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the degree of anion–cation interaction increases. Similarly, the upfield chemical shift at lower temperatures indicates cation–anion aggregation. The determination of equilibrium constants for ion association is not possible at this point since the limiting δ_i values were not resolved.

Greenbaum and co-workers[3b] have used ^{23}Na NMR measurements to indicate the presence of mobile and bound cations in a siloxane polymer electrolyte. The line width and ^{23}Na T_1 values of the Na[SO$_3$CF$_3$] siloxane(30) complexes correspond closely to their mobile species. No evidence for bound species was obtained in our studies.

Conclusions

These studies have shown that local segmental motion of the polyether chains, as probed by ^{13}C T_1 and line width measure-ments, is influenced by formation of a polymer salt complex. Both ^{13}C chemical shifts and T_1 values indicate that the ether carbons closest to the siloxane backbone are not involved in coordination of the lithium cations. As many workers have shown, the ionic conductivity of polymer salt complexes is strongly influenced by T_g. A correlation between T_1 and T_g substantiates the role of local segmental motion of the polyether chains in the ion transport process. The ^{23}Na NMR spectra of the siloxane(30)–Na[SO$_3$CF$_3$] complexes indicates extensive ion aggregation in these polymer electrolytes.

Temperature-Induced Spontaneous Emission of Uranyl Nitrate Hexahydrate

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Abstract: The spectrum of the temperature-induced spontaneous emission (TSE) from uranyl nitrate hexahydrate, UO$_2$(NO$_3$)$_2$·6H$_2$O, has been recorded for the first time. It was observed as brilliant spark-like flashes in the temperature range 100–135 K on slow cooling and warming of its crystals. The TSE, as well as photoluminescence, originates from the first excited electronic state ($^3\Pi_u$) of the uranyl ion. Each TSE pulse is accompanied by a pulsed electric charge generation between two surfaces of a single crystal. The pulsed charge appears with opposite signs for cooling and warming processes, and in good correlation with the TSE pulse. It is suggested that the internal strain formed in a crystal during the cooling and warming processes causes microcracks, which lead to irregular transient pulses of both TSE and charge generation. The mechanism of excitation of TSE is discussed in detail.

I. Introduction

Characteristic flashes of green light observed on immersing a glass tube containing single crystals of uranyl nitrate hexahydrate (UNH), UO$_2$(NO$_3$)$_2$·6H$_2$O, into liquid nitrogen have been re-ported by several workers.[1] Pant and Bist have suggested that this luminescence is related to development of electric charges in the crystal.[1] We have recently found that the UNH crystal emits light solely by changing its temperature. No external force or irradiation is necessary. In addition, it is observed both for cooling and warming processes in the temperature range 100–130 K. These characteristic features of the temperature-induced spontaneous emission (TSE) are phenomenologically different from analogous phenomena such as triboluminescence (TL), which is the mechanically induced luminescence, or thermoluminescence, which is normally defined as the light emission induced by heating the preirradiated materials containing metastable species.

Triboluminescence has recently attracted renewed attention because of its general importance in materials used for fiber communication and of its possible role in detonations in condensed media.[2-5] Reliable TL spectra of UNH have recently been reported with use of diode array detectors.[3] On the other hand, the spectroscopic features of TSE have never been recorded, obviously due to inherent problems encountered in measuring weak unpredictable flashes of variable intensity during the temperature change.

In the present work, we have measured the TSE spectra of UNH single crystals near 130 K and compared them with the corresponding photoluminescence (PL) spectra. We attempted also to make quantitative measurements on the electric voltage generated across the single crystal for the purpose of finding a correlation with the TSE pulse. On the basis of these results, we discuss the mechanism of the temperature-induced charge sepa-ration (pyroelectricity) and its relation to the TSE excitation in some detail.

