Supermolecular-Chromophore-Sensitized Near-Infrared-to-Visible Photon Upconversion

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Résumé en anglais	Selective near-IR (NIR) excitation (780 nm) of the conjugated supermolecule ruthenium(II) [15-(4?-ethynyl-(2,2?;6?,2??-terpyridinyl))-bis[(5,5?,-10,20-di(2?,6?-bis(3,3-dimethylbutoxy)phenyl)porphinato)zinc(II)]ethyne][4?-pyrrolidin-1-yl-2,2?;6?,2??-terpyridine] bis(hexafluorophosphate) (Pyr1RuPZn2) in solutions containing N,N-bis(ethylpropyl)perylene-3,4,9,10-tetracarboxylicdiimide (PDI) or tetracene gives rise to a substantial anti-Stokes energy gain (PDI, 0.70 eV; tetracene, 0.86 eV). Experimental data clearly demonstrate that this upconverted fluorescence signal is produced via Pyr1RuPZn2-sensitized triplet?triplet annihilation (TTA) photochemistry. The TTA process was confirmed by the quadratic dependence of the integrated 1PDI* emission centered at 541 nm derived from 780 nm laser excitation. The T1?Tn excited state absorption decay of Pyr1RuPZn2, monitored at 900 nm as a function of PDI concentration, revealed Stern?Volmer and bimolecular quenching constants of 10?048 M?1 and 5.9 ? 108 M?1 s?1, respectively, for the PDI triplet sensitization process. The T1?Tn PDI extinction coefficient at 560 nm (εT = 6.6 ? 104 M?1 cm?1) was determined through the triplet energy transfer method utilizing anthracene as the donor chromophore. 3PDI* transient triplet absorption dynamics observed as a function of 485 nm incident nanosecond pump laser fluence demonstrate a bimolecular 3PDI*?3PDI* TTA rate constant (kTT = 1.0 ± 0.2 ? 109 M?1 s?1). The maximum quantum yield of the supermolecule-sensitized PDI upconverted emission (ΦUC = 0.0075 ± 0.0002) was determined relative to [Os(phen)3][PF6]2 at an incident laser power of 22 mW at 780 nm. This study successfully demonstrates NIR-to-visible photon upconversion and achieves a new record anti-Stokes shift of 0.86 eV for sensitized TTA, using the supermolecular Pyr1RuPZn2sensitizer. The stability of the Pyr1RuPZn2/PDI chromophore combination is readily apparent as continuous irradiation at 780 nm produces 541 nm centered fluorescence with no significant decrease in intensity measured over time domains exceeding several hours. The molecular components of these NIR-to-vis upconverting compositions illustrate that substantial anti-Stokes energy gains via a TTA process can be effortlessly realized.
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