Molecular Triads Comprised of Boron dipyrrin-C₆₀ Dyad Connected to Either an Energy or Electron Donating Entity to Probe Sequential energy/electron Transfer Events

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Abstract. In natural photosynthesis two major processes, absorption of light energy by antenna system and transportation of that light energy to the reaction center take place efficiently. There is a growing interest to mimic these processes in artificial systems with an ultimate aim of harvesting solar energy.

In the present study, we wish to report novel molecular triads comprised of boron dipyrrin-fullerene dyad covalently linked to either an energy donating entity (En-D1-A type triads) or a secondary electron donating entity (D2-D1-A type triads) to probe sequential energy/electron transfer events. Anthracene, pyrene, fluorene and naphthalene are chosen to be energy donating (En) entities while ferrocene and triphenylamine entities are chosen as secondary electron donors (D2 - hole transfer agents) (see Scheme 1 below). Systematic spectral, electrochemical and emission studies are performed to probe sequential energy transfer followed by electron transfer events in the newly synthesized triads. Computational studies using B3LYP/3-21G* are performed to arrive at the geometry and electronic structures. Photochemical study using time-resolved emission is performed to probe electron transfer events. Further, organic photocells are being built to directly convert light energy into electricity.

Scheme 1

Experiment, Results, Discussion, and Significance.

Absorption and emission (ex 345 nm) spectra of pyrene & toluayl appended BDP compounds in DCB.
Absorption and emission (ex 350 nm) spectra of ferrocene phenyl appended BDP compounds in DCB

Summary:

1. Novel supramolecular triads featuring boron dipyrrin and fullerene as primary donor-acceptor pair are designed, synthesized and characterized by using various physico-chemical methods.
2. Electrochemical studies followed by free-energy calculations suggested possibility of photoinduced electron transfer in the triads.
3. The calculated geometry and electronic structures reveal closely spaced donor and acceptor entities in the triads.
4. The triads of the type En-D1-A reveal efficient singlet energy transfer upon excitation of En entity to the D1 entity followed by electron transfer events.
5. The triads of the type D2-D1-A show efficient fluorescence quenching suggesting occurrence of photoinduced electron transfer.
6. Further studies involving time-resolved emission and transient absorption are in progress.

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