Chem. Mater. **2000,** *12,* 1529−1535

Articles

Excited-State Behavior of Nile Blue H-Aggregates Bound to SiO_2 and SnO_2 Colloids

Chouhaid Nasr and Surat Hotchandani*

Groupe de Recherche en Énergie et Information Biomoléculaires, Université du Québec à
Trois-Rivières, C.P. 500, Trois-Rivières, Québec, G9A 5H7, Canada

Received January 27, 2000. Revised Manuscript Received April 3, 2000

The spectroscopic characterization of a cationic dye, Nile Blue A (NB), in negatively charged SnO_2 and SiO_2 colloidal suspensions has been carried out. The results show that NB, in the presence of these colloidal suspensions, forms aggregates of H-type which are nonfluorescent and have blue-shifted absorption compared to the NB monomer in aqueous solution. Laser photolysis experiments have been carried out to study the excited-state dynamics of the NB aggregates. The transient absorption measurements of NB adsorbed on SiO_2 colloids (inert support) show that the H-aggregates of NB have a relatively short-lived excitonic singlet state ($\tau = 40$ ps); the lifetime of the excited singlet of the monomer in aqueous solution is ~390 ps. On a reactive semiconductor support like SnO_2, the NB aggregates also inject electrons into SnO_2. This is characterized by the formation of the cation radical, $(NB)_2^{\bullet+}$, of the NB aggregates and by the trapping of electrons the in SnO_2 nanocrystallites. The monophotonic dependence of the formation of $(NB)_2^{\bullet+}$ on SnO_2 surface supports the charge transfer from NB aggregates to SnO_2. The rate constant for this heterogeneous electron-transfer process is $\sim 3.3 \times 10^8$ s^{-1}.

Introduction

Aggregates of organic dyes play an important role in photosensitization, xerography and imaging applications.[1−15] Of particular interest is their ability to sensitize large band-gap semiconductor materials such as silver bromide nanocrystallites in color photography. The study of aggregates is also very useful for understanding the light-harvesting and energy-transport processes in many biological systems[16] as a high concentration of the pigments is usually present in the membrane, and aggregate formation is highly possible. Because of their importance, therefore, the excited-state behavior and electron-transfer reactions of many dye aggregates have been explored.[3−13,17−23]

Aggregation is a common phenomenon observed with many dyes as their concentrations are increased.[24−34]

---

* To whom correspondence should be addressed.

(1) West, W.; Gilman, P. B., Jr. In *The Theory of the Photography Process*, 4th ed.; James, T. H., Ed.; MacMillan Publishing Co.: New York, 1977; pp 271−301.

(2) Law, K. Y. *Chem. Rev.* **1993**, *93*, 449−86; *J. Imaging Sci* **1990**, *34*, 38−44.

(3) Kemnitz, K.; Yoshihara, K.; Tani, T. *J. Phys. Chem.* **1990**, *94*, 3099−3104.

(4) Willig, F.; Spitler, M. T. *J. Imaging Sci. Technol.* **1997**, *41*, 272−282.

(5) Trösken, B.; Willig, F.; Schwarzburg, K.; Ehert, A.; Spitler, M. T. *J. Phys. Chem.* **1995**, *99*, 5152−5160; *Adv. Mater.* **1995**, *7*, 448−450.

(6) Kim, Y.-S.; Liang, K.; Law, K.-Y.; Whitten, D. G. *J. Phys. Chem.* **1994**, *98*, 984−988.

(7) Muenter, A. A.; Brumbaugh, D. V.; Apolito, J.; Horn, L. A.; Spano, F. C.; Mukamel, S. *J. Phys. Chem.* **1992**, *96*, 2783−2790.

(8) Hotchandani, S.; Das, S.; George Thomas, K.; George, M. V.; Kamat, P. V. *Res. Chem. Intermed.* **1994**, *20*, 927−938.

(9) Noukakis, D.; Van der Auweraer, M.; De Schryver, F. C. *J. Phys. Chem.* **1994**, *98*, 11745−11750.

(10) Nüesch, F.; Moser, J. E.; Shklover, V.; Grätzel, M. *J. Am. Chem. Soc.* **1996**, *118*, 5420−5431.

(11) Liu, D.; Kamat, P. V. *J. Electrochem. Soc.* **1995**, *142*, 835−839.

(12) Nasr, C.; Liu, D.; Hotchandani, S.; Kamat, P. V. *J. Phys. Chem.* **1996**, *100*, 11054−11061.

(13) (a) Liu, D.; Kamat, P. V. *Langmuir* **1996**, *12*, 2190−2195. (b) Liu, D.; Kamat, P. V. *J. Chem. Phys.* **1996**, *105*, 965−970.

(14) Hada, H.; Yonezawa, Y.; Inaba, H. Ber. *Bunsen-Ges. Phys. Chem.* **1981**, *85*, 425−30.

(15) Lenhard, J. R.; Hein, B. R. *J. Phys. Chem.* **1996**, *100*, 17287−17296.

(16) *Bioenergetics of Photosynthesis*; Govindjee, Ed.; Academic Press: New York, 1975.

(17) Sundström, V.; Gillboro, T. *J. Chem. Phys.* **1985**, *83*, 2733−2743.

(18) Wantanabe, M.; Herren, M.; Morita, M. *J. Lumin.* **1994**, *58*, 198.

(19) Khairutdinov, R. F.; Serpone, N. *J. Phys. Chem. B* **1997**, *101*, 2602−2610.

