Charge Separation in Tetrapyrrole-Graphene and Tetrapyrrole-SLGO-Fullerene Hybrids

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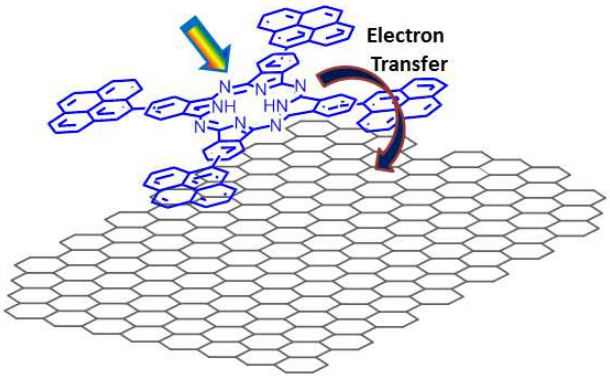
Photoinduced electron transfer is one of the most fundamental and extensively investigated of all reactions due to its importance in photosynthesis and in the development of energy harvesting and optoelectronic devices. Inspired by nature, the design and study of several elegant model systems have made possible to probe the often complex multi-step electron transfer processes. Graphene, single layer graphite, due to its remarkable optical and electrical properties has stimulated strong research interests in the areas of materials science, chemistry and physics. Graphene can be made into an active component for novel solar energy harvesting applications via donor-acceptor hybrid formation using visible-light harvesting photosensitizers.

We report herein novel, self-assembled supramolecular donor-acceptor hybrids featuring few-layer graphene as electron acceptor and custom designed phthalocyanine or zinc porphyrin bearing four pyrene entities as photosensitizer donors. The new nanohybrids have been elegantly designed, synthesized and characterized by spectral and imaging techniques. The four pyrene entities on the tetrapyrrole macrocycle facilitated π-stacking interactions with the graphene sheet resulting into soluble hybrids. Fluorescence emission studies revealed efficient quenching of the sensitizers suggesting occurrence of excited state events in the newly formed donor-acceptor hybrids. Femtosecond transient absorption spectroscopy provided clear spectral evidence for charge separation in these hybrids and the measured kinetics of charge separation were in the order of 10^{11}- 10^{12} s^{-1} revealing ultrafast charge separation. The present study opens up a venue for utilization of difluoroborane chelated azadipyrromethene in light energy harvesting donor-acceptor systems.



Further, single layer graphene oxide (SLGO) has been decorated with porphyrin and fullerene to probe photoinduced electron transfer and photocatalytic properties.