The Photophysics and Photochemistry of Porphyrins in solution and on TiO_2 crystalline thin film

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ABSTRACT

With picosecond resolution，using time-correlated single photon counting（TCSPC）,we have carried out measurements on free-base biphenylporphine（H_2BPP）and zinc biphenylporphine（ZnBPP）in benzene solution, pumping in each of the S_2 and S_1 state. We provide a model for describing the elementary intramolecular processes. The measured time scales are as follows: less than instrument response function（IRF） which is assigned to the processes of deactivation from S_2 state to S_1, 14.0 ns and 2.5 ns which are assigned to the lifetime of S_1 state in H_2BPP and ZnBPP, respectively. When O_2–induced fluorescence quenching and heavy atom effect are observed, the process of intersystem crossing（ISC） $S_1 \rightarrow T_1$ is confirmed. Since the ISC rate of different concentration of O_2 dissolved in H_2BPP solution is measured， we derived natural ISC rate coefficient and O_2-induced ISC rate coefficient $7.2 \pm 0.6 \times 10^7 s^{-1}$ are $5.3 \pm 0.2 \times 10^{10} M^{-1} s^{-1}$ and ,respectively. inter-molecular（affected by heavy atom solvents which have Cl、Br、I） 、 intra-molecular（porphyrins which have Br atom by their own）heavy atom effect and temperature effect are mentioned in this thesis.

When ZnCA$(PE)_x$BPP（x = 1、2）、ZnCATPP functionalized on TiO_2 thin film, interfacial electron transfer and inter-molecular energy transfer due to molecular aggregation are observed.