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Zeolite-Entrapped Organized Molecular Assemblies. New Evidence for Highly Efficient Adjacent Cage Dyad Formation and Constrained Rotational Mobility of Tris-Ligated Polypyridine Complexes

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The primary objectives of the present work are to investigate the extent to which an entrapped, tris-ligated polypyridine complex of divalent ruthenium is restricted from rotating within the supercage of Y-zeolite and to provide additional evidence for the high efficiency of synthetic procedures developed for the preparation of adjacent cage dyads entrapped within the Y-zeolite framework. Specifically, the Y-zeolite entrapped complex, Z-[Ru(bpy)$_2$(pypz)$^{2+}$] (where the prefix, Z, indicated a zeolite entrapped complex, bpy = 2,2′-bipyridine and pypz = 2-2-pyridylpyrazine), which contains only one reactive peripheral nitrogen atom, is shown to react with the reagent, (H$_2$O)Ru(NH$_3$)$_5$$^{2+}$, to yield the entrapped Z-[Ru(bpy)$_2$(pypz)-Ru(NH$_3$)$_5$]$^{4+}$ complex. Treatment with a large excess of bpy, according to previously documented procedures, leads to the formation of the entrapped adjacent cage dyad, Z-[Ru(bpy)$_2$(pypz)$^{2+}$/Ru(bpy)$_3$$^{2+}$], wherein the two-component complexes are entrapped in adjacent supercages. Spectroscopic measurements confirm the integrity of the component complexes and document a strong interaction between them. Most importantly, it is shown that a second treatment of this material with a large excess of the[(H$_2$O)Ru(NH$_3$)$_5$]$^{2+}$ reagent does not lead to formation of significant amounts of Z-[Ru(bpy)$_2$(pypz)-Ru(NH$_3$)$_5$]$^{4+}$; i.e., the presence of the Ru(bpy)$_3$$^{2+}$ in the cage adjacent to the primary complex shields the latter from further reaction with the ruthenium pentammine reagent. This result demonstrates that, during the formation of the Ru(bpy)$_3$$^{2+}$ secondary complex, the detached Ru(NH$_3$)$_5$$^{2+}$ fragment does not drift into remote supercages, thereby providing unequivocal evidence for the high efficiency of the synthetic procedure for adjacent cage dyad formation. Furthermore, this result also makes it clear that rotation of the tris-ligated primary complex is restricted by the confinement of the Y-zeolite supercage to the extent that the single reactive peripheral nitrogen cannot be repositioned to a different window of the surrounding supercage.

Introduction

Polypyridine complexes of divalent ruthenium, such as tris-2,2′-bipyridine ruthenium (II) [Ru(bpy)$_3$$^{2+}$] and its structural analogues, continue to attract much attention as effective photosensitizers for potentially efficient solar energy conversion devices.[1] Following early work by Lunsford and co-workers,[2] which documented the feasibility of entrapping Ru(bpy)$_3$$^{2+}$ within the supercages of Y-zeolite, Dutta and co-workers[3] demonstrated efficient photoinduced electron transfer from the ^{3}MLCT state of zeolite-entrapped Ru(bpy)$_3$$^{2+}$ to viologen acceptors occupying the neighboring cages and provided convincing evidence that the wasteful back electron-transfer process (BET) within the primary photoproduct [Ru(bpy)$_3$$^{3+}$/viologen$^{+\bullet}$] is retarded. At the same time, effective procedures for the synthesis of structurally diverse intrazeolitic complexes, including bis-2,2′-bipyridine-mono-bipyrazine ruthenium(II) complex, [Ru(bpy)$_2$(bpz)$^{2+}$], as well as many other complexes were developed in our laboratory.[4]

In one of the most impressive studies of photoinduced net charge separation, Dutta and co-workers[5] showed that reducing equivalents can be effectively transferred from an intrazeolitic viologen acceptor to an excluded, solution phase, viologen of appropriate potential, i.e., a zwitterionic neutral viologen. Though encouraging, the overall net charge separation efficiency remained relatively low, one of the responsible factors apparently being a persistent, unacceptably high, BET process within the primary photoredox pair (i.e., Ru(bpy)$_3$$^{3+}$/reduced viologen).

