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# Surface functionalization of cadmium sulfide quantum confined nanoclusters 6: Evidence of facile electronic communication between remote surface sites<sup>1</sup>

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#### Abstract

The preparation and derivatization of a series of surface functionalized  $\sim 30$  Å cadmium sulfide nanoclusters possessing surfaces of varied electron demand, tethered covalently to an electroactive fluorescent ruthenium polypyridyl complex, are described. Electrochemical analyses of these nanoclusters bearing ruthenium moieties yield a monotonic relationship between the Ru(II/III) oxidation potential and the electron withdrawing nature of the cluster surface, indicating that the electron density at the electroactive ruthenium center is indeed influenced by remote electropositive and electronegative substituents attached to the nanocluster. Further evidence of cluster mediated electronic interactions between remote surface moieties presents itself in the form of a dependence of the integrated ruthenium based MLCT emission intensity on the mole per cent of attached thiolate capping agent possessing an electron withdrawing substituent in the position *para* to the point of cluster attachment. ©2000 Elsevier Science Ltd. All rights reserved.

Keywords: CdS nanoclusters; Ruthenium(II) polypyridyls; Functionalized nanoclusters; Mesophase materials; Molecular devices

# 1. Introduction

Within the past two decades there have appeared numerous examples of experimental and theoretical investigations focused on semiconductor nanoclusters [2–7]. Many of these studies have been predicated on the future application of these interesting nanoscaled materials to molecular electronic devices [8–10]. The unique optical and electronic properties exhibited by semiconductor nanoclusters arise from the quantum size effect, which results from the splitting of the bulk semiconductor band structure into discrete, albeit closely spaced, electronic energy levels and a concurrent widening of the band gap [7]. This phenomenon becomes manifest when the size of the cluster approaches that of the exciton of the semiconductor, and can be thought of as a shift in the

behavior of the conduction electrons from Bloch wave mechanics to particle-in-a-sphere wave mechanics. To date, one fundamental question crucial to the eventual development of such proposed devices (i.e. tunnel, negative resistance and coulomb blockade devices, and single electron diodes and transistors) [11–13] still remains unanswered: will the quantum size effect lead to a loss of ability of the semiconductor to mediate electronic communication between surface groups?

Previously, we demonstrated that the electronic and physical properties of thiolate-capped CdS nanoclusters are influenced significantly by the characteristics of substituents in the position *para* to the point of attachment to the cluster on an aromatic thiolate capping agent [14–17], and we presented evidence for facile surface–core communication of conduction carriers [1]. In this contribution we present the preparation of a ruthenium polypyridyl complex which, when attached covalently to mixed surface nanoclusters via previously reported esterification methods [16], serves as an effective electrochemical and fluorescent probe of cluster

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mediated electronic communication between remote surface moieties.

# 2. Experimental

#### 2.1. Chemicals

Water was purified by passage through a Sybron-Barnstead D8902 mixed-bed ion exchange column followed by a Sybron-Barnstead D8204 activated charcoal filter. Reagent grade dimethylformamide (DMF), acetonitrile and methanol were purchased from Caledon Laboratories (Georgetown, Ont., Canada). DMF was dried over 4 Å molecular sieves for 12 h and filtered prior to use, while acetonitrile and methanol were used as received. All deuterated solvents used for <sup>1</sup>H NMR spectroscopy were purchased from Cambridge Isotope Laboratories (Andover, MA) in sealed ampules and used immediately upon opening.  $RuCl_3 \cdot xH_2O$ , sodium sulfide nonahydrate, isatin (2,3-indolinedione), 2-acetylpyridine, and sucrose were purchased from Sigma-Aldrich and used as received. Cadmium acetate (Aldrich reagent grade) was recrystallized with concurrent dehydration from glacial acetic acid and dried at 100°C in vacuo for 24 h. 4-Hydroxythiophenol was obtained reagent grade from Sigma-Aldrich and distilled at reduced pressure immediately prior to use. 4-Nitrothiophenol and 2,2'-bipyridine were obtained reagent grade from Sigma-Aldrich, recrystallized from absolute ethanol and stored in a nitrogen atmosphere at 5°C until required. Phenolic surface CdS nanoclusters (1) were prepared using the kinetic trapping method as described previously [16].

# 2.2. Mixed surface X%NO<sub>2</sub>/Y%OH quantum dot synthesis (2*a*-2*f*)

The synthesis of **2c** (16% NO<sub>2</sub>) will be discussed as a representative sample for all mixed surface 'nitro-phenolic' CdS nanoclusters (**2a–2f**). Two solutions were prepared in a 1:1:2 MeOH:MeCN:H<sub>2</sub>O (v:v:v) solvent mixture. A 20 ml cadmium acetate solution (1.7 g, 7.4 mmol) was prepared and degassed thoroughly with N<sub>2</sub>. A second solution (20 ml) of sodium sulfide nonahydrate (0.7 g, 2.9 mmol), 4-nitro-thiophenol (0.2 g, 1.3 mmol) and 4-hydroxythiophenol (1.2 g, 9.5 mmol) was degassed and added to the cadmium acetate solution yielding a yellow precipitate. The precipitate was repeatedly sonicated in water and recovered by centrifugation. The precipitate was then suspended in acetonitrile, reprecipitated upon addition of water, recovered by centrifugation, and dried in vacuo for 12 h.