II. Experimental Section

A single crystal of UNH was grown by slow evaporation of its slightly acidic solution. It was placed in a quartz tube, evacuated, and sealed with a few mTorr of water vapor to prevent possible dehydration. The bottom part of the quartz tube was immersed in liquid nitrogen, and temperature was controlled by adjusting the level of liquid nitrogen. Temperature measurements were carried out with a calibrated chromel–gold(Fe) thermocouple placed inside the tube. The cooling or warming rate of ca. 6 deg/min was found to be appropriate to observe TSE.

The PL was excited with 440 nm (Coumarine 440, ~1 mJ/pulse) radiation from an excimer-pumped dye laser (Lumonics, Models TE-430 and EPD-330) at 10 Hz. The PL or TSE emission was measured with a 0.25-m polychromator (Nikon, model G-250) equipped with a cooled intensified diode array detector (Tracor Northern, Model TN 6132).

To measure the pyroelectric voltage (V_{PyE}) pulses, thin (0.3 mm) gold-plated copper electrodes were attached by silver paint to the crystal surfaces perpendicular to the hexagonal c axis. The crystal with elec-

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(1) Pant, D. D.; Bist, H. D. *J. Sci. Ind. Res.* **1960**, *19B*, 360.
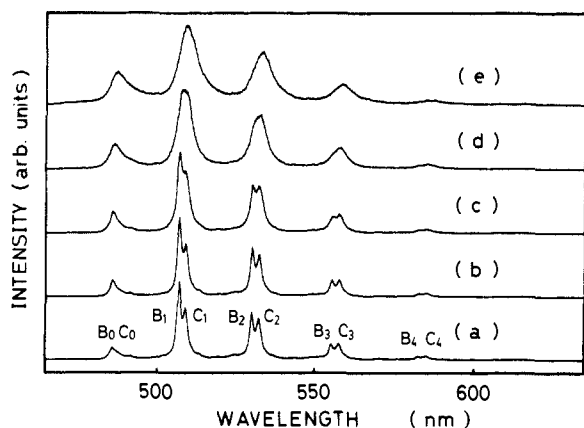(2) Zink, J. I. *Inorg. Chem.* **1975**, *14*, 555.
(3) Sweeting, L. M.; Guido, J. L. *J. Lumin.* **1985**, *33*, 167.
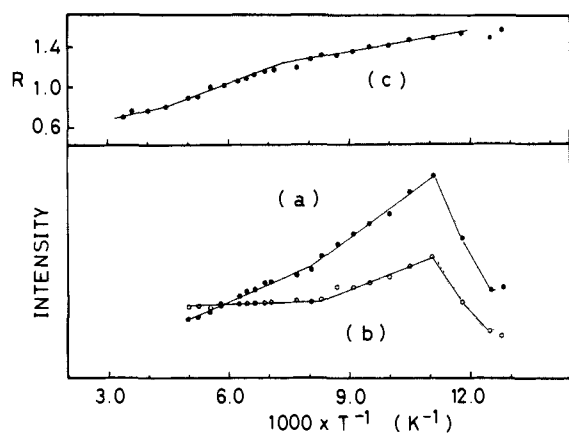(4) Leyrer, E.; Zimmermann, F.; Zink, J. I.; Gliemann, G. *Inorg. Chem.* **1985**, *24*, 102.
(5) Lin, S. H.; Wutz, D.; Ho, Z. Z.; Eyring, H. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 1245.

Figure 1. Photoluminescence spectra of uranyl nitrate hexahydrate excited at 440 nm at various temperatures: (a) 77 K, (b) 90 K, (c) 125 K, (d) 200 K, and (e) 297 K. The instrumental resolution is ~ 10 cm^{-1} (~ 0.25 nm). Base lines have been shifted for clarity.

Figure 3. The temperature-induced spontaneous emission (a) and photoluminescence (b) spectra of uranyl nitrate hexahydrate taken at ~ 130 K under the same experimental condition. The instrumental resolution is ~ 200 cm^{-1} (~ 5 nm).

