concentrations of Na_2S. The scavenging of the hole increases significantly the lifetime of conduction-band electrons resulting in a higher efficiency of interfacial electron transfer to MV^{2+}.

Direct observation of hole transfer from the valence band of a colloidal CdS particle to a solution species is possible when *N*-methyl-2-(carboxymethyl)phenothiazine (MCPTH) is employed as an electron donor.
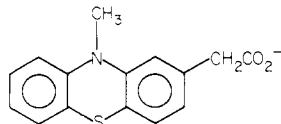
This compound adsorbs strongly to the surface of CdS particles. Its redox potential is 0.69 V (vs. NHE) and the one-electron oxidation product (MCPTH$^+$) has a characteristic absorption with a maximum at 530 nm.[32]

Upon 532-nm laser excitation of colloidal CdS (2×10^{-3} M analytical concentration, pH 6) in the presence of 10^{-3} M MCPTH, one observes formation of a transient whose absorption features are identical with those of the MCPTH cation radical. The appearance of this transient is very fast and follows essentially the time profile of the laser pulse. By use of an extinction coefficient for the cation radical of 9900 M^{-1} cm^{-1}, the concentration of MCPTH$^+$ present after the laser pulse was evaluated as 10^{-7} M.

We were interested in checking whether the yield of MCPTH$^+$ could be increased by depositing a small amount of hole-transfer catalyst, i.e., RuO_2, onto the particle surface.[6,27] The experiment was therefore repeated with CdS particles having a loading of 1% RuO_2.[33] A striking increase in the yield of MCPTH$^+$ was ob-

served that was at least 10 times higher than that obtained in the absence of RuO_2. This experiment provides unambiguous evidence for the acceleration of interfacial hole transfer by the RuO_2 deposit. We have proposed earlier that such a catalytic effect is the basis of light-induced water decomposition observed with CdS dispersions loaded simultaneously with RuO_2 and Pt.[6,27]

Conclusion

This is the first direct observation of the dynamics of interfacial electron- and hole-transfer processes from colloidal semiconductors to electron donors and acceptors in solution. A first result emerging from the present study concerns the solid-state characteristics of these particles. Despite their minute size and amorphous character, they exhibit band structure similar to the macroscopic and crystalline material. This manifests itself by distinct absorption and emission features and the fact that selective oxidation or reduction reactions can be performed with valence-band holes and conduction-band electrons, respectively, after light excitation of the particle. Important information on the dynamics of interfacial electron transfer has been obtained, which to a large extent is determined by the match of electronic levels of donor and acceptor states separated by the semiconductor/water interface. From these studies the position of the conduction or valence band of a colloidal semiconductor particle can be obtained that may deviate significantly from the value obtained for macroelectrodes. Work involving a series of different electron donors and acceptors is now in progress. This should yield a wealth of information on the detailed mechanism of charge-transfer processes across the semiconductor/electrolyte interface.

Registry No. TiO_2, 13463-67-7; CdS, 1306-23-6; BDH, 4685-14-7.

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(32) These measurements have been performed by Dr. D. Serve, visiting scientist from the University of Grenoble, France, in our laboratory and will be published shortly.

(33) The deposit of RuO_2 was produced by adding a solution of RuO_4 to the CdS dispersion as described in ref 6 and 27.

Microscopic Environment of Poly(styrenesulfonate) Macroanions. Emission and Absorption Spectra, Lifetime, and Depolarization Measurements of a Cationic Fluorescence Probe under High Pressure

Nicholas J. Turro and Tsuneo Okubo*[1]

Contribution from the Department of Chemistry, Columbia University, New York, New York 10027. Received August 3, 1981

Abstract: The absorption and fluorescence spectra, lifetimes, and fluorescence depolarizations of a cationic fluorescence probe, (11-(3-hexyl-1-indolyl)undecyl)trimethylammonium bromide, have been measured in the presence of poly(styrenesulfonate) macroanions. The probe is found to be strongly associated with the macroanions in an environment whose apparent microviscosity is ca. 150 cP. It is concluded that the hydrophobicity and viscosity experienced by the probe associated with poly(styrenesulfonate) ions are extremely high compared with those of the probe associated with typical micelles formed from ionic detergents.

