Electronic supplementary information

Nanocomposites of Carbon Quantum Dots-Nickel(II) Dithiolene as Nanolights

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Contents

(i) Materials and methods

All solvents and chemicals were purchased from commercial sources. Dimethyl acetylenedicarboxylate was purchased from Sigma-Aldrich (USA). The complex, $[PPh_4][Ni^{II}(L^{2-})(L^{1-\bullet})]$ (**1**) [L, 1,2-dicarbomethoxyethylene dithiolate], was prepared as reported earlier[7]. The single crystals of [**1**•0.25(H_2O)] suitable for X-ray diffraction were obtained by recrystallization from H_2O-MeCN (nanodiscs). The intensity data were collected on a Bruker AXS Smart APEX CCD diffractometer with graphite monochromated MoKα radiation (0.71073 Å). Data reduction and absorption corrections were done using SAINTPLUS program package. The structure was solved by direct and conventional Fourier methods and refined on F^2 by full-matrix least-squares technique using SHELXTL program package[s1]. All non-hydrogen atoms were refined anisotropically, H-atoms at idealized positions in riding mode. Selected crystallographic data of complex **1** recrystallized from H_2O-MeCN are given in Table S1. CIF of **1** (recrystallized from H_2O-MeCN) has been deposited in the Cambridge Crystallographic data centre as supplementary data no: CCDC 834592. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44)1223-336-033) or e-mail: deposit@ccdc.cam.ac.uk.

(ii) Synthesis and characterization of water soluble carbon quantum dots.

Water soluble CQDs were prepared by pyrolysis of wood wool under insufficient oxygen exposure, washing the left out carbonaceous material with alcohol to remove soluble organic impurities . This was dried and finally treated with concentrated nitric acid for couple of days to introduce acid groups (COOH) on the surface. Nitric acid containing black material was evaporated to dryness on a steam bath and the residue was treated with water and evaporated on a steam bath repeatedly to remove traces of nitric acid and nitrous oxides fumes. The final mass was washed with small quantities of cold water water 3-4 times to remove water soluble impurities and then finally sonicated in water for 3h. The smaller sizes of the CQDs were collected by 0.1 micron filtration. The CQDs used in this study are approximately 5-20 nm in size as shown by SEM, atomic force microscopic (AFM) and TEM images (Figure S1A- Figure S1C). Samples for SEM measurement was prepared by sonication of 0.5 mg carbon dots in 3 mL of HPLC grade ethanol and allowed to stand. Few drops of solution were then placed on the brass stub that was dried and finally under vacuum made gold coating. EDX analysis (Figure S2) shows the presence of carbon and oxygen only. The samples for the TEM measurements were prepared analogous to the SEM sample preparation but coated on carbon film coated copper grids. Samples for AFM measurement was prepared by placing a drop of suspension on the surface of freshly cleaved mica substrate. Emission spectra of carbon dots were recorded by PerkinElmer LS55 Fluorescence Spectrophotometer. The emission spectra of the CQDs as a function of increasing excitation wavelengths (λ_{ex}) are displayed in Figure S1D. Carbon dots due to their different sizes provide the emission over the broadest range from visible to near-infrared region as shown in Figure S1D, leading to the prospect of tunable photoluminesence and also multicolored imaging.

