Porphyrin-based Triad with Exceptionally High MFE on Phosphorescence

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Magnetic control over molecular emissivity presents interests for various fields of technology and medicine. We present experiments exploring magnetic field effects (MFE) on phosphorescence in donor-acceptor dyads and triads based on Pt porphyrins (PtP). In one triad, consisting of phosphorescent Pt porphyrin (PtP), rosamine B (RosB) and trialkoxybenzene (TAB), covalently linked together by conductive oligophenylene bridges, photoexcitation leads to two sequential reversible electron transfer processes (ET), generating two radical pairs (RP). respectively. The first rate-limiting ET originates in the local PtP triplet state, and it is slightly endergonic, competing with, but not entirely quenching the PtP phosphorescence. The second ET is exergonic, resulting in the formation of the final RP with large inter-radial distance. The RPs recombine either to the ground state (singlet channel) or back to the emissive PtP triplet state (triplet channel). The net distribution of the RP decay over the recombination channels, and hence the phosphorescence decay time and intensity, are governed by the spin dynamics in the RP(s) and are sensitive to magnetic field. The phosphorescence of the triad was found to exhibit remarkably strong positive MFE with the magnitude reaching up to ~12% in the field of a handheld toy magnet. A kinetic model was developed that allowed us to reproduce the observed behavior of the triad. Overall, this work constitutes an important step towards the design of magnetically sensitive luminescent materials, which in the future may be exploited in construction of a new kind of biological imaging probes.

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