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Polyelectrolyte-Enhanced Excimer Formation of Bis(α-naphthylmethyl)ammonium Chloride and (α-Naphthylmethyl)ammonium Chloride

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Abstract: Excimer formation of the cationic bichromophore bis(α-naphthylmethyl)ammonium chloride (NDNP) and the cationic monochromophore (α-naphthylmethyl)ammonium chloride (NMA) is found to be strikingly enhanced in the presence of the hydrophobic macroanion sodium poly(styrenesulfonate) (NaPSS). From excimer decay behavior of NDNP in aqueous NaPSS solution, it is suggested that both intramolecular and intermolecular excimers are formed in NaPSS solution with lifetimes of 23 ± 3 and 45 ± 5 ns, respectively. The enhanced excimer formation for NDNP and NMA in the presence of the macroion is suggested to result from cooperative hydrophilic and hydrophobic interactions between the probes and the macroion. Addition of sodium chloride and $Co(NH_3)_5Cl_3$ retards excimer formation of NDNP, probably via an electrostatic shielding effect. The application of high pressure (1–2610 bar) increases both the emission intensity and the lifetime of the excimers of NDNP when bound to NaPSS. The cationic mononaphthyl compound (NMA) exhibits a strikingly enhanced intermolecular excimer emission relative to that in pure water. From a kinetic analysis of emission decay data, the intermolecular excimer formation rate constant is enhanced by 3 orders of magnitude when NMA is bound to NaPSS.

Studies of the conformations of molecules bound to various kinds of molecular assemblies afford information that may be employed for an understanding of enzymatic reactions of biomolecules, i.e., reaction rate catalysis, stereoselectivity, and reaction course regulation. Recently, conformational studies have received considerable attention in the field of photochemistry, since certain photochemical techniques can be conveniently employed for this purpose. For example, the formation rate of an excited-state complex (excimer) in bichromophores (dinaphthylpropane, for example) depends on both the microviscosity of the medium and the conformational structure preceding formation of the excimer.[1] The extent of intermolecular and intramolecular excimer is also influenced by the temperature[2] and pressure[3] of the system. Recent studies demonstrated that intramolecular excimer formation depends on the interactions of probes with the surrounding media. For example, for cyclodextrins having a favorable cavity size for inclusion of the bichromophore, excimer formation[4,5a] is greatly enhanced. Micellar systems also influence the extent of excimer formation.[2,5b] In the present work, we report the influence of poly(styrenesulfonate) anions on excimer formation of a cationic bichromophore, bis(α-naphthylmethyl)ammonium chloride (NDNP), and a cationic monochromophore, (α-naphthylmethyl)ammonium chloride (NMA), in aqueous media.

Experimental Section

Materials. The preparations of bis(α-naphthylmethyl)ammonium chloride (NDNP) and (α-naphthylmethyl)ammonium chloride were described earlier.[5b] Sodium poly(styrenesulfonate) (NaPSS) was kindly donated by Dr. H. Gregor. The purification method of the polymer has been described in detail.[7] The molar extinction coefficient of the polymer at 262 nm was 403 M^{-1} cm^{-1}. Sodium *p*-toluenesulfonate (NaTS) was recrystallized twice from a water–ethanol mixture. Sodium chloride (Alfa, Ultrapure grade) was used as supplied.

Emission and Absorption Measurements. All fluorescence spectra were taken on a SPEX Fluorolog fluorimeter or on a Hitachi-Perkin-Elmer spectrometer. Fluorescence decay was obtained by using the single-photon counting technique. A stainless steel high-pressure cell (Union Giken Engineering, Hirakata, Japan) was used for high-pressure measurements.[3] A Cary 18 spectrophotometer was employed to obtain absorption spectra.

Table I. Lifetime of NDNP at 25 °C[a]

[NaPSS], M	additive	[additive], M	condition	lifetime, ns: monomer[b]	lifetime, ns: excimer[c] τ_u	lifetime, ns: excimer[c] τ_b
0.0	none	0.0	N_2 purged	24	14	
0.73×10^{-5}	none	0.0	N_2	25		42
1.5×10^{-5}	none	0.0	N_2	23	22	44
4.0×10^{-5}	none	0.0	N_2		24	46
8.0×10^{-5}	none	0.0	N_2	11	25	47
80.0×10^{-5}	none	0.0	N_2	15	23	
8.0×10^{-5}	none	0.0	O_2	11	24	46
8.0×10^{-5}	NaCl	0.1	N_2	20	15	
8.0×10^{-5}	C_2H_5OH	2.0	N_2	12	24	47
1.5×10^{-5}	$Co(NH_3)_5Cl_3$	1×10^{-4}	N_2	24	16	

[a] Concentration of NDNP = 4.0×10^{-5} M. [b] Measured at 330 nm. [c] Measured at 390–420 nm; τ_u is the short component decay, τ_b is the long component decay.

