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Bending Pyrenacenes to Fill Gaps in Singlet-Fission-Based Solar Cells

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Dedicated to Graham J. Bodwell on the occasion of his 60th birthday.

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Abstract Singlet fission is envisaged to enhance the efficiency of single-junction solar cells beyond the current theoretical limit. Even though sensitizers that undergo singlet fission efficiently are known, characteristics like low-energy triplet state or insufficient stability restrict their use in silicon-based solar cells. Pyrenacenes have the potential to overcome these limitations, but singlet-fission processes in these materials is outcompeted by excimer formation. In this work, bent pyrenacenes with a reduced propensity to stack and thus form excimers are computationally evaluated as singlet-fission materials. The energies of the S_1 , T_1 and T₂ states were estimated in a series of bent pyrenacenes by means of time-dependent density functional theory calculations. Our results show the opposite trend observed for perylene diimides, namely, an increase in the energy of the T₁ and S₁ states upon bending. In addition, we show that the energy levels can be tuned on demand by manipulating the bend angle to match the energy gap of various semiconductors that can be used in single-junction solar cells, making pyrenacenes promising candidates for singlet fission.

Key words: bent polycyclic aromatic hydrocarbons, density functional theory, pyrenacenes, ropyrenes, rylene diimides, singlet fission

Introduction

Singlet fission (SF)¹ is a spin-allowed process where one singlet exciton (S₁) is transmuted to two triplet excitons (T₁ + T₁). Because the overall mechanism relies on the production of two excitons from a single photon, SF has been implicated



as a useful process to enhance the efficiency of photovoltaic solar cells² by exceeding the Shockley–Queisser limit.³ Having in mind the simplified process for SF shown in Equation 1, it is easy to guess that the energy levels of the S₁ and T₁ excited states play a key role in the SF process.

$$S_0 + hv + S_0 \rightarrow S_1 + S_0 \rightleftharpoons {}^1(T_1 T_1) \rightleftharpoons T_1 + T_1$$

Equation 1 Schematic mechanism for SF.

In fact, the so-called "energy-matching conditions" are written as a basic requirement. Thus, for a SF sensitizer it is established that 1) the energy of S_1 should be greater than or equal to two times the energy of T_1 , in order to generate two T_1 states from one S_1 state excergically (Equation 2), and 2) the energy of the second excited triplet state (T_2) should be higher than twice the energy of T_1 , to prevent the combination of two T_1 states into a T_2 state (Equation 3).

$E(S_1) \ge 2E(T_1)$

Equation 2 First energy-matching condition for SF.

 $E(T_2) > 2E(T_1)$

Equation 3 Second energy-matching condition for SF.

SF is especially important for the development of singlejunction or dye-sensitized solar cells. The Shockley–Queisser limit on efficiency for an ideal silicon (Si)-based solar cell is 29% (considering an energy band gap E_g = 1.11 eV for Si), which can be improved up to 40% in SF-based systems according to calculations.⁴ Nevertheless, novel semiconduc-

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tors such as GaAs ($E_g = 1.43 \text{ eV}$) and perovskites ($E_g = 1.20 - 2.30 \text{ eV}$) have emerged,⁵ showing efficiencies that are competitive with Si. Thus, a dye exhibiting SF with a T₁ energy level close to E_g of any semiconductor might become a promising sensitizer for the development of highly efficient solar cells.⁶

Organic compounds such as tetracene or pentacene (Figure 1) have been proven as efficient SF sensitizers.⁷ Despite the high yield of its exoergic SF process (up to 200%), pentacene is not a suitable candidate for the development of single-junction Si-based SF solar cells because its $E(T_1)$ (0.86 eV) is significantly below E_g of Si (1.11 eV). On the other hand, tetracene undergoes endoergic SF with a yield of 133% and a matching $E(T_1)$ (1.25 eV; above $E_g(Si)$). Calculations indicate that systems with endoergic SF, facilitating the ${}^1(T_1 T_1)$ thermal dissociation, are expected to show higher device efficiencies than exoergic SF systems.⁸ Nevertheless, the main drawback of tetracene and pentacene is their low photostability, which must be tackled by modification of their chemical structure, making their synthesis challenging on a larger scale.