(20) Taguchi, T.; Hirayama, S.; Okamoto, M. *Chem. Phys. Lett.* **1994**, *231*, 561−568.

(21) Maiti, N. C.; Mazumdar, S.; Periasamy, N. *J. Phys. Chem. B* **1998**, *102*, 1528−1538.

(22) Chen, S.-Y.; Horng, M.-L.; Quitevis, E. L. *J. Phys. Chem.* **1989**, *93*, 3683−3688.

(23) (a) Horng, M.-L.; Quitevis, E. L. *J. Phys. Chem.* **1989**, *93*, 6198−6201. (b) Horng, M.-L.; Quitevis, E. L. *J. Phys. Chem.* **1993**, *97*, 12408−12415.

(24) West, W.; Pearce, S. *J. Phys. Chem.* **1965**, *69*, 1894−1903.

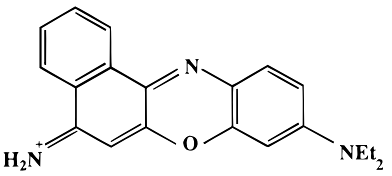
(25) Rohatgi, K. K.; Singhal, G. S. *J. Phys. Chem.* **1966**, *70*, 1695−1701.

(26) Selwyn, J. E.; Steinfeld, J. I. *J. Phys. Chem.* **1972**, *76*, 762−774.

(27) Yuzhakov, V. I. *Russ. Chem. Rev.* **1979**, *48*, 2007−2033.

10.1021/cm0000752 CCC: $19.00

Scheme 1. Structure of Cation Nile Blue A



Formation of aggregates modifies the photophysical properties of the dye. Briefly speaking, aggregation is due to the strong coupling between the molecules which causes either a blue shift or red shift in the absorption band of the aggregate. For a J-type aggregate, the absorption band is red-shifted relative to the monomer while a blue shift in the absorption is observed for an H-aggregate.[35,36] The strength of aggregation is strongly dependent on the structure of the dye molecules, the nature of the solvent, temperature, and the nature of added electrolytes. In aqueous solution, the high dielectric constant of water facilitates aggregation by reducing the repulsive force between similarly charged dye molecules.[23b]

In a recent work,[11−13] we had shown that negatively charged SiO_2 and SnO_2 colloids can also induce aggregation in various cationic dyes, for example, rhodamine, thionine, etc. The strong electrostatic interaction between cationic dye and the negatively charged oxide surface results in close packing of the dye molecules. As a result, dye aggregates are formed even at very low dye concentrations ($<10^{-5}$ M). In our continuing interest in dye aggregates with regard to their photosensitization applications, we have now studied the aggregation phenomenon of yet another cationic dye, namely, Nile Blue A perchlorate (NB).

NB, belonging to the oxazine class of dyes and possessing the structure shown in Scheme 1, is an efficient laser dye and has been employed for pulsed and CW operations. The photophysical properties of its monomeric form have been examined in detail with ultrafast techniques.[37−49] However, no major effort has been made to investigate the excited-state behavior and electron-transfer reactions of its aggregate form. To get an insight into these processes, we have deposited aggregates of NB on both inert and reactive supports. An inert or nonreactive support (like SiO_2),[50] with its conduction band at much higher energies, enables us to directly probe the excited-state dynamics of the dye undisturbed by other competing processes. On the other hand, a reactive semiconductor support, for example, SnO_2, with a conduction band situated at lower energies, can act as an electron acceptor, and thus enables us to study the charge injection process from the excited dye into the semiconductor nanocrystallites. For this reason, SiO_2 and SnO_2 colloids have been capped with H-aggregates of NB, and laser photolysis measurements have been performed to elucidate the excited-state behavior of the NB aggregates.

Experimental Section

Materials. Aqueous SnO_2 colloidal suspension (15%, particle diameter 10−15 nm) was obtained from Alfa Chemicals and was used without further purification. SiO_2 colloidal aqueous suspension (14.5%, particle diameter 3−5 nm) was obtained from NALCO Chemical Company. All the colloidal concentrations indicated in this study are expressed as molecular concentrations based on formula weights. Nile Blue A perchlorate (Laser grade) was obtained from Aldrich. All other chemicals and solvents were analytical reagents of the highest available purity.

All the measurements were made in aqueous medium ($pH \approx 9$) at room temperature. At this pH, both SnO_2 and SiO_2 exist with anionic surface charges. Absorption spectra were recorded with a Milton Roy spectronic diode array spectrophotometer. Emission spectra were recorded with a SLM-8100 spectrofluorometer system.

Laser-Flash Photolysis Experiments. Picosecond laser flash photolysis experiments were performed with 532 nm laser pulses from a mode-locked, Q-switched Quantel YG-501 DP Nd:YAG laser system (output 2 mJ/pulse, pulse width ~18 ps). The white continuum picosecond probe pulse was generated by passing the fundamental output through a D_2O/H_2O solution. The details of the experimental setup and its operation are described elsewhere.[51] Time zero in these experiments corresponds to the end of the excitation pulse. All the lifetimes and rate constants reported in this study have an experimental error of ±5%.

Nanosecond laser flash photolysis experiments were performed with a Quanta Ray model CDR-1 Nd:YAG laser system using 532 nm (second harmonic) laser pulse (~6 ns laser width) for excitation.[52] The laser

---

(28) Hamada, K.; Take, S.; Iijima, T. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 3141−3148.

(29) Arbeloa, F. L.; Ojeda, P. R.; Arbeloa, I. L. *J. Chem. Soc. Faraday Trans. 2* **1988**, *84*, 1903−1912.

