

Supporting Information

Synthesis, steady state and femtosecond transient absorption studies of resorcinol bound *ruthenium(II)* and *osmium(II)*-polypyridyl complexes on nano-TiO₂ surface in water

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1. SAED pattern of TiO_2 nanoparticles

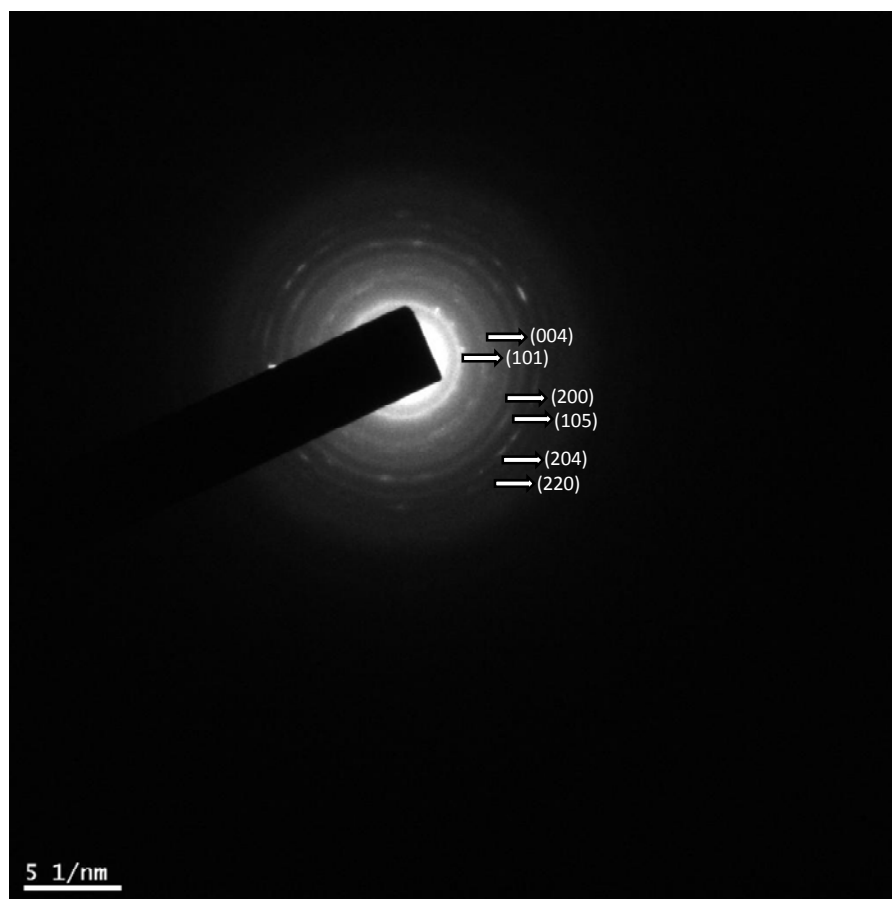


Figure S1: SAED pattern of TiO_2 nanoparticles showing the different planes of anatase phase

2. Comparison of the absorbance and the excitation spectra of **3** and **4**

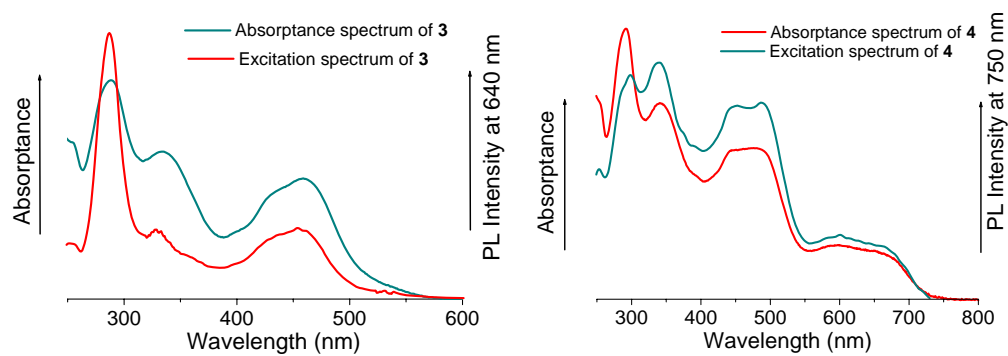


Figure S2: Comparison of the absorbance and the excitation spectra of **3** and **4**

The peak positions in the absorbance and the excitation spectra match perfectly for **3** and **4** indicating the observed luminescence is from the sensitizers itself.

