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Spectroscopic and Photophysical Studies of Charge-Transfer in a Cd_8 Thiolate Cluster Complex Containing a Coordinated *N*-Methyl-4,4′-bipyridinium Ligand

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The hybrid cluster complex $Cd_8S(SPh)_{15}(MeQ)\cdot CH_3CN$ (**1**) (MeQ^+ = *N*-methyl-4,4′-bipyridinium) was synthesized and characterized structurally by single-crystal X-ray diffraction analysis. The MeQ^+ ion is coordinated to one of the cadmium atoms of the cluster by the nitrogen atom of its pyridine group. The reflectance absorption and emission spectra of complex **1** and it's parent complex $[NEt_4]_2[Cd_8S(SPh)_{16}]$ (**2**) have been recorded and compared. DFT calculations reveal low energy cluster to ligand charge-transfer processes involving the MeQ^+ ligand.

Introduction

Hybrid nanomaterials assembled from covalently bonded organic and inorganic nanoclusters have developed into an important new research field in modern materials science. Applications for energy conversion, information storage and photo-electrochromic display,[1] chemical and biological sensors are highly sought.[2] Hybrid solar cells for the transformation of light into electricity have been the focus of considerable attention. Dye-sensitized nanocrystalline TiO_2 thin-film devices[3] and bulk heterojunction fullerene/conjugated polymer cells doped with various nanoparticle quantum dots (QDs) have been of high interest.[4,5] Advantages of QDs over conventional organic dyes in QD-sensitized solar cell include narrow luminescence emission profiles, resistance to photobleaching, and continuous absorption above the band gap,[6] but also include the production of multiexcitons by charge carrier multiplication that is not achievable by organic compounds.[3a] Efficiency of QD-sensitized cells can potentially be improved by the mechanism of multiple exciton generation (MEG) through which one absorbed high energy photon is transformed into multiple charge carriers.[7] However, the application of the MEG process requires ultrafast charge transfer from electron donors to acceptors before the Auger recombination which occurs on the 10 ps to 100 ps time scale.[7c] Elucidation of photoinduced energy and electron-transfer processes in fluorophore-QDs is important in understanding the photochemical behavior of molecules bound to semiconductor nanoparticles. There have been a number of reports of ultrafast charge transfer (CT) between QDs and the molecular electron or hole acceptors absorbed on the surface[8] and CT dynamics at the sensitizer–semiconductor nanoparticle interface.[9] More recently, ultrafast electron transfer (ET) between multiexcited CdSe QDs and the molecular electron acceptors (methyl viologen and methylene blue) adsorbed on the surface of the nanoparticles have also been investigated.[10] However, colloidal nanoparticles normally have less well-defined compositions and sizes than discrete cluster complexes. Zero-dimensional hybrid complexes based on stoichiometrically precise nanoclusters coordinated to organic fluorophore molecules could serve as valuable model systems for understanding the structures and properties of large colloidal nanoparticles and their superlattices. The structures of some CT salts of Cd(chalcogenide) cluster complexes with methyl viologen have been reported recently.[11] The methyl viologen in these salts serve to balance the charge of the clusters. The properties of these hybrids depend on the nature of the individual clusters, their spatial arrangement, and the properties of crosslinking ligands.[12] Until now, there have been few well-defined examples of covalent coassemblies between metal-chalcogenide clusters and organic ligands.[13]

N-Methyl-4,4′-bipyridinium (MeQ^+) has attracted attention because it is a strong electron acceptor and it can also serve as a ligand. It has been shown to engage readily in metal to ligand charge-transfer processes.[14] Herein we report the synthesis, structural characterization and investigation of the photophysical properties of the first example of

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a cadmium thiolate cluster complex, $Cd_8S(SPh)_{15}(MeQ)\cdot CH_3CN$ (**1**) (MeQ^+ = *N*-methyl-4,4′-bipyridinium), in which the MeQ^+ ligand is effectively coordinated to one of the cadmium atoms. The complex **1** may be good model for understanding the electron transfer (ET) dynamics at the organic molecule–nanoparticle interface which is crucial to the development of QD-based solar cells.