(30) Valdes-Aguilera, O.; Neckers, D. C. *J. Phys. Chem.* **1978**, *92*, 4286−4289; *Acc. Chem. Res.* **1989**, *22*, 171−177.

(31) Das, S.; Thanulingam, T. L.; Thomas, K. G.; Kamat, P. V.; George, M. V. *J. Phys. Chem.* **1993**, *97*, 13620−13624

(32) Fujii, T.; Nishikiori, H.; Tamura, T. *Chem. Phys. Lett.* **1995**, *233*, 424−429.

(33) Chen, H.; Herkstroeter, W. G.; Perlstein, J.; Law, K-. Y.; Whitten, D. G. *J. Phys. Chem.* **1994**, *98*, 5138−5146.

(34) Chen, H.; Farahat, M. S.; Law, K-. Y.; Whitten, D. G. *J. Am. Chem. Soc.* **1996**, *118*, 2584−2594.

(35) McRae, E. G.; Kasha, M. *J. Chem. Phys.* **1958**, *28*, 721−722.

(36) Kasha, M.; Rawls, H. R.; El-Bayoumi, M. A. *Pure Appl. Chem.* **1965**, *11*, 371−392.

(37) Grofcsik, A.; Kubinyi, M.; Jones, W. J. *J. Mol. Struct.* **1995**, *348*, 197−200.

(38) Grofcsik, A.; Jones, W. J. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 1101−1106.

(39) Lawless, M. K.; Mathies, R. A. *J. Chem. Phys.* **1992**, *96*, 8037−8045.

(40) Bigot, J.-Y.; P., M. T.; Schoenlein, R. W.; Bardeen, C. J.; Migus, A.; Shank, C. W. *Phys. Rev. Lett.* **1991**, *66*, 1138−1141.

(41) Drabe, K. E.; Cnossen, G.; Wiersma, D. A. *Chem. Phys. Lett.* **1990**, *169*, 416−420.

(42) Mokhtari, A.; Chesnoy, J.; Laubereau, A. *Chem. Phys. Lett.* **1989**, *155*, 593−598.

(43) Fragnito, H. L.; Bigot, J.-Y.; Becker, P. C.; Shank, C. V. *Chem. Phys. Lett.* **1989**, *160*, 101−104.

(44) Pollard, W. T.; Fragnito, H. L.; Bigot, J.-Y.; Shank, C. V.; Mathies, R. A. *Chem. Phys. Lett.* **1990**, *168*, 239−245.

(45) Becker, P. C.; Fragnito, H. L.; Bigot, J.-Y.; Brito Cruz, C. H.; Fork, R. L.; Shank, C. V. *Phys. Rev. Lett.* **1989**, *63*, 505−507.

(46) Brito Cruz, C. H.; Fork, R. L.; Knox, W. H.; Shank, C. V. *Chem. Phys. Lett.* **1986**, *132*, 341−344.

(47) Taylor, A. J.; Erskine, D. J.; Tang, C. L. *Chem. Phys. Lett.* **1984**, *103*, 430−434.

(48) Wise, F. W.; Rosker, M. J.; Tang, C. L. *J. Chem. Phys.* **1986**, *86*, 2827−2832.

(49) Kobayashi, T.; Takagi, Y.; Kandori, H.; Kemnitz, K.; Yoshihara, K. *Chem. Phys. Lett.* **1991**, *180*, 416−422.

(50) Kamat, P. V. *Chem. Rev.* **1993**, *93*, 267−300.

(51) Ebbesen, T. W. *Rev. Sci. Instrum.* **1988**, *59*, 1307−1309.

(52) Nagarajan, V.; Fessenden, R. W. *J. Phys. Chem.* **1985**, *89*, 2330−2335.

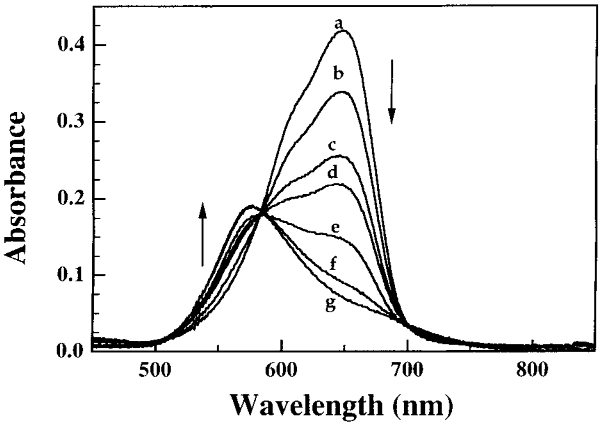


Figure 1. Absorption spectra of 16.1 μM NB in aqueous solution at different concentrations of a colloidal SnO_2 suspension: (a) 0, (b) 0.04, (c) 0.08, (d) 0.12, (e) 0.16, (f) 0.2, and (g) 0.28 mM. A corresponding concentration of SnO_2 colloidal suspension in aqueous solution without dye was used as a reference.

output was suitably attenuated to less than 5 mJ/pulse and defocused to minimize the multiphoton processes. The experiments were performed in a rectangular quartz cell of 6 mm path length with a right-angle configuration between the direction of laser excitation and analyzing light.

