Singlet Fission in Pyrene-Fused Azaacene Dimers

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Abstract: Singlet fission has emerged as a promising strategy to avoid the loss of extra energy through thermalization in solar cells. A family of dimers consisting of nitrogen-doped pyrene-fused acenes that undergo singlet fission with triplet quantum yields as high as 125% are presented. They provide new perspectives for nitrogenated polycyclic aromatic hydrocarbons and for the design of new materials for singlet fission.

Singlet fission (SF) has emerged as a promising strategy to overcome the Shockley–Queisser limit that predicts a maximum power conversion efficiency of 33.7% for a single junction device.[3] This is because, in SF, a singlet excited state (S1) splits into two triplet excited states (T1) and hence the generation of the extra exciton per absorbed photon avoids the loss of extra energy through thermalization. SF has been observed in several families of conjugated molecules and polycyclic aromatic hydrocarbons,[2] among which the acene family has shown a prominent position. For instance, acene dimers have become key to understanding how structural and electronic factors influence the dynamics of the formation and decay of triplet excitons.[3] Since SF efficiencies are known to increase with the number of linearly fused rings and pentacene is the most stable of the higher acenes, the synthesis and study of pentacene dimers have received a lot of attention,[2a,b] among which maximum triplet quantum yields (TQYs) of 200% have been reported.

However, the triplet energy of pentacene is not well-matched for use in solar cells,[4] and also, the stability of pentacene derivatives is limited in comparison to the shorter acenes.[5] On this regard, tetracene has been investigated as an alternative since it shows triplet energies above the band gap of silicon[4a,b] and is known to be more stable than pentacene.[5] Furthermore, dimers constituted by tetracene have been recently reported with TQYs > 100%.[6]

Substitutional nitrogen-doping is another potential approach to improving the properties of acenes for SF, since the resulting azaacenes are more stable than the corresponding acenes and also their energy levels can be tuned with the number and the position of the nitrogen atoms.[7] Nevertheless, azaacenes remain practically unexplored in SF and only a few studies about monomeric azaacenes in thin films have been reported.[9]

Herein, we report a family of dimers constituted by nitrogen-doped pyrene-fused acenes that undergo SF (Figure 1). This series of regioisomeric dimers are constituted by two dibenzodiazahexacene cores bridged by a phenylene linker in an ortho-, meta-, or para- substitution pattern (o-DAD, m-DAD, and p-DAD), which show the electronic structure of two diazatetracenes (highlighted in pink) as the result of the localization of sextets in the off-linear pyrene rings (highlighted in sky blue) that compartmentalize the acene backbone in smaller and more stable tetracenic residues. The combination of ultrafast transient absorption measurements with global and target analyses reveal TQYs as high as 125% and a detailed SF mechanistic insight for pyrene-fused azaacenes, which altogether provide new perspectives not only for azaacenes and nitrogenated pyrene-fused acenes, but also for the design of new materials with enhanced properties for SF.