Results and Discussion

An ORTEP diagram of the molecular structure of **1** is shown in Figure 1. The structure of **1** is similar to that of the $[Cd_8S(SPh)_{16}]^{2-}$ anion **2** reported previously[16] which contains a tetrahedral Cd_4S core having a $Cd(\mu_2\text{-}SPh)_3$ cap on each Cd_3 face and one terminal ligand SPh^- or MeQ^+ on each of the four outer cadmium atoms. Complex **1** can be viewed as a combination of the monoanion $[Cd_8S(SPh)_{15}]^-$ coordinated to the moncation MeQ^+ formed by the replacement of one of the terminal SPh^- thiolate ligands [on cadmium Cd(6)] by the MeQ^+ ligand. As shown in the Table 1, the Cd–S bond lengths range from 2.5060(8) to 2.5865(9) Å, which are comparable with those reported in the Cd-S cluster **2**.[11] The MeQ^+ ligand is coordinated to atom Cd(6) by the pyridine group. The Cd(6)–N(1) bond length is 2.339(3) Å, lies within the typical range for Cd–N values in the literature, 2.235–2.411 Å.[13b–e,15] Compound **1** is insoluble in all common solvents. It was dissolved in $[D_6]$DMSO to record an ^1H NMR spectrum, but the chemical shifts of the resonances of the MQ^+ ligand were indistinguishable from those of the free ion, and it is thus believed that the DMSO, which is itself an effective ligand, has displaced the MeQ^+ ligand from the complex.

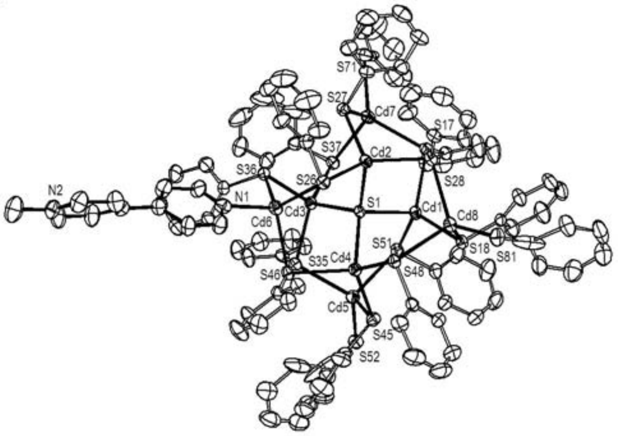

Figure 1. An ORTEP diagram of the neutral molecular structure of $Cd_8S(SC_6H_5)_{15}(C_{10}H_8N_2CH_3)$. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at the 20% probability level.

Optical Properties of the Compounds

Because of its lack of solubility and reactivity toward strong donor solvents such as DMSO, see above, the visible spectra of **1** were recorded only in the solid state by the diffuse reflectance technique. The diffuse reflectance absorption spectra of **1** over the range 300–800 nm are shown in Figure 2. For comparison diffuse reflectance absorption spectra of **2** are also shown in Figure 2. It is apparent that the spectrum of **1** is dramatically red-shifted compared with the corresponding absorptions of **2**. This dramatic change in the absorption of **1** results from low energy electronic transitions between cluster and the MQ^+ ligand. To understand the nature of the electronic transitions in **1** and **2**, time-dependent density functional molecular orbital calculations were performed on both of **1** and **2**. These calculations have revealed that the addition of MQ^+ to **1** as a ligand introduces unoccupied low-energy orbitals L – L + 3 that permit new low-energy electronic transitions. The most important one involves a transition from the cluster-based occupied molecular orbital HOMO–1 (H – 1) orbital to the unoccupied LUMO+2 (L + 2) orbital on the MQ^+ ligand **1**, see the energy level diagram on right hand side, part A of Figure 3. The calculations indicate that the low energy ab-

Table 1. Bond lengths [Å] and angles [°] for $Cd_8S(SPh)_{15}(MeQ)\cdot CH_3CN$ (**1**).