Recently, rylene derivatives and diketopyrrolopyrroles have also been established as SF sensitizers.⁹ All the past achievements notwithstanding, the door is still open for



novel and non-conventional organic SF materials.⁶ Peropyrene (**PP**), a member of the pyrenacene family (Figure 2), has been proposed as a candidate for SF; however, studies suggest that in unsubstituted **PP**, excimer formation outcompetes SF.¹⁰ Conversely, the evaluation of the SF potential of the higher homologs of the pyrenacenes, namely, teropyrene (**TP**) and quateropyrene (**QP**), is still largely unexplored despite the relatively recent synthetic access.¹¹ On the other hand, related diimide analogs such as perylene diimide (**PDI**),¹² terrylene diimide (**TDI**)¹³ or quaterrylene diimide (**QDI**)^{13b,14} have been studied in depth.



Figure 2 Systems studied in this work²¹ (rylene diimides are structural analogs of pyrenacenes (compare PDI and PP in Figure 1). Dashed bonds in the bottom-left structure indicate the oligo(methylene) bridge employed during calculations; three black dots at each end define planes 1 and 2, which define bend angle θ .

Nuckolls et al. observed that bending **PDI** along its long axis has a dramatic effect on the molecule's SF behavior,^{12b,15} increasing the rate of SF by 2 orders of magnitude and introducing control of bend angle as a tool for improving SF in organic sensitizers (Figure 1). With these discoveries in mind, we wondered about the effect of bending on the properties of promising candidates such as pyrenacenes, where bending can perform multiple functions, namely, avoiding the formation of excimers in **PP**, modifying the crystal packing

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and affecting the excited-state energy levels (Figure 1). In addition, synthetic methods to furnish some bent pyrenacene members (pyrene (**Py**) and **TP**) are well established via the methodology developed by Bodwell et al., with full control of the resulting bend angle.¹⁶ Other members of the series, namely, **PP** and **QP**, are not amenable to the same methodology.

A search for candidate compounds is often performed theoretically using computational methods. In this regard, the energies of the S₁, T₁ and T₂ states are calculated. If the computed values fulfill the energy-matching conditions (Equations 2 and 3), the proposed structure can be considered as a promising candidate for SF. Early screening carried out by Michl and co-workers suggested that either alternant closed-shell hydrocarbons or open-shell diradicals are suitable structures for SF.¹⁷ Additionally, exhaustive screenings have been reported for anthracene derivatives,¹⁸ heteroatom-based structures¹⁹ or biradicaloid chromophores.²⁰ Indeed, the proposed candidates have been proven to exhibit SF, but they usually lack thermal or photochemical stability.

Design

To this end, there is no systematic theoretical investigation on the effect of longitudinal bending on the excited-state energy levels. Thus, we propose a theoretical approach to study the excited-state levels and examine a possible trend between the energies that are relevant for SF and the bend angle in a series of pyrenacenes²¹ (Figure 2) and compare this trend with structurally related rylene diimides. We chose pyrenacenes as the model series since they exhibit high photostability and good optical properties, such as high absorptivity coefficients (100,000 L·mol⁻¹·cm⁻¹ in the case of **QP**¹⁰) and high fluorescence quantum yields (95% for **PP** in acetonitrile¹⁰).

Nuckolls et al. have provided a molecular orbital-based rationale for the experimentally observed differences in the HOMO and LUMO energies for **PDI** systems either bent or twisted along the long axis.^{15a} By considering changes in the lobe interactions in the *K*-regions upon bending (Figure 3), it is seen that in **PDI** two interactions dictate the resulting properties: 1) the energy of the HOMO is increased because of an antibonding interaction that grows as a function of the bend angle, and 2) the energy of the LUMO is decreased with increasing bend since bending bolsters a bonding interaction. Structurally related pyrenacenes studied in this work display highly similar but inverted HOMO and LUMO electronic structures with respect to the **PDI** family (Figure 3).

Applying the same analysis of the orbital-energy changes upon bending, a bonding interaction between the *K*-region lobes occurs in the pyrenacene's HOMO, decreasing the HOMO energy as a function of the bend angle. Likewise, the



Figure 3 Walsh-type diagram for HOMO and LUMO of PDI and PP, based on earlier work of Nuckolls et al.^{15a} b = bonding interactions, ab = antibonding interactions.

increasing angle drives the LUMO energy upwards because of an antibonding interaction that grows with the bend angle. Based on this analysis, the inversion in the electronic structure of the HOMO and the LUMO between the rylene diimide and pyrenacene families is expected to yield opposing trends regarding $E(T_1)$ on increasing the bend angle.