In an effort to eliminate the initial BET process, we devised a strategy based on construction of intrazeolitic organized molecular assemblies consisting of donor:sensitizer:acceptor (D:S:A) triads.[6] Specifically, solution chemistry originally reported by Lever and co-workers[7] was exploited to prepare zeolite-entrapped [Ru(bpy)$_2$(bpz)-Ru(NH$_3$)$_5$]$^{4+}$, where the pendant ruthenium pentammine fragment is coordinated to a peripheral nitrogen donor group of the primary intrazeolitic

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complex. Treatment of this material with a large excess of another polypyridine ligand [monomethyl-bipyridine, mmb] resulted in formation of a material which contained equal amounts of Ru(bpy)$_2$(bpz)$^{2+}$ and Ru(mmb)$_3$$^{2+}$. Extensive spectroscopic and photophysical studies of the material provided clear evidence for strong electronic coupling between the two intrazeolitic complexes and supported the conclusion that the secondary complex, Ru(mmb)$_3$$^{2+}$, is trapped in the supercage *adjacent* to the original (primary) complex, Ru(bpy)$_2$(bpz)$^{2+}$.[6a]

The specific polypyridine ligand of the secondary complex (i.e., mmb) was intentionally chosen so as to render the complex capable of reducing the oxidized primary (sensitizer) complex, Ru(bpy)$_2$(bpz)$^{3+}$; i.e., a sensitizer:donor dyad is thereby produced. Indeed, when the remaining cages in this material were loaded with a suitable (intrazeolitic) acceptor viologen and the material was subjected to irradiation within the absorption band of the sensitizer, substantial increases in net charge separation efficiency (by a factor of about 3.5 to 4) were realized,[6b] relative to an appropriate reference system and the system reported by Dutta and co-workers.[5]

While the detailed photophysical studies[6a] and the documented improvements in net charge separation efficiency[6b] provided convincing arguments for the effectiveness of the synthetic procedure in producing adjacent cage pairs, it seems necessary to provide more direct proof, i.e., to directly measure the extent to which the detached Ru(NH$_3$)$_5$$^{2+}$ fragment can drift to other (more remote) cages, rather than become trapped in the cage adjacent to the primary complex. To provide such an evaluation, the present work focuses attention on an intrazeolitic primary complex which contains a single peripheral nitrogen donor group, i.e., Z-Ru(bpy)$_2$(pypz)$^{2+}$, where pypz is pyridylpyrazine and the prefix Z indicates that the complex is entrapped within the zeolite supercages. Using the methodology described previously,[6a] the adjacent cage pair, Z-Ru(bpy)$_2$(pypz)$^{2+}$/Ru(bpy)$_3$$^{2+}$, has been prepared and thoroughly characterized, documenting a strong interaction between the component complexes. Most importantly, it is shown that a second treatment of this material with a large excess of the ruthenium pentammine reagent, [(H$_2$O)Ru(NH$_3$)$_5$]$^{2+}$, does not lead to formation of significant amounts of Z-[Ru(bpy)$_2$(pypz)-Ru(NH$_3$)$_5$]$^{4+}$; i.e., the presence of the Ru(bpy)$_3$$^{2+}$ in the cage adjacent to the primary complex shields the latter from further reaction with the ruthenium pentammine reagent. These results not only provide unequivocal evidence for the high efficiency of the synthetic procedure for adjacent cage dyad formation, but also make it clear that rotation of the Ru(bpy)$_2$(pypz)$^{2+}$ primary complex is restricted by the confinement of the Y-zeolite supercage, at least to the extent that the single reactive peripheral nitrogen cannot become repositioned to face a different window of the supercage, whereupon it would be expected to react with the reagent.

Experimental Section

A. Materials. The Y-zeolite sample employed for this study, provided by Union Carbide Corp., was purified before use to eliminate organic impurities as previously reported.[7] The 2-2-pyridyl-pyrazine (pypz) and Z-Ru(bpy)$_2$(pypz)$^{2+}$ (1:15 loading; i.e., one Ru^{2+} complex per 15 supercages) was available from previous studies.[8] The RuCl$_3$·3H$_2$O and Ru(NH$_3$)$_6$Cl $_3$ were purchased from Aldrich Chemical Co. and were used as received. Other chemicals used for this work were of reagent grade or better. The precursor, [Ru(NH$_3$)$_5$Cl] Cl$_2$, was prepared from Ru(NH$_3$)$_6$Cl$_3$ by a method previously described by Vogt et al.[9] The sample of [(H$_2$O)Ru(NH$_3$)$_5$](PF$_6$)$_2$ was prepared from [Ru(NH$_3$)$_5$-Cl] Cl$_2$ from the procedure initially outlined by Kuehn and Taube.[10]