Results and Discussion

A. Aggregation of Nile Blue on SnO_2 and SiO_2 Colloids. The aggregation of Nile Blue (NB) in the presence of SnO_2 and SiO_2 colloids was probed by analyzing the absorption and fluorescence spectra of the dye.

i. Absorption Spectra. Figure 1 presents the absorption changes observed upon addition of small amounts of SnO_2 colloids to the aqueous solution of NB. In aqueous solution, the monomeric dye has an absorption maximum at 650 nm. Upon addition of SnO_2 colloids, as seen, the absorption of the monomer decreases and a new band appears at shorter wavelengths ~575 nm. The appearance of the absorption band at 575 nm is at the cost of the monomeric dye, as evidenced by the decreased absorption band of the monomer at 650 nm. Similar behavior was also observed in the presence of SiO_2 colloids except that the aggregate absorption band is at about 595 nm (not shown here). It should be mentioned that the blank SnO_2 and SiO_2 colloids themselves do not have any significant absorption in the visible.

On the basis of our earlier studies with various cationic dyes,[11−13] the blue-shifted bands of NB at 575 and 595 nm in the presence of SnO_2 and SiO_2 colloids, respectively, have been attributed to the formation of H-type or card-pack aggregates of NB, and that the aggregates consist of dimer units. The presence of a single absorption band with a clean isosbestic point indicates that only two species (monomer and dimers) contribute to the absorption spectra. The aggregation process occurs in two steps: (1) association of the dye molecules with SnO_2 (or SiO_2) colloids and (2) the dye aggregation on the colloid surface, as shown below:

$$\mathrm{NB} + \mathrm{SnO_2} \rightarrow \mathrm{NB}\cdots\mathrm{SnO_2},\ \text{association} \qquad (1)$$

$$\mathrm{NB}\cdots\mathrm{SnO_2} + \mathrm{NB} \rightarrow (\mathrm{NB})_2\cdots\mathrm{SnO_2},\ \text{dimerization} \qquad (2)$$

Because of the charge neutralization on the colloid surface, the electrostatic repulsion between the dye molecules is significantly reduced, thereby facilitating the formation of aggregates. The appearance of the aggregate absorption band even at very low dye concentrations suggests that the distribution of dye molecules on SiO_2 and SnO_2 colloid surface is not random, but they are bound preferentially to adjacent surface sites as pointed out by Bergman and O'Konski.[53]

ii. Emission Measurements. NB, in its monomeric form, fluoresces strongly with an emission maximum at 675 nm in aqueous solution. Figure 2 shows the fluorescence spectra of NB in water at different concentrations of SnO_2 colloids. Upon addition of small amounts of SnO_2 colloids, the fluorescence intensity of NB decreases and practically disappears when the concentration of SnO_2 is greater than 0.3 mM. The excitation wavelength was 590 nm which is the isosbestic point for the monomers and aggregates (Figure 1). A similar decrease in fluorescence was also observed upon the addition of SiO_2 colloids, thus confirming that the cationic dye strongly interacts with the surface of the colloid. Since these colloids lead to the formation of aggregates, the absence of any new emission band supports the assumption that the dye aggregates are of H-type, as these aggregates are, in general, nonfluorescent.

The molecular exciton model proposed by McRae and Kasha[35,36] correctly predicts the nonfluorescent nature of H-aggregates. According to this model, the excited singlet state of dye aggregate (dimer) splits into two energy levels, one (S_1^-) being lower and other (S_1^+) being higher in energy than the corresponding monomeric singlet state, as is illustrated in Scheme 2. The transition to the higher state (S_1^+) is allowed for H-type aggregates, while the transition to the lower energy state (S_1^-) is allowed for J-aggregates. Consequently, the J-aggregates are found to be fluorescent while H-aggregates, because of the forbidden nature of the radiative transition $S_1^- \rightarrow S_0$ in them, are nonfluorescent.

Earlier studies of Douhal[54] have indicated that the deprotonated form of NB, formed in the presence of hydrogen accepting solvents, also possesses an absorption band at shorter wavelengths, similar to that observed by us for NB in negatively charged SnO_2 or SiO_2 colloids. However, they also observed a fluorescence band characterstic of the deprotonated form of NB at shorter wavelength (580 nm) in addition to the fluorescence of NB at 675 nm. In the present study of NB adsorbed on SiO_2 or SnO_2 colloids, no additional fluorescence band at shorter wavelength was observed. The fluorescence (Figure 2) shows only one fluorescence band which is characterstic of the monomeric NB. The blue-shifted absorption band at 575 nm for SnO_2/NB system (Figure 1) and that at 595 nm for SiO_2/NB (not shown here) are, therefore, due to the formation of the H-aggregates rather than due to the deprotonated form of NB since no corresponding fluorescence at shorter

---

(53) Bergmann, K.; O'Konski, C. T. *J. Phys. Chem.* **1963**, *67*, 2169−2177.

(54) Douhal. A. *J. Phys. Chem.* **1994**, *98*, 13131−13137.

