Supporting Information

New Ru(II)/Os(II)-polypyridyl complexes for coupling to TiO₂ surfaces through acetylacetone functionality and studies on interfacial electron-transfer dynamics

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1. Femtosecond Visible Spectrometer: The femtosecond tunable visible spectrometer has been developed based on a multipass amplified femtosecond Ti:sapphire laser system supplied by Thales, France.⁸ The pulses of 20 fs duration and 4 nJ energy per pulse at 800 nm, obtained from a self mode-locked Ti:sapphire laser oscillator (Synergy 20, Femtolaser, Austria) is amplified in a regenerative and two-pass amplifier pumped by a 20 W DPSS laser (JADE) to generate 40 fs laser pulses of about 1.2 mJ energy at a repetition rate of 1 kHz. The 800 nm output pulse from the multipass amplifier is split into two parts to generate pump and probe pulses. In the present investigation, we have used frequency doubled 400 nm as the excitation sources. To generate pump pulses at 400 nm, one part of the 800 nm output with 200 µJ/pulse is frequency doubled in BBO crystals. To generate visible probe pulses, about 3 μ J of the 800 nm beam is focused onto a 1.5 mm thick sapphire window. The intensity of the 800 nm beam is adjusted by iris size and ND filters to obtain a stable white light continuum in the 400 nm to the 1000 nm region. The probe pulses are split into the signal and reference beams and are detected by two matched photodiodes with variable gain. We have kept the spot sizes of the pump beam and probe beam at the crossing point around 500 and 300 µm, respectively. The noise level of the white light is about $\sim 0.5\%$ with occasional spikes due to oscillator fluctuation. We have noticed that most laser noise is low-frequency noise and can be eliminated by comparing the adjacent probe laser pulses (pump blocked vs. unblocked using a mechanical chopper). The typical noise in the measured absorbance change is about <0.3%. The instrument response function (IRF) for 400 nm excitation is obtained by fitting the rise time of the bleach of sodium salt of meso-tetrakis(4-sulfonatophenyl)porphyrin (TPPS) at 710 nm and is found to be 120 fs. The data analysis and fitting at individual wavelengths have been done with the LabView program which is based on differential equation with best chi-square fitting. The kinetic traces are freely fitted where both amplitudes and time constants are closely coupled. The deviation or error bar in both lifetime and amplitude is not more than $\pm 2\%$.

2. Synthesis of TiO₂ nanoparticles: TiO₂ nanoparticles have been obtained from a previous study.^{2d} Briefly, a solution of 5 ml Ti[OCH(CH₃)₂]₄ (Aldrich, 97%) in 95 ml isopropyl alcohol is added dropwise (1ml/min) to 900 mL of nanopure water (2 0 C) at pH 1.5 (adjusted with HNO₃). The solution is continuously stirred for 10-12 hours till the formation of a transparent colloid. The colloidal solution is concentrated at 35-40 0 C with a rotary

evaporator and then dried with nitrogen stream to yield a white powder. In the present work all colloidal samples (15 g/L) have been prepared by following a previously reported procedure.⁹

3. FTIR spectra of Ru(II)-polypyridyl complex (3) with pendant acetyleacetone in absence and in presence of TiO_2 nanoparticles:

To check the binding between complex **3** and TiO_2 nanoparticles, FTIR studies have been carried out. FTIR spectra have been recorded after dispersing the dye in TiO_2 nanoparticles. Such dispersion was taken on an inert surface and allowed to dry under a stream of dinitrogen gas. This was then grinded thoroughly with pre-dried KBr and the KBr pellet was used for recording the FTIR spectra. Following FTIR spectra reveals that the C=O stretching frequency on binding to TiO₂ has shifted from 1744 cm⁻¹ to 1723 cm⁻¹. This shift to a lower frequency value suggests binding of acetylacetonate group to TiO₂.



Figure S1: FTIR spectra of complex 3 in absence and in presence of TiO₂ nanoparticles.

4. Transient absorption spectrum of cation radical of 3 and 4 (uncorrected)



Figure S2: Uncorrected transient absorption spectrum of the cation radical of 3 and 4 obtained from one-electron oxidation in pulse radiolysis.

To record the transient absorption spectrum of the cation radical for complex **3** & **4**, oneelectron oxidation reaction has been carried out in aqueous solution (5% acetonitrile + 95% water) bubbled with N₂O and in the presence of N₃⁻ ion. Dye concentrations have been kept *ca*. 5 x 10⁻⁵ mol dm⁻³. **3/4** is oxidized to the corresponding cation radical by irradiation with the electron pulse. The presence of hydroxyl or azide radical allows the dye to undergo oneelectron oxidation *i.e.* loss of an electron. The reactions are given below:

H₂O \/\/\/\/\/\/\/\/\-→ H., OH.,
$$e_{aq}$$
 and other related products
 e_{aq} ⁻ + N₂O -→ N₂ + O⁻
O⁻ + H₂O -→ OH⁻ + OH
N₃ ⁻ + OH⁻ (or O⁻) -→ N₃ ⁻ + OH⁻ (or O₂⁻)
N₃ ⁻ + Dye -→ N₃ ⁻ + Dye⁻⁺