

TerpyridineCu^{II}-mediated reversible nanocomposites of single-wall carbon nanotubes: towards metallo-nanoscale architectures†

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The self-assembly of Oxi-SWNTs, based on terpyridineCu^{II} coordination, produces a thermally stable, neutral [(Oxi-SWNT)(tpyCu^{II})_m]_n nanocomposite possessing notable luminescence properties; quantitative disassembly occurred by treatment with aqueous KCN.

Metallo-polycarboxylate coordination has been commonly used for the construction of zeolitic, cage, and paddle-wheel architectures¹ via the use of transition, main-group, and rare earth metals, as well as a number of hybrid metal structures.² Recently, the assembly of pentacoordinate terpyridine–copper–carboxylate complexes^{3–5} involving three Cu^{II}–N bonds and two *cis*-oriented sites (carboxylate ions) has been reported⁶ and shown to self-assemble in specific motifs depending on the type of organic carboxylate used. The combination of SWNTs with photoactive electron donors,⁷ such as porphyrins or bipyridine ruthenium complexes,⁸ has been developed for potential applications in solar energy conversion (*ca.* 4.2% monochromatic conversion efficiency)⁹ utilizing the electron-acceptor character of the SWNTs. By means of the facile coordination of carboxylate and metal, we herein report the first nanocomposites of carboxylate-modified SWNTs mediated by tpyCu^{II} resulting in nanotube assembly and, while structurally stable, its facile disassembly in the presence of competing ligands (Scheme 1); photophysical properties are also presented. This novel and simple assembly gives rise to the use of functionalized monoterpyridines, bisterpyridines, tristerpyridines, as well as other polyterpyridine ligands³ to afford different structural morphologies.

Using the techniques reported for the preparation of crystal structures of tpyCu^{II}-polycarboxylate architectures,⁵ Oxi-SWNTs (10 mg, purchased from Aldrich: carboxylic acid; 3–6 atom%, 4–5 nm × 500–1500 nm) were dissolved in an aqueous NaOH solution (15 ml) generating a non-turbid, black solution, which was treated with an aqueous translucent green solution of tpyCu^{II} (3 mg), prepared by treatment of terpyridine with Cu(BF₄)₂ in 5 ml of water. A black precipitate immediately formed leaving a colorless aqueous solution indicative of the quantitative formation

of [(Oxi-SWNT)(tpyCu^{II})_m]_n (Fig. 1, A → C), which was collected on a nylon filter (0.2 μm, Millipore Corp.). The composite was initially washed with an aqueous solution of NaPF₆ (0.2 M) to remove any electrostatically associated tpyCu^{II}, followed by copious amounts of water to remove all water-soluble reagents, and finally with MeCN to facilitate drying. After drying *in vacuo*, the assembled [(Oxi-SWNT)(tpyCu^{II})_m]_n complex (11.7 mg) was shown to possess good thermal stability, as demonstrated by no structural change in boiling water for 12 h. The disassembly of this complex (2 mg) was induced by its suspension in water at 25 °C, followed by the addition of KCN (1 mg, **Caution:** highly toxic reagent, waste must be treated properly) resulting in a translucent pale green solution, (Fig. 1, C → E and F) after 4 h, thus supporting its deconstruction.

Morphological observations were conducted by transmission electron (TEM) and atomic force (AFM) microscopies. For the TEM a dilute sample (100 μg/100 ml) was cast onto a carbon-covered grid (Cu or Ni, 400 mesh, SPI Corp.). TEM analysis (Fig. 1E) visibly proved the morphologies of the Oxi-SWNT in association with tpyCu^{II}. Since the carboxylic acids on Oxi-SWNT are located¹⁰ on both the open-ends as well as the sidewalls, our observations indicated that the functional carboxylic moieties on the SWNT's open-ends are more likely to complex with tpyCu^{II} than those on the side wall due to enhanced site availability. When comparing the TEM of the nanocomposite (Fig. 1D) with that of the TEM of starting Oxi-SWNT (Fig. 1B), different patterns for the complex [(Oxi-SWNT)(tpyCu^{II})_m]_n could easily be distinguished (the presence of large particles indicated the typical residual metal catalyst contamination in commercial samples). The nanotubes of neat Oxi-SWNT were well distributed over the grids; whereas, the complexed [(Oxi-SWNT)(tpyCu^{II})_m]_n generally formed networks.

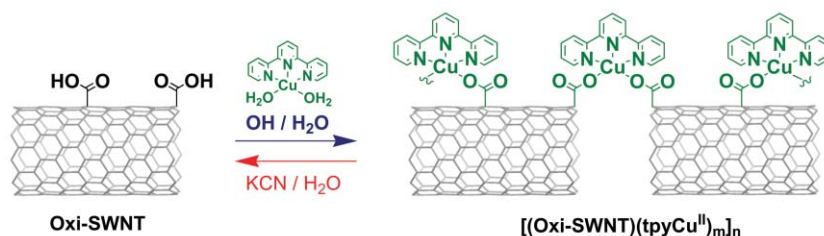
X-ray photoelectron spectroscopic (XPS, monochromatic Mg K α radiation at a power of 250 W, 93.90 eV) measurements for the parent Oxi-SWNT (Fig. 2A) showed typical graphite-carbon-like peaks (C1s) at 285 eV and O1s (from oxidized carbon) at 531 eV.¹¹ The complexed [(Oxi-SWNT)(tpyCu^{II})_m]_n (Fig. 2B) showed new peaks attributed to N1s at 398 eV along with other new peaks assigned to Cu (2p^{1/2} at 953 eV and 2p^{3/2} at 933 eV) thereby confirming the nanocomposite. The atomic O/C ratio (17.6), as determined by XPS, of neat Oxi-SWNT was reduced to 16.4 after complexing with tpyCu^{II} affording further evidence for the association. The reaction, SWNT-COONa + tpyCu^{II}(BF₄)₂ produced [(Oxi-SWNT)(tpyCu^{II})_m]_n and the by-product, NaBF₄, which was easily removed by multiple washings with water. The

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Scheme 1 Illustration of the formation and disassembly of the $[(\text{Oxi-SWNT})(\text{tpyCu}^{\text{II}})]_{m,n}$ composites.

XPS of the composite showed no evidence of either Na^+ or BF_4^- ($\text{Na}1s$ is at 1072 eV and $\text{F}1s$ at 685 eV).

In Fig. 3A, a comparison of the UV-vis data for the starting reagent (tpyCu^{II}) and the composite $[(\text{Oxi-SWNT})(\text{tpyCu}^{\text{II}})]_{m,n}$ revealed a slight bathochromic shift (*ca.* 1–2 nm) for the metal–ligand absorbance between tpyCu^{II} and $[(\text{Oxi-SWNT})(\text{tpyCu}^{\text{II}})]_{m,n}$; the intensity was, however, suppressed after functionalization. Disassembly of the complex revealed the disappearance of metal complex peaks at 320–340 nm supporting the absence of

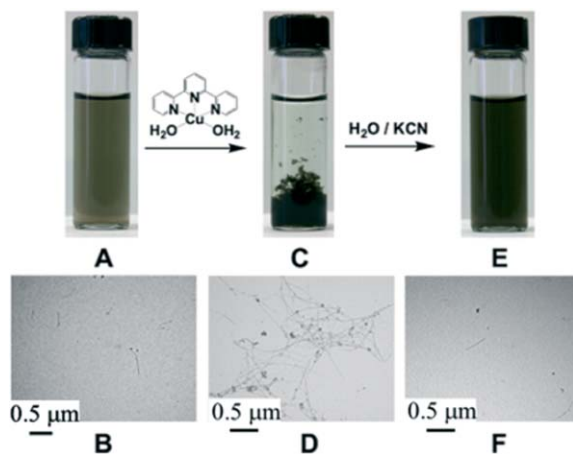


Fig. 1 (A) Oxi-SWNT in a basic aqueous solution; (B) TEM image of initial Oxi-SWNT; (C) after reaction of Oxi-SWNT with tpyCu^{II} ; (D) TEM image of the $[(\text{Oxi-SWNT})(\text{tpyCu}^{\text{II}})]_{m,n}$ composite; (E) after disassembly with KCN; and (F) recovered Oxi-SWNT after disassembly.

