Ion Pair Charge-Transfer Salts Based on Metal Chalcogenide Clusters and Methyl Viologen Cations

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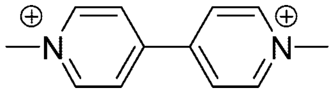
Nanosized, crystalline semiconducting II–VI materials are particularly interesting because of their potential applications in areas such as photocatalysis, electro-optics, chemical sensors, thermoelectrics, and molecular electronics.[1] To develop novel applications, it is desirable to tune the properties of chalcogenide materials through integration of metal-chalcogenide clusters with other optically active species, for example, by spatially organizing clusters with bifunctional organic ligands, or by encapsulating dye molecules within the superlattice of chalcogenide clusters.[2] The synergistic effects resulting from the uniform integration and close proximity of inorganic and organic components can dramatically alter the clusters' properties and allow a new level of control over the electronic or optical properties of chalcogenide clusters.

For a given semiconductor composition, the optical response can be tuned using the quantum confinement effect. For example, an increase in the size of CdS nanoclusters decreases the band gap and allows the optical absorption to red-shift (e.g., Cd-17, 4.26 eV; Cd-32, 3.79 eV; Cd-54, 3.51 eV).[3] However, bulk CdS (2.4 eV, ~520 nm) represents the ultimate limit in such band gap engineering.[4] For applications involving solar energy conversion, materials based on compositions such as CdS usually have low solar conversion efficiency, in part because of the low absorption in red and near-infrared (NIR) parts of the solar spectrum, the region in which the sun emits its maximum flux of photons. Efficiency could be improved by extending the range of the solar spectrum that semiconductor materials are capable of absorbing. This prospect motivates us to design new methods that can modify optical properties of metal chalcogenides, in addition to the earlier methods (e.g., size control and spatial organization) that we have employed.[2]

Scheme 1. Structure of Methyl Viologen Dication (MV^{2+})



It is well-known that upon the formation of charge transfer salts, a dramatically red-shifted absorption usually occurs. Although the charge transfer salts are well-known in various organic donor–acceptor systems, to our knowledge, no charge-transfer salts containing chalcogenide clusters are known so far. Our strategy is to create cluster-based charge transfer salts by integrating crystalline CdS semiconducting metal-chalcogenide clusters (electron-rich) with organic electron acceptors to form ion pair charge-transfer (IPCT) complexes.

Usually, charge-transfer salts (e.g., TTF-TCNQ) contain neutral donors and acceptors. Charge-transfer salts formed between cations and anions (i.e., ion pair charge-transfer or IPCT complexes) as reported here are among an interesting subclass of the donor–acceptor system.[5] Well-known IPCT complexes include those with the general formula $\{A^{2+}[ML_2]^{2-}\}$ (where A = 2,2′- or 4,4′-bipyridinium cations, and $[ML_2]^{2-}$ is a planar metal dithiolene, M = Ni, Pd, Pt, Co, Cu, Zn),[6] none of which, however, contain chalcogenide clusters.

Here, we demonstrate the use of the organic electron-poor cation (methyl viologen dication, abbreviated as MV^{2+} ($C_{12}H_{14}N_2$), Scheme 1) as the electron acceptor to organize metal chalcogenide clusters into IPCT molecular crystals.

All compounds were synthesized either by solution process or under solvothermal conditions. The starting materials metal thiolates ($Cd(SPhMe\text{-}2)_2$ (SPhMe-2 is 2-methylbenzenethiolate), $Zn(SPh)_2$ or $Cd(SPh)_2$), were prepared according to the literature procedure.[7] Thiourea is used as the S^{2-} source, which is essential for the growth of large clusters that require the presence of one or more core S^{2-} sites. These

