Energy Transfer and Electron Transfer in Meso-meso Coupled Porphyrin Arrays

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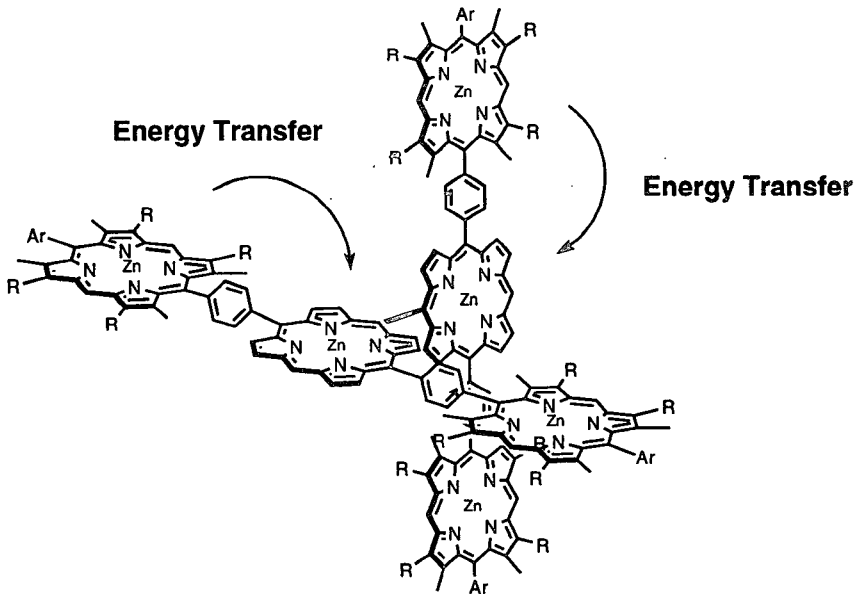
Recently, we found that treatment of zinc 5,15-diarylporphyrin with Ag(I) salt in $CHCl_3$ led to the formation of meso-meso coupled diporphyrin, triporphyrin and tetraporphyrin [1,2]. Repetition of this reaction allowed us to prepare discrete meso-meso coupled porphyrin arrays up to 32-mer. Optical properties of these porphyrin arrays which exhibit quite systematic changes upon the increase of the number of the porphyrins will be reported. When this reaction has been applied to 1,4-phenylene bridged linear porphyrin arrays in which a reactive 5,15-diaryl zinc porphyrin is flanked by octaalkyl substituted nickel porphyrins, windmill-shaped porphyrin arrays are formed in good yields. All-zinc metallated windmill porphyrin arrays constitute a new light-energy harvesting antenna system by collecting excitation energy absorbed in the peripheral porphyrins into a central meso-meso linked diporphyrin core [3]. This excitation energy flow is made more efficient by modification of the central meso-meso linked diporphyrin into bis(phenylethynyl)-substituted diporphyrin, in which the singlet excitation energy transfer proceed in ca. 6 ps time constant. We also constructed a model in which both of the energy transfer and the electron transfer occur to give a long-lived charge-separated ion pair state.



[1] A. Osuka and H. Shimidzu, *Angew. Chem. Int. Ed.*, **36**, 135 (1997). [2] N. Yoshida, H. Shimidzu, and A. Osuka, *Chem. Lett.*, 55 (1998). [3] A. Nakano, A. Osuka, I. Yamazaki, T. Yamazaki, and Y. Nishimura, *Angew. Chem. Int. Ed.*, **37**, 3023 (1998).