Yield 0.8 g. <sup>1</sup>H NMR (DMSO, ppm):  $\delta$  8.6–9.02 (m, 1H), 5.9–7.8 (m, aromatic 5H). FT-IR (KBr, cm<sup>-1</sup>): 3288 (s, v br, O–H stretch), 1654 (s), 1920, 1750 (w, 1,4-disub- $\phi$ overtone), 1613 (m), 1576 (m), 1489 (vs, NO<sub>2</sub> asymmetric stretch), 1432 (s, ring C=C), 1331 (vs, NO<sub>2</sub> symmetric stretch), 1090 (s), 822 (m), 745 (m,  $\phi$  C–H out-of-plane), 635 (m). UV–Vis (DMF, nm): 404. 2.3. Preparation of 2-(2-pyridyl)-4-carboxyquinoline sodium salt (3)

2-(2-Pyridyl)-4-carboxyquinoline was prepared using a modification of the literature preparation described by Bass and Morgan [18]. 18 g (0.12 mol) of isatin (2,3-indolinedione) and 15 g (0.12 mol) of 2-acetylpyridine were combined and stirred for 30 min. The reaction mixture was subsequently cooled to 5°C and 60 ml of 33% aqueous NaOH was added with stirring. The ensuing reaction mixture was warmed to ~ 60°C. The addition of 60 ml of ice water yielded a purple–red slurry, which was recovered by filtration and washed with water. The crude product was dissolved in a minimum of hot water and decolorized using NORIT activated carbon pellets. Upon cooling, light purple shiny crystals of the sodium salt were obtained and dried in vacuo.

Yield 18.43 g (67%). M.p.  $> 340^{\circ}\text{C}$  (literature  $> 300^{\circ}\text{C}$ ).

## 2.4. Preparation of 2-(2-pyridyl)-4-carboxyquinoline (4)

17.3 g of **3** were dissolved in 300 ml of water and titrated, with stirring, to pH 7 using 10% HCl. Off-white crystals were recovered by filtration and dried in vacuo.

Yield 13.71 g. M.p. > 300°C (literature > 300°C). <sup>1</sup>H NMR (DMSO, ppm):  $\delta$  8.99 (s, 1H), 8.78 (d, 1H), 8.76 (d, 1H), 8.62 (t, 1H), 8.21 (d, 1H), 8.05 (t, 1H), 7.75 (t, 1H), 7.56 (t, 1H). EI-MS (*m*/*z*): 250, 206.

# 2.5. Preparation of $cis-[Ru(bpy)_2]Cl_2(5)$

cis-Ru(bpy)<sub>2</sub>Cl<sub>2</sub> was prepared using a modified literature preparation as outlined by Meyer and coworkers [19]. 2.54 g of RuCl<sub>3</sub>·*x*H<sub>2</sub>O, 3.78 g (24.20 mmol) of 2,2'-bipyridine and 6.7 g (0.15 mol) of LiCl were refluxed in DMF (40 ml) under a nitrogen atmosphere for 8 h with vigorous stirring. The reaction mixture was allowed to cool to room temperature and then 200 ml of acetone was added. After standing for 18 h at 4°C, a dark solid was recovered, washed three times with 30 ml portions of water and dried in vacuo. The recovered product was subsequently Soxhlet extracted with methylene chloride for a period of 4 days. The purple methylene chloride solution was concentrated to half its original volume and the resultant shiny dark purple crystals were recovered and dried in vacuo.

Yield 1.61 g, 3.3 mmol, (14%). M.p. >  $300^{\circ}$ C. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, ppm):  $\delta$  10.00 (d, 2H), 8.30 (d, 2H), 8.13 (d, 2H), 7.91 (dd, 2H), 7.51 (dd, 2H), 7.49 (d, 2H), 6.93 (dd, 2H). UV–Vis (methanol, nm): 364, 524.

## 2.6. Preparation of $[Ru(bpy)_2(2-PCQH)]Cl_2(6a)$

cis-Ru(bpy)<sub>2</sub>Cl<sub>2</sub> (0.25 g, 0.52 mmol) was dissolved in 10 ml of methanol and a methanol solution (10 ml) containing AgNO<sub>3</sub> (0.241 g, 1.04 mmol) was added. The reaction mixture was stirred for 2 h yielding an orange solution and white precipitate. The precipitate was removed by filtration and

0.13 g (0.55 mmol) of **4** was added. The reaction mixture was refluxed for 16 h under a  $N_2$  atmosphere. The solvent was removed in vacuo, and the orange–red residue was purified by column chromatography on alumina using a 1:1 methanol:chloroform eluent.

Yield 0.31 g, 0.42 mmol (81%). M.p. 280–282°C (dec.). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>):  $\delta$  8.9 (d, 1H), 8.8 (m, 2H), 8.7 (s, 1H), 8.6 (d, 1H), 8.5 (d, 1H), 8.4 (d, 1H), 8.15 (m, 6H), 8.0 (t, 1H), 7.8 (d, 1H), 7.7 (d, 1H), 7.6 (m, 8H), 7.3 (t, 1H). FT-IR (KBr, cm<sup>-1</sup>): 3410 (m, br, OH stretch), 3070 (m, br, aromatic C–H stretch), 1610 (s, sharp, C=O stretch). UV–Vis (methanol, nm): 450, 482 shoulder. ES-MS (*m*/*z*): 334.0, 333.5, 333.0, 332.5, 332.0, 331.5, 331.0, 330.5, 330.0, 329.5, 329.0.