B. Preparation of Adjacent Cage Assembly Precursor. [Z-Ru(bpy)$_2$(pypz)-Ru(NH$_3$)$_5$] was synthesized by reacting Z-Ru(bpy)$_2$(pypz)$^{2+}$ with a 100 fold excess of [(H$_2$O)Ru(NH$_3$)$_5$](PF$_6$)$_2$, similar to the procedure reported by Sykora et al.[6a] Typically, 30 mL of degassed acetone that had undergone 3−4 freeze-pump-thaw cycles was added to a 100 mL tripleneck round-bottom flask containing 100 mg of sand brown Z-Ru(bpy)$_2$(pypz) at a loading of 1 complex per 15 supercages under *continuous flow of argon*. To this mixture was then added a 100 fold molar excess (160 mg) of the sand brown [(H$_2$O)Ru(NH$_3$)$_5$](PF$_6$)$_2$, stoichiometry based on the entrapped Ru(bpy)$_2$(pypz)$^{2+}$. The change in color of the reaction mixture advanced from sand brown to brown in under 3 min and then turned to dark brown within the next 25 min or so. The reaction mixture was magnetically stirred for 1 h to allow for complete reaction to occur. The solvent was removed from the reaction mixture by distillation to dryness. The dried solid was light-green in color. The light-green solid was then washed under an argon atmosphere with the following: 100 mL of degassed acetone (to remove unreacted [(H$_2$O)Ru(NH$_3$)$_5$](PF$_6$)$_2$), 100 mL of 25% w/v NaCl, and 100 mL of degassed deionized water (16 MO) which was purged overnight with argon. The resulting solid was a light blue-grey in color. The resulting [Z-Ru(bpy)$_2$(pypz)-Ru(NH$_3$)$_5$] sample was then additionally dried on a vacuum line at room temperature for 2−3 h.

Note: If an inert atmosphere is compromised, the formation of ruthenium red [(NH$_3$)$_5$Ru^{3+}−O−Ru^{4+}(NH$_3$)$_4$−O−Ru^{3+}(NH$_3$)$_5$]$^{6+}$ occurs. Evidence for this can be observed in the final washings with acetone and aqueous NaCl, where the filtrate is reddish-purple in color. In the absence of ruthenium red, the color of the filtrate is the characteristic yellow of [(H$_2$O)Ru(NH$_3$)$_5$](PF$_6$)$_2$.

C. Preparation of Adjacent Cage Assembly. [Z-Ru(bpy)$_2$(pypz)/Ru(bpy)$_3$] was synthesized by adding a 50-fold excess (150 equiv) of the bipyridine ligand to the precursor [Z-Ru(bpy)$_2$(pypz)-Ru(NH$_3$)$_5$]. The procedure followed is similar to that described by Sykora et al.[6a]

D. Physical Measurements. 1. Electronic Absorption Spectra. Electronic absorption spectra were recorded on a Hewlett-Packard 8452A diode array spectrometer. Spectra were recorded in the absorbance mode. To determine the relative amount of the entrapped complex within the adjacent cage assembly, the absorption spectra of the complexes liberated from the zeolite framework were obtained following the procedure described in refs 4 and 6. Briefly, a few milligrams of the zeolitic assembly was dissolved in 5 mL of diluted hydrofluoric acid (1 mL of 48% hydrofluoric acid [HF] and 4 mL of deionized water) and subsequently neutralized with 2.0 M NaOH. The solution was then centrifuged to separate the precipitated white silicate. The absorption spectrum of the extract was then recorded.