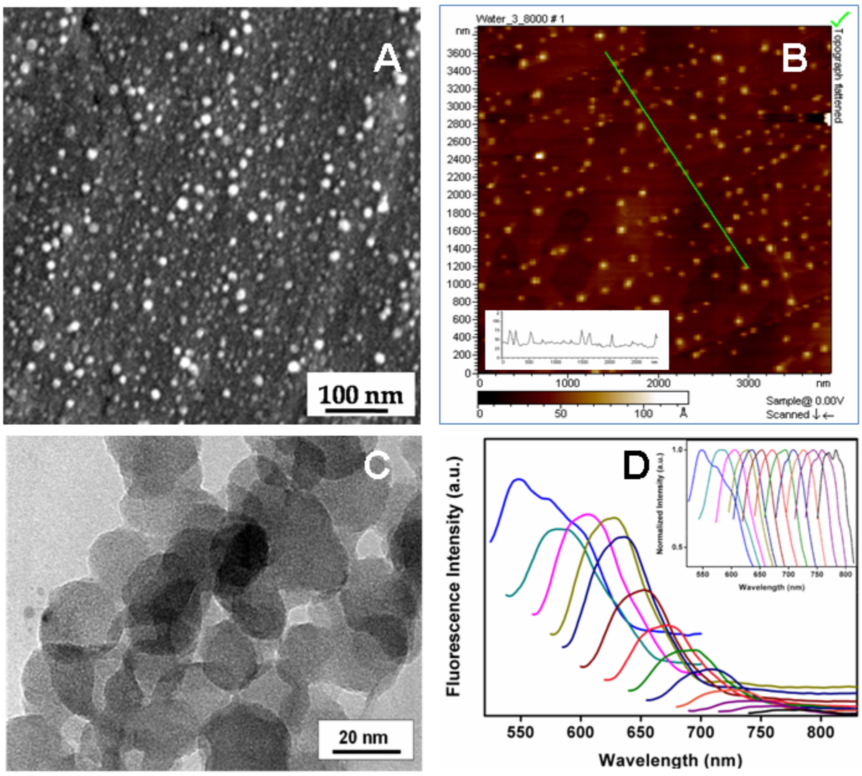


Figure S1. (A) SEM micrograph, (B) AFM topography image on mica substrate along with height histogram, (C) TEM micrograph of the water soluble CQDs, (D) Fluorescence emission spectra of carboxylated carbon dots in an aqueous solution in the visible-near IR region with progressively longer excitation wavelengths from 400 nm to 600 nm on the left in 20 nm increment; Inset, display of normalized emission spectral intensities.

(iii) Preparation of samples of nanocrystals of 1 for SEM, TEM and AFM measurements:

In a typical preparation, macroscopic and single crystals of the complex **1** were powdered finely in a passel-mortar, sonicated in H_2O-MeCN or EtOH or MeCN-Et_2O solvents for 5 min. and 5 µl of each sample was deposited onto brass stubs. The samples were dried for 3h under a table lamp, gold coated under vacuum and then mounted to SUPRA 40VP Field Emission Scanning Electron Microscope (CARL ZEISS NTS GmbH, Oberkochen (Germany) equipped with energy dispersive X-ray (EDX) facility. 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 mounted on to FEI Technai 20 U Twin Transmission Electron Microscope equipped with EDS detector. The AFM (atomic force microscopy) images are made with Pico scan Model (Molecular imaging, US) in air under ambient conditions at room temperature. Silicon nitride tip (micromesh) was used and the size of the cantilever tip (radius of curvature) was less than 10 nm. The spring (force) constant of cantilever was 1 N/m. Images were obtained by the dynamic force mode. This mode involves cantilever oscillation either by an acoustic signal (AAC) or by a magnetic signal (MAC mode), leading to an enhanced resolution and minimal damage to the samples. Samples were prepared by placing a drop of suspension on the surface of freshly cleaved mica.

(iv) Preparation of samples of nanocomposites of 1 & ws-CQDs for SEM and TEM measurements:

The nanocrystal-CQD nanocomposites were prepared by taking few single crystals of the complex **1** and few grains of CQDs in H_2O-MeCN or EtOH or MeCN-Et_2O. The suspensions were sonicated for 15 min. at ambient temperature and then were allowed to stand under argon atmosphere for 3 days. After three days, the solutions were shaken well and 5 μL of the samples were deposited on to brass stubs or carbon film coated copper grids and then subjected to SEM, TEM measurements.

(v) Preparation of samples for fluorescence microscopic measurements:

Few crystals of the complex **1** in H_2O-MeCN or EtOH or in MeCN-Et_2O with traces of CQDs were sonicated for 15 min. at ambient temperature and then were allowed to stand under argon atmosphere. After three days, 15 μL 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 on LeicaMicrosystems at magnification of 40X.

(vi) EDX analysis of the water soluble carbon quantum dots.