Results and Discussion

Poly(styrenesulfonate) (NaPSS) Induced Enhancement of Excimer Formation of Bis(α-naphthylmethyl)ammonium Chloride (NDNP). In pure water (curve 1 in Figure 1) at 4×10^{-5} M, NDNP exhibits both monomer and excimer fluorescence emissions, with the former emission being more intense than the latter. The spectra reported are uncorrected for lamp characteristics or for detector response. The relative intensity of excimer emission ($\lambda_{max} \sim 400$ nm) of NDNP, however, is strikingly enhanced upon addition of less than an equivalent amount of monomer unit of NaPSS.[8] When 2.92×10^{-5} M (monomer unit) of NaPSS was

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(1) (a) Hirayama, F. *J. Chem. Phys.* **1965,** *42,* 3163. (b) Klopffer, W.; Liptay, W. *Z. Naturforsch. A* **1970,** *25A,* 1091. (c) Kordas, A. J.; El-Bayoumi, M. A. *Chem. Phys. Lett.* **1974,** *26,* 373. (d) Goldenberg, M.; Emert, J.; Morawetz, H. *J. Am. Chem. Soc.* **1979,** *101,* 771. (e) Ito, S.; Yamamoto, M.; Nishijima, Y. *Bull. Chem. Soc. Jpn.* **1981,** *54,* 35.

(2) (a) Zachariasse, K. A.; Kuhnle, W.; Weller, A. *Chem. Phys. Lett.* **1978,** 375. (b) Turro, N. J.; Aikawa, M.; Yekta, A. *J. Am. Chem. Soc.* **1979,** *101,* 772. (c) Georgescauld, D.; Desmasez, J. P.; Lapouyade, R.; Babeau, A.; Richard, H.; Winnik, M. *Photochem. Photobiol.* **1980,** *31,* 539.

(3) Turro, N. J.; Okubo, T. *J. Am. Chem. Soc.* **1981,** *103,* 7224.

(4) Turro, N. J.; Okubo, T.; Weed, G. C. *Photochem. Photobiol.* **1982,** *35,* 325.

(5) (a) Emert, J.; Kodali, D.; Catena, R. *J. Chem. Soc., Chem. Commun.* **1981,** 758. (b) Emert, J.; Behrens, C.; Goldenberg, M. *J. Am. Chem. Soc.* **1979,** *101,* 771.

(6) (a) The biphasic decay of excimers is similar to a system involving fluorescence quenching by ions in the presence of macroions; Jonah, C. D.; Matheson, M. S.; Mersil, D. *J. Phys. Chem.* **1979,** *83,* 257. (b) The self-quenching of quinine cations may also be related to the results reported here: Taha, I. A.; Morawetz, H. *J. Polym. Sci., Polym. Chem. Ed.* **1971,** *2,* 1669.

(7) Okubo, T.; Turro, N. J. *J. Phys. Chem.* **1981,** *85,* 4034.

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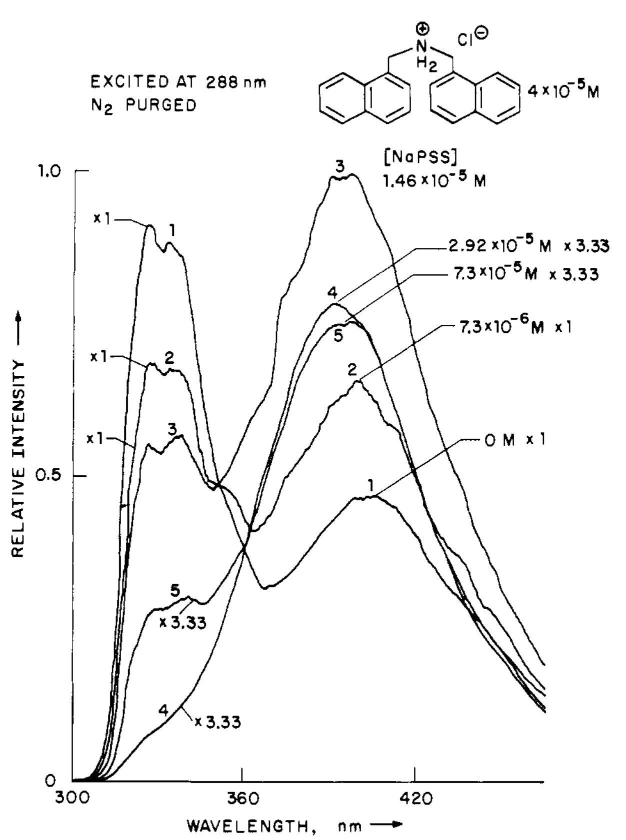

Figure 1. Fluorescence spectra of NDNP in the absence and presence of NaPSS. [NDNP] 4 × 10^{-5} M, excited at 288 nm. [NaPSS]: (1) 0 M; (2) 7.3 × 10^{-6} M; (3) 1.46 × 10^{-5} M; (4) 2.92 × 10^{-5} M; (5) 7.3 × 10^{-5} M.

added, the observed emission was almost entirely due to excimer fluorescence (curve 4, Figure 1)! Moreover, excimer emission (I_E) begins to decrease when [NaPSS]/[NDNP] > 1, while the intensity of monomer emission (I_M) ($\lambda_{max} \sim 330$ nm) undergoes an initial decrease ([NaPSS]/[NDNP] < 1) but then increases with increasing NaPSS concentration ([NaPSS]/[NDNP] > 1). Figure 2 shows the dependence of I_E/I_M, and I_E on polymer concentration. The maximum I_E/I_M occurs at ca. 4 × 10^{-5} M NaPSS, i.e., when the probe and monomer units of the polyelectrolyte are present in equivalent concentration. These results suggest that an association (or stacking) between the probe and macroanions occurs.