Dibenzodiazahexacene dimers o-DAD, m-DAD, and p-DAD are members of the pyrene-fused azaacene family that combine linear annulations (acene backbone) with periodic off-linear bisannulations (pyrene residues). Pyrene-fused azaacenes have shown a high stability as illustrated by synthesis of monodisperse nanoribbons with up to 30 linearly fused rings[10] and of polydisperse nanoribbons with approximately 80 linearly fused rings.[11] We selected dibenzodiazahexacene derivatives with TIPS-acetylene substituents because of their tetracene electronic structure, their stability,
and solubility.\cite{12} o-DAD, m-DAD, and p-DAD were synthesized following the route set out in Scheme 1. A key intermediate is the synthesis of pyrene dione A that will enable the synthesis of the dibenzodiazahexacene core and also the coupling with other units. This structure is quite challenging as it is a completely asymmetric pyrene derivative. To obtain this intermediate, we developed a new synthetic route with pyrene as the starting point that combines desymmetrization across the 2- and 7-positions and across the K-regions. The first step is the introduction of a tert-butyl group in position 2 of pyrene by Friedel–Crafts alkylation.\cite{13} Then, 2-tert-butylpyrene B was borylated on the 7-position through an iridium-catalyzed reaction (63%). Subsequently, we carried out the oxidation of one of the K-regions of pyrene C using NaIO 4 and RuCl 3 as a catalyst, which to our surprise worked very well (53%), highlighting the broad functional group compatibility of this reaction. Also the cyclocondensation of dione A and anthracenediamine D\cite{7c} was satisfactory (56%), yielding the asymmetric dibenzodiazahexacene E with a boronate ester that can be further engaged in cross-coupling reactions. Suzuki cross coupling reactions between E and diiodobenzene with conventional heating led to poor yields <7%. Conversely, when the reactions were carried out with microwave heating higher yields were obtained in shorter reaction times. The o-DAD, m-DAD, and p-DAD dimers were obtained via microwave-assisted Suzuki cross-coupling reaction between the precursor E with ortho-, meta, and para-diiodobenzene affording, respectively the desired ortho-, meta, and para compounds (25%, 45%, and 23% for o-DAD, m-DAD, and p-DAD, respectively). For reference purposes dibenzoaazahexacene (DAM) monomer was prepared by condensation of 2,7-di-tert-butyl pyrene-4,5-dione\cite{13} and anthracenediamine D\cite{7c}.

Complete synthetic procedures including 1H NMR, 13C NMR, matrix-assisted laser desorption/ionization time-of-flight high-resolution mass spectrometry (MALDI-TOF HRMS) and a X-ray crystal structure for DAM are provided in the Supporting Information.

To shed light onto electronic interactions between the two dibenzoaazahexacenes in the different dimers, we first turned to steady-state investigations in solvents with different polarity, namely toluene, THF, and benzonitrile (Figure 2a; Supporting Information, Figure S1 and Table S1). Similar absorption spectra were recorded for DAM, o-DAD, m-DAD, and p-DAD with a series of maxima in the 300–425 and the 450–700 nm ranges (Figure 2a). A closer look at the 588 and 640 nm maxima reveals that, on one hand, o-DAD, m-DAD, and p-DAD are red-shifted in comparison to DAM. The 478, 506, and 540 nm maxima, on the other hand, are blue-shifted in m-DAD and p-DAD and red-shifted on o-DAD. The extinction coefficients of o-DAD, m-DAD, and p-DAD are not doubled in comparison to that of the reference DAM. This speaks for electronic interactions in the ground state as seen for pentacene dimers.\cite{14} The computed TD-DFT spectra at B3LYP-6–311 + g(2d,p)/PBEh-3c level (Supporting Information, Figure S2) and at the M06-2X-toluene-6–311 + g-
and one oxidation wave with no remarkable differences in the half-wave potentials (Supporting Information, Table S3).

The energy levels were estimated from the electronic absorption and electrochemical measurements (Supporting Information, Tables S1 and S3), which correlate well with the DFT calculations (Supporting Information, Table S4). The optical HOMO–LUMO gaps \( E_{\text{opt}}^{\text{HOMO}} \approx 1.8 \text{ eV} \) and electrochemical HOMO–LUMO gaps \( E_{\text{CV}}^{\text{HOMO}} \approx 1.8 \text{ eV} \) are nearly identical for DAM, o-DAD, m-DAD, and p-DAD. The electrochemical LUMO levels (or electron affinities) and the electrochemical HOMO levels (or ionization potentials), which were estimated from the onset of the first reduction and the oxidation potential, respectively, are also nearly identical for DAM, o-DAD, m-DAD, and p-DAD \( E_{\text{LUMO}} \approx -3.6 \text{ eV} \) and \( E_{\text{HOMO}} \approx -5.4 \text{ eV} \). Electronic structure calculations yielded very similar relative results with subtle differences for the four studied molecules (Supporting Information, Table S4). The computed 2T1 is similar to \( S_0 \) for B3LYP in vacuum and remarkably similar for the M06-2X Hamiltonian computed in toluene (Supporting Information, Table S5) for all dimers, which therefore fulfill the energetic requirements for SF.