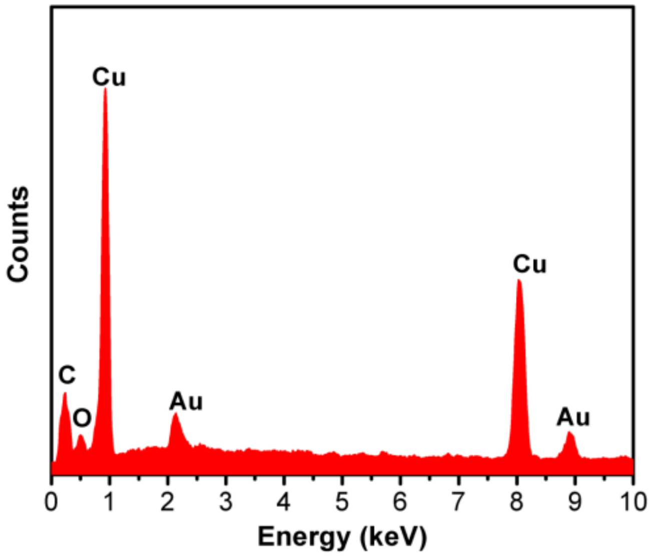
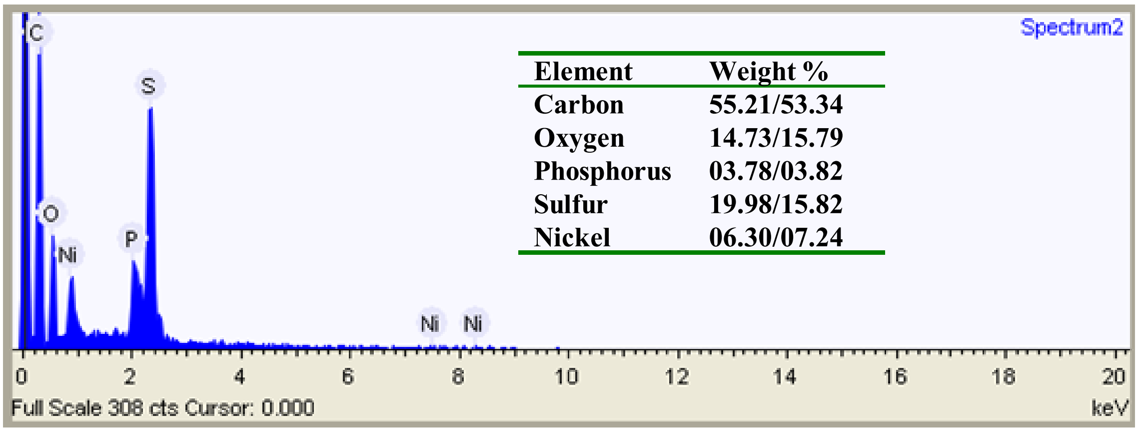


FIGURE S2. EDX analysis of the water soluble carbon quantum dots showing the presence of carbon and oxygen.

(vii) EDX analysis of the nanocrystals of 1



Element	Weight %
Carbon	55.21/53.34
Oxygen	14.73/15.79
Phosphorus	03.78/03.82
Sulfur	19.98/15.82
Nickel	06.30/07.24

FIGURE S4. EDX spot analysis (SEM) of the nanocrystals of **1** (inset, experimental and expected % weight of the constituents).

(viii) SEM micrograph of the nanocomposite of 1 and ws-CQDs prepared in H_2O-CH_3CN at low resolution.

