Inorganic Photochemistry in Organized Media

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The photochemistry and photophysics of transition metal coordination complexes can be greatly modified by incorporation into rigid hosts such as zeolites, clays, and layered inorganic solids. The microenvironment of the host can prevent decomposition processes and can promote photon-induced vectorial electron transfer [1-4]. Much of the recent interest in photochemically-active transition metal complexes in organized media is directed towards photoinduced water splitting. A high quantum yield for the production of charge-separated species necessary for H_2O cleavage can be achieved through compartmentalization of the highly energetic photoproducts.

$$H_2O \longrightarrow H_2 + {}^1/_2 O_2$$

Excitation of electron donor-acceptor pairs entrapped in zeolite supercages generates much longer-lived charge separated states since the highly reactive photoproducts are constrained with respect to diffusion. The synthesis of zeolite-entrapped $[Ru(bpy)_3]^{2+}$ can be accomplished first by impregnation of zeolite-Y with $[Ru(NH_3)_6]^{3+}$ followed by addition of excess bipyridine [5,6]. Migration of the 11Å diameter $[Ru(bpy)_3]^{2+}$ ions through the 7Å diameter intrazeolitic windows is not possible, thus preventing diffusional deactivation of excited $[Ru(bpy)_3]^{2+}$ via self-quenching.

If a mixture of $[Ru(bpy)_3]^{2+}$ and diquat (DQ^{2+}) is entrapped in a zeollite-Y host, and the zeolite particles are suspended in a solution containing proplyviologensulfonate(PVS), very long-lived charge-separation can be achieved. Electron transfer from the triplet state of $[Ru(bpy)_3]^{2+}$ to diquat, in neighboring supercages, occurs upon photoexcitation [7]. The shuttling of electrons to the zeolite-solution interface is thought to occur through a "hopping" mechanism where electrons are carried from DQ^{2+} to DQ^{2+} and eventually to propylviologensulfonate in solution [8]. Excited $[Ru(bpy)_3]^{2+}$ is capable of reducing viologens, which in turn are known to reduce water to H_2 in the presence of a Pt catalyst [9].
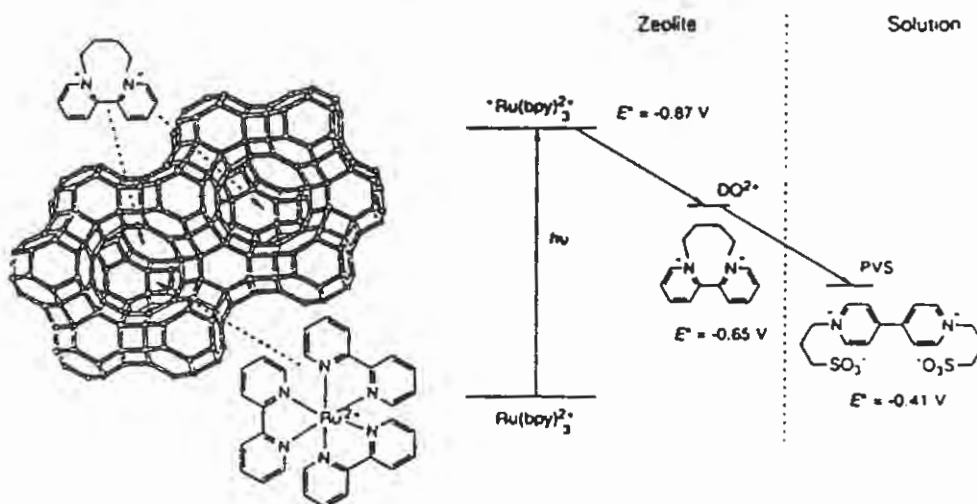
Charge recombination is entirely eliminated as a consequence of the repulsion between reduced propylviologensulfonate and the anionic zeolite cage. Early work using SiO_2 and $[Ru(bpy)_3]^{2+}$ also exhibited efficient charge-separation resulting from relay/matrix charge repulsion [10].

Another way zeolites can promote long-lived charge-separation is by immobilizing electron accepting groups bound to ruthenium centers within zeolite-L channels [11]. In this arrangement, the photooxidized ruthenium avoids reduction as a consequence of restricted motion of the reduced acceptor. Further charge-separated stabilization is possible with incorporation of benzylviologen into the zeolite channels, which takes the electron to more positive potentials and increases the lifetime by a factor of 80 [12].

Luminescent guest molecules such as $[Ru(bpy)_3]^{2+}$ can yield important information about the microenvironment of the host and about neighboring molecule interactions [13]. MLCT bands and concomitant room temperature triplet-state emission [14,15] provide a means for monitoring electron transfer processes and host microenvironmental effects.

The arrangement of $[Ru(bpy)_3]^{2+}$ ions loaded into a synthetic clay analogue, fluortetrasilicic mica, can be determined by monitoring emission intensity. $[Ru(bpy)_3]^{2+}$ in fluortetrasilicic mica doped with poly(vinylpyrrolidone) shows relative luminescence intensities that are 6 times greater than emission from $[Ru(bpy)_3]^{2+}$ in undoped fluortetrasilicic mica at low loading levels [16,17]. These clay analogues lack iron [18,19] which effectively quenches excited $Ru[(bpy)_3]^{2+}$. A comparison of the relative luminescence intensity of both polymer-doped and polymer-free layered surfaces reflect segregation of $[Ru(bpy)_3]^{2+}$ and suggests that the poly(vinylpyrrolidone) is rigid.

In conclusion, rigid assemblies facilitate the formation of charge-separated photoproducts, which is a prerequisite for efficient water cleavage. Reliable electron-transfer and luminescence studies become possible when the orientation and position of $[Ru(bpy)_3]^{2+}$ in the host is known.

References

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