#### 2.7. Preparation of $[Ru(bpy)_2(2-PCQH)](PF_6)_2(6b)$

0.2 g (0.27 mmol) of **6a** was dissolved in water and the addition of an aqueous solution of excess of  $NH_4PF_6$  resulted in the precipitation of an orange solid. The precipitate was isolated by centrifugation and washed three times with water.

Yield 0.19 g. M.p. 244–246°C (dec.). <sup>1</sup>H NMR (DMSOd<sub>6</sub>): δ 9.0 (d, 1H), 8.9 (m, 2H), 8.7 (m, 4H), 8.2 (m, 5H), 8.0 (m, 2H), 7.6 (m, 11H), 7.3 (t, 1H). ES-MS (*m*/*z*): 334.0, 333.5, 333.0, 332.5, 332.0, 331.5, 331.0, 330.5, 330.0, 329.5, 329.0.

# 2.8. Covalent attachment of **6b** to **1**, **2a–2f** via esterification (**7**, **8a–8f**)

The preparation of 7 will be presented as a representative example of the derivatization of CdS nanoclusters with polypyridyl ruthenium probe through an ester linkage. 30 mg of 6b were refluxed in SOCl<sub>2</sub> (10 ml) under a dry N<sub>2</sub> atmosphere for 3 h to yield a purple solution. The excess solvent was removed in vacuo, and 100 mg of imidazole in 10 ml of toluene were added to the purple residue and refluxed for 1.5 h. The toluene was removed and the residue was heated at 60°C in vacuo to sublime excess imidazole from the reaction flask. All procedures involving nanoclusters were carried out under subdued light. 300 mg of 1 were suspended in 10 ml of DMF with sonication. The DMF suspension was added to the reaction flask containing the imidazole derivative of 6b and stirred for 1 h. The reaction mixture was quenched with water and the resulting orange solid was isolated by centrifugation and purified through repeated sonication/centrifugation cycles in water, methanol and diethyl ether. The solid was dried in vacuo for 12 h.

Yield 105 mg. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, ppm):  $\delta$  6.0–9.2 (br M, aromatic and OH protons). FT-IR (KBr, cm<sup>-1</sup>): 3265 (s, v br, OH stretch) 1874 (w, 1,4-disub- $\phi$  overtone), 1652 (m), 1582 (m), 1488 (s), 1431 (m), 1383 (w), 1256 (s), 1170 (m), 1092 (w), 821 (m), 763 (w), 635 (w). UV–Vis (DMF, nm): 310 (shoulder), 430, 505.

## 2.9. Electrochemical analysis of 7, 8a-8f

#### 2.9.1. Electrode preparation

A homogeneous conductive carbon paste was prepared by thoroughly mixing 1.2 g of graphite powder with 200  $\mu$ l of heavy paraffin oil. Electrodes were subsequently constructed by thoroughly mixing 100 mg of the standard paste matrix with 20 mg of the nanocluster to be studied, in subdued light, until a homogeneous mixture was obtained. A ~ 2 mm thick pellet of the paste was formed in the tip of a 1 ml glass syringe (diameter ~ 2 mm) and electrical contact was achieved via the compression of a silver powder layer which was in turn addressed with a copper wire.

#### 2.9.2. Differential pulse polarography of 7, 8a-8f

Differential pulse polarography was carried out using a Cypress Inc. computer controlled potentiostat system in a 0.1 M TBAPF<sub>6</sub> acetonitrile solution with a graphite paste working electrode, platinum wire counter electrode and platinum wire pseudo-reference electrode. All electrochemical measurements were calibrated using an internal ferrocene standard. The pulse height, pulse width, and sample time for all differential pulse polarography measurements were 50 mV, 40.0 ms, and 35.0 ms, respectively. Prior to analysis, all electrolyte solutions were thoroughly degassed with argon and all experiments were carried out in an argon atmosphere.

#### 2.10. Voltammetric analysis of 6a, 6b

Cyclic voltammetry was performed with a Princeton Applied Technologies PAR 263 potentiostat/galvanostat using an electrode system which consisted of a platinum disk working electrode (diameter 0.5 mm), a platinum wire counter electrode and platinum wire pseudo-reference electrode which were separated from the bulk solution by a polished graphite frit. Samples were prepared in a stock 0.1 M TBAPF<sub>6</sub> solution in electrochemical grade dimethylformamide and degassed with dry argon prior to analysis. All measurements were done at a scan rate of 100 mV s<sup>-1</sup> and potentials were standardized using an internal ferrocene standard.

#### 2.11. Spectroscopic analyses

IR spectra were recorded as KBr pellets with a Mattson 3000 Fourier transform IR spectrometer. <sup>1</sup>H NMR spectra were performed on a Brucker ARX 400 MHz nuclear magnetic resonance spectrometer. <sup>1</sup>H NMR samples were sonicated in DMSO-d<sub>6</sub> and centrifuged prior to analysis. Electronic spectra were performed in 1 cm quartz cuvettes using a Hewlett-Packard 8452 diode array spectrometer. Solutions for fluorescence studies were thoroughly deoxygenated with argon and measurements were made using a Shimadzu RF-551 spectrofluorometric detector driven by PC-551 software.