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(1) (a) Osterloh, F. E. *Chem. Mater.* **2008**, *20*, 35. (b) Corrigan, J. F.; Degroot, M. W. In *The Chemistry of Nanomaterials: Synthesis, Properties and Applications*; Rao, C. N. R., Muller, A., Cheetham, A. K., Eds.; Wiley: Weinheim, Germany, 2004; Vol. 2, pp 418–451. (c) Feng, P.; Bu, X.; Zheng, N. *Acc. Chem. Res.* **2005**, *38*, 293. (d) Bu, X.; Zheng, N.; Feng, P. *Chem.—Eur. J.* **2004**, *10*, 3356. (e) Krebs, B.; Henckel, G. *Angew, Chem. Int. Ed.* **1991**, *30*, 769. (f) Vossmeyer, T.; Reck, G.; Katsikas, L.; Haupt, E. T. K.; Schulz, B.; Farneth, W. E.; Wang, Y. *Science* **1993**, *259*, 1426. (g) Weller, H. *Angew Chem., Int. Ed.* **1996**, *35*, 1079. (h) Weller, H. *Angew Chem., Int. Ed.* **1993**, *32*, 41. (i) Weller, H. *Adv. Mater.* **1993**, *5*, 88. (j) Weller, H. *Adv. Mater.* **1993**, *5*, 88. (k) Hsu, K. F.; Loo, S.; Guo, F.; Chen, W.; Dyck, J. S.;.; Uher, C.; Hogen, T.; Polychroniadis, E. K.; Kanatzidis, M. G. *Science* **2004**, *303*, 818. (l) Li, H.; Laine, A.; O'Keeffe, M.; Yaghi, O. M. *Science* **1999**, *283*, 1145.

(2) (a) Zheng, N.; Lu, H.; Bu, X.; Feng, P. *J. Am. Chem. Soc.* **2006**, *128*, 4528. (b) Zheng, N.; Bu, X.; Lu, H.; Chen, L.; Feng, P. *J. Am. Chem. Soc.* **2005**, *127*, 14990. (c) Zheng, N.; Bu, X.; Lauda, J.; Feng, P. *Chem. Mater.* **2006**, *18*, 4307.

(3) Zheng, N.; Bu, X.; Lu, H.; Zhang, Q.; Feng, P. *J. Am. Chem. Soc.* **2005**, *127*, 11963.

(4) Soloviev, V. N. ; Eichhofer, A.; Fenske, D.; Banin, U. *J. Am. Chem. Soc.* **2001**, *123*, 2354.

(5) Bigoli, F.; Deplano, P.; Mercuri, M. L.; Pellinghelli, M. A.; Pilia, L.; Pintus, G.; Serpe, A.; Trogu, E. F. *Inorg. Chem.* **2002**, *41*, 5241.

(6) (a) Nunn, I.; Eisen, B.; Benedix, R.; Kish, H. *Inorg. Chem.* **1994**, *33*, 5079. (b) Kirsh, H. *Comments Inorg. Chem.* **1994**, *16*, 113. (c) Kirsh, H.; Eisen, B.; Dinnebier, R.; Shankland, K.; David, W. I. F.; Knoch, F. *Chem.—Eur. J.* **2001**, *7*, 738. (d) Kirsh, H. *Coord. Chem. Rev.* **1993**, *125*, 155. (e) Hofbauer, M.; Möbius, M.; Knoch, F.; Benedix, R. *Inorg. Chim. Acta* **1996**, *247*, 147.

(7) (a) Craig, D.; Dance, I. G.; Garbutt, R. *Angew., Chem. Int. Ed.* **1986**, *25*, 165. (b) Sampanthar, J. T.; Vittal, J. J. *J. Chem. Soc., Dalton Trans.* **1999**, 1993.

