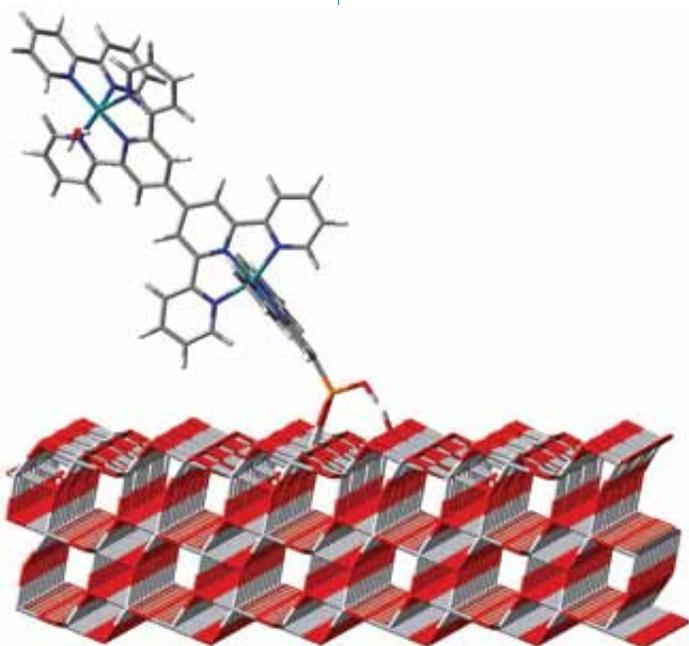


# Systematic Study of Modifications to Ru(II)-polypyridine Dyads for Electron Injection Enhancement

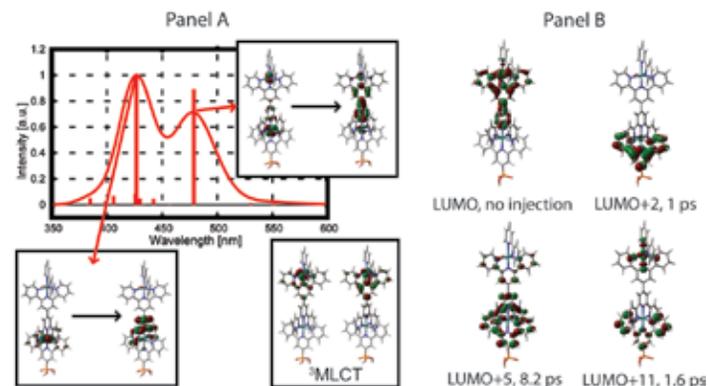
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**Fig. 1.**  $[(bpy)(H_2O)Ru(tpy-tpy)Ru(tpy)]^{4+}$  attached to (101) surface of anatase  $TiO_2$



Transition metal complexes, and particularly ruthenium polypyridine complexes, can be used as catalysts or photocatalysts capable of performing water oxidation [1] or oxidation of organic compounds.[2,3] They can also be used as chromophores to harvest solar energy due to their absorption in the visible region. Therefore, understanding the nature of the electronic excited states in transition-metal complexes is crucially important for elucidation of the mechanistic details of the photocatalyst function and design of efficient molecular devices for solar energy conversion.

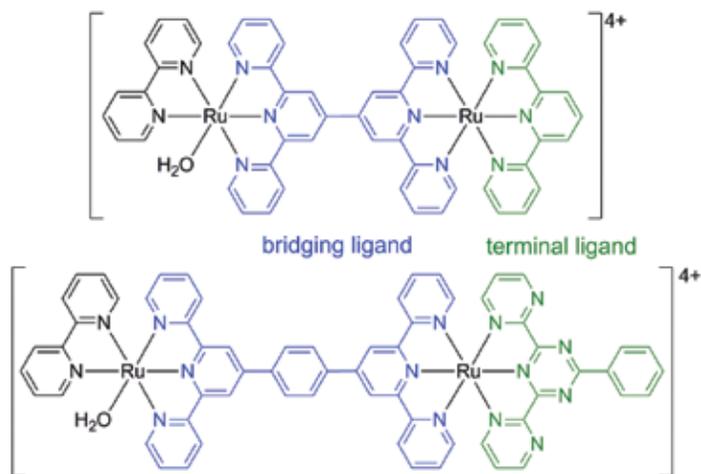
An important aspect of the molecular photocatalyst functionality is its ability to inject electrons into a metal oxide nanoparticle in order to induce charge separation and thus mimic photosynthetic charge transfer events [4-6]. This effect is usually achieved by an excitation into a metal-to-ligand charge transfer (MLCT) state that couples to the states in the nanoparticle conduction band, and this coupling drives the interfacial electron transfer (IET). IET competes with other processes that occur upon photoexcitation, such as radiative or nonradiative



**Fig. 2.** Panel A: Calculated absorption spectrum of  $[(bpy)(H_2O)Ru(tpy-tpy)Ru(tpy-PO_3H_2)]^{4+}$  with natural transition orbitals for the most intense transitions and singly occupied natural orbitals of the optimized  $^3MLCT$  state for the same molecule. Panel B: Selected virtual molecular orbitals of  $[Ru(tpy)(bpy)(H_2O)-Ru(tpy)(tpy-PO_3H_2)]^{4+}$  adsorbate obtained from extended Hückel theory, and their IET rates.

transition back to the ground state, or intersystem crossing (IC) into the lowest triplet excited state. IC plays an important role in the case of the ruthenium polypyridine complexes [7], and the excited states that lead to the electron injection into the semiconductor are a combination of initially populated singlet excited states and a thermalized  $^3MLCT$  state [8].