Both a hypochromic effect and red shift in the absorption spectra of NDNP were observed in the presence of NaPSS polyelectrolyte (Figure 3). This result suggests that interactions occur between NDNP and NaPSS in the ground state. This result contrasts with the observation[5] that inclusion of NDNP in the cavity of cyclodextrins did not lead to a significant change in the absorption spectrum of NDNP relative to that in pure aqueous solution.

The decay of the monomer (330 nm) and excimer (400 nm) of DNDP was measured in the presence of various concentrations of NaPSS (Figure 4 and Table I). Several significant points are noted: (1) the decay of excimer emission at 400 nm in pure water or in high concentration of NaPSS ([NaPSS]/[NDNP] = 20) follows a clean single-exponential decay corresponding to lifetimes of 14 and 23 ns, respectively; (2) for [NaPSS]/[NDNP] = 2–~0.3, the decay of the emission at 400 nm does not correspond to a single-exponential decay but rather to a combination of two single-exponential decays with the lifetimes of 23 ± 3 ns (τ_u) and 45 ± 5 ns (τ_b); (3) the fraction of short component (τ_u) increases with increasing NaPSS concentration; (4) the rise time or excimer emission is "instantaneous" (<2 ns). From the above observations, it is suggested that two different species exist that have similar emission wavelength around 400 nm but that possess a different lifetime. The most likely candidates are as follows: (a) one is the excimer of two naphthalene units and the other is an exciplex between a naphthalene unit and benzenesulfonate unit of the NaPSS; (b) both are excimers consisting of naphthalene units, one of which is an intermolecular excimer and the other is an intramolecular excimer.[6]

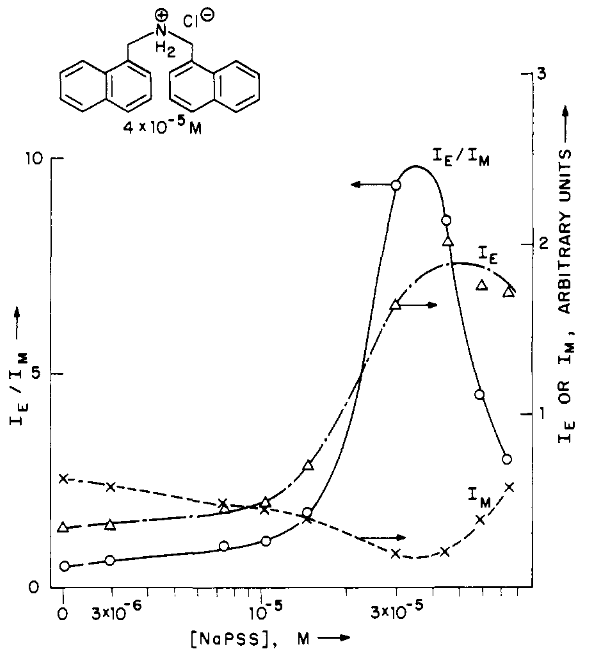

Figure 2. I_E/I_M (○), I_E (△), I_M(×) of NDNP as a function of NaPSS concentration (in monomer units). [NDNP] = 4 × 10^{-5} M, excited at 288 nm.

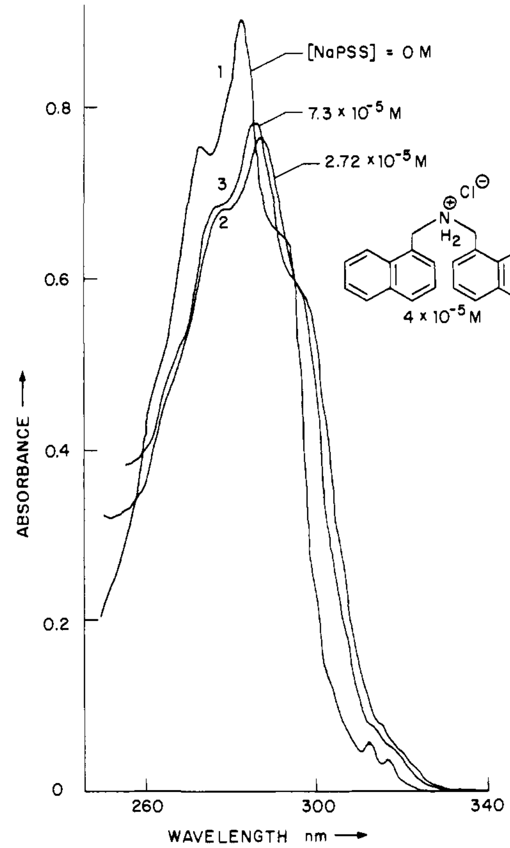

Figure 3. Absorption spectra of NDNP in the absence and presence of NaPSS. [NDNP] 4 × 10^{-5} M. [NaPSS]: (1) 0 M; (2) 2.72 × 10^{-5} M; (3) 7.3 × 10^{-5} M.

