Supporting Data

Transient absorption spectrum of di-bromo fluorescein (DBF) cation radical as obtained from pulse radiolysis in N$_2$O saturated aqueous solution.

To find out the transient absorption of the cation radical of di-bromo fluorescein (DBF) molecule, one-electron oxidation reaction was carried out in aqueous solution bubbled with N$_2$O and in the presence of N$_3^-$ ion. DBF concentration was kept ca. $10^{-4}$ mol dm$^{-3}$. DBF was oxidized to cation radical on 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:

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\begin{align*}
H_2O & \rightarrow H^+, OH^-, e_{aq}^- \text{ and other related products} \\
e_{aq}^- + N_2O & \rightarrow N_2 + O^- \\
O^- + H_2O & \rightarrow OH^- + OH^- \\
N_3^- + OH^- (\text{or } O^-) & \rightarrow N_3^- + OH^- (\text{or } O_2^-) \\
N_3^- + DBF & \rightarrow N_3^- + DBF^+ 
\end{align*}
\]
FTIR spectrum of sodium dodecyl benzene sulphonate (DBS) and DBS modified TiO\(_2\) nanoparticles.

Sodium dodecyl benzene sulphonate (DBS) absorbs strongly at 1190 cm\(^{-1}\) and less strongly at 1040 cm\(^{-1}\), due to the antisymmetric and symmetric stretching of the SO\(_3^-\) group\(^1\) (Fig A). It is clearly evident from Fig B that in presence of TiO\(_2\) nanoparticles both antisymmetric and symmetric stretching frequency of the SO\(_3^-\) group goes blue shifted absorbing at 1205 cm\(^{-1}\) and 1050 cm\(^{-1}\) (Fig B) respectively due to strong interaction between DBS and TiO\(_2\) nanoparticles through sulfonic group.

Reference:
The above figure shows the optical absorption spectra of bare and DBS modified TiO$_2$ nanoparticles. It has been observed from the figure that the optical absorption spectra of DBS-capped particles are red shifted$^1$. Absorption at longer wavelengths, which is called the absorption red shift, was also observed by Zou et.al.$^2$ with ultrafine particles (UFP) coated with surface dipole layer. The authors attributed the absorption red shift to a dipole layer that induced an attractive potential to electrons inside the UFP and led to reduction of the band gap of UFP. According to the results obtained from the steady-state absorption and FTIR measurements in the present investigation, the long wavelength can be attributed to the change in the surface structure of the nanoparticles. Once DBS molecule is capped on TiO$_2$ nanoparticles an important physicochemical process can occur. Negative hydrophilic radical of DBS (sulphonate), bind chemically to the surface of TiO$_2$. These chemically bound molecules on TiO$_2$ surface can form intra-band surface states$^3$, which can also lead to the long wavelength absorption in TiO$_2$ nanoparticles.

References:
The above figure shows steady state optical absorption spectra of DBF, DBF/DBS and DBF/TiO$_2$ in aqueous solution. Typical pH was kept in all the above solution ~ 2.8. Typical concentration of DBF in all the above solution was ~12 $\mu$M. The concentration of TiO$_2$ nanoparticles in DBF/TiO$_2$ system was 10g/L. From the above figure it is clear that there is no interaction between DBF and DBS in the ground state. Here also it is observed that in presence of TiO$_2$ nanoparticles the optical density of DBF increases and absorption spectra goes red shifted due to electronic interaction between dye and nanoparticles$^1$.

Reference: