Photoprocess of molecules encapsulated in porous solids X: Photosensitization of zeolite-Y encapsulated tris(2,2'-bipyridine– nickel-(II)ion by phenosafranine adsorbed onto the external surface of the nanoporous host

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Abstract. Tris-(2,2'-bipyridine)-nickel-(II) complex ion encapsulated by zeolite-Y host has been synthesized by ship-in-a-bottle method. Photosensitization of nickel(II) complex ($\text{Ni}(\text{bpy})_3^{2+}$) in the zeolite host by surface adsorbed phenosafranine dye was investigated by time-resolved fluorescence and absorption spectral measurements. Formation of nickel (II)-complex in the super cage of the host was ascertained by XRD, FTIR, solid-state NMR, diffuse reflectance UV-visible absorption spectroscopic techniques and ICP-OES measurements. Phenosafranine dye adsorbed on the external surface of zeolite-Y shows a decrease in fluorescence intensity with increased loading of the nickel(II) complex in zeolite-Y. Time-resolved emission studies show two excited state lifetimes for the photoexcited phenosafranine dye. Average fluorescence lifetimes of the dye in this case do not change with increase in the loading of the nickel(II) complex. However, relative contribution of short lifetime component increases when the amount of encapsulated nickel(II) complex is increased. The zeolite-Y host containing only bipyridyl ligand shows a marked decrease in fluorescence intensity. Fluorescence lifetimes of the dye however do not change with increased loading of bipyridyl while relative contribution of short lifetime component increases with an increase in the loading of bipyridyl in the host. This observation is interpreted to be due to electron transfer from the excited state of phenosafranine dye to the bipyridine. Picosecond pump-probe investigations confirm that the photoinduced electron transfer occurs from the surface-adsorbed phenosafranine in the excited state to the nickel(II) complex within zeolite-Y cavity and also to the $\text{Ni}(\text{bpy})_3^{2+}$ complex in contact with the phenosafranine dye co-adsorbed on the external surface of the host.

Keywords. Phenosafranine; photosensitization; $\text{Ni}(\text{bpy})_3^{2+}$ ion; zeolite-Y; picosecond transient absorption spectroscopy.

1. Introduction

Encapsulation of photosensitizers such as organic dyes,¹ metal complexes and semiconductor nanoparticles within the nanochannels and nanocavities of silicate host materials is of considerable interest for various applications.² Both steric and electrostatic effects of the encapsulating host influence the structure and reactivity of the encapsulated species which sometimes results in the enhancement of fluorescence lifetime³ of relaxed triplet state and products such as free radicals.⁴ Advantages of silicate hosts are their lack of absorption of visible light, relative chemical inertness and highly ordered cavities and channels of the hosts. Among the micro and mesoporous silicate hosts, zeolite-Y is of

great interest for encapsulating metal complexes due to the larger size of the super cages. In the case of zeolite-Y, three-dimensional network of approximately spherical supercage of about 1.3 nm in diameter connected tetrahedrally through 0.74 nm windows provide enough space for many coordination compounds. Since the pore diameter exceeds the entry aperture, reactants could be encapsulated through the aperture. Investigation of photoprocesses from the donor and acceptor in three-dimensional space is a key challenge in supermolecular chemistry.⁵ The ship-in-a-battle approach has been utilized in a number of interesting photophysical studies of both organic and inorganic fluorophores which are translationally trapped in the zeolite-Y host.⁶ Pore environments of the zeolites are known to alter the photophysical and photochemistry of the guest species due to the steric confinement and different dielectric properties of the aluminosilicate cages.

