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Title: Unravelling the excited state dynamics of monofunctionalized mono- and distyryl-BODIPY and

perylenediimide dyads

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Abstract:

Designing new donor-acceptor systems and probing their energy/electron transfer dynamics is essential in the context of the development of biomimetic photosynthetic systems. In this work, we have designed, synthesized and characterized dyads 1 and 2 consisting of perylenediimides (PDIs) PDI 1/PDI 2 attached at one of the β-positions of mono styryl-BODIPY (MSBDP)/distyryl-BODIPY (DSBDP) compounds. The plausible photoinduced energy transfer competing with the electron transfer process between PDI and styryl-BODIPY (STBDP) has been examined by different spectroscopic studies. Steady-state emission studies revealed quenching of the PDI emission upon PDI excitation in both the dyads due to charge transfer from STBDP to PDI. From electrochemical measurements, Gibbs free energies for charge-separation (Δ GCS) were calculated that indicated energetically favourable charge transfer from STBDP to PDI to yield PDI'--STBDP'+ in both dyads 1 and 2. Further conclusive evidence for the occurrence of photoinduced charge separation from MSBDP/DSBDP to PDI 1/PDI 2 in dyads 1 and 2 was obtained from femtosecond transient absorption studies. Charge separation as well as charge recombination in dyad 1 (τ CS \sim 157/2.19 ps and τ CR \sim 838/35.2 ps in toluene/chloroform) was faster compared to dyad 2 ($\tau CS \sim 257/14.6 \text{ ps}$ and $\tau CR \sim 1032/127.8 \text{ ps}$ in toluene/chloroform). These studies suggest that STBDP-PDI dyads are interesting candidates owing to their intriguing photophysical properties for bioinspired photosynthetic systems.

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