Cd(1)–S(1)	2.5248(7)	S(1)–Cd(2)–S(27)	102.65(2)
Cd(1)–S(17)	2.5234(8)	S(26)–Cd(2)–S(28)	116.17(3)
Cd(1)–S(18)	2.5262(8)	S(27)–Cd(2)–S(28)	115.58(3)
Cd(1)–S(51)	2.5328(8)	S(26)–Cd(2)–S(27)	113.62(3)
Cd(2)–S(1)	2.5232(7)	S(1)–Cd(2)–S(26)	99.59(2)
Cd(2)–S(26)	2.5543(8)	S(1)–Cd(3)–S(37)	106.71(2)
Cd(2)–S(27)	2.5108(8)	S(35)–Cd(3)–S(37)	117.47(3)
Cd(2)–S(28)	2.5060(8)	S(1)–Cd(3)–S(35)	103.98(2)
Cd(3)–S(1)	2.5169(7)	S(36)–Cd(3)–S(37)	111.37(3)
Cd(3)–S(35)	2.5338(8)	S(1)–Cd(3)–S(36)	101.35(2)
Cd(3)–S(36)	2.5627(8)	S(35)–Cd(3)–S(36)	114.02(2)
Cd(3)–S(37)	2.5129(8)	S(1)–Cd(4)–S(48)	103.06(2)
Cd(4)–S(1)	2.5116(7)	S(1)–Cd(4)–S(45)	110.99(3)
Cd(4)–S(45)	2.5143(8)	S(45)–Cd(4)–S(48)	114.40(3)
Cd(4)–S(46)	2.5567(7)	S(1)–Cd(4)–S(46)	99.63(2)
Cd(4)–S(48)	2.5131(8)	S(46)–Cd(4)–S(48)	119.35(2)
Cd(5)–S(52)	2.5249(8)	S(45)–Cd(4)–S(46)	108.11(3)
Cd(5)–S(35)	2.5744(8)	S(35)–Cd(5)–S(52)	116.85(3)
Cd(5)–S(51)	2.5805(8)	S(51)–Cd(5)–S(52)	105.90(3)
Cd(5)–S(45)	2.5865(9)	S(35)–Cd(5)–S(51)	104.79(3)
Cd(6)–S(46)	2.5277(8)	S(45)–Cd(5)–S(52)	113.65(3)
Cd(6)–S(26)	2.5294(8)	S(35)–Cd(5)–S(45)	109.65(3)
Cd(6)–S(36)	2.5335(8)	S(45)–Cd(5)–S(51)	104.81(3)
Cd(6)–N(1)	2.339(3)	N(1)–Cd(6)–S(46)	105.69(7)
Cd(7)–S(17)	2.5848(9)	N(1)–Cd(6)–S(26)	104.47(7)
Cd(7)–S(27)	2.5981(8)	S(26)–Cd(6)–S(46)	109.76(3)
Cd(7)–S(37)	2.5930(8)	N(1)–Cd(6)–S(36)	106.72(7)
Cd(7)–S(71)	2.5320(10)	S(36)–Cd(6)–S(46)	112.88(2)
Cd(8)–S(18)	2.5610(8)	S(26)–Cd(6)–S(36)	116.36(3)
Cd(8)–S(28)	2.5826(8)	S(17)–Cd(7)–S(71)	122.68(3)
Cd(8)–S(48)	2.5890(7)	S(37)–Cd(7)–S(71)	117.52(3)
Cd(8)–S(81)	2.4909(9)	S(17)–Cd(7)–S(37)	100.25(3)
		S(27)–Cd(7)–S(71)	99.08(3)
S(1)–Cd(1)–S(17)	103.98(2)	S(17)–Cd(7)–S(27)	106.68(3)
S(17)–Cd(1)–S(18)	114.89(3)	S(27)–Cd(7)–S(37)	110.13(2)
S(1)–Cd(1)–S(18)	107.31(2)	S(18)–Cd(8)–S(81)	119.31(3)
S(17)–Cd(1)–S(51)	116.19(3)	S(28)–Cd(8)–S(81)	115.84(3)
S(1)–Cd(1)–S(51)	100.64(2)	S(18)–Cd(8)–S(28)	101.96(3)
S(18)–Cd(1)–S(51)	112.00(3)	S(81)–Cd(8)–S(48)	105.44(3)
S(1)–Cd(2)–S(28)	106.51(2)	S(18)–Cd(8)–S(48)	106.03(2)
		S(28)–Cd(8)–S(48)	107.47(3)

