Chemistry of Water Soluble Carbon Nanotubes and Carbon Quantum Dots with Group IB Metal-Dithiolenes: Structural and Photophysical Insights

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(i) Materials and methods

All solvents and chemicals were purchased from commercial sources. Disodium salt of maleonitrile dithiolate (Na_2mnt) was synthesized according to a reported procedure.[1] Functionalized carbon quantum dots (f-CQDs) were prepared as described previously.[40] Elemental analysis was performed on Perkin-Elmer 2400 microanalyser. The electronic absorption spectroscopic measurements were conducted on a Perkin-Elmer Lambda 35 spectrometer. Infrared spectra were measured on a Bruker Vertex 70 FT-IR spectrometer. ^1H NMR spectral measurements were done on JEOL-500 MHz NMR spectrometer. Scanning electron microscopic measurements were done by coating the samples on brass stubs and scanned using the SUPRA 40VP Field Emission Scanning Electron Microscope (CARL ZEISS NTS GmbH, Oberkochen (Germany) equipped with energy dispersive X-ray (EDX) facility. TEM measurements were done by coating the samples on to carbon film coated copper grids and scanned using the FEI Technai 20 U Twin Transmission Electron Microscope equipped with EDS detector. Fluorescence microscopic measurements were done by depsoiting the samples on microscopic glass slides and scanned on Leica Microsystems at magnification of 40X.

ii) Synthesis and characterization of –COOH functionalized multiwalled water soluble carbon nanotubes (f-CNTs).

Water soluble multiwalled CNTs (f-CNTs) were synthesized by nitric acid oxidation of commercially available multiwalled CNTs. Commerically available MW-CNTs (1 g) were taken up in fuming nitric acid (HNO_3, 35 ml) in a 50m ml round bottomed flask and heated under reflux for 12 h. The system was allowed to cool down and stand at room temperature for further

12 h and then the supernatant HNO_3 acid was decanted carefully and the residue was hand shaken with distilled water (50 ml) and allowed to stand at room tempearture for 6 h. The supernatant water layer was decanted and the CNT containing residue was further hand shaken with 50 ml distilled water and allowed to stand and then the water layer was removed. This procedure was repeated 6 times and then the residue was dried over boiling water bath to get the shining and 100% pure sample (as per SEM, TEM) of functionalized multiwalled CNTs (f-CNTs) that are highly soluble in water.

(iii) Synthesis and characterization of silver (I) dithiolene (1).

The silver(I) dithiolene complex $[PPh_4]_3[\{Ag(mnt)\}_2I]$ (**1**) was synthesized by stirring silver(I) iodide (0.234 g; 1 mM) with disodium salt of maleonitrile dithiolate (0.28g; ~2 mM) in MeCN (50 ml) at 18 ºC for 6h. The reaction mixture was filtered and PPh_4Br (0.8 g, ~2 mM) was added to the pale yellow colored filtrate and stirred for further 2h allowed to stand for further 4h and then filtered. Diethyl ether (200 ml) was added to the filtrate followed by the addition of 50 ml of distilled water which yielded the complex (**1**) as pale yellow colored powder. Recrystallization of this pale yellow powder from H_2O-MeCN mixture yielded pale orange colored spheres which were not suitable for X-ray diffraction. Yield, 0.9g, 55%. Data for **1**: C, H, N elemental analysis calculated for $C_{80}H_{60}Ag_2IN_4P_3S_4$, C, 58.55, H, 3.68, N, 3.41; Found, C, 58.48, H, 3.73, N, 3.45. FT-IR (KBr disc, cm^{-1}): 3055(w), 2182(s, ν_{CN}), 1583 (w), 1481 (w), 1435(s), 1107(s), 995(m), 751(m), 722(s), 687 (s), 526(s) (w, weak, m, medium, s, strong). ^1H NMR, (500 MHz, CD_3CN, ppm) δ, 7.91 (t, 1H), 7.86 (m, 2H), 7.70 (m, 2H).

(iv) Synthesis and characterization of copper (II) dithiolene (2).

The complex $[PPh_4]_2[Cu(mnt)_2]$ (**1**) was synthesized by the reaction of copper(II) chloride dihydrate (0.17 g; 1 mM) with disodium salt of maleonitrile dithiolate (0.28g; ~2 mM) in MeCN (50 ml) at 18 ºC for 6h. The reaction mixture was filtered and PPh_4Br (0.8 g, ~2 mM) was added to the brown filtrate and stirred for further 2h allowed to stand for further 4h and then filtered. Diethyl ether (200 ml) was added to the filtrate which precipitated the complex (**2**) as brown powder. Recrystallization from MeCN yielded black single crystals suitable for X-ray diffraction. Yield, 0.8g, 78%. Data for **1**: C, H, N elemental analysis calculated for $C_{56}H_{40}CuN_4P_2S_4$, C, 65.77, H, 3.94, N, 5.48; Found, C, 65.95, H, 3..88, N, 5.54. FT-IR (KBr disc, cm^{-1}): 3055(w), 2190 (s, ν_{CN}), 1460 (w), 1448 (s), 722(s), 687 (s), 526(s) (w, weak, m, medium, s, strong).