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Entrapment of transition metal complexes of ruthenium, cobalt and nickel with 2,2'-bipyridine in zeolite-Y has attracted particular attention to solar energy conversion applications, photochemical molecular devices and photocatalysis.⁷ Photoreduction of carbon dioxide to carbon monoxide is an important process and it has been shown that photocatalysis by $\text{Ni}(\text{bpy})_3^{2+}$ in the presence of triethylamine in acetonitrile, reduces carbon dioxide to carbon monoxide.⁸ At present, many researchers are investigating the donor-acceptor systems in different zeolite hosts.^{2b,9} Nickel (II) ion forms mono, bis and tris complexes with 2,2'-bipyridine as ligand when encapsulated in zeolite-Y. These complexes are known to be present in cavities and channels depending upon the coordination state of the nickel ion and steric hindrances induced by the host structure.¹⁰ This study is an attempt to investigate the visible light-induced electron transfer from surface adsorbed phenosafranine to the $\text{Ni}(\text{bpy})_3^{2+}$ complex within zeolite-Y host (scheme 1).

Phenosafranine is known to be an efficient photosensitizer for energy conversion in dye-sensitized solar cells.¹¹ Encapsulation of coordination compound in the zeolite-Y host has been reported by an elegant method earlier.¹² Photosensitization of titanium dioxide nanoparticles encapsulated in the zeolite host by surface-adsorbed phenosafranine in the excited state is reported earlier.¹³ Recently, researchers mainly focused on electron transfer processes in solid host because the solid host materials help to prevent back electron transfer and also stabilize the charge transfer species for a long time. Nature of electron transfer processes in nanocavity of the silicate host is investigated by steady state and time-resolved fluorescence lifetime and picosecond pump-probe techniques.

2. Experimental

2.1 Materials

Zeolite-Y was procured from SudChemie India Ltd. 2, 2'-bipyridine (bpy) and NiCl_2 were purchased from Alfa Aesar. Solvents used in this study were purchased from Qualigens Chemicals. Phenosafranine dye in the monocationic chloride form was obtained from Aldrich.

2.2 Sample preparation

Zeolite-Y is stirred with 1 M sodium chloride solution for 2 h to remove extra framework impurities such as iron. The solid was washed further with excess volume

of triply distilled water until the filtrate showed negative test for chloride ion with silver nitrate solution. The resulting sample was calcined at 530°C in a muffle furnace for 12 h and the samples were then stored in an airtight container and used as such for further studies. Crystallinity of the zeolite-Y was confirmed by powder XRD pattern as listed in the database (<http://www.iza-structure.org/databases/>).

Nickel ion exchanged zeolite-Y (Ni-Y) was prepared from Na^+ -Y by treating it with 1.0 mM NiCl_2 solution for 4 h. The resulting zeolite-Y after ion exchange was washed with deionized water until the silver ion test for chloride was negative. Ni-Y was dried at 100°C and stored in airtight container. The bpy-exchanged zeolite-Y was prepared by mixing weighed amount of bpy dissolved in ethanol along with 1.0 g of dry zeolite-Y. The mixture was stirred for 12 h and the resulting bpy-zeolite-Y (bpy-Y) was washed with excess volume of water and dried at 100°C.

Incorporation of $\text{Ni}(\text{bpy})_3^{2+}$ into Na^+ -exchanged zeolite-Y was carried out similar to the procedure of Quayle and Lunsford.¹² 0.5 g of Ni^{2+} -zeolite-Y was taken in a 50 mL flask to which 0.05 g of 2,2'-bipyridine ligand dissolved in ethanol was added. The mixture was stirred under reflux for 2 h. During the course of the reaction, the colour of the solid changes from white to pink indicating formation of $\text{Ni}(\text{bpy})_3^{2+}$ in the zeolite-Y supercages. In order to remove $\text{Ni}(\text{bpy})_3^{2+}$ complex that might have formed on the external surface of zeolite-Y, the $\text{Ni}(\text{bpy})_3^{2+}$ -incorporated zeolite-Y was washed several times with aqueous NaCl solution (0.1 M, 50 mL). The solid was washed with hot ethanol and dried at 100°C and then stored in an airtight container. Total amount of nickel present in zeolite-Y containing the $\text{Ni}(\text{bpy})_3^{2+}$ complex was estimated by ICP-OES. Concentration of nickel complex within the zeolite-Y was estimated separately by dissolving 50 mg of the $\text{Ni}(\text{bpy})_3^{2+}$ -Y in hydrofluoric acid (5 mL, 10% V/V) and concentration of nickel complex was then estimated from the absorbance in the visible region.^{10a}

Phenosafranine-loaded $\text{Ni}(\text{bpy})_3^{2+}$ -Y was prepared by stirring an aqueous solution of the dye with known amount of $\text{Ni}(\text{bpy})_3^{2+}$ and zeolite-Y for about 4 h. The resulting coloured solid was filtered and washed with excess amount of water until the filtrate showed no absorbance at 520 nm for phenosafranine; the obtained sample was dried at room temperature.