### 2.12. Transmission electron microscopy

Transmission electron microscopy (TEM) was performed using a Phillips EM-301 transmission electron microscope. Nanocluster samples were prepared by placing a few drops of freshly sonicated and centrifuged DMF suspension of the desired cluster (2.5 mg of nanocluster in 3 ml of solvent) onto J.B.EM Services (Pointe Claire, Dorval, Que.) JBS-183 300 mesh carbon coated copper grids (cleaned in acetone, chloroform and again in acetone followed by air drying). The excess solvent was drawn off with a piece of filter paper while holding the grid in non-capillary forceps, leaving aggregates as well as individual nanoclusters adhering to the grid surface. Grids were then air dried at room temperature. Size calibration was performed using a precision silicon grid of 21600 lines cm<sup>-1</sup>.

# 3. Results and discussion

The covalent attachment of an electroactive transition metal fluorophore to the surface of a semiconductor nanocluster offers an opportunity to probe the electronic interactions between remote surface moieties as mediated by the quantum dot core. All 'parent' CdS nanoclusters were prepared using a modification of the kinetic trapping method (Scheme 1) thus providing control of the cluster size and surface composition while facilitating the introduction of chemically active moieties [1,14–17,20]. We have successfully controlled the electron withdrawing/donating properties of nanocluster organic surface layers through careful consideration of the surface capping agent composition employed in the initial reaction mixture. By incorporating



predetermined mole percentages of an electronegative surface moiety (4-nitrothiophenolate) and an electron donating surface moiety (4-hydroxythiophenolate), we have prepared a series of CdS quantum dots (2a–2f) with varied surface electronic properties as well as surface moieties which are easily derivatized via well established esterification methods [16].

Proton NMR analyses of 2a-2f show characteristic homogeneous peak broadening with superimposed structure similar to that discussed for other CdS nanocluster systems indicative of the multiple chemical shift environments and slow cluster tumbling on the NMR timescale [1,14,15,21]. Regions of the <sup>1</sup>H NMR spectra of 2a-2f can be assigned to aromatic ( $\sim 6-8$  ppm) and phenolic protons (8.5-9.95 ppm). The integration of these broadened regions provides a suitable determination of the relative percentages of 4hydroxythiophenolate and 4-nitrothiophenolate actually incorporated as surface caps. The <sup>1</sup>H NMR spectrum of 2a, corresponding to 6 mol% 4-nitrothiophenolate, is shown in Fig. 1. For all mixed surface nanoclusters (2a–2f), <sup>1</sup>H NMR integration ratios indicate that the fraction of 4-nitrothiophenolate surface caps is somewhat greater than that defined by the relative solution mercaptan concentrations during cluster synthesis; this is expected considering the relative acidities of 4-nitrothiophenol  $(pK_{a(SH)} = 4.5)$  [22] and 4-hydroxythiophenol  $(pK_{a(SH)} = 6.75)$  [23]. A summary of the <sup>1</sup>H NMR spectra and surface compositions for 2a-2f are included in Tables 1 and 2, respectively.

All mixed surface nanoclusters prepared in this work (2a-2f) lie in a 20–30 Å size regime. The diameters of nanoclusters with low percentages of surface tethered  $\phi$ -NO<sub>2</sub> (2a) may be determined by applying tight binding band theory analysis to data obtained from electronic spectroscopy as previously described, and are in good agreement with measurements obtained by TEM and X-ray analysis [14–17,24– 26]. Unfortunately, the diameters of clusters with surface mole percentages of the 4-nitrothiophenolate exceeding



Fig. 1. <sup>1</sup>H NMR spectrum of **2a** in DMSO-d<sub>6</sub> showing distinctive signals from aromatic and phenolic protons.

Table 1 Summary of <sup>1</sup>H NMR analysis of **2a–2f** and **8a–8f** in DMSO-d<sub>6</sub>

Compound	vs. TMS
2a	8.60–9.05 (br m, 0.94H, OH proton), 6.0–7.3 (br m, 4H, aromatic proton)
2b	8.60–9.01 (br m, 0.93H, OH proton), 6.0–7.8 (br m, 4H, aromatic proton)
2c	8.50–9.60 (br m, 0.84H, OH proton), 6.0–7.7 (br m, 4H, aromatic proton)
2d	8.60–9.20 (br m, 0.78H, OH proton), 5.7–7.8 (br m, 4H, aromatic proton)
2e	8.70–9.21 (br m, 0.49H, OH proton), 5.8–7.8 (br m, 4H, aromatic proton)
2f	9.95 (br m, 0.03H, OH proton), 6.7–8.25 (br m, 4H, aromatic proton)
7	6.0–9.2 (broad and structured, aromatic and phenolic H)
8a	5.9–9.5 (broad and structured, aromatic and phenolic H)
8b	5.5–9.4 (broad and structured, aromatic and phenolic H)
8c	5.7–10.0 (broad and structured, aromatic and phenolic H)
8d	5.8–10.0 (broad and structured, aromatic and phenolic H)
8e	6.0–10.0 (broad and structured, aromatic and phenolic H)
8f	6.5–10 (broad and structured, aromatic)

Table 2

Yield and surface composition data for 2a–2f

Compound	Yield (g)	Theoretical NO <sub>2</sub> <sup>a</sup> (%)	Observed NO <sub>2</sub> <sup>b</sup> (%)
2a	0.63	1	6
2b	0.67	5	7
2c	0.66	10	16
2d	0.64	15	22
2e	0.58	50	51
2f	0.55	90	97

<sup>a</sup> From mole ratio of 4-nitrothiophenol in reaction mixture.

