

Physicochemical Characterization of Novel Subphthalocyanines Axially Substituted with a Tetracyanobuta-1,3-diene-aniline Moiety

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The development of inexpensive, renewable energies plays a crucial role in ensuring a sustainable and environmental friendly energy supply, whereby solar energy exhibits a great potential due to its high abundance. The development and design of artificial photosynthetic systems comprising electron donor-acceptor (D–A) ensembles that mimic the biological light energy conversion processes displays a promising approach towards more cost-effective photovoltaic devices. Among the molecular building blocks used for the construction of such light-powered, electroactive ensembles subphthalocyanines (SubPcs) – cone-shaped 14 π -electron aromatic compounds – hold a privileged position owing to their intense panchromatic absorptions, excited state energies above 2.0 eV, low reorganization energies in photoinduced electron transfer reactions, and a rich redox chemistry tunable by different peripheral functionalizations.^[1,2] Of particular interest as electroactive counterparts are nonplanar, acetylene-derived push-pull chromophores featuring intense low-energy charge transfer absorptions.^[3]

In light of the aforementioned, we present two novel D–A conjugates, in which a 1,1,4,4-tetracyanobuta-1,3-diene (TCBD)-aniline moiety has been introduced, for the first time, at the axial position of two SubPcs peripherally substituted with hydrogen (H₁₂SubPc) or fluorine atoms (F₁₂SubPc). In-depth physicochemical studies of both SubPc-TCBD-aniline derivatives including a wide range of electrochemical as well as steady state and time-resolved spectroscopic techniques revealed unique photophysical features never observed before in any SubPc- or TCBD-based derivative. On one hand, H₁₂SubPc-TCBD-aniline presents significant ground state charge transfer (CT) interactions between the electron-donating H₁₂SubPc and the axial electron-withdrawing TCBD (Fig. 1a). On the other hand, its perfluorinated analogue gives rise to an intense, broad fluorescence undergoing a bathochromic shift with increasing solvent polarity due to the formation of an intramolecular exciplex (Fig. 1b).

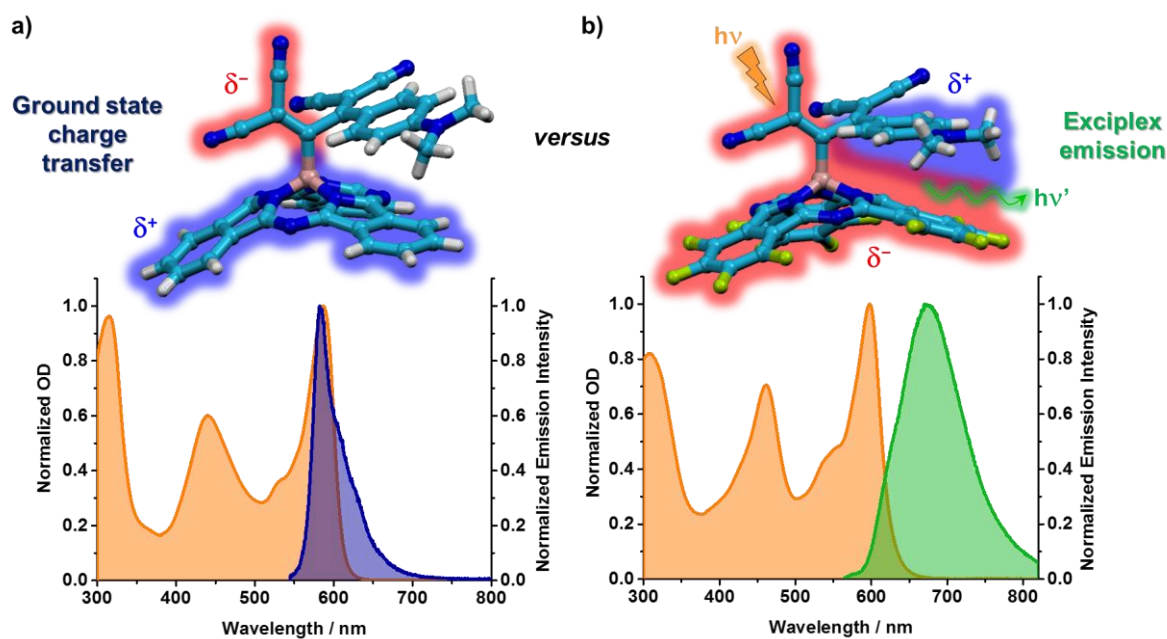


Figure 1. Top: Lateral-view (with respect to the SubPc-TCBD-aniline B–C bond) of the X-ray crystal structure of a) H_{12} SubPc-TCBD-aniline and b) F_{12} SubPc-TCBD-aniline with the electron donor marked in blue and the electron acceptor marked in red. Bottom: Normalized steady state absorption (orange) and fluorescence spectra of a) H_{12} SubPc-TCBD-aniline (dark blue, $\lambda_{\text{ex}} = 530 \text{ nm}$, $c = 2.05 \times 10^{-6} \text{ M}$) and b) F_{12} SubPc-TCBD-aniline (green, $\lambda_{\text{ex}} = 550 \text{ nm}$, $c = 8.90 \times 10^{-6} \text{ M}$) recorded in toluene.

Such exciplex emission stems from a polarized CT state, which is a direct result of the unique three-dimensional geometry adopted by the F_{12} SubPc-TCBD-aniline allowing for intramolecular interactions in the excited state between the spatially close electron-rich aniline and F_{12} SubPc. The formation of an exciplex in terms of a radical-ion pair stabilized through-space, which was corroborated by time-dependent absorption and fluorescence studies, is, to the best of our knowledge, a finding completely peerless in the context of SubPc- and TCBD-based chemistry. Complementary transient absorption studies on both SubPc-TCBD-aniline derivatives demonstrated the occurrence of photoinduced charge separation processes, which, together with the aforementioned ground and excited state features, render these systems promising materials for applications in the field of molecular photovoltaics.

References:

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