2.3 Characterization

BET surface area, pore volume and pore size distribution of $\text{Ni}(\text{bpy})_3^{2+}$ -loaded zeolite-Y samples were

Scheme 1. Graphical representation of phenosafranine adsorption on surface of Na-Y and Ni(bpy)₃²⁺-Y and respective picoseconds transient absorption spectra.

determined using volumetric adsorption equipment (ASAP 2010 micrometric USA) at 77 K. The sample was degassed under vacuum at 373 K prior to data collection. Powder X-ray diffraction patterns were recorded using a diffractometer with CuK α radiation ($\lambda = 1.5406$ Å). UV-visible diffuse reflectance spectra of powder zeolite-Y sample were collected using Agilent 8453 spectrophotometer equipped with labsphere RSH-HP-8453 reflectance accessory. The solid state NMR spectra were obtained in a Bruker 500 MHz spectrometer and the IR spectrum was obtained in a Perkin-Elmer equipment. Steady state fluorescence measurement of the dye-loaded zeolite-Y powder samples was carried out using Jobin-Yuon Fluoromax-4 spectrophotometer at 45° in the front-face configuration. Time-resolved fluorescence measurements were carried out using IBH time-correlated single photon counting setup. Samples were excited at 470 nm and

fluorescence decay was measured at the front-face configuration with suitable cut-off-filters to avoid scattered light. Data analysis was carried out by the software provided by IBH (DAS-6) which is based on deconvolution technique using non-linear least square method and the quality of the fit is ascertained by the value $\chi^2 < 1.2$ and weighted residuals.

Ultrafast transient absorption experiments were carried out using mode-locked Nd:YAG laser system PY61C-10, (532 nm, 5 mJ/pulse, FWHM 35 ps, 10 Hz repetition rate). White light probe was generated by focusing fundamental laser output (1064 nm) through a cylindrical quartz cuvette containing 10 mL water and 10 mL D₂O mixture. Probe light intensity is very weak beyond 750 nm. Optical delay line provided a pump beam time window of 2.45 ns with a step resolution of 3.33 ps. The pump beam was attenuated at 1 mJ/pulse with a spot size of 4 mm diameter at the

sample position, where it was merged with the white light incident on the sample cell at the front-face configuration. The scattered 532 nm laser beam was filtered using band pass filter and the reflected probe light was focused on a 200 μm core fibre connected to an Ocean Optics SD2000 UV-Vis CCD spectrophotometer (400 to 800 nm). Typically, 100 excitation pulses were averaged to obtain the transient absorption spectrum at the set delay time. All the experiments were conducted at ambient temperature.

3. Results and Discussion

3.1 Characterization of tris-(2, 2'-bipyridine)-nickel-(II) ion encapsulated into the zeolite-Y host

Diffuse reflectance spectrum of $\text{Ni}(\text{bpy})_3^{2+}$ complex entrapped in zeolite-Y with absorption maximum at 536 nm as shown in figure 1 is assigned to a d-d transition ${}^3\text{A}_2 - {}^3\text{T}_1(\text{F})$. Absorption spectrum of the complex, $\text{Ni}(\text{bpy})_3(\text{ClO}_4)_2$, dissolved in neat ethanol shows absorption maximum of d-d transition ${}^3\text{A}_2 - {}^3\text{T}_1(\text{F})$ band at 518 nm.^{10a} Recently, we have investigated the charge transfer photochemistry of $\text{Ni}(\text{bpy})_3^{2+}$ in aqueous solution which shows the ligand oxidation process.^{13a} A red shift in the absorption maximum of the complex in the zeolite-Y host lattice indicates that the $\text{Ni}(\text{bpy})_3^{2+}$ complex is in the environment of the zeolite-Y supercage which is supported by structural and surface area measurements. The IR spectra of bpy-Y ligand, $\text{Ni}(\text{bpy})_3^{2+}$ -Y and Na-Y are shown in figure 2. The band over the region of 1350–1500 cm^{-1} corresponds

Figure 1. Absorption spectrum of $\text{Ni}(\text{bpy})_3^{2+}$ complex in i) aqueous solution and ii) encapsulated into the zeolite-Y.