<sup>b</sup> Determined from <sup>1</sup>H NMR analysis.

about 7% (**2b–2f**) cannot be evaluated reliably using electronic spectroscopy as the excitonic absorption of the CdS cluster is obscured by the intense  $n \rightarrow \pi^*$  transition of the  $\phi$ -NO<sub>2</sub> chromophore. For these systems, TEM analysis alone was performed to evaluate cluster dimensions. A summary of spectroscopic and TEM determined diameters for **2a–2f** may be found in Table 3.

FT-IR spectra of KBr pellets of 2a-2f show absorptions characteristic of the pendant surface groups. As expected, broad absorptions indicative of phenolic functionalities appear at ca. 3300 cm<sup>-1</sup> for 2a-2f, while the spectra lack the characteristic –SH stretch at 2580 cm<sup>-1</sup>, thus confirming exclusive thiolate binding of surface moieties. A complete summary of the FT-IR spectra for 2a-2f appears in Table 4.

Polypyridyl complexes of ruthenium have been widely studied [27], and are well known for their stability, long lived charge transfer excited states, intense phosphorescence and well characterized electrochemical properties. Numerous examples of correlations between metal centered electrochemical potentials and electronic properties of chemical moieties on substituents on ligands exist in the literature. The

Table 3 Electronic spectroscopy and cluster dimension data for **2a–2f** and **8a–8f** 

Compound	$\lambda_{\max}$ (nm)	TBT diameter (Å) <sup>a</sup>	TEM diameter (Å) <sup>b</sup>
2a	340 (shoulder), 410	24	$26 \pm 7$
2b	404		$27\pm7$
2c	404		$23\pm7$
2d	404		$25\pm7$
2e	404		$26\pm7$
2f	326, 404		$24\pm7$
7	365	27	$25\pm7$
8a	340 (shoulder)	24	$28\pm7$
8b	404		$29\pm7$
8c	404		$27\pm7$
8d	404		$26\pm7$
8e	404		$24\pm7$
8f	326, 404		$25\pm7$

<sup>a</sup> Estimated using tight binding band theory.

 $^{\rm b}$   $\pm$  7 Å represents the resolution of the transmission electron microscope.

strong dependence of the metal centered oxidation potential upon electron donating and withdrawing properties of substituted fragments affords a means to probe the effectiveness of a ligand (or nanocluster) to mediate the electronic influence of a remote functionality on a metal center. Indeed, Meyer and coworkers [28-31], as well as others [32-35], have demonstrated that a  $[cis-Ru(bpy)_2]$  fragment serves as an effective probe for the electron interaction of a third ligand with the ruthenium metal center.

Although ruthenium polypyridyl species have previously been attached to TiO<sub>2</sub> nanoparticles by Meyer and coworkers [36,37], and although these materials exhibited interesting properties of solar energy conversion with monochromatic efficiencies of 0.30, no detailed discussion of the electrochemical analysis nor the affects of remote substituents on the ruthenium(II/III) oxidation potential was offered. Hence, we endeavored to link covalently an electroactive polypyridyl ruthenium fluorophore to the surface of quantum sized cadmium sulfide where it serves to probe the extent to which the semiconductor core mediates electron demand between surface groups. To facilitate the covalent attachment of a polypyridyl ruthenium complex to a phenolic surface CdS nanocluster, it was necessary to replace a single bipyridine ligand of  $[Ru(bpy)_3]^{2+}$  with a polypyridyl analog bearing a carboxylic acid moiety. 2-(2'-Pyridyl)-4carboxyquinoline (4) offers a carboxylic acid group suitable for esterification and was prepared using the coupling reaction of 4-acetylpyridine and isatin (2,3-indolinedione) as described by Bass and Morgan [18].

The 2D-COSY analysis of **4** shows numerous aromatic signals, the most striking of which is a singlet appearing at 9.0 ppm assigned to the proton in the 3 position. The electron impact mass spectrum of **4** shows a parent peak at m/z = 250 corresponding to the loss of a proton and a fragmentation pattern including an intense peak at m/z = 206 arising from the loss of  $-CO_2$ . Scheme 2 illustrates the reaction of **4** with

