Photoinduced multiple electron transfer processes in ruthenium(II)-chromium(III) dyad or metallo-supramolecular wire.

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Chromium(III) polypyridinyl complexes exhibit rich photophysical and electrochemical properties, notably excited states that can be quenched by electron transfer and a series of one reversible reduction processes between three different states.^[11] These aspects are particularly interesting in electron storage devices and for catalysis. However Cr(III) complexes are poorly investigated as redox catalyst in the literature.^[2] In this context we investigated the photoredox behavior of $[Cr(tpy)_2]^{3+}$ (tpy = terpyridine) in the presence of sacrificial electron donor (PPh₃, TEA). Under irradiation, the complex can be reduced twice successively to form a $[Cr(tpy)_2]^+$ species. In the presence of $[Ru(bpy)_3]^{2+}$ (bpy = 2,2' bipyridine) as external photosensitizer, the kinetics of the photoreduction is accelerated. Based on these first results, we developed two heterobinuclear assemblies based on the covalent association of $[Ru(bpy)_3]^{2+}$ and $[Cr(tpy)_2]^{3+}$ subunits : a 1-D coordination polymer and a Cr(III)-Ru(II) dyad [figure 1]. Both structures anchored on ITO behave as photoanode. The magnitude and photostability of the photocurrent will also be discussed during the presentation, as well as preliminary results regarding the catalytic ability of $[Cr(tpy)_2]^{3+}$ towards H₂ generation.

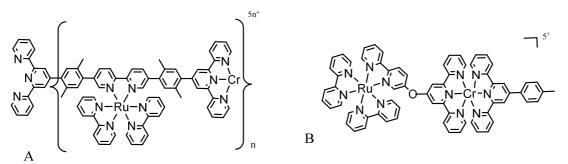


Figure 1. Schematic representation of the heteronuclear Ru(II)-Cr(III) studied architectures; A: 1-D molecular wire, B: Ru(II)-Cr(III) dyad.

References:

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