sorption (Figure 3) is formally a cluster to ligand charge-transfer transition (CLCT). In the absence of the MQ$^+$ ligand, anion **2** shows only high energy transitions from the cluster-based occupied MOs: HOMO (H), HOMO–1 (H–1), HOMO–2 (H–2) and HOMO–3 (H–3) to the cluster-based unoccupied MOs: LUMO (L), LUMO+1 (L+1), LUMO+2 (L+2) and LUMO+3 (L+3), see left hand side of Figure 3 (A). Feng recently reported that an MV^{2+} salt of anion **2** also exhibits highly red-shifted absorptions in the UV/Vis spectrum and attributed this to charge-transfer effects.[11]

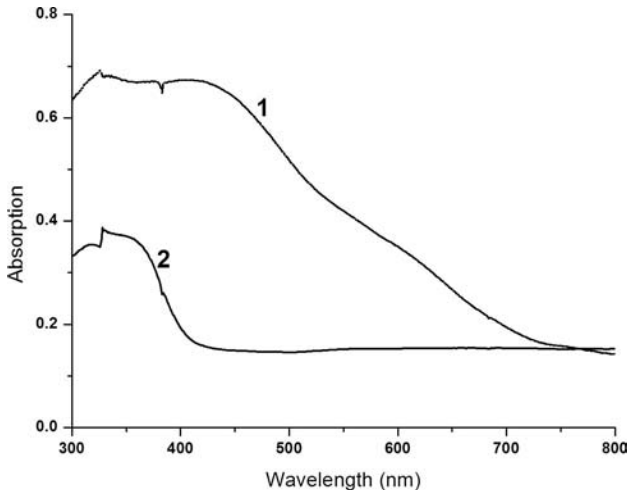

Figure 2. Solid-state absorption spectra of $Cd_8S(SPh)_{15}MeQ$ (**1**) and $[NEt_4]_2[Cd_8S(SPh)_{16}]$ (**2**).

It was reported extensively in the literature that the photophysical properties and composition of QDs are strongly dependent on the nature of surface ligands.[16] The diffuse reflectance excitation and emission spectra of **1** and **2** in the solid state are shown in Figure 4. Comparison shows that the emission from **1** at 484 nm is greatly reduced compared to that of **2** which lies at essentially the same position. This is attributed to quenching effects caused by electron transfers from the excited state to the MeQ$^+$ ligand. Viologens are strong electron acceptors that readily engage in electron transfer reactions[17] and have been shown to form a variety of intra- and intermolecular charge-transfer (CT) complexes with a wide range of donors including halides,[18] ferrocyanide,[19] carboxylate anions,[20] amines,[21] phenols, arenes[22] and calixarenes.[23] Recently, methylviologen have also been used as electron acceptor for CdSe QDs and the fluorescence of QDs can be totally quenched.[10] The calculated results of **1** and **2** show that CT from the nanoclusters to MeQ$^+$ ligand may lead to quenching of the fluorescence.