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charge transfer salts were obtained as intensely red crystals,[8–10] even though all starting materials are either colorless or pale-yellow. The structures were determined from single-crystal X-ray diffraction data collected at 150 K on an APEX II CCD diffractometer.[11–13]

The crystal structure analysis of IPCT 1−3 reveals that these materials are made of tetrahedral clusters and charge-balancing MV^{2+} cations (Figure 1). As reported previously, tetrahedral clusters can be classified into three different series: supertetrahedral clusters (T*n*), capped supertetrahedral clusters (C*n*), and pentasupertetrahedral clusters (P*n*).[1c] For example, the P1 cluster (a typical composition: $[Cd_8S(SPh)_{16}]^{2-}$) is the first member of the P*n* series, whereas the T3 cluster (a typical composition: $[Cd_{10}S_4(SPh)_{16}]^{4-}$) is the third member of the T*n* series. T*n* clusters can be considered as regular tetrahedrally shaped fragments of cubic ZnS type lattice and *n* is the number of metal layers in each cluster.[1k,14] The P*n* clusters can be conceptually constructed by coupling four T*n* clusters (e.g., four CdS_4 T1 clusters) onto each face of antisupertetrahedral clusters (e.g., T-*1*, SCd_4) of the same order. An antisupertetrahedral cluster (e.g., T-1, SCd_4) is defined here as having the same geometrical feature as that of the T*n* cluster (e.g., T1 CdS_4) with the positions of cations and anions being exchanged.

Single-crystal structure analysis shows that IPCT-1 (formula: $[(MV^{2+})(Cd(SPhMe\text{-}2)Cl_3)^{2-}]$, Figure 1a) is an ion-pair charge-transfer complex that employs MV^{2+} as a cation and T1 cluster as an anion. The T1 unit has a central Cd^{2+} ion coordinated to three Cl^- ions and one −SPhMe-2 ligand. The distance of the Cd−S bond is 2.4749 Å and the Cd−Cl bond lengths range from 2.4769 to 2.4882 Å. The deep-red color of crystals together with the dramatically red-shifted UV−vis absorption spectrum suggest that this material is an ion-pair charge-transfer complex.