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

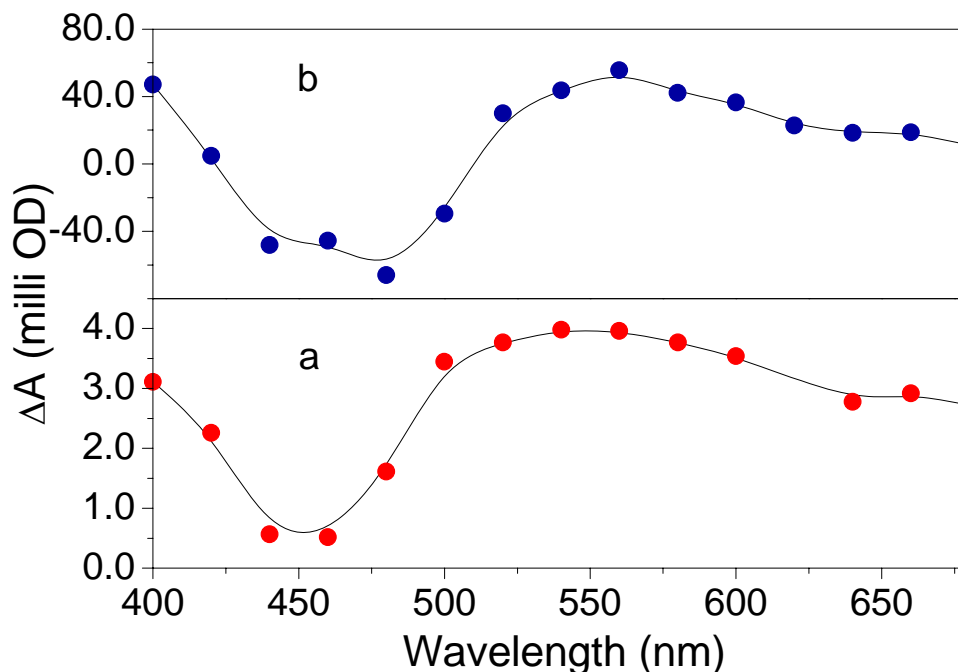
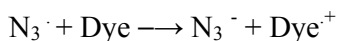
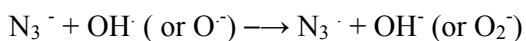
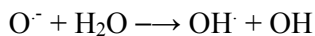
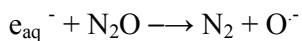
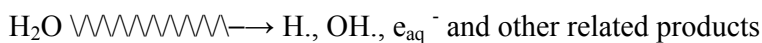


Figure S3: Transient absorption spectrum of the cation radical of (a) **3** and (b) **4** obtained from one-electron oxidation in pulse radiolysis.

To record the transient absorption spectrum of the cation radical for complex **3** & **4**, one-electron oxidation reaction has been carried out in aqueous solution (5% acetonitrile + 95% water) bubbled with N_2O and in the presence of N_3^- ion. Dye concentrations have been kept *ca.* $5 \times 10^{-5} \text{ mol dm}^{-3}$. **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 one-electron oxidation *i.e.* loss of an electron. The reactions are given below:



We would like to point out a very important thing. Since the cation radical spectra obtained from pulse radiolysis studies and shown in Fig. S1 are not corrected for free dye absorption

(please see the heading of this section), it would not be wise to infer about excited states being present or not from these (even if the ΔA values are all positive). Correction for free dye absorption has not been done because our aim is just to show the band position of the cation radical and it can be seen that they match well in Fig. S1 and in the transient absorption spectrum of **3/4**-TiO₂ system shown in Fig. 7 of the manuscript.

4. Kinetic trace for the decay of the cation radical in **4**-TiO₂ system

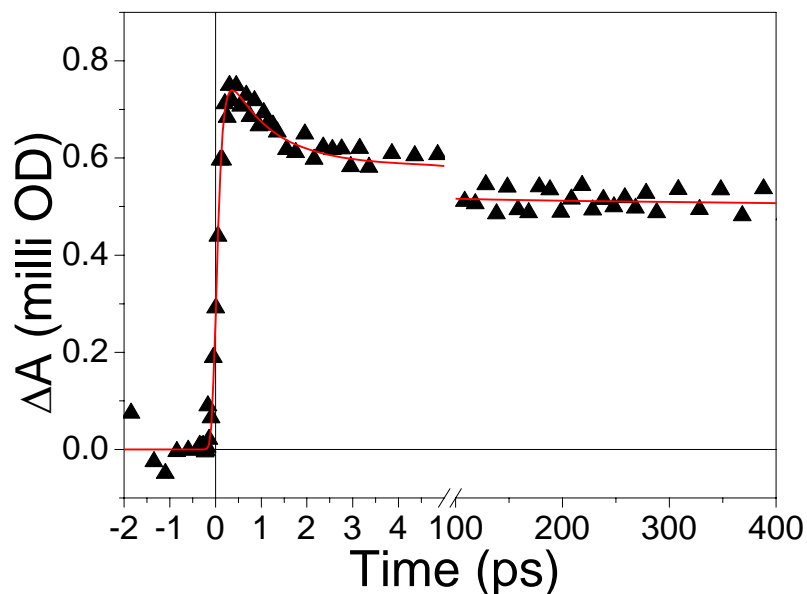


Figure S4: Kinetic trace for the decay of the cation radical in **4**-TiO₂ system at 620 nm. The kinetic trace can be fitted with the following parameters - < 120 fs (+100%), 0.9 ps (-29.4%), 22 ps (-9.4%), > 400 ps (-61.2%).