(v) Synthesis and characterization of gold (III) dithiolene (2).

The gold(III) dithiolene complex $[PPh_4][Au(mnt)_2]$ (**2**) was synthesized by stirring gold(III) chloride (0.3 g; 1 mM) with disodium salt of maleonitrile dithiolate (0.3 g; ~2 mM) in MeCN (50 ml) at 18 ºC for 6h. The yellow reaction mixture was filtered and PPh_4Br (0.4 g, ~1 mM) was added to the yellow colored filtrate, stirred for further 2h and allowed to stand for further 4h and then filtered. The complex (2) was precipitated as a yellow powder upon addition of diethyl ether (200 ml). Recrystallization of this pale yellow powder from MeCN yielded yellow single crystals which were suitable for X-ray diffraction. Yield, 0.4 g, 49%. Data for **2**: C, H, N elemental analysis calculated for $C_{32}H_{20}AuN_4PS_4$, C, 47.06, H, 2.47, N, 6.86; Found, C, 46.85, H, 2.39, N, 6.82. FT-IR (KBr disc, cm^{-1}): 3050(w), 2193(s, ν_{CN}), 1481 (w), 1435(s), 722(s), 687 (s), 526(s) (w, weak, m, medium, s, strong).

(vi) Preparation of samples of nanospheres of (1), (2) and doughnuts of (3) for SEM and TEM measurements.

In a typical preparation, macroscopic, crystalline samples of (**1)** - (**3**) were powdered finely in a pestle-mortar, sonicated in H_2O-MeCN for 5 min. and 5 □l of each sample was deposited onto brass stubs. The samples were dried for 3h under a table lamp and then subjected to scanning electron microscopic analysis. The samples for TEM measurements were prepared in a similar fashion to SEM sample preparation but the samples were deposited on carbon film coated copper grids (400 square mesh), dried for 3h under table lamp and then transmission electron microscopic analysis was carried out.

(vii) Preparation of samples of f-CNT composites (4) - (6) for SEM and TEM measurements.

The composites of f-CNTs (**4**) - (**6**) were prepared by taking single crystals of the dithiolene complexes (**1)** - (**3**) and f-CNTs in H_2O-MeCN solvents respectively. The suspensions were sonicated for 15 min. at ambient temperature and then were allowed to stand under argon atmosphere for 5 days. After five days, the solutions were shaken well and 5 □L of the samples were deposited on to brass stubs or carbon film coated copper grids and then subjected to SEM, TEM measurements.

(viii) Preparation of samples of f-CQD composites (7) - (9) for SEM and TEM measurements.

The composites of f-CQDs (**7**) - (**9**) were prepared by taking single crystals of the dithiolene complexes (**1)** - (**3**) and f-CQDs in H_2O-MeCN solvents respectively. The suspensions were sonicated for 15 min. at ambient temperature and then were allowed to stand under argon atmosphere for 5 days. After five days, the solutions were shaken well and 5 □L of the samples

were deposited on to brass stubs or carbon film coated copper grids and then subjected to SEM, TEM measurements.

(ix) Preparation of samples for fluorescence microscopic measurements:

Few crystals of the complex (**1)** in H_2O-MeCN with f-CNTs or f-CQDs were sonicated for 15 min. at ambient temperature and then were allowed to stand under argon atmosphere. After five days, 15 □L of the sample solutions were deposited on a glass slide and allowed to dry for 3h under a table lamp and then subjected to fluorescence microscopic measurements.

(x) Lattice packing in crystals of $[PPh_4][Au(mnt)_2]$ (3).