Figure 2. Temperature dependence of the photoluminescence spectra of crystalline uranyl nitrate hexahydrate. Curves a and b are the relative peak intensities $I(B_1)$ and $I(C_1)$ of the B_1 and C_1 bands, respectively, taken at the peak positions at 77 K. Curve c denotes the variation of ratio R ($=I(B_1)/I(C_1)$) with temperature. The sudden drop of intensities below 90 K may be unreliable due to the liquid nitrogen level interfering with the emission measurement.

trodes was placed in a quartz tube in the same manner as in the TSE measurement. Signal was taken by thin leadwires out of the tube, which were terminated by a 100 kΩ load resistor. The luminescence pulses (V_{TSE}) appearing across the photomultiplier load were also measured simultaneously on a two-channel storage oscilloscope to examine the time correlation between V_{PyE} and V_{TSE}.

III. Results

A. Photoluminescence (PL). Typical PL spectra are given in Figure 1. They are essentially the same as those previously reported and assigned to the $^3\Pi_u \rightarrow {}^1\Sigma_g^+$ transition in the UO_2^{2+} ion.[1,6] The B series in Figure 1 is due to the totally symmetric ν_1 mode (868 cm^{-1}) in the ground state of the UO_2^{2+} ion and the C series is due to a superposition of the asymmetric U–O bond-stretching mode ν_3 (945 cm^{-1}) on each false ν_1 origin.[7]

The ratio R of the intensities at the B and C bands [$I(B)/I(C)$] is plotted against $1/T$ in Figure 2 (curve c). A regular enhancement in R with decreasing temperature is seen in the range 130–200 K. The slope of R changes around 130 K and remains constant for 100–130 K, where TSE is observed. This observation would suggest a change of the immediate environment of the UO_2^{2+} ion in this temperature range.

B. The Temperature-Induced Spontaneous Emission (TSE). The TSE spectrum of UNH is given in Figure 3a. Brilliant flashes observed in the crystal are mainly responsible for the spectrum. The flashes were observed for a freshly prepared transparent
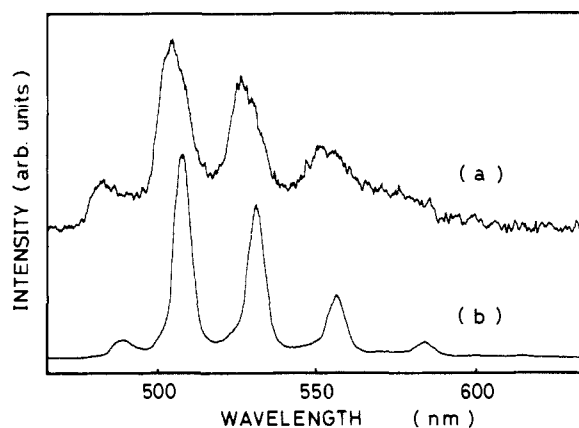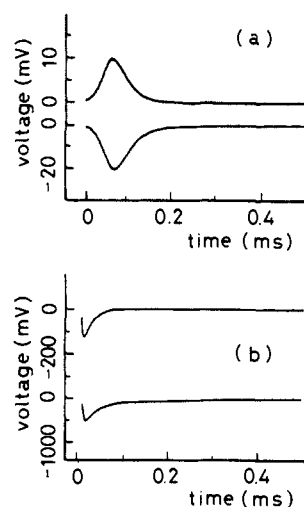
Figure 4. Pyroelectric voltage (top), V_{PyE}, and TSE voltage (bottom), V_{TSE}, recorded simultaneously from a single crystal of uranyl nitrate hexahydrate during (a) cooling and (b) warming processes in the temperature range 100–135 K.

crystal and lasted for several cooling and warming cycles in the temperature range 100–130 K. Then the crystal became opaque gradually and lost the ability for TSE. The opacity seems to be due to microcrack formation after repeated cooling and warming. The following observations are noted:

(i) A comparison of a and b in Figure 3 reveals that, except for a small blue shift, the general features of the TSE spectrum are the same as those of PL. It is therefore assigned to the $^3\Pi_u \rightarrow {}^1\Sigma_g^+$ transition in the UO_2^{2+} ion.