Figure 2. IR spectra of (a) zeolite-Y, (b) bpy-Y and (c) $\text{Ni}(\text{bpy})_3^{2+}$ -Y.

to the ring vibrations of bpy ligands. The IR spectra of zeolite-Y did not show any peak in this region. The IR band observed around 1453 cm^{-1} and 1415 cm^{-1} in figure 2b is attributed to the different vibrational modes of bipyridine ring with C_2 symmetry.^{13d} Symmetry changes to C_{2v} on complexation with nickel (II) ions and the frequency of the bpy ring vibrations get blue shifted to 1453 and 1440 cm^{-1} . The shift in IR frequencies of $\text{Ni}(\text{bpy})_3^{2+}$ -Y complexes as compared to that of free bpy ligand also supports formation of $\text{Ni}(\text{bpy})_3^{2+}$ -Y in the supercages of zeolite-Y. Samples were washed thoroughly with a solution of sodium chloride which removes any complex adsorbed on to the external surface of the host. Proton NMR spectra of the solid samples show the characteristic bpy features in the region 6.0–9.0 ppm. (figure S1). It is thus concluded that the $\text{Ni}(\text{bpy})_3^{2+}$ complex is indeed encapsulated by the zeolite-Y host. Quayle and co-workers have reported that the location of large, transition metal complexes either within or on the external surfaces of Faujasite-type zeolites can be determined from the analysis of the XRD pattern of the host lattice.^{12,14} Accordingly, the relative peak intensities of the (220) and (311) in the XRD pattern show that the intensity of peak at the (220) is considerably reduced in the host when the complex is encapsulated in the super cage. Ratio of intensities of the (220) reflection to that of the intensity for the (311) reflection is found to be 1.57 for the zeolite host without the complex; and when the complex is encapsulated in the surfaces, the corresponding ratio is determined to be 0.66 and 0.59 for the samples as given in table 1. The XRD patterns for zeolite-Y (Na^+) alone and with $\text{Ni}(\text{bpy})_3^{2+}$ in the zeolite-Y host are shown in figure 3.

Table 1. Adsorption characteristics of zeolite-Y encapsulated with nickel complex, nickel ion and bpy

Sample	BET surface area, (m ² /g)	Micropore volume, (m ³ /g)	% nickel loading	Conc. in μ mol/g	Ratio of I ₂₂₀ /I ₃₁₁
Na-Y	738	0.35	0.00	—	1.57
Ni-Y	669	0.32	1.32	—	1.24
Ni(bpy) ₃ ²⁺ -Y(1)	613	0.31	0.31 ^a	11	0.66
Ni(bpy) ₃ ²⁺ -Y(2)	545	0.27	1.22 ^a	17	0.59
Bpy-Y	675	0.32	0.00	174	1.19

^aPart of the nickel is not coordinated (<10%); the values are total nickel estimated from ICP-OES estimation.

Figure 3. XRD pattern of (a) Na-Y and (b) Ni(bpy)₃²⁺-Y(1.22% loading), (c) Ni-Y and (d) Ni(bpy)₃²⁺ adsorbed on the surface of zeolite-Y.