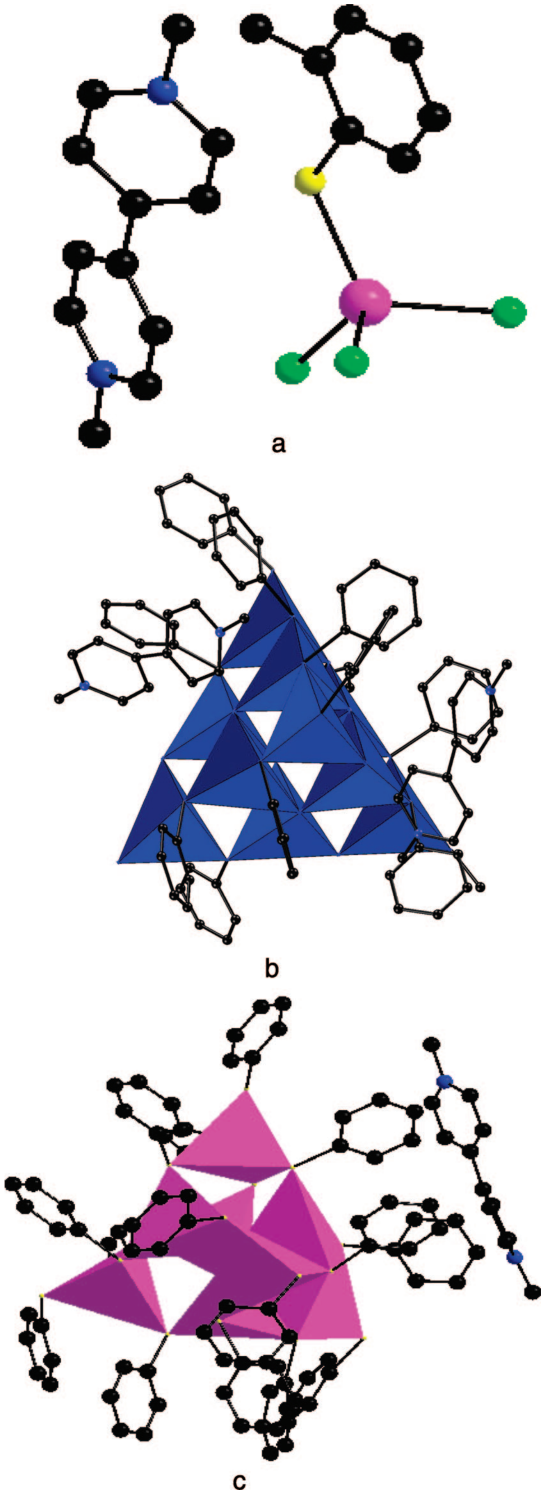

Figure 1. Structures of (a) IPCT-**1**, (b) IPCT-**2**, and (c) IPCT-**3**. (a) Purple, Cd; green, Cl atom; yellow, S atom; blue, N; black, C atom. (b) Blue tetrahedra, ZnS_4. (c) Purple tetrahedra, CdS_4.

The composition of IPCT-2 is $MV_2[Zn_{10}S_4(SPh)_{15}Cl]$, which consists of supertetrahedral T3 clusters, $[Zn_{10}S_4(SPh)_{15}Cl]^{4-}$ (Figure 1b). In a T3 cluster, all metal sites are four-coordinate, but none of the sulfur sites are tetrahedrally coordinated. There are 12 bicoordinated −SPh sites on six edges of each supertetrahedron and four tricoordinated S^{2-} ions on each face of the supertetrahedron.

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(8) IPCT-**1** ($C_{19}H_{21}CdCl_3N_2S$): A mixture of $Cd(SPhMe\text{-}2)_2$ (200mg), $MVCl_2$ (50 mg), DMF (5.0 g), and methanol (5.0 g) was placed in a glass vial and stirred for 1 h to form a clear red solution. The solution was then sealed and kept unstirred for 1 month. The red crystals were filtered and washed with methanol three times. Yield: 55%.

(9) IPCT-**2** ($C_{114}H_{103}Zn_{10}ClS_{19}N_4$): A mixture of $Zn(SPh)_2$ (150mg), thiourea (49mg), $MVCl_2$ (15mg), and acetonitrile (7.0g) were placed in a vial and stirred for 1 h. The vial was then sealed and heated at 85°C for 5 days. After being cooled to room temperature, red crystals were harvested in 45% yield.

(10) IPCT-**3** ($C_{110}H_{97}Cd_8N_3S_{17}$): A mixture of $Cd(SPh)_2$ (180 mg), thiourea (49 mg), $MVCl_2$ (15 mg), and acetonitrile (7.0 g) were placed in a vial and stirred for 30 min to form a clear red solution. The solution was then sealed and kept unstirred for 1 month and the dark-red crystals were obtained in 75% yield.

(11) Crystal data for IPCT-**1** ($C_{19}H_{21}CdCl_3N_2S$): monoclinic, space group $P2_1/n$, $M = 528.19$, $a = 8.23000(10)$Å, $b = 17.8611$ (2)Å, $c = 15.3995$ (2)Å,β= 95.0630 (10)°, $V = 2254.85(5)$Å^3, $Z = 4$, $T = 150(2)$ K, $D_c = 1.556$ g cm^{-3}, $F(000) = 1032$, Mo Kαradiation ($\lambda = 0.71073$Å), $R_1 = 0.0424$ and $wR_2 = 0.1249$, $S = 1.026$.

