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Communication

Chemical control of photoinduced charge-transfer direction in a tetrathiafulvalene-fused dipyrrylquinoxaline difluoroborate dyad

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A new approach for a compact annulation of tetrathiafulvalene (TTF) and dipyrrylquinoxaline difluoroborate (QB) is presented, leading to strong electronic interactions between the TTF and QB units. Regulation of distinct photoinduced charge flows within this dyad is achieved by external stimuli, which is also verified by TD-DFT calculations.

Inspired by the unidirectionality of electron transfer evidenced in photosystem II, special attention has been devoted to efficient control of electron flow in π-conjugated ensembles consisting of electron donor (D) and acceptor (A) subunits. However, regulating the direction of intramolecular charge transfer (ICT) over multiple pathways present in such D-A systems remains a big challenge. An in-depth understanding of this key issue is a prerequisite for the successful implementation of organic molecules in photovoltaics, electronics and photonics. Their intrinsic electronic properties are governed by the extent of communication between D and A units which can be fine-tuned by the meticulous choice and modification of the D-A architectures as well as external stimuli such as coordination, protonation, redox, and light. Very recently, a fullerene-phenothiazine dyad was reported to show in situ switchable molecular photodiode-like behaviour by regulating the redox state of phenothiazine. Our strategy involves a direct annulation of a redox-active π-electron donor TTF (black part, Chart 1) and a strong chromophore dipyrrylquinoxaline difluoroborate (QB, blue part, Chart 1) leading to the formation of the TTF-QB dyad. QB is analogous to BODIPY (boron dipyrromethene) with high extinction coefficient and fluorescence quantum yield and can act as an π-electron acceptor. In stark contrast to the previously reported TTF-BODIPY ensembles, TTF-QB absorbs strongly in the visible spectral region due to a strong effective ICT dominated by one-electron excitation from the HOMO localized on the TTF moiety to the LUMO on the QB core, indicative of largely enhanced electronic communication between them. On the other hand, TTF-BQ featured with a peripheral pyrrolic NH unit, is envisaged to form a hydrogen bond with a fluoride, leading to an ICT from the HOMO mainly localized on the pyrrolylquinoxaline-fluoride adduct to the LUMO on the pyrrolylquinoxaline difluoroborate coordination moiety. Moreover, upon chemical oxidation of the TTF subunit to its radical cation TTF•+, a reverse ICT from the QB to the TTF moiety would occur. As a consequence, chemical regulation of photoinduced charge flow within this compact multicomponent dyad is fulfilled.

In the present contribution, the synthesis and electronic properties of TTF-QB in response to external stimuli including H-bonded fluoride adduct and chemical oxidation are discussed.
characterized. 1H NMR and mass spectrometric data match well with its predicted molecular structure.

The electrochemical properties of TTF-QB, the free ligand TTF-PQ and the reference compounds dipyrrolylquinolizine (PQ) or QB in CH2Cl2 were investigated by cyclic voltammetry (Figures S1-S2, Table S1). TTF-QB undergoes two reversible oxidation processes at 0.78 and 1.10 V to the TTF radical cation and dication states and one reversible reduction process at -0.81 V, corresponding to the reduction of the QB subunit. Upon complexation of the PQ unit with one equivalent of BF3, both oxidation and reduction potentials are positively shifted, indicative of the enhanced π-electron withdrawing ability of the quinoxaline core due to B–N bond formation between the nitrogen lone pair and the vacant π-orbital of the boron atom. It can therefore be deduced that the resultant QB subunit acts as a stronger π-electron acceptor than the quinoxaline unit itself. A separation between the onset oxidation and reduction potentials leads to an electrochemical HOMO-LUMO gap of 1.37 eV for TTF-QB, which is significantly reduced compared to that for TTF-PQ (1.91 eV).

