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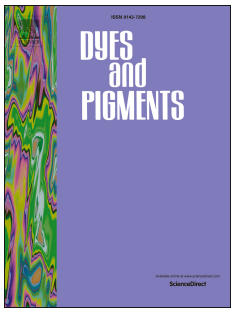

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ACCEPTED MANUSCRIPT

Amplified singlet oxygen generation in metallated-porphyrin doped conjugated polymer nanoparticles.

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Abstract

We report on the mechanism and efficiencies of singlet oxygen $O_2(^1\Delta_g)$ generation of nanoparticles (NP) of the conjugated polymer (CP) poly(9,9-dioctylfluorene-alt-benzothiadiazole) (F8BT) doped with platinum octaethylporphyrin (PtOEP) suspended in water. A detailed study of the photophysics of these NP, using stationary and time-resolved absorption and emission techniques, indicates that $O_2(^1\Delta_g)$ is generated by the triplet excited state of F8BT and not by that of PtOEP, as previously observed for other porphyrin doped CP NP. $O_2(^1\Delta_g)$ quantum yields (Φ_Δ) were measured by quantifying the characteristic phosphorescence of $O_2(^1\Delta_g)$ in the NIR region (~ 1268 nm). It was found that incorporation of relatively small amounts of PtOEP to F8BT NP results in a significant increase of Φ_Δ. NP containing 10% PtOEP (w/w) show a $\Phi_\Delta \sim 0.24$, which is 3 times larger than that observed for undoped F8BT NP, and larger than the reported for most water-soluble porphyrins. Φ_Δ were also calculated from the oxidation rates (v_0) of 3-10-(2-carboxyethyl) anthracene (ADPA), a well-known chemical $O_2(^1\Delta_g)$ trap. Unexpectedly, this method was found to significantly overestimate the Φ_Δ values due to the adsorption of ADPA on the surface of NP. The ADPA / NP adsorption process was characterized using a simple adsorption model yielding an (average) equilibrium constant of $\sim 8 \times 10^3$ M^{-1} and an (average) number of NP-binding sites of ~14000. These

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