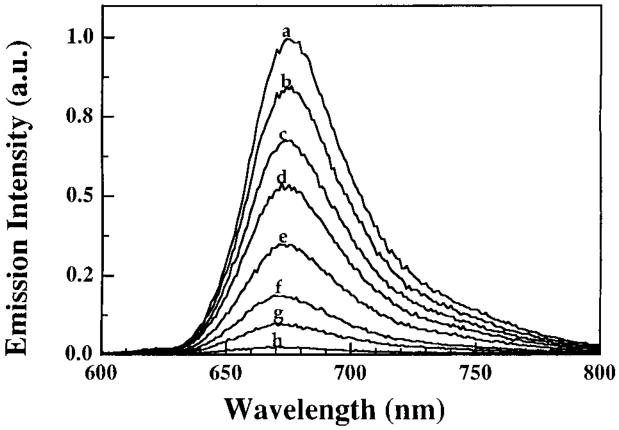
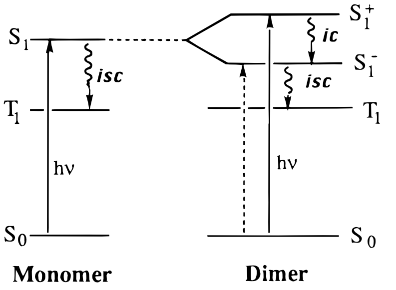


Figure 2. Emission spectra of 4 μM NB in aqueous solution at different concentrations of a colloidal SnO_2 suspension: (a) 0, (b) 0.04, (c) 0.08, (d) 0.12, (e) 0.16, (f) 0.2, (g) 0.24, and (h) 0.28 mM. The excitation wavelength was 590 nm which is the isosbestic point, and emission spectra were corrected for the instrument response.

Scheme 2. Energy Levels (S = Singlet and T = Triplet) of Monomer and Dimer[a]



[a] *isc* and *ic* represent the intersystem crossing and the internal conversion processes, respectively.

wavelength is observed and since H-aggregates are nonfluorescent.

B. Characterization of the Excited States of NB. A pump−probe technique was used to characterize absorption characteristics of the excited states of monomeric and aggregated NB. The short laser pulse (532 nm, pulse width 18 ps) was used for direct excitation while the continuum pulse served as a probe (see Experimental Section for details). Such a pump−probe technique facilitates the detection of short-lived excited states and other transients formed in the subnanosecond time domain.

i. NB Monomer. NB in micromolar concentration is essentially present as monomers in aqueous solutions. The transient absorption spectra recorded at different time intervals following the laser pulse excitation of NB in water (monomeric form) are presented in Figure 3. The difference absorption spectrum exhibits a bleaching at wavelengths greater than 570 nm and a maximum in the region of 525 nm. The bleaching at 635 nm is due to the depletion of the ground state of the dye as it is converted into the excited singlet state of NB, $^1(NB)^*$, with absorption at 525 nm. The decay of the absorption at 525 nm shown in Figure 4A matches very well with the recovery of bleaching at 635 nm (Figure 4B), which confirms that the transient absorption at 525 nm originates from $^1(NB)^*$. Analysis of the first-order decay kinetics of this singlet state gives a lifetime of 390 ps.

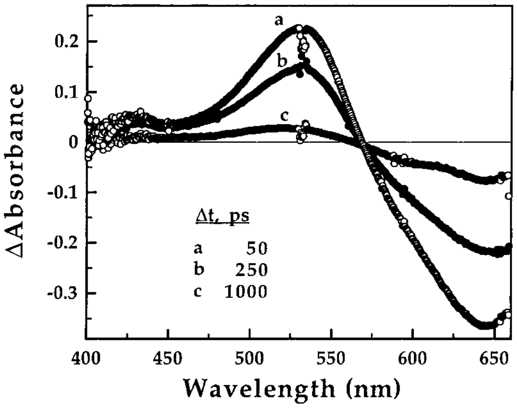


Figure 3. Time-resolved transient absorption spectra recorded following 532 nm laser excitation of an aqueous solution of 20.5 μM NB. The spectra were recorded at Δt = 50, 250, and 1000 ps after laser pulse excitation.

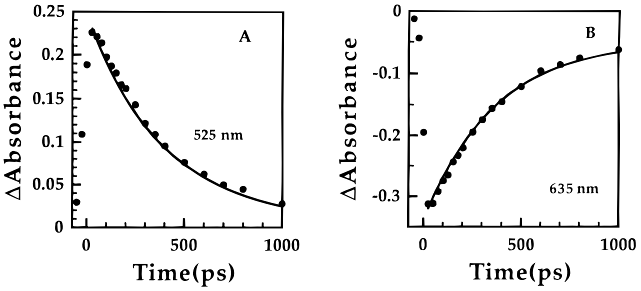


Figure 4. Absorption−time profile spectra recorded following 532 nm laser excitation of an aqueous solution of 20.5 μM NB at (A) 525 nm and (B) 635 nm.

Grofcsik et al.[37] and Grofcsik and Jones[38] reported a value of 418 ps for lifetime of $^1(NB)^*$, while Dutt and co-workers,[55] using time-resolved fluorescence depolarization sepectroscopy with photon counting technique, obtained a value of 380 ps. Considering the experimental error, the agreement between the observed value of lifetime 390 ps in the present study with the literature data is quite good. The spectrum recorded after 4 ns (not shown in Figure 3) shows a small amount of the ground-state bleaching that fails to recover. This residual bleaching which persists following the decay of the singlet excited state is attributed to the formation of triplet excited state.

ii. NB Aggregates. It is shown above that upon addition of negatively charged SnO_2 or SiO_2 colloids, H-aggregates of NB are formed on the surface of the colloids. Thus, in principle, excited-state dynamics of NB aggregates could be studied both in the presence of SnO_2 and SiO_2 colloids. However, since SiO_2 colloids provide an inert support, it facilitates the examination of the excited-state behavior of the aggregate without any perturbation caused by the support. SnO_2, on the other hand, as discussed later, participates in an electron-transfer process. Thus, to probe the excited-state dyanmics of the NB aggregates undisturbed by other processes, a small amount of SiO_2 colloids was added to the aqueous solution of NB, and laser photolysis experiments were carried out.