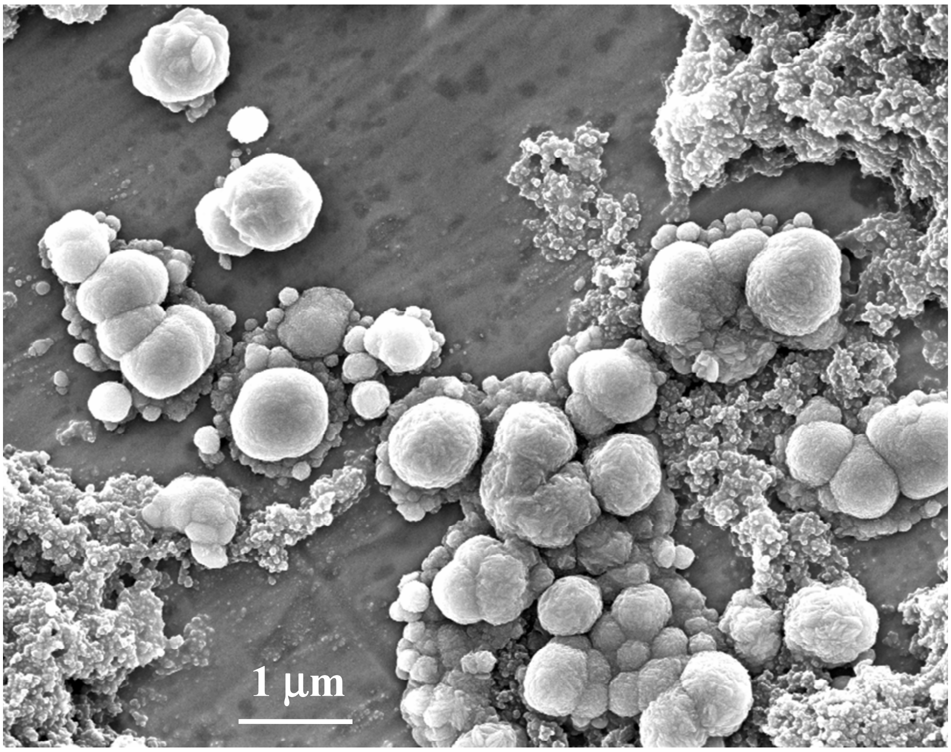


FIGURE S5. SEM micrograph of the nanocomposite of **1** and ws-CQDs prepared in H_2O-CH_3CN at low resolution.

(ix) SEM micrograph of the nanocomposite of 1 and ws-CQDs prepared in H_2O-CH_3CN at low resolution.

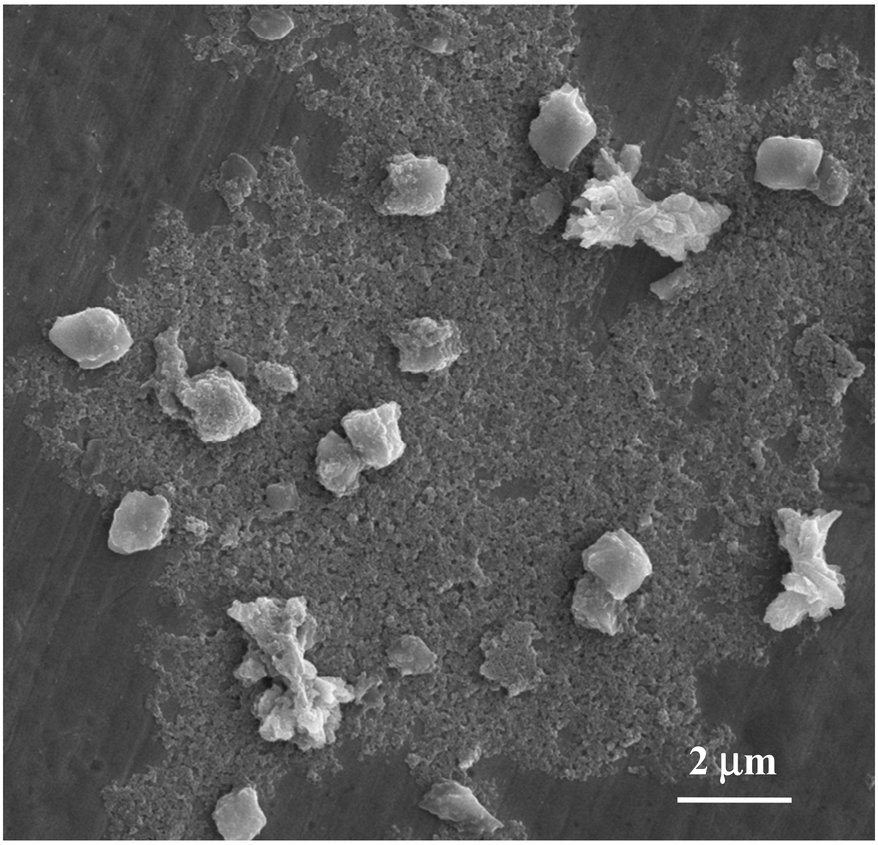


FIGURE S6. SEM micrograph of the nanocomposite of **1** and ws-CQDs prepared in EtOH at low resolution.