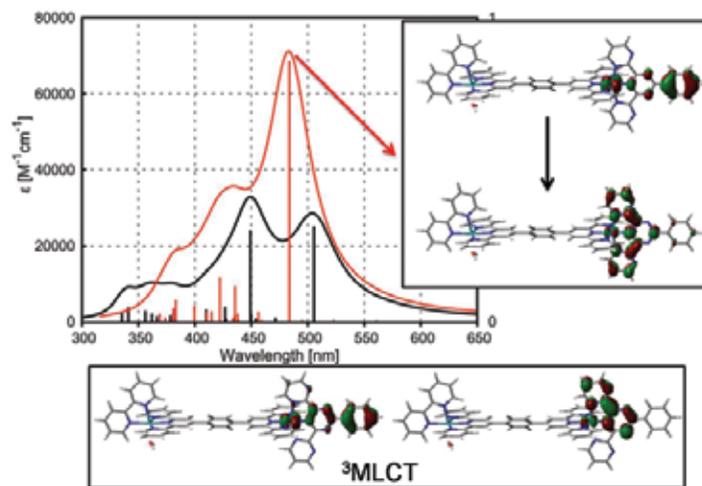
We have studied absorption properties and IET dynamics in a prototype photocatalytic assembly [3]  $[(bpy)(H_2O)Ru(tpy-tpy)Ru(tpy)]^{4+}$  ( $[Ru(tpy)(bpy)(H_2O)]^{2+}$  - model catalyst,  $[Ru(tpy)_2]^{2+}$  - chromophore; tpy = 2,2':6',2''-terpyridine and bpy = 2,2'-bipyridine) attached to an anatase  $TiO_2$  nanoparticle via a phosphonic acid linker. Density functional theory (DFT) was used to obtain the ground-state geometry of the catalyst-chromophore-nanoparticle assembly (see Fig. 1), as well as the absorption spectrum and the lowest triplet excited state of  $[(bpy)(H_2O)Ru(tpy-tpy)Ru(tpy-PO_3H_2)]^{4+}$ . Wave packet quantum dynamics simulations based on extended Hückel Hamiltonian [9] were used to obtain the IET rates from the excited states localized on the catalyst-chromophore assembly into the nanoparticle.



**Fig. 3.** Chemical structure of the original catalyst-chromophore dyad (top) and the modified catalyst-chromophore dyad (bottom).

The absorption spectrum obtained using the time-dependent DFT formalism in the visible region for the free  $[(bpy)(H_2O)Ru(tpy-tpy)Ru(tpy-PO_3H_2)]^{4+}$  molecule is shown in panel A of Fig. 2. The two most intense peaks correspond to the excitation of the electron into the orbitals characterized by the electron density on the bridging tpy-tpy ligand. Natural transition orbitals, which describe these excitations, are also shown in Fig. 2. The excited  $[(bpy)(H_2O)Ru(tpy-tpy)Ru(tpy-PO_3H_2)]^{4+}$  molecule can also undergo intersystem crossing into the  $^3MLCT$  state, in which the excited electron localizes on the tpy-tpy bridging ligand as well (also shown in panel A of Fig. 2). Panel B of Fig. 2 shows selected virtual molecular orbitals of the  $[(bpy)(H_2O)Ru(tpy-tpy)Ru(tpy-PO_3H_2)]^{4+}$  adsorbate obtained with the extended Hückel theory, and their IET rates.

While the IET occurs at a 1-10 ps rate from the orbitals localized on the terminal tpy( $PO_3H_2$ ) ligand attached to  $TiO_2$ , the most intense transitions, as well as long-lived  $^3MLCT$  state, are characterized by the spatial localization of the excited electron on the bridging tpy-tpy ligand. The bridging tpy-tpy ligand is only weakly coupled with the  $TiO_2$  nanoparticle, which leads to an inefficient IET in the investigated catalyst-chromophore-nanoparticle assembly. Therefore,



**Fig. 4.** Top panel: Absorption spectra of the original dyad (black) and modified dyad (red) and the natural transition orbitals corresponding to the most intense excitation in the visible region. Bottom panel: Lowest triplet MLCT state of the modified dyad.

we explored a series of 18 modifications to the bridging and terminal ligands, based on previously synthesized molecules, in order to find a related catalyst-chromophore assembly that would favor electronic excitations into the terminal terpyridine ligand with a strong electronic coupling to the semiconductor [10].

After investigating various modifications, we found that both introduction of a spacer group (such as phenylene or alkane) into the tpy-tpy bridge and replacement of the terminal terpyridine group by a more extended  $\pi$ -conjugated ligand are necessary to capture the excitations next to the attachment group that links to the surface. An example of a successfully modified dyad is shown in Fig. 3. The modified dyad displays both intense absorption into the terminal heteropyridine ligand, and electron localization on the

modified terminal ligand in the lowest  $^3MLCT$  state, which should lead to the efficient IET upon attachment to the  $TiO_2$  nanoparticle.

In conclusion, we have shown that the excited state properties of the prototype catalyst-chromophore dyad can be tuned by the use of different bridging ligands and modifications to the terminal ligand. These results have implications for the design of photocatalysts and dye-sensitizer assemblies based on Ru(II)-terpyridine compounds.

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