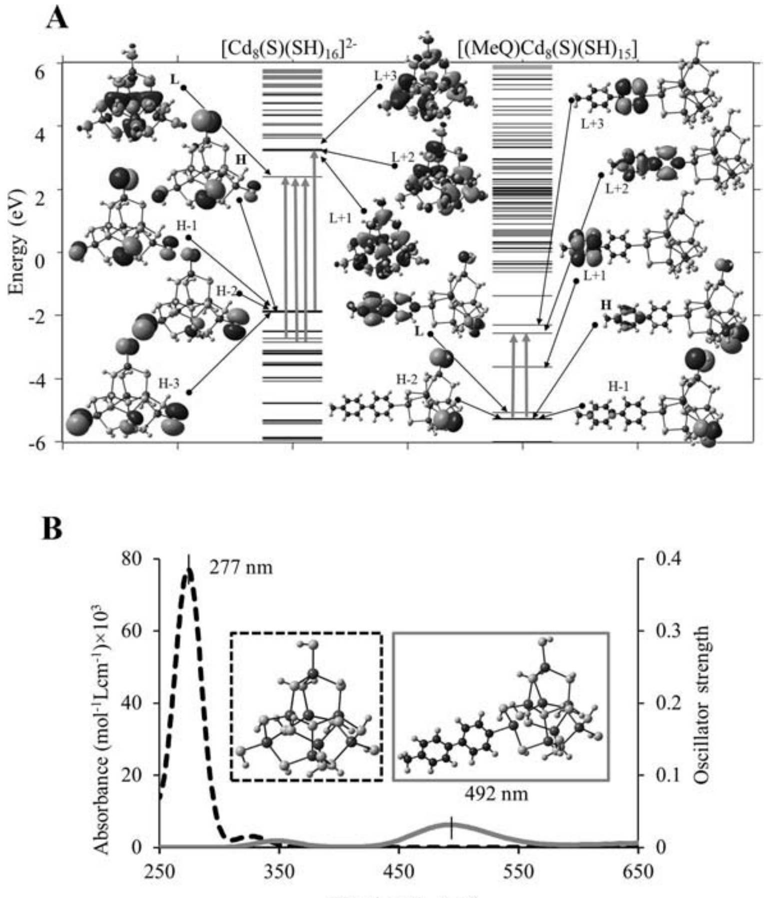

Figure 3. TD-DFT calculated cluster complexes **1** (right) and **2** (left). A: Energy states and electronic transitions. B: Absorption spectra of **1** (solid) and **2** (dotted).

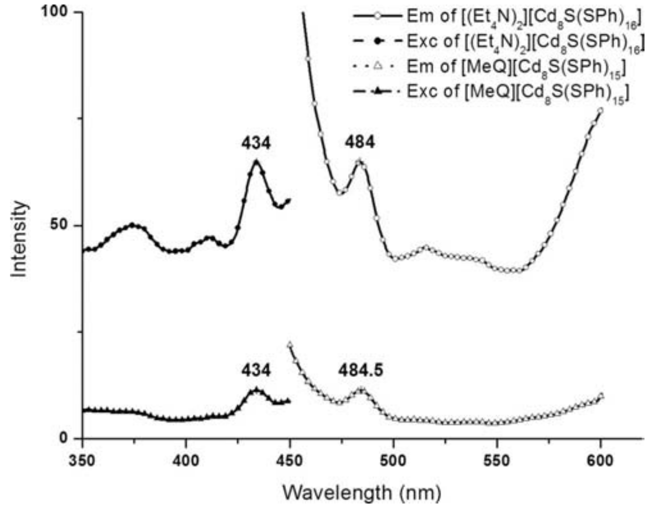

Figure 4. Fluorescence spectra of $Cd_8S(SPh)_{15}MeQ$ (**1**) and $(Et_4N)_2[Cd_8S(SPh)_{16}]$ (**2**).

Conclusions

MeQ^+ has been shown for the first time effectively binding with nanocluster to form a stable CT complex which exhibits dramatically red-shifted UV/Vis absorptions compared to the parent nanocluster, and fluorescence can be greatly quenched by MeQ^+. The complex can serve as an excellent model for understanding electron-transfer dynamics at the organic molecule–nanoparticle interface, which is crucial to the development of many nanoparticle-based photonic devices, especially QD-based solar cells.

Experimental Section

General Remarks: The $Cd(SPh)_2$,[24] $[NEt_4]_2[Cd_8S(SPh)_{16}]$,[25] and [MeQ]I[26] were synthesized according to reported procedures. Other materials were purchased from Alfa Aesar and were used as received. ^1H NMR spectra were recorded on a Mercury 300 spectrometer operating at 300.1 MHz.

