Photochemistry I – Problems

Series E

1. The cyanine dye Cy-3 ($\Delta E_{0,0}$ = 2.4 eV) is used as an initiator in a photo-lithographic process along with *N*-phenylglycine (NPG) as an electron donor and the electron acceptor MCP^+. Write all thermodynamically feasible electron transfer reactions that can result from the photo-excitation of the dye.

   Write electron back transfer processes and calculate for each of them the corresponding standard Gibbs energy ΔG_r^0 of the reaction. Standard oxydation potentials ϕ^0 (vs. the standard calomel electrode) are provided for all three participants.

   ϕ^0 (S^+/S) = + 1.63 V/SCE
   ϕ^0 (NPG^+/NPG) = + 0.25 V/SCE
   ϕ^0 (MCP^+/MCP) = – 0.65 V/SCE.

2. a) CMV^- is a carboxyl derivative of methylviologen (*N,N'*-dimethyl-4,4'-bipyridinium). This anion is strongly adsorbed on the surface of TiO_2 nanoparticles in aqueous colloidal suspension at *pH*=1. Titanium dioxide is characterized naturally by a stoichiometric oxygen deficiency, which results in a very strong *n*-doping of the semiconductor material.
   Write all photoredox processes expected upon irradiation of the oxide at λ = 347.1 nm and estimate in each case the value of standard Gibbs energy for the electron transfer reaction.

   ϕ^0 (CMV^-/CMV^{2-}) = + 0.04 V/NHE
   ϕ_{CB} (TiO_2) = – 0.12 V/NHE
   E_g (TiO_2) = 3.2 eV.

   b) What are the values of ΔG^0 for the same processes in the case where intrinsic TiO_2 (undoped) is irradiated with low intensity UV light, such as the stationary concentration of out-of-equilibrium charge carriers in the solid is 10^{17} cm^{-3}.

   $N_V = N_C = 10^{21}$ cm^{-3} .

3. 10-methyl-acridinium (MA^+) in solution in acetonitrile is irradiated in the presence of a large concentration of *p*-tritolylamine (TTA). While the forward photoinduced electron transfer reaction is practically quantitative, the quantum yield for the formation of TTA^+ radical cation is only $\Phi = 5\%$. Knowing that the total reorganization energy for the photoredox reaction is $\Lambda = 1.06$ eV and that the rate constant for charge separation in the geminate pair is $k_s = 3\times10^9\ s^{-1}$, determine the rate constant k_{et} of the photoinduced electron transfer process and that (k_b) of the charge recombination reaction.

ϕ^0 (MA^+/MA) = – 0.18 V/NHE
$\Delta E_{0,0}$ (MA^+) = 2.66 eV
ϕ^0 (TTA^+/TTA) = 1.42 V/NHE