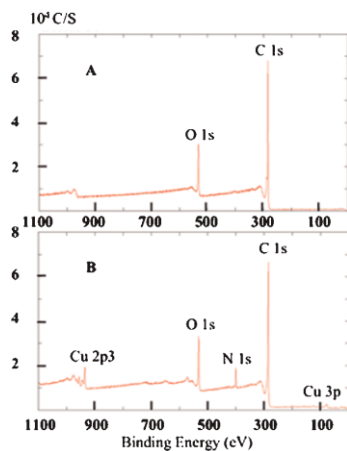


Fig. 2 XPS spectra of (A) a neat Oxi-SWNT film, and (B) a film of the $[(\text{Oxi-SWNT})(\text{tpyCu}^{\text{II}})]_{m,n}$ complex.

terpyridine-based connectivity, which is consistent with the TEM and AFM observations. The photoluminescence experiments were conducted in an aqueous suspension or solution at the same concentrations ($\sim 2 \times 10^{-7}$ M) with an excitation wavelength of 290 nm. The corresponding emission spectra¹² are shown in Fig. 3 B. Photoluminescence for $[(\text{Oxi-SWNT})(\text{tpyCu}^{\text{II}})]_{m,n}$ was observed with a strong emission peak at 357 nm. After disassembly, a new peak at 347 nm appeared which was also observed after treatment of the starting tpyCu^{II} with aqueous cyanide suggesting that this peak is due to Cu–CN coordination; the detailed mechanism is currently under investigation.

To further confirm the coordination-directed complexation and disassembly process, a droplet of the resultant suspension (100 $\mu\text{g}/500$ ml in DI water) was deposited on the surface of freshly cleaved mica and dried under ambient conditions. Fig. 4 shows the AFM images for the pure Oxi-SWNT (Fig. 4a, note: the bright particles are for the contaminated metal catalyst in these commercial complexes) and disassociated Oxi-SWNTs (Fig. 4c), in which the isolated nanotubes where tubular lengths (< 2 μm) and diameters

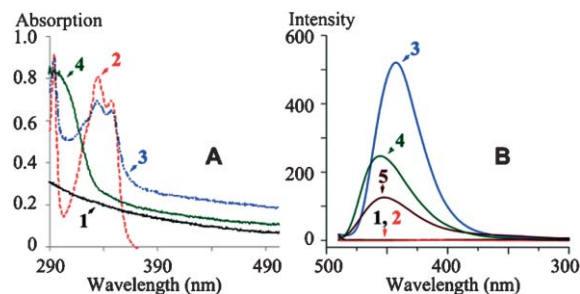


Fig. 3 (A) UV-vis absorption spectra of (1) Oxi-SWNT, (2) tpyCu^{II} , (3) $[(\text{Oxi-SWNT})(\text{tpyCu}^{\text{II}})]_{m,n}$, (4) disassembly of $[(\text{Oxi-SWNT})(\text{tpyCu}^{\text{II}})]_{m,n}$. (B) Emission spectra of (1) Oxi-SWNT, (2) tpyCu^{II} , (3) $[(\text{Oxi-SWNT})(\text{tpyCu}^{\text{II}})]_{m,n}$, (4) disassembly of $[(\text{Oxi-SWNT})_2\text{tpyCu}^{\text{II}}]_n$, (5) disassembly of the tpyCu^{II} complex; all experiments were performed in aqueous solution.