(12) Crystal data for IPCT-**2** ($C_{114}H_{103}Zn_{10}ClS_{19}N_4$): orthorhombic, space group $P2_12_12_1$, $M = 2827.29$, $a = 18.6605(7)$Å, $b = 18.6586(7)$Å, $c = 33.9833(15)$Å, $V = 11832.3(8)$Å^3, $Z = 4$, $T = 150$ (2) K, $D_c = 1.587$ g cm^{-3}, $F(000) = 5744$, Mo Kαradiation ($\lambda = 0.71073$Å), $R_1 = 0.0976$ and $wR_2 = 0.2627$, $S = 0.976$. Because of the particular geometry of the T3 cluster in IPCT-2, the surface−SPh ligands can adopt more than one energetically similar crystallographic positions, which leads to the crystallographic disorder of these groups and associated high R-factor.

(13) Crystal data for IPCT-**3** ($C_{110}H_{97}Cd_8N_3S_{17}$): monoclinic, space group $P2_1/c$, $M = 2905.13$, $a = 15.2608$ (2)Å, $b = 27.9174$ (5)Å, $c = 26.4792$ (4)Å,β= 110.7760 (10)°, $V = 11043.8$ (3)Å^3, $Z = 4$, $T = 150$ (2) K, $D_c = 1.747$ g cm^{-3}, $F(000) = 5736$, Mo Kαradiation ($\lambda = 0.71073$Å), $R_1 = 0.0574$ and $wR_2 = 0.1477$, $S = 1.030$.

(14) (a) Cahill, C. L.; Ko, Y.; Parise, J. B. *Chem. Mater.* **1998**, *10*, 19. (b) Cahill, C. L.; Parise, J. B. *J. Chem. Soc., Dalton Trans.* **2000**, 1475.

In addition, there are three terminal −SPh groups and one Cl^- ion at four corners of the cluster. In the structure reported here, the charge of each T3 cluster is balanced by two methyl viologen cations. The zinc−sulfur bond lengths are in the range of 2.2612−2.4310 Å.

IPCT-3, $(MV)(CH_3CN)[Cd_8S(SPh)_{16}]$, (Figure 1c) consists of octanuclear cadmium clusters ($[Cd_8S(SPh)_{16}]^{2-}$, P1 cluster) and charge-balancing cations MV^{2+}. Different from the T3 cluster, the P1 cluster has a central S^{2-} anion, which is coordinated to four inner Cd atoms. The central SCd_4 (anti-T1) unit is capped by four CdS_4 (T1) units. All Cd atoms exhibit four-coordinate tetrahedral coordination. The Cd−S bond lengths are in the range of 2.4457−2.6047 Å. The P1-type clusters with various compositions have been found in other metal chalcogenides, however, none of those known in the literature exhibits charge-transfer behavior observed in this work.[15–20]

The diffuse reflectance spectra were recorded on a Shimadzu UV-3101PC double-beam, double-monochromator spectrophotometer by using $BaSO_4$ powder as 100% reflectance reference. As shown in Figure 2, The spectra of IPCT-1, IPCT-2, and IPCT-3 show a broad range of absorption in the visible range from about 400 to 600 nm. The absorption onsets occur at about 650 nm for IPCT-**1**, 760 nm for IPCT-**2**, and 740 nm for IPCT-**3**, which suggest that the band gaps of IPCT-1, IPCT-2, and IPCT-3 were 1.91, 1.63, and 1.68 eV, respectively. For comparison, UV−visible absorptions of methyl viologen dichloride ($MV^{2+}Cl_2$), regular T3 cluster in the form of $TMA_4Zn_{10}S_4(SPh)_{16}$, and regular P1 cluster in the form of $TMA_2Cd_8S(SPh)_{16}$ (TMA = tetramethylammonium) were also measured (Figure 2). None of these three salts are charge-transfer salts and they all show the absorption onsets at much shorter wavelengths: 400 nm for $MV^{2+}Cl_2$, 380 nm for $TMA_4Zn_{10}S_4(SPh)_{16}$, and 350 nm for P1 ($TMA_2Cd_8S(SPh)_{16}$). Clearly, the dramatically red-shifted UV−visible absorption observed in IPCT-**1**, IPCT-**2**, and IPCT-**3** results from the synergistic effect between metal chalcogenide anions and MV^{2+} cations, which is consistent with the formation of charge-transfer salts between chalcogenide anions and MV^{2+} cations.