Femtosecond (fs-TAS) and nanosecond transient absorption (ns-TAS) measurements were performed to gather a more detailed understanding of the excited-state dynamics. Fitting the differential absorption data with a combination of multiwavelength and target analyses sheds light onto lifetimes, quantum yields, and species associated spectra (SAS). In the case of DAM (Supporting Information, Figures S9–S12), 505 nm excitation experiments are best fit by a kinetic model that is based on the sequential formation of three species, namely \( (S_0), (S_1)_{\text{SOL}}, \) and \( (T_1) \) (Supporting Information, Figure S13 and Table S6). TQYs of 12% and 8% for DAM in toluene and benzonitrile were, respectively obtained.\(^{17}\) To establish the triplet excited state features, we turned to triplet–triplet energy-transfer experiments using N-methylfulleropyrrolidine (N-MFP, 8.0 × 10^−5 m) as a triplet sensitizer using 480 nm (800 nJ) photoexcitation (Supporting Information, Figures S14–S17).

Fitting the fs-TAS and ns-TAS data of m-DAD (Supporting Information, Figures S18–S21) required the use of a four-species kinetic model (Supporting Information, Figure S22 and Table S7). After excitation at 505 nm, the singlet excited state \( (S_0)_{\text{hex}} \) undergoes solvent reorganization to afford \( (S_0)_{\text{sol}} \) that transforms quickly and directly into a correlated triplet excited state \( (T_1) \). The last step in the sequence is spin decoherence that results in the uncorrelated triplet excited state \( (T_1)_{\text{sol}} \) (Supporting Information, Figure S22 and Table S7). TQYs for \( (T_1) \) and \( (T_1)_{\text{sol}} \) are 70% and 27% in toluene and 30% and 32% in benzonitrile, respectively. Fitting the fs-TAS/ ns-TAS data for o-DAD (Figure 3a,b; Supporting Information, Figures S23–S26 and Table S8) and p-DAD (Supporting Information, Figures S27–S30 and Table S9) necessitated the modifications of the deactivation mechanism. In this case, \( (S_0)_{\text{hex}} \), which is a virtual inter-
DAD. The immediate outcome of using benzodiazahexacenes in o-DAD has a strong effect on the S₁→S₂ transition, which combines contributions with a sizable charge-transfer (CT) character owing to the transfer of charge between the two aromatic tetracene moieties (Supporting Information, Figures S31–S33). While in the case of m-DAD and p-DAD the S₁→S₂ transition is not red-shifted because the two tetracene units are spatially decoupled (Figure 2a; Supporting Information, Figures S31 and S32). This direct contact is also reflected experimentally by the higher fluorescence quenching on o-DAD (Figure 2b). To check the DFT findings, we also computed the excited states of the o-DAD-H model system (this is an o-DAD model in which the TIPS groups have been exchanged by H) at the NEVPT2(8,8)/def-SV(P) level. This yielded two local excitation (LE) states at 2.28 and 2.39 eV and two darker CT states at 2.36 and 2.37 eV, which confirms the M06-2X finding yet also suggesting that these CT states might be nearly degenerate to the LE S₁.

In conclusion, we have reported the synthesis of a new family of regioisomeric diazatetracene trimers constituted of two dibenzodiazahexacene units linked by a phenylene ring in an ortho, meta, and para substitution pattern. In o-DAD the two tetracenes are in close contact, while in the case of m-DAD and p-DAD the two tetracenes are spatially decoupled, as demonstrated by a combination of electronic absorption and photoluminescence measurements and theoretical calculations. Femtosecond (fs-TAS) and nanosecond transient absorption (ns-TAS) measurements reveal how the enhanced electronic communication in o-DAD gives rise to a TQY >100%. Overall this work provides new application perspectives for pyrene-fused azacenes, but also for the design of new materials with enhanced properties for SF, in which the triplet energy and the stability are better suited for use in solar cells.