Sodium poly(styrenesulfonate) (NaPSS) is a strongly hydrophobic synthetic macroanionic polymer. The chemical structure of this polyelectrolyte is well characterized and is quite simple when compared with polyelectrolytes that compose biomolecules. Knowledge of the physicochemical properties of NaPSS in solution may be helpful for the understanding of the fundamental aspects

of solutions of more complex biomolecules. Many thermodynamic and kinetic studies on NaPSS in which hydrophobic interactions were found to be very important in the determination of solution properties have been reported;[2] i.e., electrostatic interactions alone

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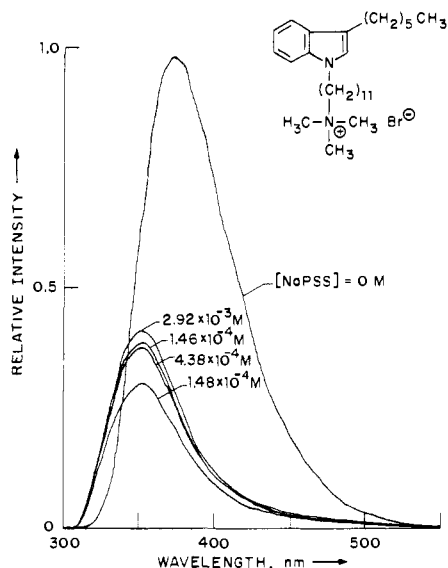(1) Department of Polymer Chemistry, Kyoto University, Kyoto, Japan.

Figure 1. Fluorescence spectra of 6-In-11$^+$ in the presence of NaPSS at 25 °C. Polymer concentration dependence. [6-In-11$^+$] = 2 × 10^{-5} M excited at 290 nm.

Table I. Fluorescence Lifetime, Molecular Anisotropy, and Microviscosity of 6-In-11$^+$ in the Presence and Absence of NaPSS at 25 °C^a

[NaPSS], M	λ_{max}, nm	τ, ns	r	η, cP
0	374	15.3	0	1
1.46 × 10^{-4}	353	6.2	0.016	160
4.38 × 10^{-4}	352	6.2	0.014	140
1.46 × 10^{-3}	351	6.2	0.015	150
2.92 × 10^{-3}	350	6.2	0.016	160
7.15 × 10^{-3}	350	6.2	0.015	150

^{a} [6-In-11$^+$] = 2 × 10^{-5} M.

Table II. Fluorescence Lifetime, Molecular Anisotropy, and Microviscosity of 6-In-11$^+$ in the Presence of NaPSS under High Pressure at 25 °C^a

	[NaPSS], M	pressure, bar				
		1	450	990	1540	2070
τ, ns	0	15.2	16.3	16.5	17.1	16.9
	7.15 × 10^{-4}	6.1	6.4	6.3		6.9
	1.46 × 10^{-3}	6.3	6.6	6.4		6.7
r	1.46 × 10^{-3}	0.015	0.014	0.017	0.018	0.017
η, cP	1.46 × 10^{-3}	150	150	180	190	180

^{a} [6-In-11$^+$] = 2 × 10^{-5} M.

Table III. Temperature Dependence of Fluorescence Lifetime, Molecular Anisotropy, and Microviscosity of 6-In-11$^+$ in the Presence of NaPSS^a at Atmospheric Pressure

	temperature, °C					
	10	17	25	33	40	48
τ, ns	6.8	6.5	6.2	6.1	5.4	4.9
r	0.014	0.021	0.015	0.018	0.024	0.026
η, cP	150	230	150	180	230	230

^{a} [NaPSS] = 1.46 × 10^{-3} M.

were insufficient to understand the results. However, most of these investigations were concerned with macroscopic properties. Reports probing the microscopic properties of polyelectrolytes are few. A luminescence probe[3] provides a very convenient method of obtaining the information about the microenvironment of molecular assemblies such as micelles, membranes, and liquid crystals. For example, the emission parameters of ionic aromatic molecules such as 1-anilinonaphthalene-4-sulfonate (ANS) display a high sensitivity toward environmental polarity.[3]

Recently, we synthesized a series of fluorescent probes including (11-(3-hexyl-1-indolyl)undecyl)trimethylammonium bromide (6-In-11$^+$).[4] The fluorescence maximum (λ_{max}) and the lifetime (τ) of this probe were found to be very sensitive to the environmental polarity; i.e., λ_{max} and τ are 374 nm and 16 ns, respectively, in pure water but shift to 350 nm and 4–8 ns in detergent solutions.[4,5]

In the present report, we have investigated the microenvironment of poly(styrenesulfonate) anions by employing 6-In-11$^+$ as a fluorescent probe.