(ii) Figure 3 shows that the main peaks in the TSE spectrum are blue shifted by 180 cm^{-1} with respect to those of the PL spectrum. There is about a 70-cm^{-1} blue shift of the PL peaks on going from 297 to 130 K. The additional blue shift of ~ 180 cm^{-1} at ~ 130 K on going from the PL to TSE spectra must be a characteristic feature of the TSE phenomenon.

(iii) The PL spectra recorded after measuring the TSE spectra showed little evidence for blue shift, excluding the possibility of any irreversible change in the crystal to account for the blue shift.

C. The Pulsed Voltages due to Pyroelectricity (V_{PyE}) and TSE (V_{TSE}). To comprehend the TSE mechanism, the time profile of the pyroelectric voltage V_{PyE} was measured during the cooling and warming cycles and compared with the TSE pulse measured as a voltage V_{TSE} across the photomultiplier load. Typical voltage displays are given in Figure 4a (cooling) and Figure 4b (warming). The peak values of V_{PyE} and V_{TSE} and the rise and decay times τ_R and τ_D, respectively, are summarized in Table I for typical cooling and warming cycles. The following features are noteworthy:

(6) McGlynn, S. P.; Smith, J. K. *J. Mol. Spectrosc.* **1961**, *6*, 164.
(7) Bist, H. D. et al. (to be published).

Table I. Typical Pulse Characteristics for the Pyroelectric Voltage (V_{PyE}) and TSE Voltage (V_{TSE}) for a Single Crystal of Uranyl Nitrate Hexahydrate during Cooling and Warming Processes around 130 K

process	PyE			TSE		
	V^a	$\tau_R{}^b$	$\tau_D{}^c$	V^a	$\tau_R{}^b$	$\tau_D{}^c$
cooling	+10	25	40	−20	25	40
warming	−130	5	20	−500	5	30

[a] Peak voltage in units of mV. [b] Rise time in units of μs. [c] Decay time in units of μs.

(i) The pyroelectric pulses of varying peak voltages are observed in the whole range of temperature (100–135 K) where TSE has been noticed. The sign of V_{PyE} is reversed for cooling and warming processes.

(ii) The V_{PyE} and V_{TSE} pulses are coincident with each other; they reach the peak at the same time within experimental error, and the peak voltages and the rise and decay times vary in parallel.

(iii) Appreciable pulse-to-pulse variations were observed both for τ_R (5–50 μs) and τ_D (20–60 μs) for V_{PyE} and V_{TSE}.

(iv) In addition to the correlation between V_{PyE} and V_{TSE}, τ_R and τ_D are also correlated with each other both in PyE and TSE, namely, a longer τ_R is followed by a longer τ_D, and vice versa.

IV. Discussion

A. Internal Stress and Pyroelectricity. It has been shown that TSE can be observed by slow cooling and warming. A sudden cooling or warming of a crystal was not effective. It occurs in a narrow range of temperature between 100 and 135 K where the temperature gradient of the intensity ratio R in PL differs from that of the high-temperature region. In addition, it is a reversible phenomenon for cooling and warming processes, although a crystal tends to become opaque after repeated cooling and warming. Microcracks could be formed due to the internal stress caused by temperature change, or they could accompany the phase transition. Although we have presently no direct evidence for the latter, the behavior of R mentioned above would suggest the possibility of a second-order phase transition in this temperature range. This point will be discussed elsewhere in more detail.[7]

At room temperature, UNH is known to be piezoelectric with a noncentrosymmetric space group $Cmc2_1$.[8] Such a crystal exhibits piezoelectricity on application of mechanical force in a certain direction. The crystal of this symmetry could also exhibit pyroelectricity which is defined as charge development across the crystal during the temperature change.

