

Magnesium Porphyrin-Fullerene Dyads: Synthesis, Electrochemistry and Photo-induced Electron Transfer

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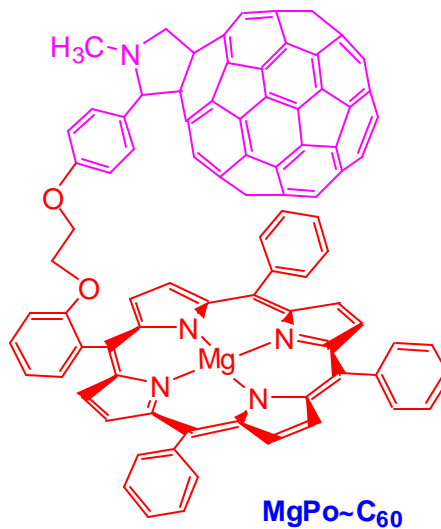
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Photoinduced charge-separation and charge-recombination reactions in a newly synthesized magnesium porphyrin-fullerene dyad (Scheme 1) are reported in coordinating and noncoordinating solvent solutions. The synthesis of the dyad was accomplished by functionalizing *meso*-tetraphenylporphyrin at the *ortho* position of one of the aryl groups to possess a fulleropyrrolidine entity through a flexible ethylene dioxide bridge. In *o*-dichlorobenzene, 0.1 M (TBA)ClO₄, the synthesized dyad exhibited six one-electron reversible redox reactions within in the potential window of the solvent and the measured redox potentials and steady-state fluorescence data revealed higher free-energy change for charge separation ($-DG_{et}$) as compared to the earlier reported for zinc porphyrin-fullerene dyads.¹ Charge-transfer interactions between the electron donor, magnesium porphyrin and electron acceptor, fullerene entities were also revealed by spectroscopic and computational studies performed by *ab initio* B3LYP/3-21G(*) methods.

Scheme 1



The excited state photochemical events were monitored by both steady-state and time-resolved emission as well as nanosecond transient absorption techniques. The main emission quenching pathway involved electron transfer from the singlet excited magnesium porphyrin to the C₆₀ moiety irrespective of the nature of the solvent. Relatively long-lived charge separated states ($\tau_{RIP} = 350\text{-}550$ ns) were observed for the studied dyad depending upon the solvent conditions.

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References

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