Experimental Section

Materials. (11-(3-Hexyl-1-indolyl)undecyl)trimethylammonium bromide was available from previous studies.[4] Sodium poly(styrenesulfonate) (NaPSS, a gift of Dr. H. Gregor, Columbia University, molecular weight = 4 × 10^5) was purified by dialysis against deionized pure water for 2 weeks and then by ion-exchange chromatography with cation and anion ion-exchange resin columns. The molar extinction coefficient at 262 nm was 403.

Spectroscopy under High Pressure. Absorption and fluorescence spectra were measured on Cary 18 and Spex Fluorolog spectrophotometers, respectively. Fluorescence decay was measured by the single photon counting technique.[5] Fluorescence depolarization was obtained on a Spex Fluorolog provided with a polarization accessory. The fluorescence intensities were corrected following the method of Azumi and McGlynn.[6] The evaluation of the apparent microviscosity (η) was done by using eq 1 from measurements of the molecular anisotropy (r).[7,8]

$$r^{-1} = r_0^{-1}(1 + k\tau T/\eta V) \qquad (1)$$

(2) See, for example: (a) Rice, S. A.; Nagasawa, M. "Polyelectrolyte Solutions"; Academic Press: New York, 1961. (b) Ise, N. "Polyelectrolyte and Their Applications", Selegny, E., Rembaum, A., Eds., Dordrecht-Holland: D. Reidel, 1975. (c) Skerjanc, T.; Dolar, D.; Leskovsek, D. *Z. Phys. Chem. (Frankfurt am Main)* **1967**, *56*, 207, 218; **1970**, *70*, 31. (d) Okubo, T.; Ise, N. *J. Am. Chem. Soc.* **1973**, *95*, 2293, 4031.

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(5) Turro, N. J.; Tanimoto, Y. *Photochem. Photobiol.* **1981**, *34*, 173.

(6) Azumi, T.; McGlynn, S. P. *J. Chem. Phys.* **1962**, *37*, 2413.

In eq 1 r_0 is the limiting molecular anisotropy when $T/\eta \rightarrow 0$; k and T have the usual meanings. τ is the fluorescence lifetime and V denotes the molecular volume of 6-In-11$^+$ ($r_0 = 0.1$, $V = 3.0 \times 10^{-24}$ cm^3/molecule).[5] The details of the high-pressure cell were described in a previous paper.[9]

Results

Fluorescence and Absorption Spectra. The fluorescence maximum, λ_{max}, of 6-In-11$^+$ in aqueous solution (Figure 1) undergoes a shift to shorter λ_{max} upon NaPSS addition, i.e., from 374 nm in water to 351 nm upon addition of NaPSS. This shift in λ_{max} indicates that the probe experiences a strongly hydrophobic environment when it becomes associated with PSS macroions. It was noted that for concentration of NaPSS lower than 1 × 10^{-5} M, precipitation occurred. It is seen (Figure 1) that the intensity of fluorescence decreased significantly with initial addition of NaPSS and then increased slightly with further addition. The reason for the initial decrease is not yet clear. In part, this may be due to the quenching with a trace of coexisting impurities, though the polymer was purified as completely as possible.

The influence of high pressure on the fluorescence spectra is demonstrated in Figure 2. Within the experimental error, the λ_{max} value does not shift with pressure from one to 2000 bar. The fluorescence intensity was relatively insensitive to applied pressure, decreasing very slightly (3–11% decrease at 2070 bar).