Figure 5 illustrates the difference absorption spectra of the excitonic singlet state of H-aggregates formed on

---

(55) Dutt, G. B.; Doraiswamy, S.; Periasamy, N.; Venkataraman, B. *J. Chem. Phys.* **1990**, *93*, 8498−8513.

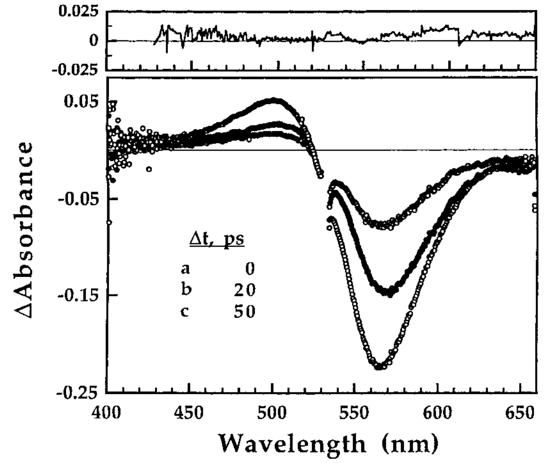


Figure 5. Time-resolved transient absorption spectra recorded following 532 nm laser excitation of an aqueous solution containing 20.5 μM of NB and 1 mM of SiO_2 colloidal suspension. The spectra were recorded at $\Delta t = 0$, 20, and 50 ps after laser pulse excitation.

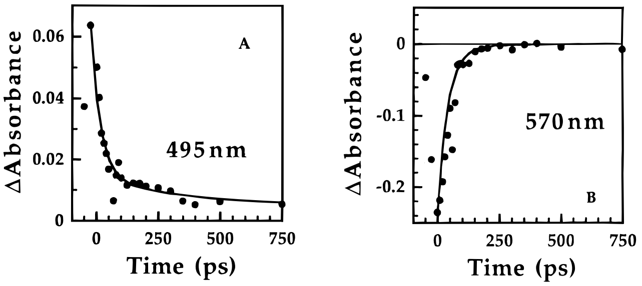


Figure 6. Absorption−time profile spectra recorded following 532 nm laser excitation of an aqueous solution containing 20.5 μM of NB and 1 mM of SiO_2 at (A) 495 nm and (B) 570 nm.

SiO_2 colloids at different time intervals. The transient spectrum recorded immediately after the 532 nm laser pulse excitation ($\Delta t = 0$ ps) shows an absorption band at 495 nm and a bleaching maximum at wavelengths greater than 520 nm. The bleaching corresponds to the ground-state depletion of the dye aggregates as they get converted into the singlet excited state of aggregates, $^1(NB)_2^*$, with absorption at 495 nm. This band is blue-shifted (~30 nm) compared to that for monomeric $^1(NB)^*$ at 525 nm (Figure 3). It should be pointed out that the blank experiements carried out with SiO_2 suspension alone, without the dye, did not exhibit any detectable transient absorption following 532 nm laser pulse excitation.

The analysis of the decay of the absorption band at 495 nm presented in Figure 6A shows that it is biexponential with lifetimes of 40 and 400 ps. The bleaching recovery at 570 nm also shows a similar biexponential behavior with lifetimes of 50 and 380 ps (Figure 6B). We attribute these two lifetimes to the excited states of NB dimer and monomer, i.e., to $^1(NB)_2^*$ and $^1(NB)^*$, respectively. The observation of $^1(NB)^*$, with $\tau \approx 380$ ps, is possibly due to the excitation of NB that failed to adsorb on SiO_2 and thus failed to form aggregates. The major component of the decay of the absorption at 495 nm, however, is due to short-lived $^1(NB)_2^*$.

Since the transition to the upper state is allowed for H-type aggregates, the laser excitation leads to the population of S_1^+ state which quickly relaxes to the S_1^- state by internal conversion. Thus, S_1^- is the state that we actually observe as the transient in the excited-state spectrum of the aggregate. Since, $S_1^- \rightarrow S_0$ radiative transition is forbidden, the deactivation of S_1^- proceeds via internal conversion to the ground state and/or intersystem crossing to generate the excited triplet state (Scheme 2).

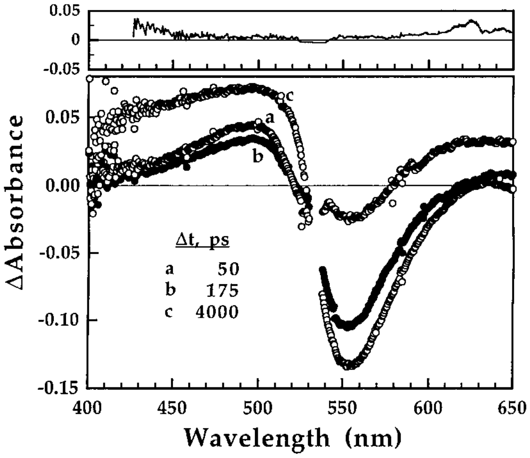


Figure 7. Time-resolved transient absorption spectra recorded following 532 nm laser excitation of an aqueous solution containing 20.5 μM of NB and 1 mM of SnO_2 colloidal suspension. The spectra were recorded at $\Delta t = 50$, 175, and 4000 ps after laser pulse excitation.

C Heterogeneous Electron Transfer at SnO_2/NB Interface. The semiconductor SnO_2 colloids with a conduction band at lower energy provides a reactive support. Thus, besides promoting the dimerization of NB on its negatively charged surface, it can also participate in electron-transfer process.