The dark blue TTF-QB strongly absorbs over an extended range within the UV-Vis spectral region (Figure 1). A strong and broad absorption band (ε = 2.3 × 10^4 M^-1 cm^-1) peaked at 610 nm is attributed to an ICT transition from the TTF unit to the QB fragment as confirmed theoretically (vide infra). A series of less-intense absorption bands is observed between 550 nm and 350 nm, followed by a very intense absorption band centered at 310 nm. These spectral features are in stark contrast with those of the free ligand TTF-PQ. On the one hand, its lowest energy absorption band is hypsochromically shifted by 120 nm, as evidenced by its purple-red colour. This observation is ascribed to the formation of N–H···F hydrogen bonds, as previously observed during the titration of the ligand TTF-PQ with the fluoride anion.12 Concomitantly, the emergence of a strong absorption band at 410 nm occurs at the expense of the absorption band around 310 nm. Upon addition of 80 equiv. of TBAF, no further noticeable spectral changes are observed. The final spectrum resembles that of the reference QB in the presence of 80 equiv. TBAF, by exhibiting three distinct electronic transitions (Figure S4). As expected, all these transitions are bathochromically shifted and much stronger in TTF-QB than in QB, by virtue of the large extended π-conjugation that substantially lowers the energy level of the LUMO. In the following, quantum-chemical calculations demonstrate that the lowest energy transition of TTF-QB, when H-bonded to fluoride, corresponds to an ICT from the pyrrole–F unit to the QB moiety, suggesting that the direction of the ICT in TTF-QB can be regulated by adding F.

Intramolecular electronic interactions between the TTF and QB units in the TTF-QB dyad have further been explored by UV-Vis-NIR spectroscopy, whereby a chemical oxidation of TTF-QB was carried out by successive addition of NOSbF5 aliquots at room temperature. As depicted in Figure 3, a progressive reduction of the absorbance of both π-π* and ICT transitions at
310 nm and 610 nm, respectively, is accompanied with a concomitant emergence of new absorption bands at 736 nm and around 1040 nm which reach their maximum values upon addition of 2.5 equiv. of NOSbF$_5$. These new transitions are characteristic of the TTF radical cation species TTF$^+$* within a D-A ensemble. We note that in previously reported studies on oxidised D-A compounds, the lowest energy absorption band is assigned to the dimeric radical cation species arising from enforced intermolecular interactions. In the actual multicomponent molecule, however, the two lowest energy electronic transitions in the NIR around the asymmetric 1040 nm absorbance show a back CT character, which is corroborated by TD-DFT calculations in the following.

To characterise and verify the various electronic transitions, TD-DFT calculations were accomplished using the Gaussian 16 package at the B3LYP/6-31G(d,p) level of theory. After DFT relaxation to within default thresholds, TD-DFT calculations of the 40 lowest excited states were carried out and the absorption spectra extracted with GaussSum 3.0. The predicted absorption spectra of TTF-QB, its fluoride adduct and its oxidised form are in fairly good agreement with experimental results (Tables S2-S7, Figure S11). Compared to TTF-PQ, TTF-QB reveals in particular an absorption onset at a much larger wavelength. This lowest energy absorption band, peaked at 610 nm, is attributed to the dimeric radical cation species arising from enforced intermolecular interactions. In the actual multicomponent molecule, however, the two lowest energy electronic transitions in the NIR around the asymmetric 1040 nm absorbance show a back CT character, which is corroborated by TD-DFT calculations in the following.

The calculated excitations reveal that upon photoexcitation, the charge flow is directed in the reverse direction, hence from the QB to the TTF unit which is now the acceptor site (Figure 4c, Tables S6, S7). Moreover, the calculated excitations $D_0$$\rightarrow$$D_n$ (n ≥ 3) cover well the experimental absorption features at wavelengths around 800 nm and lower.

a) TTF-QB

b) Fluoride adduct

In conclusion, the key finding is that, through external stimuli like fluoride binding or oxidation reaction, the directionality of a photoinduced charge flow within a multichromophoric D-A system can be regulated. TD-DFT calculations allow the characterisation of the ground- and excited electronic states, which in turn reveals the different directions and locations of charge flow within the intricate but still compact molecule. These obtained results pave the way to manipulate photoinduced CT through various pathways by judicious design.
and chemical modification for potential applications in optoelectronic devices.

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Conflicts of interest
There are no conflicts to declare.

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Table of Content

Chemical regulation of a distinct photoinduced charge flow over multiple pathways present in an electron donor-acceptor dyad is demonstrated.