Figure 3 shows the absorption spectra of 6-In-11$^+$ in the presence of NaPSS. The optical density associated with the probe increased with NaPSS concentration, a result consistent with an

(7) Shinitzky, M.; Dianoux, A. C.; Gitler, C.; Weber, G. *Biochemistry* **1971**, *10* 2106.

(8) We used here the formula (eq 1) of an isotropic rotation as our probe following previous work (see ref 5). Although 6-In-11$^+$ is a long molecule, the actual spatial structure is likely to be near spherical or ellipsoidal because of folding or association of the long hydrocarbon group with itself or other groups as a result of strong hydrophobic forces.

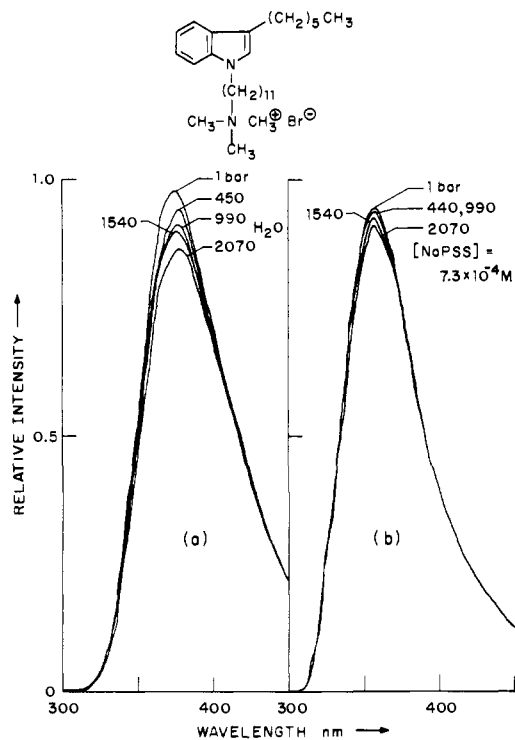(9) Turro, N. J.; Okubo, T. *J. Am. Chem. Soc.*, in press.

Figure 2. Fluorescence spectra of 6-In-11⁺ in the presence (a) and absence (b) of NaPSS at 25 °C. Pressure dependence. [6-In-11⁺] = 2 × 10⁻⁵ M, [NaPSS] = 7.3 × 10⁻⁴ M. excited at 290 nm.
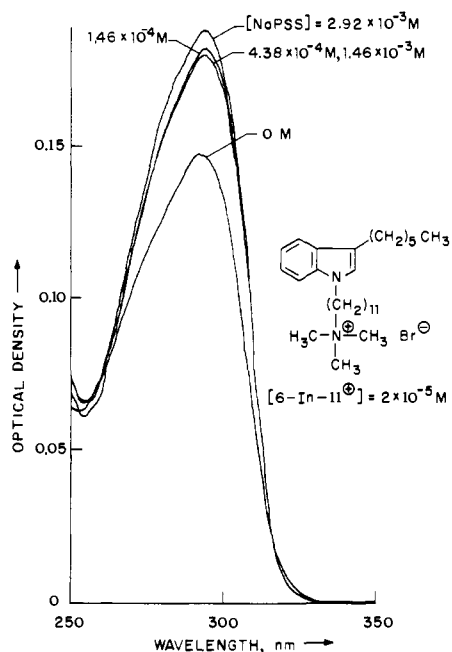

Figure 3. Absorption spectra of 6-In-11⁺ in the presence of NaPSS at 25 °C. [6-In-11⁺] = 2 × 10⁻⁵ M.

increase in decreasing polarity of the probe environment.[4] Thus, we conclude that the probe experiences a highly hydrophobic environment.

Fluorescence Lifetimes. The typical fluorescence lifetime (τ) of 6-In-11⁺ in NaPSS solution is ∼6 ns, but is quite insensitive to polymer concentration. This value of τ is smaller than that for the probe in ionic micelles but is larger than that of cyclohexane (4 ns).[4,5] These results are consistent with the conclusion that the hydrophobicity around the PSS anions experienced by the probe is high and intermediate in value to those of micelles and *n*-hexane. Although the probe lifetime and the probe environment were quite insensitive to pressure, the probe lifetime in the presence

Table IV. Influence of NaCl on the Fluorescence Lifetime, Molecular Anisotropy, and Microviscosity of 6-In-11⁺ in the Presence of NaPSS at Atmospheric Pressure

	[NaCl], M				
	0	0.001	0.003	0.01	0.03
τ, ns	6.2	5.0	4.9	4.9	4.8
r	0.015	0.018	0.015	0.016	0.014
η, cP	150	150	120	130	110

of NaPSS decreased more significantly with rising temperature (Table III). From the temperature dependence of τ, the apparent activation free energies ($\Delta G^{\ddagger}$), enthalpies ($\Delta H^{\ddagger}$), and entropies ($\Delta S^{\ddagger}$) were evaluated as follows: 6.9 kcal/mol⁻¹, 2.7 kcal/mol⁻¹, and −14 eu in H₂O, and 6.2 kcal/mol⁻¹, 0.87 kcal/mol⁻¹, and −18 eu in aqueous NaPSS solution. Furthermore, τ was found to decrease with addition of NaCl (Table IV).

Molecular Anisotropy and Microviscosity. The experimental results on the molecular anisotropy (r) and the microviscosity (η) are compiled in Tables I–IV. The uncertainty of η is fairly large (±20%), since the experimental error of r is fairly large (±15%). Irrespective of polymer concentration, η was essentially constant and was extremely large, ca. 150 cP. High pressure increased τ and η values, with the latter being significantly affected. The increase of r and η with rising temperature (Table III) may be explained as the result of enhanced hydrophobicity with temperature. The decrease in r and η with NaCl addition is interpreted to result from an electrostatic shielding effect of added salt on the attraction forces between the probe cations and the macroanions.

Discussion

The values of τ (ns) of 6-In-11⁺ for various systems including the present work[4,5] with NaPSS occur in the order H₂O (16) > SDS (12) > HDTCl (10) > HDTBr (7) > NaPSS (6) > cyclohexane (4). The values of λ_{max} (nm) are in the order H₂O (374) > SDS (357) ∼ HDTCl (∼357) > HDTBr (355) > NaPSS (352) > cyclohexane (340). The values for SDS were estimated by using the negative probe 11-(3-hexyl-1-indolyl)dodecyl sulfate (6-In-11⁻). Since this ordering is related to the order of strength of hydrophobicity experienced by the probe, we conclude that the hydrophobicity of PSS ions is very high compared to that of micelles. For micelle systems, the probes are expected to take locations at or near the micelle surface and not deep in the micelle core. On the other hand, in the case of NaPSS solution, the cationic probe (6-In-11⁺) may be very close to the PSS anions because of strong attraction with both electrostatic and hydrophobic interactions. This difference in the average probe position explains the low polarity or high hydrophobicity experienced by the probe associated with PSS ions. The insensitivity of τ and λ_{max} toward NaPSS concentration supports a strong attractive interaction between the macroions and their gegenions (probes).

The order of magnitude of the apparent microviscosity η (cP) of typical micelles and NaPSS, which were evaluated from various measurements (intramolecular excimer, fluorescence depolarization, etc.),[3-5,7,10] is H₂O (∼1) < SDS (∼15) < HDTCl (∼30) < HDTBr (∼40) < NaPSS (∼150) < HDTBr + cetyl alcohol(200–300) < HDTBr + 1-hexadecanesulfonate (∼400).

The extremely large value of η observed for NaPSS (∼150 cP) may be due to the strong restriction of the movement of the probe which results from the striking electrostatic and hydrophobic forces between the probes and the macroanions. We should note here that the HDTBr + 1-hexadecanesulfonate system shows a surprisingly large value of η, i.e., ∼400 cP.[7] This is due to the very strong attraction with both electrostatic and hydrophobic interactions between cationic HDTBr micelle and the anionic 1-hexadecanesulfonate.[7]

In Table III it is seen that r and η increase with rising temperature. This tendency strongly suggests the very important

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contribution of the hydrophobic interactions between the probes and PSS ions, because the hydrophobic interactions are generally reinforced with rising temperature.[11]