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(8) The emission intensity of NaPSS is much weaker than that of NDNP.

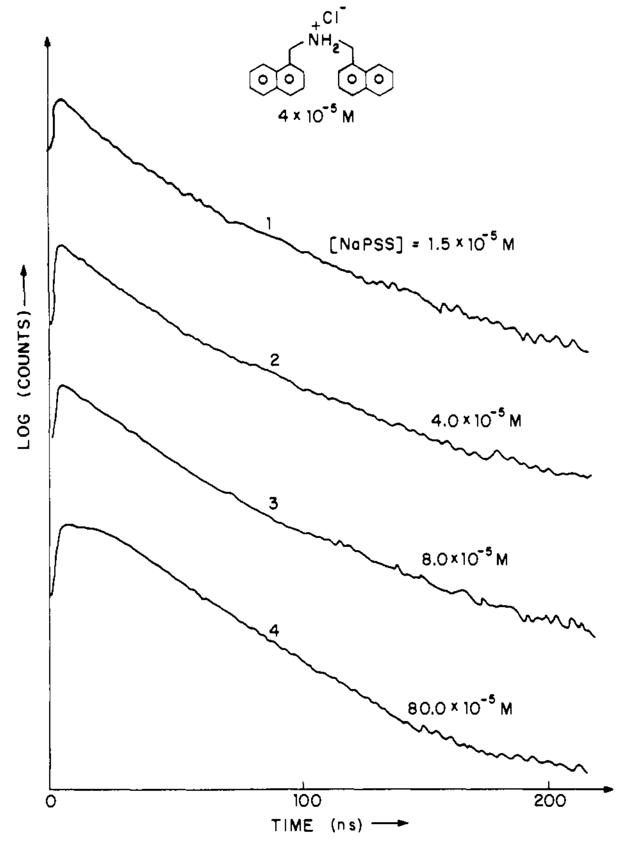

Figure 4. Typical traces of the decay of NDNP excimer fluorescence (400 nm) in the presence of NaPSS. [NDNP] 4 × 10^{-5} M. [NaPSS]: (1) 1.5 × 10^{-5} M; (2) 4.0 × 10^{-5} M; (3) 8.0 × 10^{-5} M; (4) 80.0 × 10^{-5} M;

The former possibility (excimer and exciplex) was ruled out by the following observations: (1) The decay behavior is the same, independent of the analyzing wavelength in the range 390–420 nm. This suggests strongly that the same species is responsible for the emission around 400 nm. (2) The emission intensity at 400 nm at high concentration of polyelectrolyte ([NaPSS]/[NDNP] = 20) is ~20% of the emission at equivalent concentration of the NDNP and NaPSS. (3) The decay of the long-lived emission at 400 nm is similar to the decay of excimer of (α-naphthylmethyl)ammonium chloride in NaPSS solution (vide infra).

The assignment of intra- and intermolecule excimer formation is consistent with the NaPSS concentration dependence of the emission intensity and decay behavior. When the [NaPSS]/[NDNP] ratio increases, intermolecular excimer formation decreases, as does the total emission intensity, and the decay behavior will approach that of high concentration of NaPSS ([NaPSS]/[NDNP] = 20).

Both monomer and excimer emission are not significantly influenced by oxygen saturation of the solutions. Addition of ethanol did not show a significant effect on the emission intensity or on the decay behavior of the emissions (Table I). However, addition of sodium chloride decreased the intensity of the excimer and monomer emissions (Figure 5), and eventually ([NaCl] > 0.1 M) the ratio of excimer to monomer emission reached the same value as that in pure water. This observation may be due to an electrostatic shielding effect of the salt on the attraction between the cationic probes and the anionic macroions. By comparison of the emission spectra, absorption spectra, and time-resolved emissions of monomer and excimer in the presence of high concentration of NaCl (>0.1 M) in polyelectrolyte solution and in water, it is concluded that NDNP is forced compeltely into water, i.e., all the measured properties are identical in 0.1 M NaCl polyelectrolyte solution and in water. Similarly (Table I), addition of $Co(NH_3)_5Cl_3$ to NDNP polyelectrolyte solution retards the intensities of monomer and excimer emissions, but a concentration of only 1 × 10^{-4} M is needed to achieve the same behavior as 0.1 M NaCl.

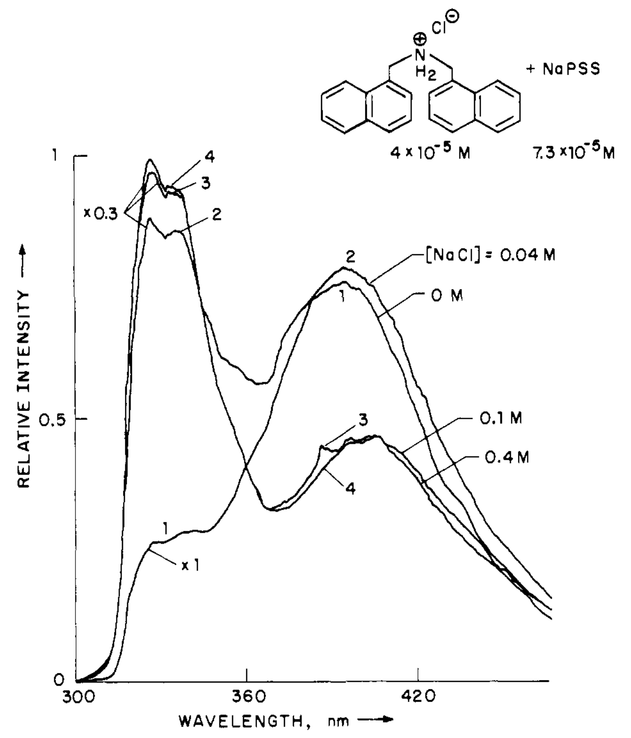

Figure 5. Influence of NaCl on the fluorescence spectra of NDNP + NaPSS + H_2O system. [NDNP] 4 × 10^{-5} M, [NaPSS] 7.3 × 10^{-5} M. [NaCl]: (1) 0 M; (2) 0.04 M; (3) 0.1 M; (4) 0.4 M.

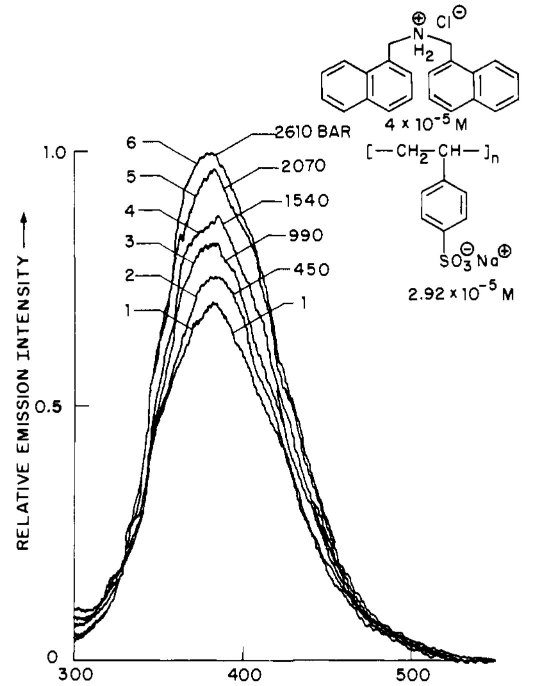

Figure 6. Influcence of high pressure on the fluorescence spectra of NDNP + NaPSS + H_2O system. [NDNP] 4 × 10^{-5} M, [NAPSS] 2.92 × 10^{-5} M. (1) 1 bar; (2) 450 bar; (3) 990 bar; (4) 1540 bar; (5) 2070 bar; (6) 2610 bar.

Both the fluorescence intensity and lifetime of the NDNP excimer emission in the pressence or absence of NaPSS increased ca. 20–30% by applying 2610 bar of pressure (Figure 6 and Table II). This enhancement of excimer formation by applied pressure may be due to the predominant "icelike" structure effect, because this effect is accompanied by a decrease in volume in the course of binding between macroions and their gegenions, whereas the

Table II. Fluorescence Lifetimes of NDNP under High Pressure at 25 °C

			lifetime, ns	
[NDNP], M	[NaPSS], M	pressure, bar	monomer	excimer
4×10^{-5}	0.0	1	24	14
4×10^{-5}	0.0	990	24	20
4×10^{-5}	0.0	2070	15	16
4×10^{-5}	2.92×10^{-5}	1		48^a
4×10^{-5}	2.92×10^{-5}	990		49^a
4×10^{-5}	2.92×10^{-5}	1540		49^a
4×10^{-5}	2.92×10^{-5}	2070		57^a

[a] Measured for long-lived decay.

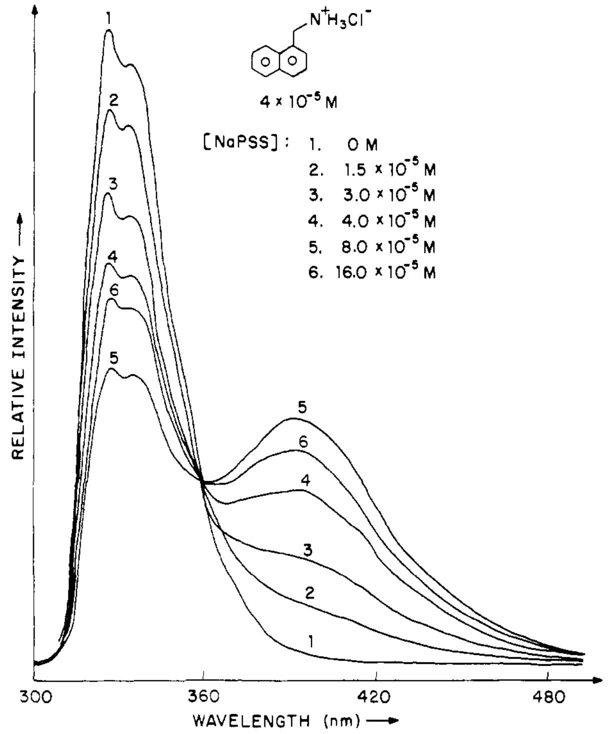

Figure 7. Fluorescence spectra of NMA in the absence and presence of NaPSS. [NMA] 4×10^{-5} M, excited at 288 nm. [NaPSS]: (1) 0 M; (2) 1.5×10^{-5} M; (3) 3.0×10^{-5} M; (4) 4.0×10^{-5} M; (5) 8.0×10^{-5} M; (6) 16.0×10^{-5} M.

electrostatic dehydration effect by the binding reaction is accompanied by an increase in volume.[9] Thus, the former, but not the latter, is expected to show an enhanced effect upon application of high pressure.

Poly(styrenesulfonate) (NaPSS) Induced Excimer Formation of (α-Naphthylmethyl)ammonium Chloride. In pure water at concentration below 1×10^{-3} M, the cationic mononaphthyl compound (NMA) shows only monomer fluorescence with $\lambda_{max} \sim 330$ nm. However, in aqueous polyelectrolyte solution (NaPSS), NMA exhibits both monomer and intermolecular excimer ($\lambda_{max} \sim 400$ nm) emissions even at concentrations as low as 4×10^{-5} M (Figure 7). This striking induction of intermolecular excimer formation observed upon addition of a hydrophobic macroanion strongly suggests the formation of aggregates of NMA molecules that are electrostatically bound to the polyelectrolyte. This kind of association is similar to the binding of ionic dyes to ionic biomolecules.[10]

Table III. Kinetic Rate Constants at 25 °C

rate constant^a	in water	at 8×10^{-5} M NaPSS
k_1	$(2.1 \pm 0.3) \times 10^{9}$	$(2.3 \pm 0.3) \times 10^{12}$
k_{-1}	$(0.5\text{–}4) \times 10^{7}$	$(2\text{–}6) \times 10^{7}$
k_M	$(2.9 \pm 0.3) \times 10^{7}$	$(2.9 \pm 0.3) \times 10^{7}$
k_D	$(1.9 \pm 0.3) \times 10^{7}$	$(1.9 \pm 0.3) \times 10^{7}$

[a] See eq 1 for definition of rate constants.

The kinetic analyses of excimer formation in pure water and in aqueous NaPSS solution were made in order to obtain more information about the enhancement of excimer formation that is induced by NaPSS. The scheme of photophysical kinetics, including the excimer formation process, is given in eq 1, where

$$\begin{tikzcd} M^* \arrow[d, shift left, "k_M"] & +M \arrow[r, shift left, "k_1"] & (M\text{---}M)^* \arrow[l, shift left, "k_{-1}"] \arrow[lld, "k_D"] \\ M \arrow[u, shift left, "h\nu"] & & \end{tikzcd} \tag{1}$$

k_1 and k_{-1} are the excimer formation and dissociation rate constants, respectively, and k_M and k_D are decay rate constants (including radiation and radiationless decay) for monomer and excimer, respectively. The theoretical response functions $I_M(t)$ and $I_D(t)$, for monomer and excimer fluorescence, are derived by

$$I_M(t) = C_M(e^{-\lambda_1 t} + Ae^{-\lambda_2 t})$$
$$I_D(t) = C_D(e^{-\lambda_1 t} - e^{-\lambda_2 t})$$

where C_M, C_D, A, λ_1, and λ_2 are given as functions of the rate constant,[11] and

$$\lambda_{1,2} = \tfrac{1}{2}[k_M + k_D + k_1[M] + k_{-1} \pm \{(k_D\, k_{-1} - k_M - k_1[M])^2 + 4k_1k_{-1}[M]\}^{1/2}$$
$$\lambda_1 + \lambda_2 = k_M + k_D + k_{-1} + k_1[M]$$

λ_1 and λ_2 can be obtained from the experimental risetime of excimer emission and the decay of monomer and excimer emissions.[11] The rate constant k_1 can be obtained from the linear plot of $\lambda_1 + \lambda_2$ as a function of NMA concentration, k_M from the monomer lifetime at [NMA] → 0, and k_D from the excimer lifetime at [NMA] → ∞. The results are shown in Table III. From the table, it can be seen that k_1 (excimer formation rate constant) is dramatically enhanced (3 orders of magnitude) by 8×10^{-5} M NaPSS. This enhancement is rationalized as the result of interactions of the electrostatic field of NaPSS with ions of the same charge such as NMA.[12]

It has been recognized[13] that, depending on the charge of the macroion and probe, the dependence of reaction rates on concentrations may deviate dramatically from that observed in conventional homogeneous solution. For example, when the macroion and the probe have the opposite charge, probe molecules and quenchers of the same charge may be "concentrated" in the region of space near the polyion. This will lead to enhanced quenching relative to homogeneous solution. Also, adjustment of polyion concentration or of probe concentration can lead to a reduction when the polyion (monomer) concentration is increased beyond that equivalent to the probe/quencher concentration, since the probe/quencher ions must then be distributed among a number of polymer domains and the local concentrations of probe and quencher are decreased. Finally, if the concentrations of probe/quencher ions are higher than the concentration of binding sites on the polyion, two kinetically distinct situations may occur: separate quenching of the excited probe both in the polyion domain and in the bulk aqueous domain.[6]

The behavior of the probe emission (Figures 1 and 2) as a function of polyion concentration can be understood in the fol-

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(9) (a) Ise, N.; Maruno, T.; Okubo, T. *Proc. R. Soc. London, Ser. A* **1980**, *370*, 485. (b) Okubo, T.; Maruno, T.; Ise, N. *Ibid.* **1980**, *370*, 501. (c) Maruno, T.; Okubo, T.; Ise, N. *Ber. Bunsenges. Phys. Chem.* **1981**, *85*, 667.

(10) See, for example: (a) Michaelis, L. *J. Phys. Chem.* **1950**, *54*, 1. (b) Bradley, D. F.; Wolf, M. K. *Proc. Natl. Acad. Sci. U.S.A.* **1959**, *45*, 944. (c) Bradley, D. F.; Lifson, S. "Molecular Assication in Biology"; Pullman, B., Ed.; Academic Press: New York, 1968. (d) Schwarz, G.; Klose, S. *Eur. J. Biochem.* **1972**, *29*, 249.

(11) Birks, J. B.; Dyson, D. J.; Munro, I. H. *Proc. R. Soc. London, Ser. A* **1963**, *275*, 575.

(12) Ise, N.; Okubo, T. *Macromolecules* **1978**, *11*, 439 and references therein.

(13) Morawetz, H. *Science (Washington, D.C.)* **1979**, *203*, 405; *Sven. Kem. Tidskr.* **1967**, *79*, 309; *J. Am. Chem. Soc.* **1969**, *91*, 563; **1970**, *92*, 7532.

lowing terms. In aqueous solution (at 4×10^{-5} M probe concentration), only unimolecular emission (monomer and excimer) is observed. The addition of very low levels of polyion (7.3×10^{-6} M) results in substantial extraction of the probe from the aqueous domain to that of the polyion. Both intermolecular and intramolecular excimer formations are enhanced, and the contribution of probe emission from the aqueous phase is significantly decreased. Eventually, at $\sim 5 \times 10^{-5}$ M polyion concentration, the fluorescence intensity maximizes. Further addition of polyion causes separation of probe molecules over the larger number of available sites, and the intermolecular component decreases, allowing the monomer emission to become more pronounced.

Summary

The excimer emissions of NDNP and NMA are dramatically enhanced in the presence of polyelectrolyte (NaPSS) in aqueous solution. This enhancement is attributed to the association (due to hydrophilic, electrostatic, and hydrophobic interactions) of the probes with microanions. The intermolecular excimer formation rate constant, k_1, of NMA is enhanced by 10^3 in the presence of 8×10^{-5} M NaPSS. Both intramolecular and intermolecular excimer formation of NDNP occur in the presence of NaPSS in aqueous solution. NaCl and $Co(NH_3)_5Cl_3$ retard excimer formation, while high pressure increases both the emission intensity and the lifetime of the excimer of NDNP.

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Registry No. NDNP, 17018-62-1; NaPSS, 25704-18-1; NMA, 39110-74-2.