Adsorption and desorption isotherms using nitrogen gas for zeolite-Y and Ni(bpy)₃²⁺ complex exchanged zeolite-Y are shown in figure S2. Adsorption and desorption isotherms for zeolite-Y and nickel(II) ion, bpy and Ni(bpy)₃²⁺ complex encapsulated with zeolite-Y show typical hysteresis loop; the surface area and pore volume characteristics of zeolite-Y encapsulated with Ni(bpy)₃²⁺ complexes are given in table 1. BET surface area of Na⁺-ion-exchanged zeolite-Y is measured to be 739 m²/g; whereas in the case of nickel (II) ion

exchanged zeolite-Y, BET surface area is 669 m²/g. Observed decrease in the BET surface area for the nickel (II) loaded sample is due to factors related to the size of the metal cations and presumably complex formation with the water molecules present in the host lattice. The bpy and Ni(bpy)₃²⁺ complex loaded zeolite-Y samples show BET surface area of 675 and 545 m²/g, respectively. With an increase in the loading of nickel (II) complex into the zeolite-Y, a decrease in the BET surface area and micropore volume is observed

indicating that the nickel (II) complex is entrapped in the zeolite-Y cavity. Both BET surface area and the XRD patterns of nickel (II) complex loaded zeolite-Y reveal that $\text{Ni}(\text{bpy})_3^{2+}$ complex is indeed present inside the nanocavities of zeolite-Y. Dutta and Severance^{2b} reported the ratio of $\text{Ru}(\text{bpy})_3^{2+}$ ion to the empty supercages in Faujasite; using the data provided; it was estimated that the nickel (II) complex is encapsulated in approximately 30:1 (1.27% sample) and 45:1 (0.31% sample) ratio of the available supercages of the host for the two samples considering that the identical host holds one complex in the cavity.

3.2 Photophysics of phenosafranine adsorbed onto the external surface of the zeolite-Y in presence of $\text{Ni}(\text{bpy})_3^{2+}$ complex, bpy ligand and nickel (II) ion

Diffuse reflectance spectra of the dye adsorbed onto the zeolite-Y with various loading levels of $\text{Ni}(\text{bpy})_3^{2+}$ complex in the zeolite are shown in figure 4. The dye, phenosafranine is known to be adsorbed only onto the external surface of zeolite-Y as the molecular dimension of the dye is too large to be encapsulated in the supercage (scheme 1). The dye adsorbed onto the surface of zeolite-Y-containing $\text{Ni}(\text{bpy})_3^{2+}$ complex exhibits absorption maximum at 520 nm which is similar to that of the dye in zeolite-Y11a indicating that the ground state and excited state electronic spectral properties of the dye are not altered significantly due to the encapsulation of $\text{Ni}(\text{bpy})_3^{2+}$ complex into the nanocavity of zeolite-Y (figure 4). Fluorescence intensity of the dye shows a decrease with increase in the loading of the $\text{Ni}(\text{bpy})_3^{2+}$ complex in zeolite-Y on excitation of the adsorbed dye at 520 nm. Observed decrease in fluorescence intensity is presumably due to the following processes: (i) electron transfer from surface-adsorbed

phenosafranine in the excited state to the $\text{Ni}(\text{bpy})_3^{2+}$ complex inside the zeolite-Y cavity or (ii) quenching of fluorescence intensity by excess of $\text{Ni}(\text{II})$ -ion present in zeolite host. It is known that paramagnetic ions enhance the intersystem crossing process resulting in decrease of fluorescence intensity of many organic compounds. On the other hand, a decrease in fluorescence intensity may also be due to trivial absorbance of some light by the nickel (II) complex. In order to understand further the nature of the quenching process of the fluorescence from the dye adsorbed on to the surface of the $\text{Ni}(\text{II})$ -ion exchanged zeolite-Y and zeolite-Y containing only the bipyridine ligand, the steady state emission behaviour of these samples is investigated.

Diffuse reflectance spectra and fluorescence emission spectra of phenosafranine adsorbed onto the zeolite-Y with various loading levels of $\text{Ni}(\text{II})$ ion in the zeolite-Y host are shown in figure S2. Phenosafranine adsorbed on zeolite-Y with increase in the loading level of nickel (II) ion shows an increase in fluorescence intensity as compared to that of the dye adsorbed on to the Na^+ -exchanged zeolite-Y. Firor and Seff¹⁵ reported that when Na^+ ion is exchanged by nickel(II) ion into the zeolite-Y, nickel ion induces the dissociation of one proton per water molecule to form three $\text{Ni}(\text{II})\text{-OH}(\text{Si}, \text{Al})$ linkages per nickel(II) ion. Hence, observed increase in fluorescence intensity is due to the formation of $\text{Ni}(\text{II})\text{-OH}(\text{Si}, \text{Al})$ linkage in the zeolite-Y framework which reduces the extent of interaction between Al-O-Si group present in the zeolite-Y and the dye molecule. Based on this, decrease in fluorescence intensity is suggested to be due to processes other than quenching of phenosafranine excited state by paramagnetic nickel (II) ion adsorbed onto the host.