2. Diffuse Reflectance Spectra. Diffuse reflectance spectra were recorded on a Model UV-2501 PC Shimadzu spectrophotometer equipped with an intergrating sphere attachment. The zeolite samples were measured as KBr pellets, where pellets with an identical content of plain Na−Y zeolite were used as blanks. The spectra were recorded in the transmittance mode and were numerically corrected via Kubelka−Munk manipulation.[11]

3. Electronic Emission Spectra. Zeolite samples (approximately 50 mg) were transferred to a conventional 5 mm i.d. NMR tube. Electronic emission spectra were acquired employing a conventional Raman spectrometer (Spex Model 1403 double monochromator equipped with a Spex Model DM1B controller and a Hammamatsu R928 photomultiplier tube) with the 457.9 nm line from a Spectra-Physics Model 2025-05 argon ion laser as the excitation source. The spinning 5 mm i.d. NMR tube was illuminated by a laser beam focused through a glass lens (typical power at the sample was between 5 and 10 mW), and the emission from the sample was collected with a conventional two-lens collecting system. To avoid fluctuation in the excitation power during these measurements, the laser was operated in the constant power mode. Typically, the results of five measurements for each sample were averaged, and this value was considered to be the observed emission intensity.

4. Resonance Raman Spectra. Resonance Raman spectra were acquired using the same instrumental setup as described for the

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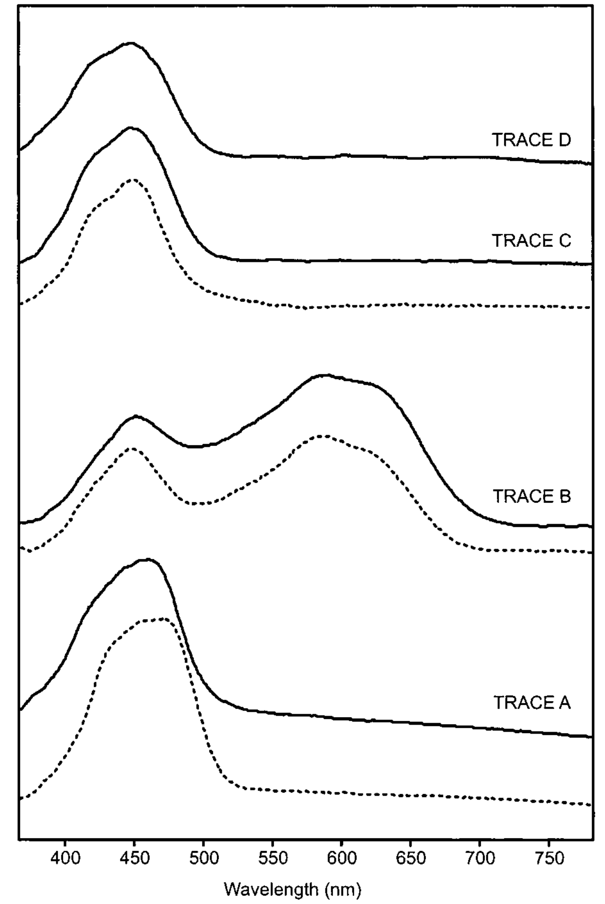

Figure 1. Diffuse reflectance spectra. Z-[Ru(bpy)$_2$(pypz)$^{2+}$] (trace A), Z-[Ru(bpy)$_2$(pypz)-Ru(NH$_3$)$_5$$^{4+}$] (trace B), Z-[Ru(bpy)$_2$(pypz)$^{2+}$/Ru(bpy)$_3$$^{2+}$] (trace C), [Z-Ru(bpy)$_2$(pypz)$^{2+}$ + Z-Ru(bpy)$_3$$^{2+}$] (trace D). Dotted lines are absorption spectra of corresponding HF extracts.

electronic emission spectra. The excitation line employed was the 457.9 nm line from the argon ion laser (typical power at the sample was between 100 and 110 mW) Spectra of zeolite-entrapped compounds were obtained from the solid samples prepared for the emission studies above using the spinning NMR tube device.