Table 4	
A summary of FT-IR assignments of KB	r pellets of 2a–2f and 8a–8f

Compound	Wavenumber $(cm^{-1})$		
2a	3272 (s, br, OH stretch), 1870 (vw, 1,4-disub- $\phi$ overtones), 1582 (m), 1486 (s, NO <sub>2</sub> asymmetric stretch), 1427 (m), 1356 (w), 1231 (s), 1170 (s), 1090 (w), 819 (w), 633 (w)		
2b	3250 (s, br, OH stretch), 1875 (vw, 1,4-disub- $\phi$ overtones), 1578 (s), 1486 (s, NO <sub>2</sub> asymmetric stretch), 1425 (m, ring C=C), 1364 (m), 1169 (s), 1086 (m), 1006 (m), 818 (m), 740 (w, NO <sub>2</sub> symmetric stretch), 630 (w)		
2c	3288 (s, v br, O–H stretch) 1654 (s), 1920, 1750 (w, 1,4-disub-φ overtone), 1613 (m), 1576 (m), 1489 (vs, NO <sub>2</sub> asymmetric stretch), 1432 (s, ring C=C), 1331 (vs, NO <sub>2</sub> symmetric stretch), 1090 (s), 822 (m), 745 (m, NO <sub>2</sub> symmetric stretch), 635 (m)		
2d	3440 (s, br, OH stretch), 1874 (vw, 1,4-disub- $\phi$ overtones), 1625 (m, br), 1573 (m, br), 1498 (m, NO <sub>2</sub> asymmetric stretch), 1428 (m, ring C=C), 1331 (m, NO <sub>2</sub> symmetric stretch), 1255 (w, br), 1084 (w, br)		
2e	3445 (m, br, OH stretch), 3078 (m, br), 1868 (vw, 1,4-disub- $\phi$ overtones), 1603 (m, sharp), 1573 (m, sharp), 1509 (s, NO <sub>2</sub> asymmetric stretch), 1427 (m, ring C=C) 1338 (s, NO <sub>2</sub> symmetric stretch), 1180 (w, br), 1110 (w, br), 1084 (w, br), 850 (m, shrp), 740 (w, NO <sub>2</sub> symmetric stretch)		
2f	3390 (w, br, OH stretch), 3092 (w, aromatic C–H stretch), 1918, 1788 (vw, 1,4-disub- $\phi$ overtones), 1646 (w), 1509 (s, NO <sub>2</sub> asymmetric stretch), 1432 (m, ring C=C),1340 (s, NO <sub>2</sub> symmetric stretch), 1175 (w), 1104 (w), 1082 (m), 846 (m), 736 (m, NO <sub>2</sub> symmetric stretch), 678 (w), 529 (w)		
7	3265 (s, v br, OH stretch) 1874 (w, 1,4-disub-φ overtone), 1652 (m, C=O stretch), 1582 (m), 1488 (s, NO <sub>2</sub> asymmetric stretch), 1431 (m, ring C=C), 1383 (w), 1256 (s), 1170 (m), 1092 (w), 821 (m), 763 (w), 635 (w)		
8a	3250 (s, v br, OH stretch) 1882 (w, 1,4-disub- $\phi$ overtone), 1651 (m, C=O stretch), 1579 (m),1489 (s, NO <sub>2</sub> asymmetric stretch), 1429 (m, ring C=C), 1258 (s), 1169 (m), 1090 (w),1009 (w), 823 (m), 763 (m), 635 (m), 512 (w)		
8b	3240 (s, v br, OH stretch), 1872 (w, 1,4-disub-φ overtone), 1654 (m, C=O stretch), 1578 (m),1489 (s, NO <sub>2</sub> asymmetric stretch), 1431 (m, ring C=C), 1259 (s), 1172 (m), 1090 (w),1009 (w), 823 (m), 762 (m), 635 (m), 512 (w)		
8c	3290 (s, v br, OH stretch), 1880 (w, 1,4-disub-φ overtone), 1650 (m, C=O stretch), 1578 (m),1490 (s, NO <sub>2</sub> asymmetric stretch), 1428 (m, ring C=C), 1255 (s), 1169 (m), 1088 (w),1006 (w), 822 (m), 753 (m), 635 (m)		
8d	3288 (s, v br, OH stretch), 3001 (m, sharp, aromatic C–H stretch), 1878 (w, 1,4-disub- $\phi$ overtone), 1654 (m, C=O stretch), 1576 (m),1490 (s, NO <sub>2</sub> asymmetric stretch), 1432 (m, ring C=C), 1258 (s), 1170 (m), 1090 (w), 912 (w), 823 (m), 745 (m), 635 (m)		
8e	3350 (s, v br, OH stretch) 1870 (w, 1,4-disub- $\phi$ overtone), 1647 (m, C=O stretch), 1575 (m),1503 (s, NO <sub>2</sub> asymmetric stretch), 1426 (m, ring C=C), 1272 (s), 1175 (m), 1090 (w), 827 (m), 743 (m), 632 (m)		
8f	3380 (s, sharp, OH stretch), 3022 (m, sharp, aromatic C–H stretch), 1888 (w, 1,4-disub-φ overtone), 1651 (m, C=O stretch), 1572 (m),1406 (s, NO <sub>2</sub> asymmetric stretch), 1429 (m, ring C=C), 1256 (s), 1165 (w), 1090 (m), 1085 (m), 1009 (w), 850 (m), 740 (m), 682 (w), 648 (m), 535 (w)		





*cis*-Ru(bpy)<sub>2</sub>Cl<sub>2</sub> yielding ruthenium polypyridyl complex (**6a**) bearing a carboxylic acid functionality which may be exploited as a point of covalent attachment to CdS nanoclusters. The <sup>1</sup>H NMR of **6a** is illustrated in Fig. 2, and shows a series of multiplet signals in the aromatic region of the spectrum ( $\sim$ 7.0–10.0 ppm), all of which have been assigned with the aid of 2D NMR. The most striking feature of the <sup>1</sup>H NMR spectrum of **6a** is a singlet appearing at 8.67 ppm arising from the unique proton in the 3 position of the 2-2'-pyridylcarboxyquinoline ligand. Peak assignments, chemical shifts, integration ratios and coupling constants for the 2D-COSY spectrum of **6a** are reported in Table 5.