In the present case, the pure pyroelectric mechanism could be excluded for the following reasons; we have observed no voltage for the periods between the successive pulse signals. This means that slowly developing charges are neutralized by ions adsorbed on the crystal surfaces (as normally experienced in the case of pyroelectric light detectors). The appearance of pulsed voltage should then be due to some sudden change in the crystal. However, it is difficult to devise any mechanism which leads to a sudden temperature rise and fall accounting for the observed PyE pulses with opposite signs. On the other hand, the temperature change could also induce the piezoelectric charge since it causes an anisotropic internal stress in the UNH crystal (the "false" pyroelectricity). In this model, the most plausible mechanism accounting for the sudden change would be the formation of microcracks which reduces the internal stress and, thereby, polarization inside the crystal. This instantaneous change leaves the adsorbed ions on the surfaces, giving rise to the voltage pulse which decays as the surface charge discharges through the crystal (see section B below). The scheme could also account for the observation of opposite signs of V_{PyE} for cooling and warming processes, since the direction of stress and hence the sign of initial polarization are opposite for cooling and warming. It also accounts for the fact that the crystal becomes opaque and shows no TSE after repeated cooling and warming. Probably the crystal, which is opaque due to microcracks, cannot produce sufficient internal

stress anymore. On the other hand, the opposite signs of V_{PyE} can hardly be understood on the basis of the (pure) pyroelectricity combined with the microcrack formation, since it would release the strain energy and result in local temperature rise both for cooling and warming processes, which should give rise to pulses with the same sign for both processes. Therefore we can conclude that the piezoelectricity coupled with the internal stress caused by temperature change is responsible for the observed charge separation.

B. Excitation Mechanism. Little has been discussed so far on the mechanism of excitation of TSE. In the following, we shall discuss some of the mechanisms proposed so far for TL[4,5] and examine their applicability to TSE.

The intramolecular distortion mechanism has been suggested for some organic systems emitting TL at room temperature.[9,10] This mechanism assumes that the internal stress causes appreciable deformation of $UO_2{}^{2+}$ in the direction of one or more normal modes. If a particular deformation leads to the crossing of the potential curves of the ground and $^3\Pi_u$ states, the latter has a chance to be populated when the stress is removed and the molecule returns to its initial structure. Zink has discussed the possibility of applying this mechanism to TL of UNH and concluded that a reasonable range of the distortion of the stretching bond of $UO_2{}^{2+}$ would be insufficient to allow the highest occupied molecular orbital (π_g) to cross the lowest unoccupied molecular orbital (δ_u). It is also difficult with this model to understand the simultaneous building up of the charge separation and TSE.

The development of charge separation across the crystal suggests the possibility of discharge-excited luminescence from $UO_2{}^{2+}$. The necessity of evacuation for TSE to be observed and the occasional observation of glow-like emission would be in favor of this mechanism. The role of charged microcrack surfaces inside a crystal has been emphasized by Zink in the discussion of TL.[11,12] He derived kinetics for the creation and annihilation of charged crack surfaces. In deriving the temporal behavior of TL emission,[13] he assumed implicitly a rapid radiative lifetime of emitting species and explained the temporal behavior of TL as determined by that of cracks. This model could account for the observed behavior of V_{TSE} and V_{PyE}.