Figure 7 shows the time-resolved spectra following 532 nm laser pulse excitation of an aqueous solution of NB in the presence of SnO_2 colloids. The difference spectrum (spectrum a), recorded immediately after the laser pulse excitation, exhibits an absorption maximum at 495 nm and a bleaching at 560 nm. The absorption at 495 nm is due to the singlet excitonic state $^1(NB)_2^*$ of NB dimers, similar to that observed in the presence of SiO_2 colloids. However, the picture that emerges at longer time scale is quite different (spectrum c, Figure 7). New absorption bands in the region of 480−520 and 650 nm are obtained.

The absorption at 480−520 nm has been attributed to the formation of the cation radical of NB dimers and is the result of charge injection from excited NB dimers, $(NB)_2^*$, into the conduction band of the SnO_2 colloids:

$$(NB)_2^* + SnO_2 \rightarrow (NB)_2^{\bullet+} + SnO_2(e) \qquad (3)$$

where $(NB)_2^{\bullet+}$ is cation radical of NB dimer and SnO_2(e) represents the electrons trapped in SnO_2 nanocrystallites.

It is worth noting that the formation of $(NB)_2^{\bullet+}$ was seen only in the presence of SnO_2 colloids and not with the SiO_2 ones. Since the conduction band of SnO_2 ($E_{CB} \approx 0.0$ V vs NHE at pH 7 or −0.12 V at pH 9)[56] is significantly lower in energy than that of SiO_2 ($E_{CB} \approx -4.5$ V vs NHE at pH 7 or −4.62 V at pH 9),[56] the charge injection process is energetically favored in the SnO_2/

---

[56] Kajiwara, T.; Hasimoto, K.; Kawai, T.; Sakata, T. *J. Phys. Chem.* **1982**, *86*, 4516−4522.

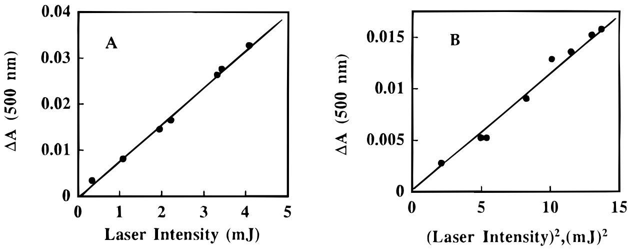


Figure 8. Dependence of transient absorption at 500 nm on (A) laser intensity, following 532 nm excitation of an aqueous solution containing 20.5 μM of NB and 1 mM of SnO_2 colloidal suspension and on (B) square of laser intensity following 532 nm laser excitation of an aqueous solution containing 20.5 μM of NB and 1 mM of SiO_2 colloidal suspension.

$(NB)_2$* system in contrast to that in SiO_2/$(NB)_2$*. Reaction 3 further suggests that as a result of charge injection, one would expect to see the formation of trapped charges in the SnO_2 nanocrystallites. The broad absorption at ~660 nm observed in spectrum c (Figure 7) is consistent with the characterstic absorption in the red region (>600 nm) reported for trapped electrons in metal oxide colloids,[57-62] and thus validates the charge injection from NB aggregates into SnO_2 nanocrystallites.

To further ensure that the formation of cation radical $(NB)_2^{\bullet+}$ in the presence of SnO_2 colloids, was indeed due to the charge injection process from excited H-aggregates of NB, $(NB)_2$*, into the SnO_2 nanocrytallites, the formation of $(NB)_2^{\bullet+}$ on SnO_2 and SiO_2 surfaces was recorded as a function of laser excitation intensity. As shown earlier,[50] depending on its nature, the support material can promote the oxidation of the adsorbate in two different ways. In the first case (SnO_2 system), the support material directly participates in the electron-transfer process with the adsorbate and produces cation radical, while in the second case (SiO_2 system), the support material brings about oxidation via excited-state ionization of the adsorbate. Thus, both support materials yield the same product, i.e., the cation radical of the adsorbate, however, the production of cation radical is a monophotonic process on SnO_2 while it is a multiphotonic on SiO_2.

In other words, one should expect the yield of $(NB)_2^{\bullet+}$ to vary linearly with intensity of light ($n = 1$, n is the exponent of light intensity) in the presence of SnO_2 colloids, while the formation of $(NB)_2^{\bullet+}$ in the presence of SiO_2 colloids should be seen only at relatively high excitation intensities with $n > 1$. Parts A and B of Figure 8 display the dependence of the yield of cation radical $(NB)_2^{\bullet+}$ on relative intensity of the laser pulse. The maximum absorbance at 500 nm recorded immediately after the nanosecond laser pulse (pulse width 6 ns) was taken as a measure of the relative yield of $(NB)_2^{\bullet+}$. From the figures, it is evident that the production of $(NB)_2^{\bullet+}$ is proportional to the intensity of the laser pulse on SnO_2 surface (Figure 8A) but depends on the square of the laser intensity on SiO_2 surface (Figure 8B). This confirms our observation that a monophotonic charge injection process is the dominant process on the SnO_2 semiconducting surface, while a biphotonic photoionization mechanism is operative on the surface of the inert SiO_2 support.