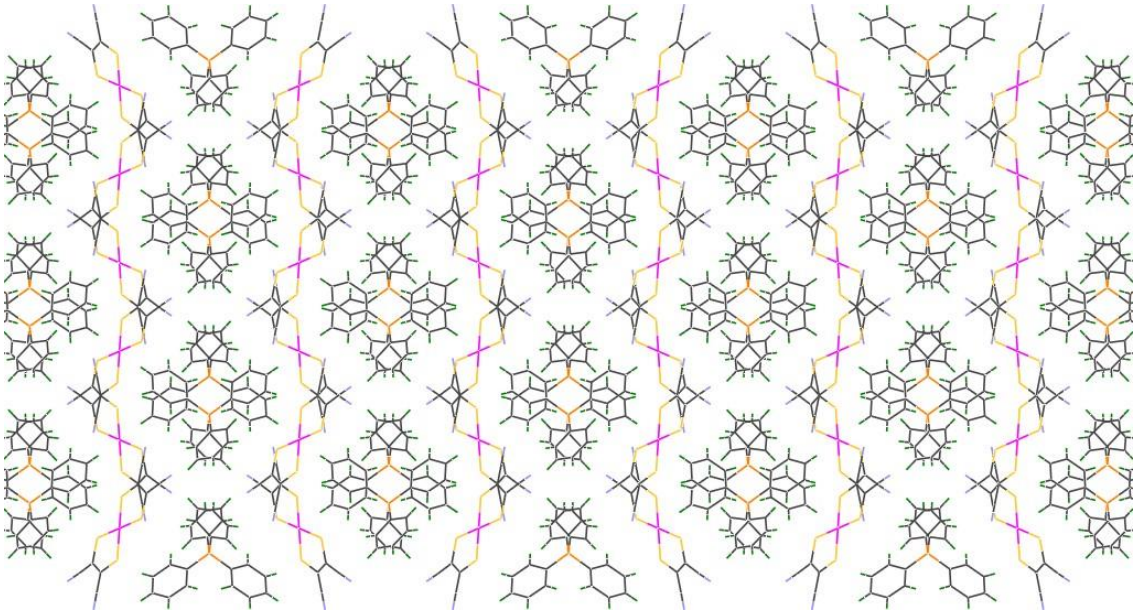

Figure. 1. Lattice packing in crystals of (3) along z-axis. Carbon, Dark grey; Hydrogen, Green, Gold, Magenta, Nitrogen, Blue, Sulfur, Yellow.

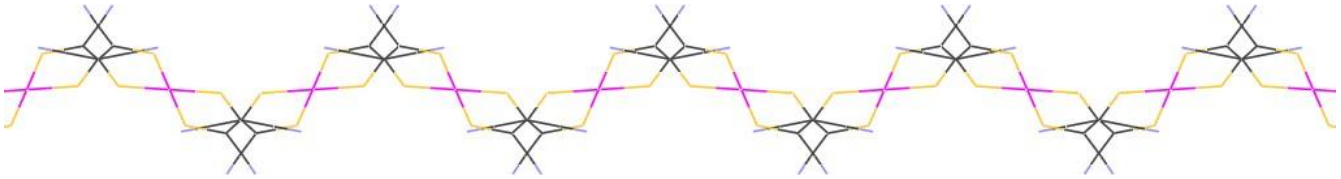

Figure 2. Threaded structure with an outward orientation of the –CN substituents of $[Au(mnt)_2]$ anions in crystals of (**3**).

Compounds 1, 4, and 7 nanospheres' normalised fluorescence emission spectra were obtained at an excitation wavelength (λ_{ex}) of 488 nm. In the visible spectrum, all three systems have broad emission bands; compound 1 and compound 7, for example, display closely overlapping maxima centred about 590 nm, suggesting similar emissive states. Compound 4, on the other hand, has a larger and more blue-shifted emission profile with a maximum at 560 nm, indicating variations in the electrical structure and/or packing within the supramolecular assemblies. Increased intermolecular interactions and aggregation-induced effects within the nanospheres may be responsible for the spectrum widening and redshift seen for compounds 1 and 7. By highlighting differences in emission maxima and band shape resulting from different self-assembly settings, the normalised intensity draws attention to relative spectral properties.

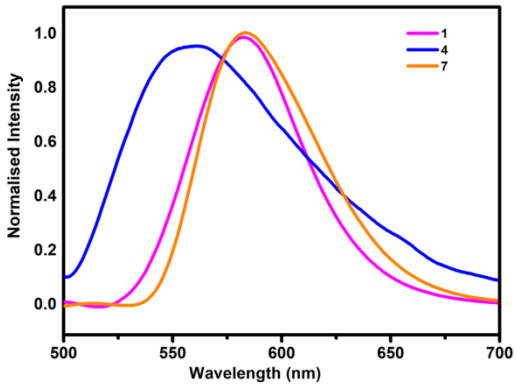

Figure 3. Fluorescence spectras of nanospheres of 1,4 and 7 at excitation at λ, 488 nm.

Table 1. Crystal data for $[PPh_4][Au(mnt)_2]$ (**3**).

Compound	(**3**)
Empirical formula	$C_{32}H_{20}AuN_4PS_4$
Formula weight	816.70
Temperature (K)	120
Wave length MoK□ (Å)	0.71073
Crystal system	Orthorhombic
Space group	C2/c
a/(Å)	23.570(3)
b/(Å)	11.6239(16)
c/(Å)	11.3776(15)
Volume ($Å^3$)	3117.2(7)
Z	4
Density (Mg/m^3)	1.740
Absorption coefficient (mm^{-1})	5.068
F(000)	1592
Crystal size (mm)	0.06X0.05X0.03
θ- range for data collection (º)	1.9 to 25
Unique reflections	7754

Observed reflections	2755
Absorption correction	Empirical
Data/restraints/parameters	2755/0/192
Goodness of fit on F^2	1.064
Final R_1 values [I>2σ(I)]	0.0331
Final wR(F^2) values [I>2σ(I)]	0.829
CCDC number	882226