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Synthesis and photophysical study of unsymmetrical porphyrin arrays

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Porphyrin-based dimers, trimers and oligomers have received considerable attention as models for the study of electron transfer and energy transfer processes in photosynthesis. Multiporphyrin arrays are also attractive because of their potential use in nonlinear optics, molecular devices and photodynamic therapy of cancer. An unsymmetrical porphyrin array with two different porphyrin units is an ideal model to study photoinduced processes. Core-modified porphyrins in which one or two pyrrole rings are replaced by five-membered heterocycles like thiophene and furan exhibited novel physico-chemical properties which are quite different from N_4 porphyrin systems. Connecting the core-modified porphyrins with N_4 porphyrins would result in unsymmetrical porphyrin arrays and study of their photodynamics would be helpful in understanding the factors that govern the photoinduced processes. In this paper, we report the synthesis and characterization of unsymmetrical porphyrin arrays comprising of heterosubstituted porphyrin (N_3S and N_2S_2) and N_4 porphyrin subunits. Phenyl and diphenyl ethynyl groups are used as links which provide rigidity to the arrays and thereby allow strong interaction between the porphyrin units. Steady state fluorescence data indicate that the energy transfer between the porphyrin units depends on the link.