A photoconversion-tunable photosensitizer with diversified excitation and excited-state relaxation pathways

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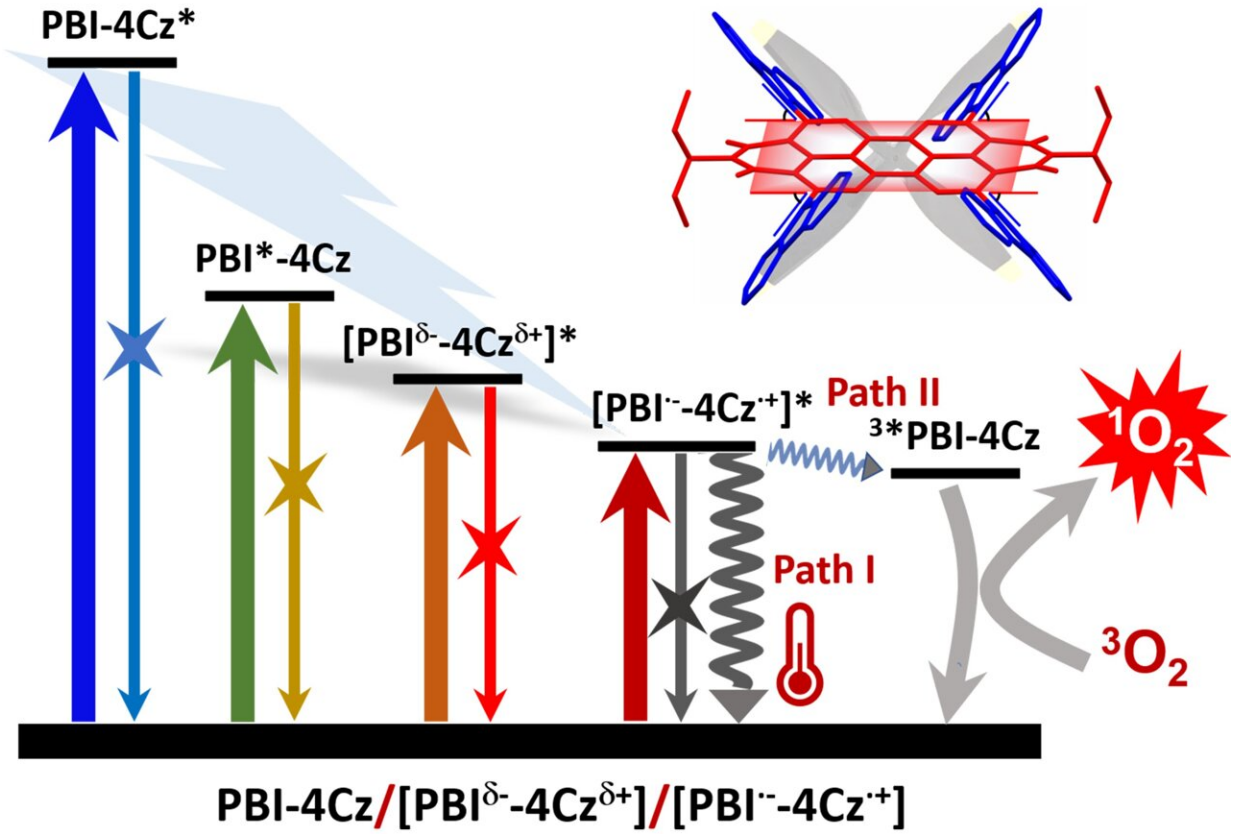

Charge separation state of PBI–4Cz are exclusively formed when photoexcited at different wavelengths. Energy dissipation of the resulting charge-separated state is subjected to the toggle between charge recombination toward ground states (Path I) and intersystem-crossing toward excited triplet states (Path II). Credit:

In a paper published in *Science China Chemistry*, scientists present an orthogonal carbazole-perylene bisimide pentad, which is a photoconversion-tunable photosensitizer with diversified excitation and excited-state relaxation pathways.

Integrating multiple photosensitive properties into an "all-in-one" photosensitizer shows great promise for the treatment of cancers owing to synergistic effects among them. However, the development of such photosensitizers, especially those where a single laser source is needed, remains a challenge.

The researchers report an orchestration of electron donor and acceptor in a propeller-like pentad, PBI-4Cz, where four carbazole (Cz) units are covalently linked at the ortho-positions of the perylene bisimide (PBI) core. Strong intramolecular donor-acceptor interaction significantly quenches the luminescence and largely extends the absorption spectrum to near-infrared region.

Excited state dynamics investigated via femto- and nanosecond transient absorption spectroscopy revealed exclusive charge separation of PBI-4Cz within initial 0.5 ps when photoexcited, regardless of which intermediate is involved. Energy dissipation of the resulting charge-separated state is toggles between intersystem crossing toward an excited triplet state and charge recombination to ground state. The relative importance of the two paths can be tuned by microenvironmental polarity, which endows PBI-4Cz remarkable performance of singlet oxygen generation (>90.0%) in toluene and photothermal conversion (~28.6%) in DMSO.

The work not only show the promise for multifunctional photo-theranostics, but also provides a prototype for designing high-performance photosensitizers with tunable photoconversion pathways through harnessing the intrinsic photostability and excited state processes of a heavy-atom-free PBI derivative.

More information: Zhaolong Wang et al, Orthogonal carbazole-perylene bisimide pentad: a photoconversion-tunable photosensitizer with diversified excitation and excited-state relaxation pathways, *Science China Chemistry* (2021). DOI: 10.1007/s11426-021-1154-0

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