Electrochemical analysis of **6a** shows a well defined reversible Ru(II/III) oxidation process at 1.27 V versus SCE as well as a reversible 2-2'-pyridylcarboxyquinoline reduction at -1.26 V and two reversible bipyridine reductions at -1.57 and -1.93 V versus SCE. In addition, an irreversible chloride oxidation is also observed at 1.18 V versus SCE and will preclude any accurate measurement of changes in the Ru(II/III) oxidation potential of probes tethered to functionalized nanoclusters. Thus, **6a** was converted to the corresponding hexafluorophosphate salt (**6b**) by treatment with excess aqueous NH<sub>4</sub>PF<sub>6</sub>. The electrochemical analysis of **6b** shows a reversible Ru(II/III) oxidation at 1.27 V versus SCE and three reversible ligand reductions at -1.26, -1.57 and -1.93 V versus SCE, with the chloride oxidation absent.

Electronic and emission spectroscopy of **6a** and **6b** shows the expected MLCT absorptions (450 nm and 482 nm shoulder) and MLCT emission maxima (652 nm), respectively (Fig. 3).

The <sup>1</sup>H NMR spectra of all  $[Ru(bpy)_2(PCQ)]^{2+}$  functionalized CdS nanoclusters (7, 8a–8f, Scheme 3) in this



Fig. 2. 1D- and 2D-COSY <sup>1</sup>H NMR analysis of **6a**; detailed peak assignments and coupling constants may be found in Table 5.

Table 5 <sup>1</sup>H NMR-COSY assignments for **6a** 

Proton	Chemical shift ( $\delta$ , ppm vs. TMS)	$J_{\mathrm{H-H}}~(\mathrm{Hz})$
3	8.67 (s)	
5	8.44 (d)	8.412
6	$\sim$ 7.6 (t in m)	
7	7.27 (t)	7.628
8	$\sim 7.5$ (d in m)	
9	~7.5 (d in m)	
10	8.01 (t)	7.840
11	~7.5 (t in m)	
12	~ 8.2 (m)	
13	8.80 (d)	8.396
14	$\sim 8.2 \text{ (t in m)}$	
15	7.5 (t in m)	
16	7.74 (d)	5.564
17	8.2 (d in m)	
18	7.4 (t in m)	
19	$\sim 8.2 \text{ (t in m)}$	
20	8.503 (d)	8.160
21	7.837 (d)	5.484
22	7.6 (t in m)	
23	8.2 (t in m)	
24	8.930 (d)	8.188
25	8.589 (d)	8.204
26	~7.6 (t in m)	
27	8.2 (t in m)	
28	8.806 (d)	8.396



Fig. 3. Emission spectrum of an argon saturated DMF solution of **6b**;  $\lambda_{\text{exc}}$  = 430 nm.



work show homogeneously broadened peaks similar to those observed for all nanoclusters discussed previously (4a-4e),

indicating that the cluster core remained intact throughout the derivatization process. The most striking change noted when comparing the <sup>1</sup>H NMR spectrum of the ruthenium derivatized CdS functionalized nanoclusters to that of the parent quantum dots is a loss of definition (Fig. 4(b)) between the phenolic and aromatic signal regions previously reported for the corresponding parent nanocluster counterparts (Fig. 4(a)). The increased complexity in the <sup>1</sup>H NMR suggests that, as expected, the derivatization process caused an increase in the number of proton environments on the cluster surface. Table 1 summarizes the <sup>1</sup>H NMR spectroscopy of **7**, **8a–8f**.

FT-IR assignments of KBr pellets of **7** and **8a–8f** are summarized in Table 2 The appearance of an absorbance at  $\sim 1650 \text{ cm}^{-1}$  not present in similar spectra of **1** and **2a–2f** confirms the formation of an ester linkage between the phenolic surface functionalities and  $[\text{Ru}(\text{bpy})_2(\text{PCQ})]^{2+}$ . Another significant observation is the appearance of a sharp absorption at 3381 cm<sup>-1</sup>, characteristic of a non-hydrogen bonded –OH, in the FT-IR spectrum of **8f**, confirming a loss of interaction between surface –OH moieties. Fig. 5 shows the FT-IR spectrum of a KBr pellet of **8f**.

The electronic spectra of CdS quantum dots derivatized with **6b** and bearing low molar percentages of 4-nitrothiophenolate surface caps (**8a**) show the characteristic excitonic shoulder arising from the semiconductor core, while the MLCT absorptions of the pendant ruthenium polypyridyl center are masked by the presence of a weak absorption shoulder arising from the  $n \rightarrow \pi^*$  transition of the  $-NO_2$ . For clusters with greater than about 7 mol% 4-nitrothiophenolate caps, both the excitonic shoulder of the cluster core and the MLCT absorptions of the pendant  $[Ru(bpy)_2(PCQ)]^{2+}$  are hidden by the intense absorption attributed to the  $n \rightarrow \pi^*$  transition of the  $-NO_2$  functionality. The electronic spectrum of **7** is shown in Fig. 6 as a representative example of clusters having surfaces without  $-NO_2$  moieties.

For clusters showing excitonic absorptions, **7** and **8a**, it is possible to approximate the core diameter using a tight binding band approach as previously described [24–26]. All of the presented clusters have been found to lie in a size regime of ca. 27 Å. Good agreement was found between tight binding band theory approximations and TEM analyses for clusters **2a**, **7**, and **8a**. A summary of cluster dimensions for **7** and **8a–8f** may be found in Table 3.