Photochemistry of $Ru(bpy)_3^{2+}$

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Abstract: Temperature-dependent lifetime data in dichloromethane are reported for the emitting charge-transfer excited state of $Ru(bpy)_3^{2+}$ (^{3}CT) (bpy is 2,2′-bipyridine) under photochemical (NCS^- salt) and nonphotochemical (PF_6^- salt) conditions. Temperature-dependent lifetime data have also been obtained in dichloromethane for the salts $[Ru(bpy)_2(py)_2](PF_6)_2$ (py is pyridine) and $[Ru(phen)_3](PF_6)_2$ (phen is 1,10-phenanthroline) as have temperature-dependent quantum-yield data for photochemical loss of bpy, $[Ru(bpy)_3]X_2\ (+h\nu) \rightarrow [(bpy)_2RuX(bpy)]X \rightarrow (bpy)_2RuX_2 + bpy$, for the salt $[Ru(bpy)_3](NCS)_2$ ($\phi_p(25\ °C) = 0.068$). The data obtained here, combined with the data and suggestions made earlier by Van Houten and Watts (ref 2 and 11) based on their experiments in water, suggest a detailed view of the microscopic events which lead to photosubstitution. Initial excitation leads to a charge-transfer state largely triplet in character, ^{3}CT. The CT state undergoes thermal activation to give a d–d excited state. The d–d state undergoes further thermal activation by loss of a pyridyl group to give a five-coordinate intermediate which is apparently square pyramidal in structure. The fate of the intermediate is capture of a sixth ligand, either by solvent or an anion held close to the activated metal center by ion-pairing or by chelate ring closure to return to $Ru(bpy)_3^{2+}$. Capture by solvent or an anion leads to a six-coordinate, unidentate bpy intermediate $(bpy)_2(L)Ru^{II}(py\text{–}py)$ which can either undergo chelate ring closure and loss of L to return to $Ru(bpy)_3^{2+}$ or loss of bpy to give photoproducts. At room temperature and above, $Ru(bpy)_3^{2+}$ is in an intrinsic sense relatively reactive photochemically in either dichloromethane or water. The apparent solvent effect between dichloromethane and water may arise largely from the thermodynamic and/or kinetic preferences of the six-coordinate unidentate bpy intermediate and not in steps involving excited states. The apparent photochemical stability of $Ru(bpy)_3^{2+}$ in water is a consequence of the dominance of chelate ring closure and not of an inherently low photochemical reactivity.

Introduction

Although the excited-state properties of $Ru(bpy)_3^{2+}$ (bpy is 2,2′-bipyridine) have been studied in detail[2-7] and the excited state(s) have provided the basis for a number of interesting applications,[8,9] the photochemical properties of this and related complexes have been largely neglected. The photochemical decomposition of $Ru(bpy)_3^{2+}$ in water[10,11] and DMF[12,13] has been studied, and a marked enhancement in quantum yield has been noted in dichloromethane.[14] In related complexes, photochemical substitution in *cis*-$Ru(bpy)_2(py)_2^{2+}$ (py is pyridine) has been shown to be of synthetic value[15] and both photochemical cis $\rightleftharpoons$ trans isomerization and ClO_4^- oxidation have been observed for $Ru(bpy)_2(H_2O)_2^{2+}$.[16]

We report here the results of detailed photochemical and photophysical studies on $Ru(bpy)_3^{2+}$ and the related complexes $Ru(phen)_3^{2+}$ (phen is 1,10-phenanthroline) and $Ru(bpy)_2(py)_2^{2+}$ in dichloromethane solution. When combined with the earlier results of Van Houten and Watts,[10,11] a detailed picture begins to emerge of the mechanistic and excited-state properties which lead to the observed photochemistry.

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(1) Department of Chemistry, University of Chemistry, University of Arkansas, Fayetteville, Ark. 72701.

(2) Van Houten, J.; Watts, R. J. *J. Am. Chem. Soc.* **1975**, *97*, 3843.

(3) Balzani, V.; Moggi, L.; Manfrin, M. F.; Bolletta, F.; Laurence, G. S. *Coord. Chem. Rev.* **1975**, *15*, 321.

(4) Hager, G. D.; Crosby, G. A. *J. Am. Chem. Soc.* **1975**, *97*, 7031. Hipps, K. W.; Crosby, G. A. *Ibid.* **1975**, *97*, 7042.

(5) Meisel, D.; Matheson, M. S.; Mulac, W. A.; Rabani, J. *J. Phys. Chem.* **1977**, *81*, 1449.

(6) Creutz, C.; Sutin, N. *Proc. Natl. Acad. Sci. U.S.* **1975**, *72*, 2858.

(7) Felix, F.; Ferguson, J.; Güdel, H. U.; Ludi, A. *J. Am. Chem. Soc.* **1980**, *102*, 4096.

(8) (a) Balzani, V.; Bolletta, F.; Gandolfi, M. T.; Maestri, M. *Top. Curr. Chem.* **1978**, *75*, 1. (b) Meyer, T. J. *Isr. J. Chem.* **1977**, *15*, 200.

(9) (a) Meyer, T. J. *Acc. Chem. Res.* **1978**, *11*, 94. (b) Sutin, N. *J. Photochem.* **1979**, *10*, 19.

(10) Van Houten, J.; Watts, R. J. *J. Am. Chem. Soc.* **1976**, *98*, 4853.

(11) Van Houten, J.; Watts, R. J. *Inorg. Chem.* **1978**, *17*, 3381.

(12) Hoggard, P. E.; Porter, G. B. *J. Am. Chem. Soc.* **1978**, *100*, 1457.

(13) Wallace, W. M.; Hoggard, P. E. *Inorg. Chem.* **1979**, *18*, 2934.

(14) Gleria, M.; Minto, F.; Beggiato, G.; Bortolus, P. *J. Chem. Soc., Chem. Commun.* **1978**, 285.

(15) Durham, B.; Walsh, J. L.; Carter, C. L.; Meyer, T. J. *Inorg. Chem.* **1980**, *19*, 860.

(16) Durham, B.; Wilson, S. R.; Hodgson, D. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 600.

0002-7863/82/1504-4803$01.25/0