Unique multiphthalocyanine coordination systems: vibrationally hot excited states and charge transfer states that power high energy triplet charge separated states

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Controlling molecular architecture of well-organized organic building blocks and linking their functionalities with the impact of solar-light converting systems constitutes a grand challenge in materials science. Strong absorption cross-sections across the visible range of the solar spectrum as well as fine-balanced energy- and redox-gradient are all important features that pave the way for either funneling excited state energy or transducing charges. In light of this, we used thiopyridyl-phthalocyanines (PcSPy) and ruthenium (tert-butyl)-phthalocyanines (RuPc) as versatile building blocks and demonstrated the realization of a family of multi-functional PcSPy-RuPc 1-4 by means of axial coordination. Sizeable electronic couplings between the electron donors and acceptors in PcSPy-RuPc 1-4 govern ground-state as well as excited-state reactivity. Time-resolved techniques, in general, and fluorescence and transient absorption spectroscopy, in particular, helped to corroborate a rapid charge separation next to a slow charge recombination (Figure 1). Key to these charge transfer characteristics are higher lying, vibrationally hot states of the singlet excited states in parallel with a charge transfer state and the presence of several heavy atom effects that are provided by ruthenium and sulfur. As such, our advanced investigations (Figure 2) confirm that rapid charge separation evolves from both higher lying, vibrationally hot states as well as from a charge transfer state, populating charge separated states, whose energies exceed those of the singlet excited states. Charge recombination involves triplet rather than singlet charge separated states, which delays the charge recombination by one order of magnitude.

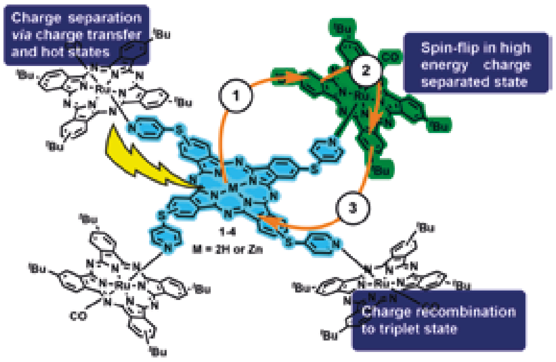

FIGURE 1
Versatile building blocks of thiopyridyl-phthalocyanines and ruthenium (tert-butyl)-phthalocyanines (PcSPy-RuPc).

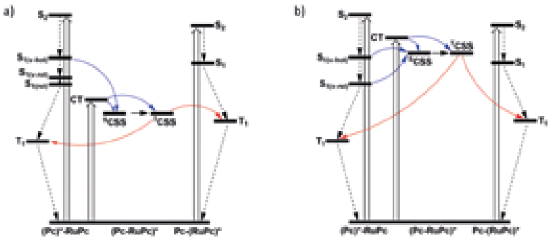

FIGURE 2
Jablonski scheme of pentamers a) $H_2PcSPy_4[RuPc]_4$ (3) and b) $ZnPcSPy_4[RuPc]_4$ (4) derived from GloTarAn analysis of femtosecond pump–probe experiments. Charge separation and charge recombination pathways are highlighted in blue and red, respectively.