Results and Discussion

A. Spectral Properties. 1. Electronic Absorption and Diffuse Reflectance Spectra. Shown in Figure 1 are the diffuse reflectance (DR) spectra of the zeolite-entrapped adjacent cage dyad [Z-Ru(bpy)$_2$pypz^{2+}/Ru(bpy)$_3$$^{2+}$] and its precursors, along with the absorption spectra (dotted lines) of solutions of the components liberated from the zeolite matrix upon its dissolution with dilute HF. The DR spectrum of Z-Ru(bpy)$_2$pypz^{2+}, shown in trace A, matches that previously reported.[8] The envelope of absorption bands spanning the region between 400 and 500 nm are assignable to the $Ru^{2+} \rightarrow$ bpy MLCT (~420 nm) and $Ru^{2+} \rightarrow$ pypz MLCT (~460 nm) transitions.[12,13] The spectrum of the material derived from reaction with the (H$_2$O)Ru(NH$_3$)$_5$$^{2+}$ reagent (trace B) exhibits an additional absorption band near 590 nm. On the basis of well-documented spectral properties of a similar material, [Z-Ru(bpy)$_2$bpz-Ru(NH$_3$)$_5$$^{4+}$],[6a] and corresponding solution phase complexes,[14] this band is assignable to the Ru → pypz MLCT transition associated with the pendant ruthenium pentammine fragment. It is important to note that the ratio of intensities of the two absorption bands (i.e., A_{590}/A_{453}) decreases for samples prepared using lower amounts of the (H$_2$O)Ru(NH$_3$)$_5$$^{2+}$ reagent. Thus, when a 100-fold excess of the reagent is used (corresponding to a loading of 6.7 molecules of reagent per supercage), the measured ratio is 1.21. However, when a 5-fold excess is used (corresponding to a loading of 0.33 molecule of reagent/per supercage), the measured ratio is only 0.92, indicating that a significant fraction of the entrapped primary complex, Ru(bpy)$_2$(pypz)$^{2+}$, had not been derivatized; i.e., this material contains some fraction of “isolated” primary complexes having no secondary complex in the adjacent cage.

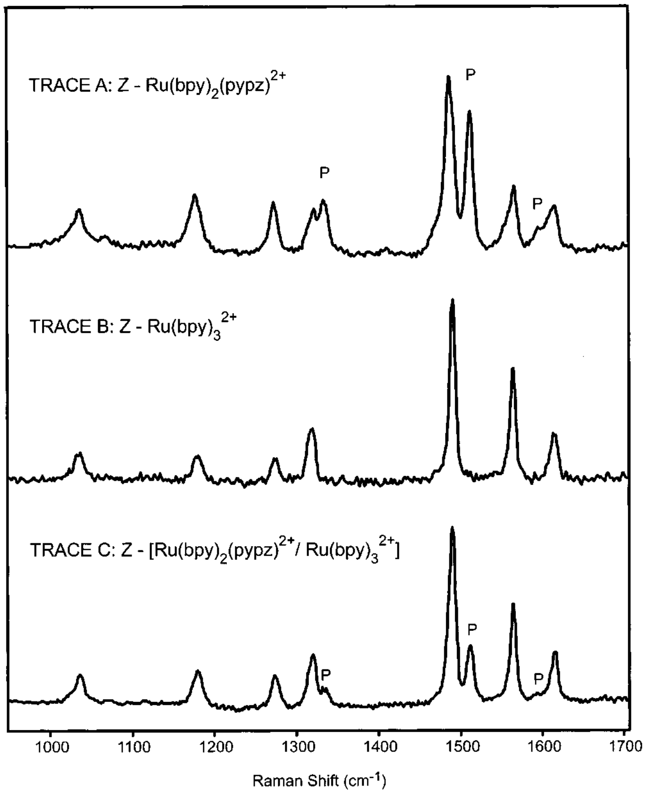

Figure 2. Resonance Raman spectra. Z-[Ru(bpy)$_2$(pypz)$^{2+}$] (trace A), Z-[Ru(bpy)$_3$$^{2+}$] (trace B), Z-[Ru(bpy)$_2$(pypz)$^{2+}$/Ru(bpy)$_3$$^{2+}$] (trace C). The 457.9 nm line from Argon ion laser used for excitation. The features designated with a P are attributable to the pyrazine fragment of the pyridylpyrazine ligand.

In trace C of Figure 1 are shown the DR spectrum of [Z-Ru(bpy)$_2$(pypz)$^{2+}$/Ru(bpy)$_3$$^{2+}$] and the electronic absorption spectrum of the solution resulting from the HF dissolution of the zeolite matrix of this material (dotted line), while trace D gives the DR spectrum of a mechanical mixture obtained by combining equal quantities of Z-Ru(bpy)$_2$(pypz)$^{2+}$ and Z-Ru(bpy)$_3$$^{2+}$. As can be seen by comparison of traces C and D, the spectrum of the intrazeolitic adjacent cage dyad matches quite well the trace obtained for the mechanical mixture. Thus, the DR spectrum of the targeted material is entirely consistent with that expected for a zeolite sample which contains equivalent amounts of the two component complexes.

