cm⁻¹ (see Fig. 6 insert).⁵ The tangential mode (G-band) of the complex at *ca*. 1590 cm⁻¹ remained unchanged compared to that of the Oxi-SWNTs. Since ionic coordination does not induce additional sp³ hybridized carbon defects, there is no significant change of the intensity ratio of the D and G bands (I_D/I_G) .³⁰

Electrochemical measurements were conducted in order to follow the construction of the nanocomposite. Electrochemical experiments were performed using a potentiostat connected to a three-electrode cell. A glassy carbon disk (diameter = 1 mm) was used as the working electrode; Pt and Ag wires were used as counter and pseudo-reference electrodes (all potentials were referenced to the ferrocenium|ferrocene couple, denoted as $Fc^+|Fc\rangle$, respectively. All experiments were obtained using a scan rate of 100 mV s⁻¹ and 0.1 M Bu₄NPF₆ in DMF as an electrolytic solution, previously purged with ultrapure N₂, at 298 K.

The cyclic voltammetry (CV) response of Ru-hexamer metallomacrocycle (2, 0.1 mM) was obtained in DMF (Fig. 7A) at 298 K. The CV reveals two reversible peaks at -1.61 and -1.86 V, associated with the redox processes of the terpyridine moieties.³⁴ The anodic waves, detected between 0.2–0.7 V, are related to the oxidation of the aryl ether groups anchored to $2.^{35}$ Also, another anodic wave was observed at a more positive potential (0.90 V) corresponding to the irreversible oxidation of the ruthenium atoms suggesting that the redox centers in 2 were buried by the large ethylene glycol chains. Therefore, electron transfer between 2 and the electrode surface is reasonably slow.³⁶

Since Oxi-SWNT³⁷ and $[(Oxi-SWNT)_n(2)_m]$ showed low solubility in the electrolytic medium, their CVs were obtained by preparing modified electrodes, as follows: 150 µL cm⁻² of Oxi-SWNT suspension (1.4 mg per mL of pure DMF) or $[(Oxi-SWNT)_n(2)_m]$ previously precipitated in pure water, transferred using a micropipette and carefully positioned on



Fig. 7 Cyclic voltammograms obtained in DMF + 0.1 M Bu_4NPF_6 for (A) 0.1 mM of water soluble Ru-hexamer **2**, and modified electrodes with a film of (B) Oxi-SWNT or (C) [(Oxi-SWNT)_n(**2**)_m] nanocomposite. All experiments were conducted at 298 K and using a scan rate of 100 mV s⁻¹.

the electrode surface. Once the solvent was removed, the Oxi-SWNT or $[(Oxi-SWNT)_n(2)_m]$ -modified electrodes were immediately immersed in the electrolytic medium.

While voltammograms obtained for Oxi-SWNT films (Fig. 7B) revealed a capacitive behavior for the electrodes, based on carbon nanotubes;34 those obtained for [(Oxi- $SWNT_{n}(2)_{m}$ films (Fig. 7C) showed one cathodic peak at -1.13 V, associated with the quasi-reversible redox processes of the terpyridine moieties (during the inverse potential scan this peak can be observed at 0 V). This observation can be explained by invoking the electronic properties of carbon nanotubes.¹⁰⁻¹³ According to previous TEM images obtained for the nanocomposites (Fig. 1C and D), it is possible to consider carbon nanotubes as the main support of hexamer- Ru^{II} units. In this way, during the cathodic scan, π -electron conjugation in the carbon nanotubes easily allows the reduction of terpyridine moieties (Fig. 7C); however, during the inverse potential scan, the oxidation of terpyridines needs additional energy, since carbon nanotubes are poor electron donors (see their capacitive behavior in Fig. 7B).¹⁰⁻¹³ In essence, the oxidation of terpyridines in the nanocomposite should be energetically disfavored. A similar effect is observed for Ru^{II} oxidation in [(Oxi-SWNT)_n(2)_m], since the corresponding potential (1.35 V, Fig. 7C) was measured at a more positive value than that previously observed for 2 in solution (0.90 V, Fig. 7A).

Surface coverage of **2** in the modified electrode with $[(\text{Oxi-SWNT})_n(2)_m]$ nanocomposite was estimated to be 1.24×10^{-8} mol cm⁻² using the terpyridine-related cathodic peak and eqn (1),³³

$$\Gamma = \frac{Q}{zFA} \tag{1}$$

in which Q is the integrated charge below the peak (Fig. 7C), z is the number of electrons transferred per mol of studied sample, F is Faraday's constant (96500 C equiv⁻¹), and A represents the electrode area in cm².

Anodic waves related to oxidation of the aryl ether groups were not observed (Fig. 7C). A probable explanation for this is that aryl ether groups can be oxidized in polar media, such as DMF (dielectric constant 36.7) or MeCN (37.5),²⁹ but the oxidation process is more difficult in non-polar media, such as CH_2Cl_2 (8.93)³¹ or SWNT (3.24).³⁵ It is noteworthy that the low dielectric constant for SWNT is also consistent with the capacitive behavior observed for the modified electrodes, based on Oxi-SWNT (Fig. 7B).

Conclusion

In conclusion, the multi-ion pair association of Ru-hexamer **2** and Oxi-SWNT was successfully prepared; the self-assembly phenomenon to form the complex was verified by the immediate precipitation, as well as the TEM and AFM images, XPS, IR, UV-vis spectroscopy, and CV. Competing counterion reagents, such as NH_4PF_6 and KPF_6 , can readily disassemble the non-covalently linked composite at 25 °C. This self-assembly method shows potential for use in solar cell conversion or electronic nanodevices, since the components of the nanocomposites afford entry into the formation of tailored molecular surfaces capable of yielding dense electron storage and release devices as well as components for photovoltaic devices due to the ability of the macrocycles to act as sensitizers; such studies are currently in progress.

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