Diffuse reflectance and fluorescence spectra of the dye adsorbed onto the zeolite-Y with different

Figure 4. Diffuse reflectance spectra (a) and emission spectra (excitation at 520 nm) (b) of phenosafranine adsorbed on zeolite-Y encapsulated with various loading levels of $\text{Ni}(\text{bpy})_3^{2+}$ complex (i: 0%, ii: 0.26%, iii: 0.31%, iv: 0.47% and v: 1.22%).

loading level of 2, 2'-bipyridine present in the zeolite-Y is shown in figure 5. Diffuse reflectance absorption spectra of the samples with different concentrations of bpy in zeolite-Y indicate an increase in the absorbance at 242 and 290 nm (figure S3). The $\pi \rightarrow \pi^*$ transition of bpy encapsulated in zeolite-Y is observed at 242 and 290 nm; for the bpy dissolved in ethanol, absorption maxima are observed at 234 and 280 nm. This observed significant red shift in the absorption spectrum with the bpy present in zeolite-Y host reveals that the bpy is more strongly adsorbed in the zeolite-Y host. Such type of red shift in the absorption maximum was reported^{2c} in the case of bpy encapsulated in silicalite-1 and ZSM-5. Phenosafranine shows a decrease in fluorescence intensity with increasing load of bpy in zeolite-Y as shown in figure 5b. Observed decrease in fluorescence intensity is suggested to be due to electron transfer from the dye in the excited state to bpy in zeolite-Y host. In order to further understand the excited state processes, we have carried out fluorescence lifetime measurement and picosecond transient absorption spectral studies.

3.3 Fluorescence lifetime studies of phenosafranine adsorbed on zeolite-Y in the presence of Ni(II) ion, bpy ligand and Ni(bpy)₃²⁺ complex

In aqueous solution, fluorescence decay from the excited state of phenosafranine corresponds to a single exponential lifetime of 0.82 ns.^{11a,13c} In the case of phenosafranine adsorbed on the zeolite-Y, the fluorescence decay profile fits satisfactorily with bi-exponential functions with the lifetimes of 0.44 ns (48.19%) and 1.18 ns (51.81%). The observed shorter lifetime component is due to interaction of the dye with Al-O-Si group and longer lifetime component is attributed to interaction of the dye with (-Si-OH) group.

In the case of the dye adsorbed onto the nickel (II) exchanged zeolite, a bi-exponential decay with lifetimes of 0.22 ns (12.53%) and 1.32 ns (88.77%) is observed. Formation of nickel (II)-OH-(Si,Al) linkage is likely to prevent interaction of the dye with the available H-O-Si group resulting in an increase in the relative amplitude of the longer lifetime component. Time-resolved fluorescence measurement of phenosafranine adsorbed on the zeolite-Y surface with increase in the loading of Ni(bpy)₃²⁺ complex further elucidates quenching mechanism involved in these systems.