Synthesis of $Cd_8S(SPh)_{15}(MeQ)\cdot CH_3CN$ (1): A mixture of $Cd(SPh)_2$ (180 mg, 0.58 mmol), thiourea (50 mg, 0.65 mmol), and [MeQ]I (54 mg, 0.18 mmol) was placed in 5 mL of acetonitrile solvent in a 25 mL flask and stirred for 30 min to form a clear orange solution. The solution was then sealed and left undisturbed for one week. Orange crystals of **1** formed and were separated by filtration and washed with acetone three times;. yield 43% based on $Cd(SPh)_2$. ^1H NMR (300 MHz, DMSO, 333 K): δ = 9.10 (d, 2 H pyridinium), 8.85 (d, 2 H pyridinium), 8.58 (d, 2 H pyridinium), 8.00 (d, 2 H pyridinium), 7.40–7.38 (m, 9 H, thiolate), 7.28–7.26 (m, 18 H, thiolate), 6.89–6.92 (m, 48 H, thiolate), 4.34 (s, 3 H, $-CH_3$); 2.49 (s, acetonitrile) ppm. $C_{103}H_{89}Cd_8N_3S_{16}$ (2780.93): calcd. C 44.48, H 3.22, N 1.51; found: C 44.20, H 3.01, N 1.10.

Photophysical Properties Measurements: Solid-state reflection spectra were measured as micron-sized crystalline powders between quartz plates with Perkin–Elmer Lambda 35 spectrophotometer with 50 mm Labsphere RSA-PE-20 Integrating Sphere. $BaSO_4$ powder was used as 100% reflection reference. Solid state Fluorescence spectra were recorded as micron-sized crystalline powders between quartz plates with Perkin–Elmer LS55 with Front Surface Reflectance accessory. The samples measured are weighed with the same molar amounts and in 4-mm cell under the same measurement conditions.

Crystallographic Analyses: Data were collected by using a Bruker SMART APEX CCD-based diffractometer using Mo-K_α radiation (λ = 0.71073 Å). The raw data frames were integrated with SAINT$^+$ program by using a narrow-frame integration algorithm.[27] Correction for Lorentz and polarization effects were also applied with SAINT$^+$. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied for each analysis by using the program SADABS. All structures were solved by a combination of direct methods and difference Fourier syntheses, and refined by full-matrix least-squares on F^2, using the SHELXTL software package.[28] All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in geometrically idealized positions and included as standard riding atoms during the least-squares refinements. Crystal data, data collection parameters, and results of the refinements are listed in Table 2.

Table 2. Crystallographic data of $Cd_8S(SPh)_{15}(MeQ)\cdot CH_3CN$ (**1**).

Complex	**1**
Empirical formula	$C_{103}H_{89}Cd_8N_3S_{16}$
Formula weight	2780.93
Temperature /K	293(2)
Wavelength /Å	0.71073
Crystal system, space group	monoclinic, $P2_1/n$
Unit cell dimensions *a* /Å	21.4707(8)
b /Å	17.8881(7)
c /Å	28.0447(11)
β /°	90.353(1)
Volume /Å^3	10770.9(7)
Z	4
Calculated density /g cm^{-3}	1.715
Absorption coefficient /mm^{-1}	1.903
F(000)	5472
Theta range for data collection θ /°	2.57–25.35
Reflections collected	117094
Independent reflections	19690 [R_{int} = 0.0425]
Reflections with [$I > 2\sigma(I)$]	14357
Parameters/restraints	1156/4
GooF	0.997
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0439$, $wR2 = 0.1269$
All data	$R1 = 0.0662$, $wR2 = 0.1468$
Largest diff. peak and hole /e Å^{-3}	1.462 and –0.901

CCDC-799804 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational Details: Density-functional theory (DFT)[29] and time-dependent DFT (TD-DFT)[30] calculations at the B3PW91/LANL2DZ/6-31G(*d*) level of theory were performed. This level of theory includes the Becke three-parameter hybrid exchange functional[31] with the Perdew–Wang correlation functional;[32] in addition, a contribution to exchange energy calculated according to Hartree–Fock (HF) but using the Kohn–Sham molecular orbitals instead of the HF ones was used. The Double-Zeta Los Alamos National Laboratory basis set LANL2DZ[33,34] for Cd atoms and the 6-31G(*d*)[35,36] for C, O, S, and H were used. All structures are tested to be local minima and all calculations were performed with the program GAUSSIAN-09.[37]

Acknowledgments

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