The properties of the covalently attached ruthenium moieties on 7 and **8a–8f** offer two independent methods for the investigation of the electronic processes mediated by the semiconductor core, emission spectroscopy and electrochemistry. All of the presented ruthenium functionalized nanoclusters (7 and **8a–8f**) exhibit MLCT emission characteristic of the tethered ruthenium moiety (**6b**) at ca. 652 nm as shown in Fig. 7. Variation of the mole percentage of 4-nitrothiophenolate surface cap results in a unique relationship between the mole percentage of 4-nitrothiophenolate surface functionality and the integrated fluorescence intensity (Fig. 8(a)). There is an observed rapid decrease in integrated



Fig. 5. FT-IR spectrum (KBr pellet) of 8f showing C=O and OH stretching frequencies at 1651 and 3380 cm<sup>-1</sup>, respectively; detailed assignments may be found in Table 4.

emission intensity as the mole percentage of 4-nitrothiophenolate cap increases from 0 to  $\sim 50\%$  followed by a range of slight decrease in intensity for mole percentages between

680



Fig. 7. Emission spectrum of a DMF suspension of **8f**;  $\lambda_{\text{exc}} = 430$  nm.



Fig. 8. Observed dependence of (a) ruthenium based MLCT emission integrated intensity and (b) ruthenium(II/III) oxidation potential on mole per cent 4-nitrothiophenolate surface functionality for **7**, **8a–8f**.

~50 and ~97%. From this analysis, it is evident that the MLCT emission characteristics are effectively quenched by only a few caps bearing remote electron withdrawing substituents, indicating that electronic communication mediated by the semiconductor core is indeed occurring. Interestingly, electrochemical studies of the same series of ruthenium derivatized nanoclusters exhibit a similar relationship (Fig. 8(b)). Differential pulse polarography of a graphite mull of 7 and **8a–8f** shows a broad reversible oxidation process arising from the pendant ruthenium center which shifts between 0.497 and 0.747 V versus SCE with increased mole percentage of 4-nitrothiophenolate surface.

These phenomena may be explained on the basis of a coremediated electronic inductive effect. The valence and conduction band edges of bulk CdS are 1.36 V and -1.18 V, respectively, relative to an SCE reference [38]. The quantum size effect symmetrically widens the observed band gap of bulk CdS ( $E_g$ =2.54 eV) to 3.65 eV for ~30 Å diameter CdS nanoclusters, providing a valence band edge of 1.92 V versus SCE and a conduction band edge at -1.74 V versus SCE at the core interior. However, we have previously shown that changes in the electronic properties of the cluster capping agent, as predicted by the Hammett  $\sigma_p$  parameter, result in an ultimate change in the electronegativity of the cluster surface [1], consequently shifting the positions of the conduction and valence band edges at the cluster core/cap interface, relative to the respective levels in the core interior.

If one considers an electron rich surface (7), the valence and conduction bands bend up, rendering the surface relatively electropositive (Fig. 9(a)), which in turn increases the electron density at a pendant ruthenium center via a cluster mediated inductive mechanism, and shifts the Ru(II/III) oxidation potential of the pendant Ru(bpy)<sub>2</sub>(PCQ) moiety (1.27 V versus SCE for the free complex; 0.497 V versus SCE for 7). This dramatic change in Ru(II/III) oxidation potential for cadmium sulfide nanocluster tethered ruthenium polypyridyl probes is comparable to that observed for functionalized TiO<sub>2</sub> clusters [36,37] and is in good agreement with the value of 0.59 V versus SCE determined using the literature analysis of ruthenium based MLCT absorptions as described by Lever and Dodsworth [35].

We report here that as the mole ratio of 4-nitrothiophenolate cap increases from 0 to 0.97, the oxidation potential of the pendant  $[Ru(bpy)_2(PCQ)]^{2+}$  moiety increases from



Fig. 9. (a) Electron donating surface caps on Ru-tagged CdS nanoclusters (**7**, **8a–8f**) result in an upward bending of the valence and conduction bands, decreasing the cluster surface electronegativity, which in turn results in an increase of electron density at the ruthenium center lowering the Ru(II/III) oxidation potential. (b) Electron withdrawing surface caps cause the conduction and valence bands to bend downward, consequently increasing the cluster surface electronegativity and increasing the Ru(II/III) oxidation potential.

The core-mediated inductive model is also consistent with the observed quenching of the Ru based MLCT emission. In the case of an electron rich surface (7), the conduction band edge is bent up above the PCQ  $\pi^*$  level, and the excited  $\pi^*$ electron of [Ru(bpy)<sub>2</sub>(PCQ)]\* remains localized within the ligand orbital, ultimately relaxing via MLCT emission. Conversely, for a relatively electronegative surface, the conduction band edge bends below the PCQ  $\pi^*$  level, resulting in electron capture and concurrent fluorescence quenching.

## 4. Conclusions

We have presented the synthesis and characterization of a series of CdS nanoclusters having controlled surface electron demand, and bearing an electroactive ruthenium polypyridyl fluorophore. Electrochemical and emission studies of these interesting materials have yielded conclusive evidence that electronic communication can indeed be mediated by CdS nanoclusters via a core-mediated inductive mechanism. These results further suggest the possibility that surface functionalized semiconductor nanoclusters may possess device activity.

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