Photo-Induced Charge Separation in TiO2/Porphyrin Bilayers Studied by Time-Resolved Microwave Conductivity

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Interfacial charge separation following flashphotolysis of bilayers consisting of an 80 nm thick, smooth layer of anatase TiO₂ coated with a layer of a (metallo)porphyrin has been studied using the electrodeless, timeresolved microwave conductivity (TRMC) technique. The kinetics, efficiency, and action spectrum of charge separation have been determined. The nature of the central metal substituent is found to have a dramatic influence on the photoconductivity transients observed. Both singlet and triplet photosensitization occur with the former dominant for the metal-free and zinc derivatives and the latter for the palladiumporphyrin complex. The enhancement of the triplet mechanism for the Pd derivative is attributed to a much greater rate of intermolecular triplet energy diffusion resulting from the heavy-atom effect on spin-orbit coupling. Because of this, yields of charge separation per incident photon as high as 12% are found for a TiO₂/PdP bilayer on excitation in the Soret band.