Fluorescence decay observed for phenosafranine in Ni(bpy)₃²⁺ complex entrapped zeolite is fitted satisfactorily to bi-exponential function with $\chi^2 < 1.5$. In the case of Ni(bpy)₃²⁺ complex loaded zeolite-Y, observed fluorescence lifetimes of the dye are not affected significantly with an increase in the loading of the nickel complex into the zeolite-Y cavity as indicated in figure 6, whereas relative amplitude of the short lifetime component increases with increased loading of the nickel complex. Recently, Corma and co-workers^{9c} studied electron transfer from the excited state of Ru(bpy)₃²⁺ present at the external cups of ITQ-2 zeolite to methyl viologen, MV²⁺ included in the independent and not-connected channels. After incorporation of MV²⁺, a significant decrease in emission intensity of Ru(bpy)₃²⁺ was observed with emission lifetime essentially unaffected. Emission data is interpreted to be due to contact quenching between the excited states of Ru(bpy)₃²⁺ and MV²⁺ in close proximity. Excited state of Ru(bpy)₃²⁺ ion shows normal emission properties when MV²⁺ is not in the vicinity of the complex. It has also been observed that TiO₂ encapsulated with MCM-41 and porous silicates also show contact quenching by the excited states of different dyes.^{13c} Based on these results, it is suggested that photosensitization of Ni(bpy)₃²⁺ complex by

Figure 5. Diffuse reflectance spectra (a) and emission spectra (excitation at 520 nm) (b) of phenosafranine adsorbed on zeolite-Y encapsulated with various loading levels of bpy (i: 0%, ii: 0.26%, iii: 0.31%, iv: 0.47% and v: 1.22%).

Figure 6. Fluorescence lifetime (Left picture) and relative amplitude (Right) of phenosafranine adsorbed on zeolite-Y encapsulated with various loading levels of Ni(bpy)₃²⁺ complex (i: 0%, ii: 0.26%, iii: 0.31%, iv: 0.47% and v: 1.22%).

surface-adsorbed excited state of phenosafranine occurs only when the dye and Ni(bpy)₃²⁺ complex (complex is present when dye is located closer to the pore opening of zeolite-Y host) are found in close proximity in the zeolite host material. If the Ni(bpy)₃²⁺ complex is present in the interior of the host material, quenching process does not occur and it is suggested that only a static quenching mechanism is indicated with the excited state of the dye and Ni(bpy)₃²⁺ complex are in contact.

While average fluorescence lifetime of the dye is found to be unchanged with increasing loading of bpy in zeolite-Y, relative contribution of shorter lifetime component is increased with increase in the loading of bpy as shown in figure S4. Observed increase in relative amplitude of shorter lifetime component is attributed to the electron transfer process occurring from the surface-adsorbed phenosafranine to the bpy present in the zeolite-Y host. In order to further confirm the electron transfer processes in zeolite host, we have carried out the picosecond pump-probe transient absorption studies (vide infra).

3.4 Absorption spectral studies of the transient observed on photolysis in picosecond time domain by pump-probe techniques

Excitation of the solid sample of phenosafranine adsorbed onto the external surface of the nanoporous host, Zeolite-Y, using 532 nm laser pulse, shows broad transient absorption band starting from 630 nm with maximum absorbance at 730 nm (figure 7, Z-Y-Ps). The transients observed are suggested to be due to formation of the excited triplet state of the dye (reported absorption maxima at ~700 and 790 nm in aqueous solution^{11b}) trapped electron and oxidized

Figure 7. Transient absorption spectra of phenosafranine adsorbed onto the Ni(bpy)₃²⁺-Y, Na-Y, Ni-Y and bpy-Y (excitation at 532 nm probe: white light delay: 133 ps).

phenosafranine radical. In presence of nickel bipyridyl complex ion, Ni(bpy)₃²⁺ in the cavity, the dye present at the external surface of the host on excitation with 532 nm laser pulse shows transient absorption with essentially a band at $\lambda_{\text{max}} \approx 680$ nm with a shoulder red shifted by 10 nm and another feature with maximum at 580 nm (figure 7, Ni(bpy)₃²⁺-Y-Ps). It is interpreted that in the presence of the nickel complex, transient absorption with maximum at 730 nm which is due to the trapped electron disappears and the well-defined absorption band observed at 675 nm is suggested to be due to the phenosafranine-oxidized radical and the transient spectral feature at 575 nm is due to the bipyridyl anion radical.¹⁶ The absorbance maximum observed at 680 nm is interpreted to be due to the triplet state of the phenosafranine dye. Absorption spectra of the oxidized form of phenosafranine dye and

the triple state of phenosafranine are well-documented in the literature.^{13c} $\text{Ni}(\text{bpy})_3^{2+}$ ion encapsulated in the supercages of the host is reduced by the electron produced from the excited dye resulting in the formation of bpy anion radical. In the picosecond pump-probe results depicted in figure 8, further decay of the phenosafranine cation radical reacting with the other species is not well-characterized. The dye adsorbed on $\text{Ni}(\text{bpy})_3^{2+}$ complex entrapped zeolite-Y (figure 8) shows transient maxima at 570 and 675 nm corresponding to the anion radical of bpy and cation radical of the dye, respectively. Generation of $\text{bpy}^{\cdot-}$ and $\text{PS}^{\cdot+}$ within the pulse duration on the picosecond laser excitation indicates that the quenching process is due to interaction between the excited dye and the $\text{Ni}(\text{bpy})_3^{2+}$ complex in contact with each other or mediated by water molecules or the lattice. It is known that on photolysis of 2,2'-bpy co-adsorbed with DABCO in zeolite-Y, the radical anion is observed as the major species with the transient electronic absorption spectra (broad absorption around 540 nm) as reported earlier.¹⁶ Phenosafranine adsorbed on the nickel(II) ion exchanged zeolite-Y shows transient absorption maxima at ~ 680 nm (figure 9). These observations are best correlated with the steady state and time resolved fluorescence spectral studies of the dye in nickel (II) ion exchanged zeolite-Y as indicated in scheme 1.

Based on the picosecond transient absorption spectral studies, we conclude that electron transfer occurs from the excited state phenosafranine to entrapped $\text{Ni}(\text{bpy})_3^{2+}$ complex into zeolite-Y. Phenosafranine adsorbed on

Figure 8. Transient absorption spectra of phenosafranine adsorbed onto the $\text{Ni}(\text{bpy})_3^{2+}$ complex loaded zeolite-Y (inset; plot of change in absorbance at 680 nm corresponding to the delay time). (Excitation at 532 nm probe: white light).

Figure 9. Transient absorption spectra of phenosafranine adsorbed onto the Ni-exchanged zeolite-Y (inset; plot of change in absorbance at 680 nm corresponding to the delay time) (excitation at 532 nm probe: white light).

bpy-loaded zeolite-Y does not show such type of transient spectra which indicates that electron transfer may be very fast from the dye to bpy in zeolite host. There have not been many detailed investigations in the literature on the time-resolved excited state processes of dyes adsorbed on the surface of porous materials. The excited state produced from the dye in homogeneous solution and microheterogeneous media undergoes redox processes in presence of appropriate quenchers. In these media, quenching of the excited state of the dye is known to occur by diffusion process in solution. However, in the solid surface, the excited state formed undergoes charge transfer processes by contact quenching when the quencher is present in the vicinity of the excited state or mediated through lattice in presence of adsorbed water molecules. Investigations reported on the present systems are important to understand the excited state processes in nanoporous solids for many applications in device fabrication, sensors, and in other areas.

4. Conclusion

Diffuse reflectance spectra and XRD pattern show that $\text{Ni}(\text{bpy})_3^{2+}$ complex is present in the nanocavity of zeolite-Y. Crystallinity of the host is not significantly affected due to encapsulation of bpy and $\text{Ni}(\text{bpy})_3^{2+}$ complex by the silicate which is confirmed by XRD and BET surface area measurement. Photophysics and photochemistry of the dye adsorbed on zeolite-Y in absence and presence of $\text{Ni}(\text{bpy})_3^{2+}$ complex have been studied using fluorescence lifetime and picosecond transient

absorption techniques. Results of this study show that electron transfer occurs from the excited state of the surface-adsorbed phenosafranine to $\text{Ni}(\text{bpy})_3^{2+}$ complex entrapped zeolite-Y cavity.

Supplementary Information

NMR spectra of complex encapsulated in the zeolite-Y, adsorption and desorption isotherms of N_2 on zeolite-Y containing different loading of $\text{Ni}(\text{bpy})_3^{2+}$ complex and absorption and emission spectra of bpy in zeolite host are available as supplementary information (figures S1–S5) and can be seen at www.ias.ac.in/chemsci.

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