2. Resonance Raman Spectra. Shown in Figure 2 are the RR spectra obtained for the materials of interest here. In traces A and B are shown the RR spectra of Z-Ru(bpy)$_2$(pypz)$^{2+}$ and Z-Ru(bpy)$_3$$^{2+}$, respectively. As is explained fully elsewhere,[15]

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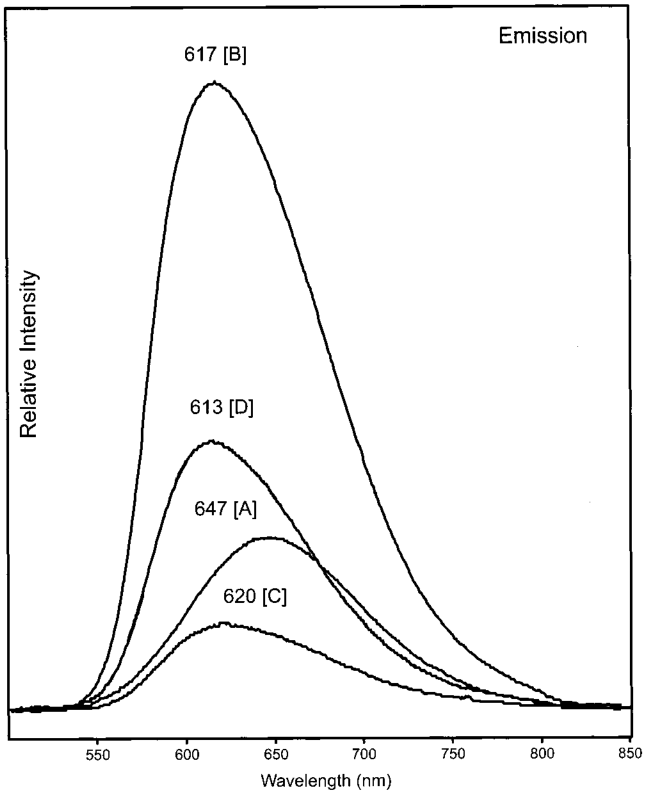

Figure 3. Emission spectra. Z-[$\mathrm{Ru(bpy)_2(pypz)^{2+}}$] (trace A), Z-[$\mathrm{Ru(bpy)_3^{2+}}$] (trace B), Z-[$\mathrm{Ru(bpy)_2(pypz)^{2+}/Ru(bpy)_3^{2+}}$] (trace C), [Z-$\mathrm{Ru(bpy)_2(pypz)^{2+}}$ + Z-$\mathrm{Ru(bpy)_3^{2+}}$] (trace D, described elsewhere as mechanical mixture or MM). Laser excitation line used 457.9 nm.

the vibrational modes of the coordinated pypz ligand can be classified according to specific fragments of the structure. One set of features is attributable to vibrations involving movement of the atoms of the pyridine periphery and overlap some of the modes of the coordinated bipyridine ligands.[16,17] However, a second set of bands, labeled "P" in Figure 2, correspond to modes attributable to the periphery of the pyrazine fragment and exhibit frequencies which are similar to some modes of a coordinated 2,2′-bipyrazine.[18] Thus, the intensities of the modes labeled P in these spectra, relative to the unlabeled modes, reflect the relative concentrations of the two complexes in the particles. Specifically, the RR spectrum of the adjacent cage dyad system [Z-$\mathrm{Ru(bpy)_2(pypz)^{2+}/Ru(bpy)_3^{2+}}$] (trace C) is entirely consistent with that expected, the features appearing in the spectrum coinciding exactly with those observed in traces A and B. Once again, we wish to point out that, for the sample which was prepared using a smaller amount of the reagent, $\mathrm{(H_2O)Ru(NH_3)_5^{2+}}$, the relative intensities of the modes labeled P are greater than those observed for the material prepared with a large excess of the reagent. This fact indicates that the concentration of the $\mathrm{Ru(bpy)_3^{2+}}$ is lower relative to the primary, $\mathrm{Ru(bpy)_2(pypz)^{2+}}$, complex; an observation consistent with the results obtained by DR spectroscopy, showing that isolated excess $\mathrm{Ru(bpy)_2(pypz)^{2+}}$ complexes are present if insufficient amounts of the pentammine reagent are used.

