Synthesis, structure and photophysical properties of ferrocenyl or mixed sandwich cobaltocenyl ester linked *meso*-tetratolylporphyrin dyads

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Streszczenie

We report here the design and synthesis of porphyrin–metallocene dyads consisting of a metallocene [either ferrocene or mixed sandwich η^5-$[C_5H_4(COOH)]Co(\eta^4$-$C_4Ph_4)$ connected *via* an ester linkage at *meso* phenyl position of either free-base or zinc porphyrin. All these dyad systems were characterized by various spectroscopic and electrochemical methods. A dimeric form of this molecule was observed in the X-ray crystal structure of Zn-TTPCo. The absorption spectra of all four dyads indicated the absence of electronic interactions between porphyrin macrocycle and metallocene in the ground state. However, interestingly, in all four dyads, fluorescence emission of the porphyrin was quenched (19–55%) as compared to their monomeric units. The quenching was more pronounced in ferrocene derivatives rather than cobaltocenyl derivatives. The emission quenching can be attributed to the excited-state intramolecular photoinduced electron transfer from metallocene to singlet excited state of porphyrin and the electron-transfer rates (k_{ET}) were established in the range 1.51×10^8 to 1.11×10^9 s^{-1}. They were found to be solvent dependent.

Adres publiczny

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