(x) TEM micrograph of the nanocomposite of 1 and water soluble CQDs.

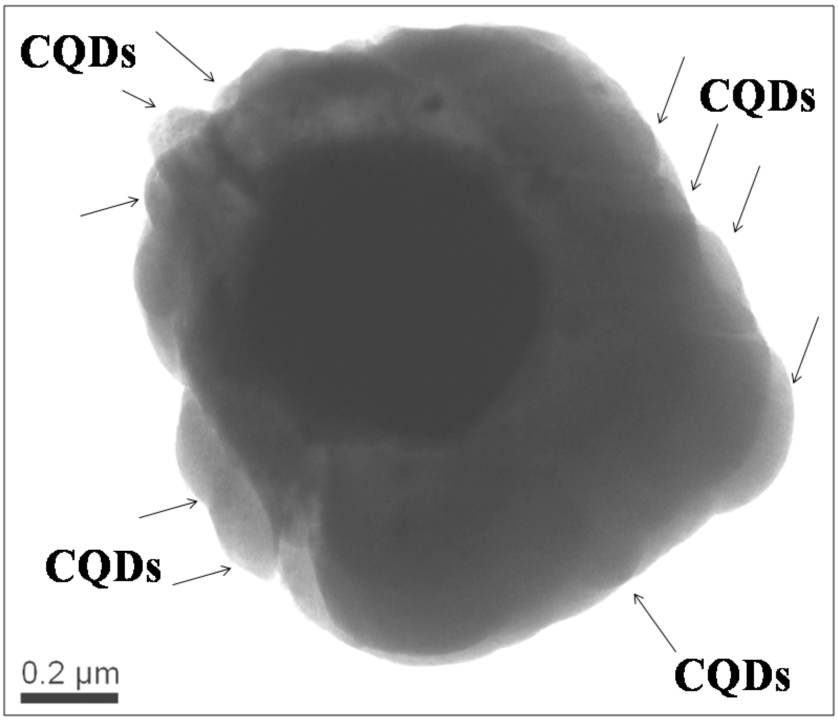
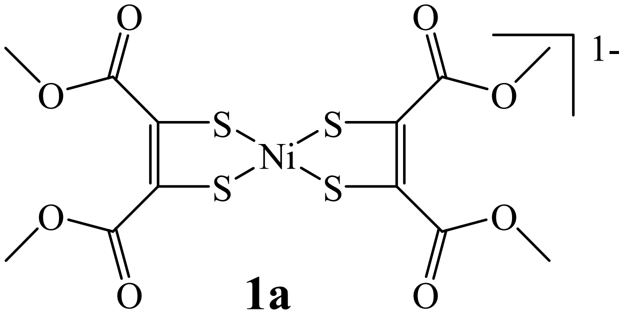
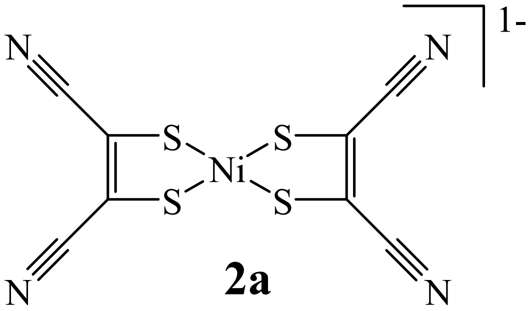


FIGURE S9. Display of TEM micrograph of the nanocomposite of **1** and water soluble CQDs highlighting the CQDs embedded into the nanocrystal of **1**.

(xi) Structures of the anions 1a and 2a in dithiolene complexes [PPh_4][$Ni^{II}(L^{2-})(L^{1-\bullet})$] (1) and [$PPh_4$][$Ni(mnt)_2$] (2).