The possibility of the dynamic and/or static quenching of the probe with PSS macroanion itself must also be considered in interpreting our results. Photophysical properties of NaPSS have not been studied in detail. We find that NaPSS does not significantly quench the luminescence of several fluorescence and phosphorescence probes such as bis(α-binaphthylmethyl)ammonium chloride, α-naphthylmethylammonium chloride, and *n*-(4-bromo-1-naphthoyl)alkyltrimethylammonium bromides. We also

found the strong monomer and excimer emission for NaPSS aqueous solution.[12] Furthermore, the absorption maxima of 6-In-11$^+$ did not show any change in the presence of NaPSS as is seen in Figure 3. These results are consistent with small or negligible dynamic quenching of the probe by NaPSS. In addition, very strong association between the cationic probes and the macroanions will not be favorable to the dynamic quenching with NaPSS.

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On the Connection between the Photochemistry and the Jahn–Teller Effect of the Excited Doublets in Octahedral Cr(III) Complexes

A. Ceulemans, D. Beyens, and L. G. Vanquickenborne*

Contribution from the Department of Chemistry, University of Leuven, 3030 Heverlee, Belgium. Received January 26, 1981

Abstract: In octahedral Cr(III) complexes, the lowest excited doublets are more reactive than the (equiconfigurational) ground state but less than the lowest excited quartets. Moreover, the spatially degenerate doublets are characterized by negligible Jahn–Teller interactions while the degenerate quartets are subject to a large Jahn–Teller energy splitting. Both effects are shown to be related to certain specific features of half-filled shell states.

I. Introduction

It is the purpose of this paper to discuss two apparently unrelated features of the lowest excited doublet states of the octahedral Cr(III) complexes. In the first place, these states are claimed to exhibit an enhanced substitution activity with respect to the ground state; in the second place, although they are orbitally degenerate, they do not appear to be subject to any significant Jahn–Teller distortions.

It is well-known that the dominant reaction modes of the Cr(III) photosubstitutions proceed via the first excited quartet states.[1] Yet, the photoactivity of the doublets is measurable, and the substitution rates are definitely larger than in the ground state. Since both the ground state and the first excited doublets correspond to the same configuration, one generally assumes that substitutions in both cases take place along the same (associative) reaction mechanism. Recently Adamson[2] formulated a set of empirical rules connecting the doublet photoactivity and the phosphorescence lifetime of the Cr(III) complexes. Although this proposal has been stimulating further work on the doublet reactivity,[3] the basic reason for the difference in behavior between quartet ground state and doublet excited states remains unclear.

Several discussions on the photochemistry of octahedral Cr(III) complexes refer to a vacant t_{2g} orbital, supposedly characterizing the excited t_{2g}^3 doublet states.[4,5] The picture of two electrons,

paired in a single d orbital while leaving one t_{2g} orbital "entirely vacant",[4] suggests a certain similarity to the ground state of the very labile d^2 systems, such as Cr(IV) or V(III) complexes. On these grounds, the t_{2g}^3 doublet states are predicted to be very reactive toward bimolecular association reactions.

A closer examination of the detailed properties of the relevant Cr(III) doublet states might contribute to a better understanding of their behavior. In the present paper, we intend to show that the vacant orbital idea is not valid and that the association reactions of the Cr(III) complexes are determined by the specific properties of half-filled shell systems. In the last sections of this paper, we will show that the same properties are also at the basis of the Jahn–Teller behavior.

II. t_{2g} Occupation and Associative Interactions

Figure 1 shows the well-known state energy diagram corresponding to the t_{2g}^3 configuration in octahedral symmetry. Representative wave functions are shown schematically (only one component is given for each state). The functions are based on the three usual real t_{2g} orbitals (d_{xz}, d_{yz}, d_{xy}); more explicit and complete sets of functions can be found in the literature.[6,7]

The first excited doublet states ^2E and $^2T_{1g}$ are degenerate to first order in perturbation theory. As a result of configuration interaction (mainly with $t_{2g}^2e_g^1$ states), ^2E_g is slightly stabilized with respect to $^2T_{1g}$.

Because of the generalized Unsöld theorem, the three t_{2g} orbitals are equally occupied in any octahedral eigenstate, in the present

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