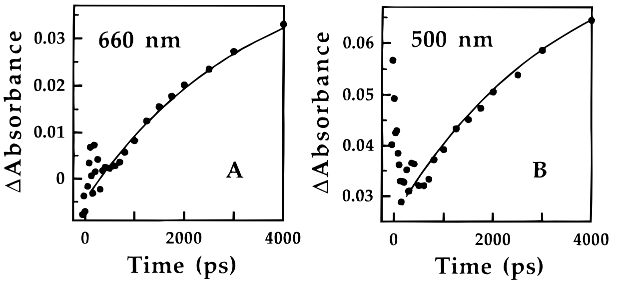


Figure 9. Absorption–time profile spectra recorded following 532 nm laser excitation of an aqueous solution containing 20.5 μM of NB and 1 mM of SnO_2 at (A) 660 nm and (B) 500 nm.

To get an insight into the kinetics of the charge injection process, the absorption–time profiles at 500 and 660 nm, following the excitation of NB dimers adsorbed on SnO_2 colloids, were recorded and are presented in Figure 9. It should be recalled that these wavelengths are characteristic of the formation of the cation radical $(NB)_2^{+\bullet}$ and of the trapped electrons in SnO_2 nanocrystallites, (SnO_2(e)), respectively. Analysis of both these traces shows that they exhibit an exponential growth with lifetimes of 3 and 3.12 ns, respectively, which corresponds to an heteregeneous electron-transfer rate constant of 3.3×10^8 s^{-1}. In our opinion, this is probably the first demonstration of the participation of H-aggregates of NB in a charge injection process. Blank experiments carried out with SnO_2 colloidal suspension without NB did not exhibit any detectable transient absorption.

One may now ask which excited state (singlet or tripet) of NB aggregates injects electrons in semiconductor SnO_2 nanocrystallites? There are several examples in the literature that report charge injection from an excited dye into large band gap semiconductors to occur from both singlet and triplet states.[12,13,63-67] In our earlier study with rhodamine 6G H-aggregates adsorbed on SnO_2 colloids, we showed that the charge injection occurred from the singlet state of the rhodamine aggregates.[12] In the present work, however, we rule out the participation of the singlet state of the NB aggregates in the charge injection process since the singlet excitonic state $^1(NB)_2$* has a very short lifetime ~40 ps and, moreover, there is no evidence from the figure for either the formation of the dye radical cation $(NB)_2^{\bullet+}$ or the phenomenon of electron trapping in SnO_2 on this time scale. Further, the absorption profile at 500 nm (Figure 9B) shows that the growth in absorption of the

---

(57) Bedja, I.; Hotchandani, S.; Kamat, P. V. *J. Phys. Chem.* **1993**, *97*, 11064–70.

(58) Bedja, I.; Hotchandani, S.; Kamat, P. V. *J. Phys. Chem.* **1994**, *98*, 4133–4140.

(59) Rothenberger, G.; Moser, J.; Graetzel, M.; Serpone, N.; Sharma, D. K. *J. Am. Chem. Soc.* **1985**, *107*, 8054–9.

(60) Skinner, D. E.; Colombo, D. P. J.; Cavaleri, J. J.; Bowman, R. M. *J. Phys. Chem.* **1995**, *99*, 7853–7856.

(61) Bahnemann, D.; Henglein, A.; Lilie, J.; Spanhel, L. *J. Phys. Chem.* **1984**, *88*, 709–711.

(62) Howe, R. F.; Graetzel, M. *J. Phys. Chem.* **1985**, *89*, 4495–99.

(63) Eichberger, R.; Willig, F. *Chem. Phys. Lett.* **1990**, *141*, 159–73.

(64) Ryan, M. A.; Fitzgerald, E. C.; Spitler, M. T. *J. Phys. Chem.* **1989**, *93*, 6150–6.

(65) Ryan, M. A.; Spitler, M. T. *J. Imaging Sci* **1989**, *33*, 46–9.

(66) Willig, F.; Eichberger, R.; Sundaresan, N. S.; Parkinson, B. A. *J. Am. Chem. Soc.* **1990**, *112*, 2702–7.

(67) Liu, D.; Kamat, P. V.; George Thomas, K.; Thomas, K. J.; Das, S.; George, M. V. *J. Chem. Phys.* **1997**, *106*, 6404–6411.

cation radical is preceded by the decay of the excitonic singlet state. The kinetics shown in Figure 9 thus support that the triplet state of the NB aggregates is responsible for the charge injection into SnO_2 colloids. Involvement of the triplet state in the charge injection process was also observed for cresyl violet adsorbed on SnO_2 colloids.[13b]

Conclusion

The present study shows that the cationic dye Nile Blue (NB) easily forms aggregates in negatively charged SnO_2 and SiO_2 colloidal suspensions. These aggregates are of H-type which have blue-shifted absorption band with respect to the monomeric absorption and are nonfluorescent. The laser photolysis experiments of NB adsorbed on SiO_2 colloids (inert support) suggest that the excitonic singlet states of the aggregates are relatively short-lived ($\tau \approx 40$ ps) and form an excited triplet state via intersystem crossing. With NB adsorbed on SnO_2 colloids (reactive support), the excited state of the aggregate also injects electrons into SnO_2 nanocrystallites. The rate constant for this heterogeneous electron transfer, evaluated from the growth of the cation radical of the NB aggregate, $(NB)_2^{\bullet+}$, and from electron trapping in SnO_2 nanocrystallites, is 3.3×10^8 s^{-1}. The triplet state of the aggregate is believed to be participating in this charge-transfer process.

Acknowledgment. We thank Dr. Prashant Kamat for helpful discussions and valuable suggestions. The work described herein was supported by the Natural Sciences and Engineering Research Council of Canada. C.N. is grateful to Ministère de l'Éducation Nationale du Maroc for a fellowship and for partial financial support from the Radiation Laboratory, University of Notre Dame.

CM0000752