In the present case, a slow building up of internal stress due to temperature change causes the charge separation through the piezoelectric effect. As discussed above, these charges are likely compensated by ions adsorbed on the surfaces since no voltage has been observed for the periods between the successive PyE signals. Probably the rate of charge neutralization due to the adsorbed molecular ion from the outer atmosphere is faster than that of charge creation inside a crystal. After the strain increases to some threshold value, microcracks are formed in the crystal, causing the reduction of stress. The bulk polarization in the crystal decreases suddenly leaving the ions on the outer surfaces, which lead to the pulsed voltage between the electrodes. The surface charges will partially be neutralized by the discharge through the measuring circuit, which is detected as a voltage pulse (V_{PyE}), while remaining charges appear at the microcrack surfaces and are neutralized by a discharge across the microcrack. This internal discharge through microcracks should excite the $UO_2{}^{2+}$ ion near the crack surfaces through electron bombardment and/or UV irradiation.

It would be of some interest to examine the relative energy consumed internally to that consumed in the measuring circuit; the energy E observed as V_{PyE} is calculated as

$$E = \int (V_{PyE}^2/R) \, dt \approx (V_0^2/R)\tau$$

where $R = 100$ kΩ is the load resistance for the PyE measurement, V_0 is the peak PyE voltage, and τ is the half-width of the PyE pulse. Typical values $V_0 \sim 10$ mV and $\tau \sim 70$ μs give $E \sim 7$

(8) Taylor, J. C.; Mueller, M. H. *Acta Crystallogr.* **1965**, *19*, 536.

(9) Robinson, G. W. *J. Chem. Phys.* **1967**, *47*, 1967.
(10) Zink, J. I.; Kaska, W. C. *J. Am. Chem. Soc.* **1973**, *95*, 7510.
(11) Zink, J. I. *J. Am. Chem. Soc.* **1974**, *96*, 6775.
(12) Zink, J. I. *Naturwissenschaften* **1981**, *68*, 507.
(13) Chandra, B. P.; Zink, J. I. *Phys. Rev.* **1980**, *B21*, 816.

$\times 10^{-14}$ J. If this energy is converted completely into visible photons (energy $\sim 4 \times 10^{-19}$ J), the total number of photons is $7 \times 10^{-14}/4 \times 10^{-19} \sim 2 \times 10^5$. Taking account of the light collection efficiency (~ 0.004), the number of photons collected per diode array channel is ~ 0.8, which could hardly be detected. Considering also the efficiency of energy conversion from discharge to emission, the energy consumed for the excitation of TSE should be several orders of magnitude higher than E estimated above. Namely, most of the electrical energy must be used in the internal discharge across the microcracks.

The rise and decay times and pulse width of V_{TSE} exhibit a pulse-to-pulse variation in synchronism with V_{PyE}. The fastest decay time of TSE ($\sim 20 \mu s$) is shorter than the normal decay time (~ 0.7 ms) for PL.[14] These facts indicate that the excited state involved in TSE must have a much faster decay rate than that in PL. Generally the PL emission from UO_2^{2+} shows no dependence on the excitation wavelength;[15] i.e., there is no possibility of emission from vibrationally excited $^3\Pi_u$ state. Therefore the shorter lifetime of TSE cannot be explained on this basis. The most plausible explanation for this would be that the UO_2^{2+} ions near the crack surface are involved in TSE where the environment of the ions is different from that in the bulk and results in a faster nonradiative decay from the vibrationless $^3\Pi_u$ state. The blue shift of the TSE spectrum with respect to the PL spectrum should also be due to the unusual environment near the crack surfaces.

C. Summary. We have shown that TSE observed for a single crystal of UNH has the same spectroscopic origin as photoluminescence ($^3\Pi_u \rightarrow {}^1\Sigma_g^+$ transition in UO_2^{2+}) with a remarkable blue shift. Simultaneous time-resolved measurements of the TSE and PyE pulses have established the correlation between the luminescence and the electric charge separation. The piezoelectricity coupled with microcrack formation has been revealed to be the main cause for the temperature-induced charge separation. It has also been suggested that the charge neutralization across the microcrack is most probably responsible for the TSE excitation. This mechanism is essentially the same as that proposed so far for TL, except that the stress is not caused by an external force but caused internally by temperature change. We hope that the present investigation would reveal not only the mechanism of TSE and charge separation accompanied but also some further details of the TL phenomenon. We have also suggested the possibility of phase transition involved in the process. Further investigation on the crystal structure and thermal measurements would clarify this point.