1a



2a

(xii) Table S1. Crystal data of 1 recrystallized from H_2O-CH_3CN.

Empirical formula	$C_{36}H_{32}NiO_{8.25}PS_4$	
Formula weight	814.54	
Temperature (K)	100(2)	
Wave length MoKα (Å)	0.71069	
Crystal system/Space group	Triclinic/P-1	
Unit cell dimensions (Å), (°)	a = 10.844(5)	α = 85.742(5)
	b = 10.972(5)	β = 82.695(5)
	c = 15.617(5)	γ = 82.424(5)
Volume ($Å^3$)/Z	1823.8(13)/2	
Density (Mg/m^3)	1.483	
Absorption coefficient (mm^{-1})	0.856	
F(000)	842	
θ range for data collection (°)	2.20 to 25.00	
Unique reflections	6251	
Observed reflections	2786	
Completeness to θ = 25.00°	97.3%	
Absorption correction	Empirical	
Refinement method	Full matrix least-squares on F^2	
Data/parameters	6251/463	
Goodness of fit on F^2	0.939	
Final R indices [$I>2\sigma(I)$]	$R_1 = 0.0999$, $wR_2 = 0.2311$	
R indices (all data)	$R_1 = 0.2066$, $wR_2 = 0.3109$	

(xiii) Perspective view of the anion [Ni^{II}(L^{2-})(L$^{1-\bullet}$)] in single crystals of the complex 1 obtained by X-ray crystallography

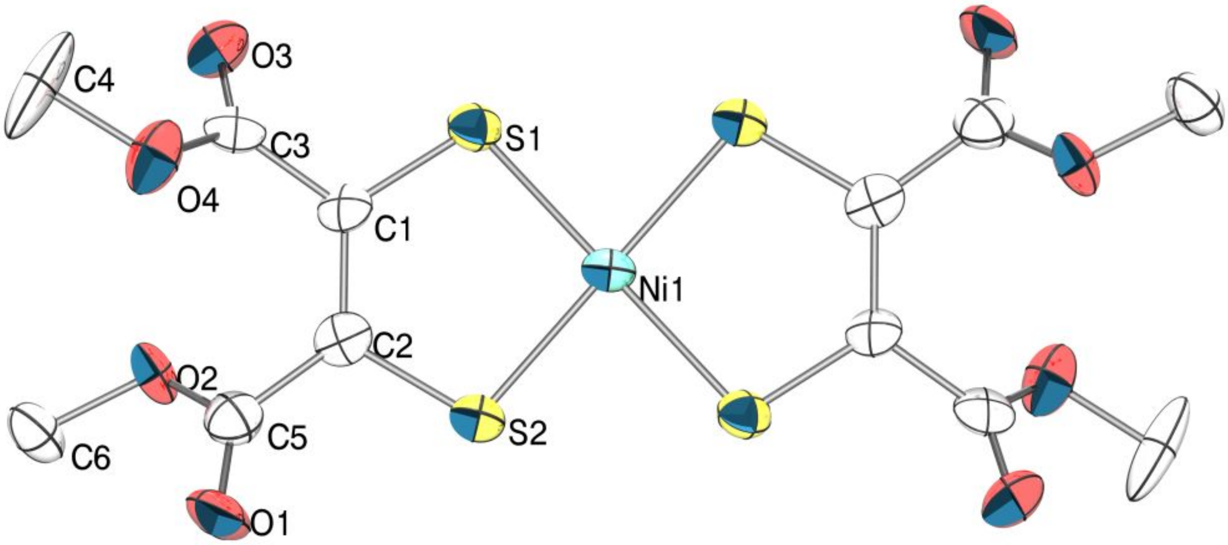


FIGURE S10. Perspective view of the anion [Ni^{II}(L^{2-})(L$^{1-\bullet}$)] in single crystals of the complex (**1**). Selected bond distances (Å): Ni(1)-S(1), 2.143(3); Ni(1)-S(2), 2.135(3); S(1)-C(1), 1.684(12); S(2)-C(2), 1.723(12).

(xiv) Reference

S1. G. Sheldrick, *Acta. Cryst.,* 2008, **A64**, 112.