3. Emission Spectra. Figure 3 illustrates the electronic emission spectra of key materials of interest in this work. In trace A is given the previously reported[8] spectrum of Z-$\mathrm{Ru(bpy)_2(pypz)^{2+}}$, which exhibits a maximum at 647 nm. As has been well established,[12,13] the emission from these tris-ligated polypyridine complexes of divalent ruthenium involves a transition from the lowest lying ^{3}MLCT state, which is properly formulated as $[\mathrm{Ru(III)}L'_2L^{-\bullet}]^{2+}$ (where the L ligand possesses the lower energy p* orbital); i.e., in this case the lowest lying (triplet) metal-to-ligand-charge-transfer (^{3}MLCT) excited state is properly formulated as $[\mathrm{Ru(III)(bpy)_2(pypz^{-\bullet})}]^{2+}$, as has been effectively demonstrated by transient RR spectroscopy.[15] The emission spectrum of the sample of Z-$\mathrm{Ru(bpy)_3^{2+}}$, shown in trace B, is identical to that reported previously[4,19] and consistent with the well-documented emission spectrum of this complex.[12]

Also shown in Figure 3 is the emission spectrum of the adjacent cage dyad material (trace C), [Z-$\mathrm{Ru(bpy)_2(pypz)^{2+}/Ru(bpy)_3^{2+}}$], as well as the spectrum (trace D) of the MM, a material composed of equal parts of the two zeolite-entrapped reference complexes; i.e., [Z-$\mathrm{Ru(bpy)_2(pypz)^{2+}}$ + Z-$\mathrm{Ru(bpy)_3^{2+}}$]. What is most significant here is the fact that the relative intensity of the emission is substantially reduced for the adjacent cage dyad material relative to that observed for the MM sample. This behavior is similar to that which has been observed for several other adjacent cage dyad materials[6,19] and has been reasonably attributed to the intimate contact between adjacent cage partners, which can give rise to an additional (efficient) nonradiative decay process. As is discussed in detail in those works, one or more electron- or energy-transfer quenching mechanisms are energetically allowed to varying degrees.

4. Summary of Spectroscopic Properties. The studies described above document the formation of a zeolite-based material which contains two tris-ligated ruthenium polypyridine complexes whose electronic absorption and emission and RR spectral properties, both inside the zeolite matrix and upon liberation into aqueous solution, are consistent with those expected for these materials, with no evidence being obtained for the presence of contaminants. While the observed emission intensity for this material, relative to appropriate reference materials, is consistent with the proposal that the component complexes are spatially arranged so as to be susceptible to additional decay pathways which decrease the lifetimes and emission intensities, such data do not totally exclude the possibility that some fraction of the secondary complex, $\mathrm{Ru(bpy)_3^{2+}}$, may have been formed in cages remote from the primary partner complex, $\mathrm{Ru(bpy)_2pypz^{2+}}$. However, the results of further studies, summarized below, do effectively address this issue.

B. Evidence for Highly Efficient Adjacent Cage Dyad Formation. To the extent that the formation of the secondary complex, $\mathrm{Ru(bpy)_3^{2+}}$, in the cage adjacent to the primary complex, $\mathrm{Ru(bpy)_2pypz^{2+}}$, is efficient, it may be expected that the primary complex would possibly be shielded from further reaction with the $\mathrm{(H_2O)Ru(NH_3)_5^{2+}}$ reagent upon a second treatment. In Figure 4 are shown the DR spectra of the initially formed adjacent cage dyad material (trace A) along with that obtained for the product (trace B) resulting from a second treatment with the reagent using the same conditions as were employed for the initial reaction. It is important to note that in trace B no new bands appear near the region of 590−600 nm; i.e., there is no evidence for further addition of the $\mathrm{(H_2O)Ru(NH_3)_5^{2+}}$ reagent to the primary complex, $\mathrm{Ru(bpy)_2pypz^{2+}}$. It is also important to point out that this result also provides insight into the extent of rotation that can be experienced by such entrapped tris-ligated polypyridine complexes.