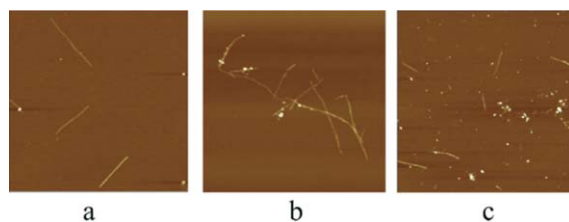


Fig. 4 A typical AFM image of (a) oxidized SWNTs (scan area: $3.3 \mu\text{m} \times 3.3 \mu\text{m}$, z scale: 0–20 nm), (b) hyperbranched SWNTs by coordination (scan area: $3.7 \mu\text{m} \times 3.7 \mu\text{m}$, z scale: 0–50 nm), and (c) disassociated SWNTs (scan area: $5.3 \mu\text{m} \times 5.3 \mu\text{m}$, z scale: 0–30 nm).

(4 ± 1.5 nm) are clearly shown. Fig. 4b shows the [(Oxi-SWNT)(tpyCu^{II})_m]_n composite. Chiu *et al.*¹³ reported less than 2% connections for the pristine nanotubes, compared to 30% intermolecular nanotube junctions derived from amide cross-linking. Analysis of the AFM and TEM images gives rise to a possible inter-connecting network for the [(Oxi-SWNT)(tpyCu^{II})_m]_n suggesting a more than 80% cross-linked assembly. Numerous differing linkages (see supporting information†) were observed that further confirm the formation of inter-nanotube junctions mediated by the two reaction sites of tpyCu^{II}. Self-assembly of the SWNTs with tpyCu^{II} connectivity gives rise to the possible linkages, such as head-to-head (V model), head-to-wall (T or Y models), and a few wall-to-wall (X model). Due to the more hindered wall-sites of the Oxi-SWNTs, the first two modes of connectivity are favored; these assembly combinations were formed in a ratio of 5 : 6 : 1, respectively. And, further supporting the formation of the [(Oxi-SWNT)(tpyCu^{II})_m]_n, luminescence experiments revealed emission at 357 nm upon excitation at 290 nm that was presumably due to the expanded π-conjugation.

In conclusion, the self-assembly of Oxi-SWNTs based on terpyridineCu^{II} coordination, produced a thermally stable, neutral [(Oxi-SWNT)(tpyCu^{II})_m]_n composite; disassembly occurred upon treatment with aqueous KCN. TEM and AFM microscopies revealed the resultant connections between the carboxylate-modified SWNTs. Also the XPS, Raman, IR, UV-vis spectra, and cyclic voltammetry further confirmed the formation of [(Oxi-SWNT)(tpyCu^{II})_m]_n. Luminescence measurements showed an emission peak at 357 nm after complexation. Based on the overall observations, the new and simple method to assemble and disassemble the electrically conductive organic nanotubes, in a nearly quantitative procedure, has been demonstrated. The controlled, self-assembly for the construction of carbon nanotube lattices with metal complexes gives rise to a new strategy for building metallo-nanomaterials that could find potential application in nanoscale electronic devices.‡

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Notes and references

‡ **Experimental Section: Synthesis of the Oxi-SWNT-tpyCu^{II} complex:** Terpyridine-Cu(BF₄)₂ (3 mg; ESI-MS (*m/z*) 314.7 amu for tpyCu^{II} + F⁻) aqueous solution, prepared according to a published procedure,⁵ was added to a basic, oxidized single-wall carbon nanotube (10 mg) aqueous solution at 25 °C with agitator and sonication for 1 h, the reaction was monitored by TLC (SiO₂, eluent; MeCN : saturated aqueous KNO₃ : water, 10 : 1 : 1) showing that no terpyridine-metal complexes remained in the clear aqueous solution. The precipitate was collected on a nylon filter and sequentially washed with a NaPF₆ aqueous solution (0.2 M, 3 × 5 ml) followed by copious amounts of water, and finally with 2 × 5 ml of CH₃CN, then dried *in vacuo* to afford a black solid (11.7 mg) in nearly quantitative yield. **Disassembly of the complex:** 2 mg of the complex of [(Oxi-SWNT)(tpyCu^{II})_m]_n was suspended in 8 ml of water at 25 °C, and then 1 mg of KCN was added with stirring for 4 h followed by sonication for 1 h.

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