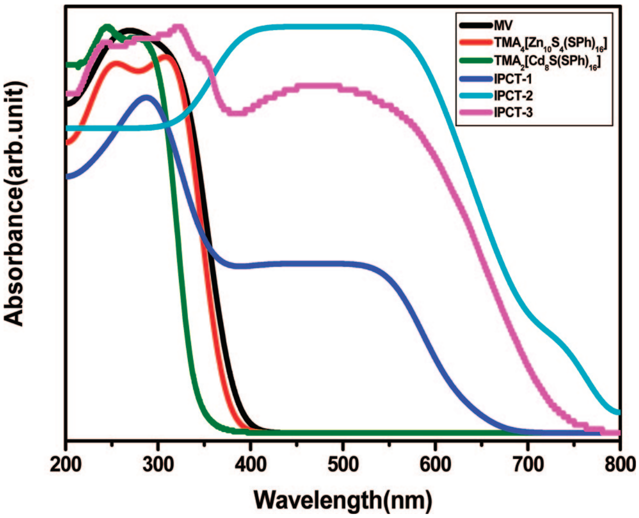

Figure 2. UV−vis absorption spectra of $MVCl_2$ (black line), $TMA_4[Zn_{10}S_4(SPh)_{16}]$ (red line), $TMA_2[Cd_8S(SPh)_{16}]$ (green line), IPCT-1 (blue line), IPCT-2 (cyan line), and IPCT-3 (purple line).

In conclusion, metal-chalcogenide clusters have been shown for the first time to form ion-pair charge-transfer (IPCT) salts with methyl viologen (MV^{2+}). The resulting salts exhibit dramatically red-shifted UV−visible absorptions, which provides a new way to control optical and electronic properties of metal chalcogenides, particularly in relation to their potential applications in the solar spectrum.

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Supporting Information Available: Crystallographic data including positional parameters, thermal parameters, and bond distances and angles (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Lee, G. S. H.; Craig, D. C.; Ma, I.; Scudder, M. L.; Bailey, T. D.; Dance, I. G. *J. Am. Chem. Soc.* **1988**, *110*, 4863.

(16) Lee, G. S. H.; Fisher, K. J.; Craig, D. C.; Scudder, M. L.; Dance, I. G. *J. Am. Chem. Soc.* **1990**, *112*, 6435.

(17) Xie, J.; Bu, X.; Zheng, N.; Feng, P. *Chem. Commun.* **2005**, 4916.

(18) Burth, R.; Gelinsky, M.; Vahrenkamp, H. *Inorg. Chem.* **1998**, *37*, 2833.

(19) (a) Manos, M. J.; Iyer, R. G.; Quarez, E.; Liao, J. H.; Kanatzidis, M. G. *Angew. Chem., Int. Ed.* **2005**, *44*, 3552. (b) Palchik, O.; Iyer, R. G.; Liao, J. H.; Kanatzidis, M. G. *Inorg. Chem.* **2003**, *42*, 5052. (c) Palchik, O.; Iyer, R. G.; Liao, J. H.; Kanatzidis, M. G. *Z. Anorg. Allg. Chem.* **2004**, *42*, 5052.

(20) (a) Zimmerman, C.; Melullis, M.; Dehnen, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 4269. (b) Dehnen, S.; Brandmayer, M. K. *J. Am. Chem. Soc.* **2003**, *125*, 6618. (c) Melullis, M.; Zimmerman, C.; Anson, C. E.; Dehnen, S. *Z. Anorg. Allg. Chem.* **2003**, *629*, 2325. (d) Brandmayer, M. K.; Clerac, R.; Weigend, F.; Dehnen, S. *Chem.—Eur. J.* **2004**, *10*, 5147.