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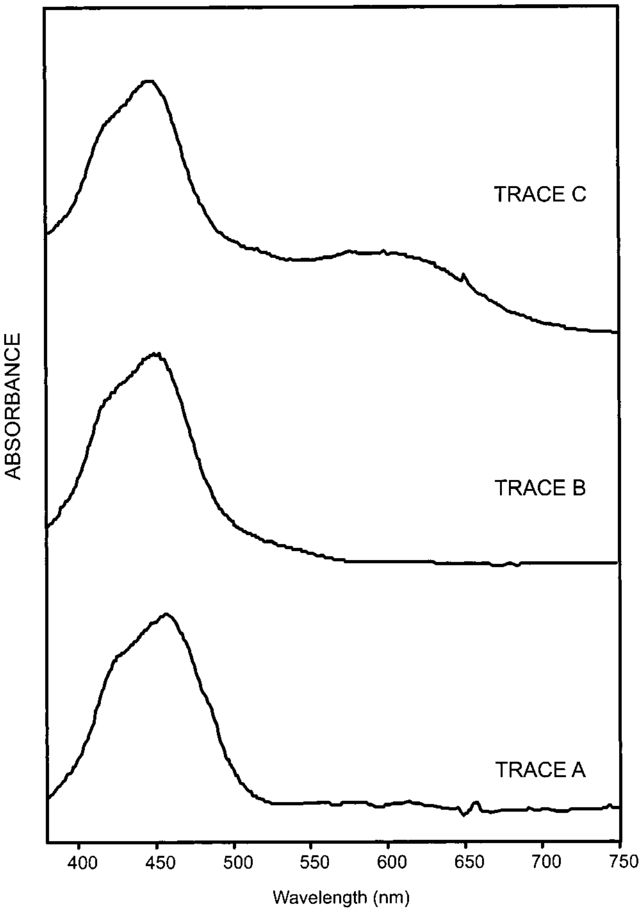

Figure 4. Diffuse reflectance spectra. (trace A), adjacent cage dyad Z-[Ru(bpy)$_2$(pypz)$^{2+}$/Ru(bpy)$_3$$^{2+}$]; (trace B), After second treatment of sample in trace A with (H$_2$O)Ru(NH$_3$)$_5$(PF$_6$)$_2$; (trace C), Product of reaction of (H$_2$O)Ru(NH$_3$)$_5$(PF$_6$)$_2$ with a Z-[Ru(bpy)$_2$(pypz)$^{2+}$] sample known to contain isolated Ru(bpy)$_2$(pypz)$^{2+}$ complexes.

Thus, inasmuch as large scale rotations of the primary complex would position the reactive peripheral nitrogen donor toward a “vacant” adjacent supercage, where it would be expected to react with the excess of the pentammine reagent, absence of this product provides strong evidence that rotation of the primary complex is restricted by the confined environment of the Y-zeolite supercage, at least to the extent that the single reactive peripheral nitrogen does not become exposed to another window of the surrounding supercage.

In order further support the contention that it is the presence of the secondary complex in the adjacent cage which prevents the reaction with the pentammine reagent, rather than some other factor which arises because of the subsequent purification procedures, the material which had been generated using a low ratio of the reagent in the initial preparation was also subjected to a second treatment. As can be seen in Figure 4, trace C, the second treatment of this material, which is known to contain isolated Ru(bpy)$_2$pypz^{2+} complexes, does exhibit the 590 nm absorption band characteristic of attachment of the reagent to the peripheral pyrazyl nitrogen, demonstrating that the inherent reactivity of the primary complex toward the pentammine reagent is not compromised by the synthetic and purification procedures.

Conclusions

The present work describes the successful preparation of the zeolite-entrapped adjacent cage complex, [Z-Ru(bpy)$_2$(pypz)$^{2+}$/Ru(bpy)$_3$$^{2+}$]. The observed spectroscopic properties confirm sample integrity and document an intimate spatial organization of the component complexes. Most importantly, it is shown that a second treatment of this material with a large excess of the ruthenium pentammine reagent, [(H$_2$O)Ru(NH$_3$)$_5$]$^{2+}$, does not lead to formation of significant amounts of Z-[Ru(bpy)$_2$(pypz)-Ru(NH$_3$)$_5$]$^{4+}$; i.e., the presence of the Ru(bpy)$_3$$^{2+}$ in the cage adjacent to the primary complex shields the latter from further reaction with the ruthenium pentammine reagent. These results not only provide unequivocal evidence for the high efficiency of the synthetic procedure for adjacent cage dyad formation, but also make it clear that rotation of the tris-ligated primary complex is restricted by the confinement of the Y-zeolite supercage to the extent that the individual polypyridine ligands are not free to rotate toward different windows.

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