(14) Leung, A. F. *J. Phys. Chem. Solids* **1982**, *43*, 467.
(15) Dieke, G. H.; Duncan, A. B. F. *Spectroscopic Properties of Uranium Compounds*; McGraw Hill: New York, 1949.

Surface Derivatization and Isolation of Semiconductor Cluster Molecules

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Abstract: We describe a synthesis of nanometer-sized clusters of CdSe using organometallic reagents in inverse micellar solution and chemical modification of the surface of these cluster compounds. In particular we show how the clusters grow in the presence of added reagents and how the surface may be terminated and passivated by the addition of organoselenides. Passivation of the surface allows for the removal of the cluster molecules from the reaction medium and the isolation of organometallic molecules which are zinc blende CdSe clusters terminated by covalently attached organic ligands. Preliminary cluster characterization via resonance Raman, infrared, and NMR spectroscopy, X-ray diffraction, transmission electron microscopy, and size-exclusion chromatography is reported.

Large inorganic cluster molecules are interesting as representatives of a state of matter intermediate between molecules and crystalline solids.[1] The differences are especially evident in molecules that are fragments of the lattice of infinite solid-state compounds.[2] Recent studies of bare semiconductor crystallites (stabilized as colloids) have described electronic properties that depend on the size of the colloidal particles[3] and have thereby yielded insight into the transition from the molecular regime to the solid state. It is important for further examination of this transition to be able to prepare and isolate true molecules of the semiconductor solid that are size-selected, having from 100 to 10^4 atoms, are soluble in convenient solvents, and are chemically protected from growth and aggregation into bulk solids.

Colloids of II–VI crystallites small enough (≤ 50 Å) to have incomplete band structure were first prepared by arrested precipitation in homogeneous solution.[3] Better size control and dispersion stability were achieved by arrested precipitation in structured media (zeolites, inverse micelles, polymer films, etc.).[4]

(1) (a) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 56. (b) Fenske, D.; Ohmre, J.; Hachgenei, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 993. (c) Sola, J.; Do, Y.; Berg, J. M.; Holm, R. H. *Inorg. Chem.* **1985**, *24*, 1706–13.
(2) Vargaftik, M. N.; Zagorodnikov, V. P.; Stolyarov, I. P.; Moiseev, I. I.; Likholobov, V. A.; Kochubey, D. I.; Chuvilin, A. L.; Zaikovsky, V. I.; Zamaraev, K. I.; Timofeeva, G. I. *J. Chem. Soc., Chem. Commun.* **1985**, 937. (b) Dance, I. G.; Choy, A.; Scudder, M. L. *J. Am. Chem. Soc.* **1984**, *106*, 6285. (c) Dance, I. G. *Polyhedron* **1986**, *5*, 1037.
(3) (a) Brus, L. E. *J. Phys. Chem.* **1986**, *90*, 255. (b) Brus, L. E. *New J. Chem. (France)* **1987**, *11*, 123.

(4) (a) Meyer, M.; Wallberg, C.; Kurihara, K.; Fendler, J. H. *J. Chem. Soc., Chem. Commun.* **1984**, 90. (b) Fendler, J. H. *Chem. Rev.* **1987**, *87*, 877. (c) Llanos, P.; Thomas, J. K. *Chem. Phys. Lett.* **1986**, *125*, 299. (d) Daunhauser, T.; O'Neil, M.; Johansson, K.; Whitten, D.; McLendon, G. *J. Phys. Chem.* **1986**, *90*, 6074. (e) Pileni, M. P., private communication, 1986. (f) Wang, Y.; Herron, N. *J. Phys. Chem.* **1987**, *91*, 257.