The HOMO and the LUMO are occupied by one electron each in the S_1 and T_1 states, while the two electrons are paired in the HOMO in the S_0 state. Consequently, for rylene diimides, S_1 and T_1 suffer less from the antibonding interaction in the HOMO than S_0 and profit from the bonding interaction in the LUMO, resulting in their stabilization relative to S_0 . As a net result, the S_1 and T_1 energies, reported relative to S_0 , are decreased. For pyrenacenes, an opposite trend is observed, namely, an increase in the S_1 and T_1 energies upon bending (Figure 3). This opens up an exciting opportunity for pyrenacenes to push their $E(T_1)$ beyond the energy band gap of Si to higher band gaps of semiconductors such as GaAs, metal dichalcogenides or perovskites.

Results and Discussion

The calculated²² energy values for the T_1 , S_1 and T_2 excited states of **Py**, **PP**, **TP** and **QP** are gathered in Table S1. These

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calculated values reveal that the energy of the T_1 state, $E(T_1)$, increases with increasing bend angle. This trend is in stark contrast to the series of rylene diimides studied previously.^{15a} which display the opposite trend (Figure 4), as predicted in the Design section by the frontier molecular orbital analysis (Figure 3). The energy of the S_1 state, $E(S_1)$, tends to increase with increasing bend angle but less so than that of $E(T_1)$, meaning that the SF process becomes more endoergic upon bending pyrenacenes (Figure 5). A similar trend is observed when plotting $E(T_1)$ and $E(S_1)$ against the HOMO-LUMO gap, correlating the energy of the HOMO and the LUMO with the energies of the T_1 and S_1 states (Figures S19, S21, S23, and S25). The energy of the T_2 state, $E(T_2)$, remains almost unaltered upon bending (Table S1). Slight conformational changes are observed in the excited states compared to the ground state, where the bend angle increases in the T₁ and S₁ states.



Figure 4 In stark contrast to rylene diimides (red), the energy of the T_1 state of pyrenacenes (green) increases with the bend angle, in accord with the prediction shown in Figure 3.

In the case of **Py**, $E(T_1)$ jumps from 1.01 to 2.13 eV after a slight bending (28.4°). Then, it moves up to 2.34 eV by bending the structure to 106.5° (Figure S18). The computed $E(T_1)$ value is far from matching the E_g of Si, but it might fit one of the emerging semiconductors with higher E_g values, such as transition metal dichalcogenides (TMDCs; e.g., MoS₂ monolayer, 1.90 eV or WS₂ monolayer, 2.10 eV).²³

Remarkably, in the case of **PP**, $E(T_1)$ moves from 1.38 to 1.83 eV after bending up to 174.8° (Table S1). This observation is notable since slightly bent **PP** can be used to build Si- or even GaAs-based single-junction devices, while **PP** bent to a higher degree is a good match for some perovskites (Figure 6). In addition, the contortion of **PP** might influence

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Figure 5 Upon bending, the SF process in pyrenacenes is more endoergic.



Figure 6 $E(T_1)$ of pyrenacenes can be tuned by bending to match E_g of a desired semiconductor.

the crystal packing as observed for **PP**–CPP hybrids,²⁴ since the formation of excimers, which is the main drawback of flat **PP**,¹⁰ would be suppressed. The SF process is expected to be endoergic (Figure 5) since the effect of bending on $E(S_1)$ and $E(T_2)$ is not as strong as that on $E(T_1)$.

The same trend continues for **TP**. In flat **TP**, the energy levels match the first energy condition (Equation 2) with $E(S_1) = 2.76 \text{ eV}$ and $E(T_1) = 1.08 \text{ eV}$, slightly lower than E_g of Si (1.11 eV). Notably, $E(T_1)$ can be adjusted to the requirements of Si, perfectly matching its E_g when **TP** is bent to



35.5° (Figure 6). Moreover, $E(T_1)$ can be lifted up to 1.34 eV or even higher when bent like the bridged derivatives reported by Bodwell and coworkers,^{16c} fulfilling the criteria for the preparation of GaAs-based devices (Figure 6). $E(S_1)$ trends downward, making the process more endoergic with increasing bend angle (Figure 5), while $E(T_2)$ remains unchanged.

QP is the largest member of the pyrenacene family studied in this work. Its energy levels in the flat geometry are similar to pentacene $(E(S_1) = 1.86 \text{ vs.} 1.83 \text{ eV} \text{ and}$ $E(T_1) = 0.90$ vs. 0.86 eV for **QP** and pentacene, respectively) and SF is expected to be exoergic. The advantage of **OP** is that its extinction coefficient and photostability are higher than in pentacene, which should improve the performance of single-junction **QP**-based solar cells. $E(T_1)$ in **QP** can be adjusted to match $E_{g}(Si)$ by bending **QP** in the range of 124-167° (Figure 6). The effect of curvature is less pronounced in **QP** compared to the other studied pyrenacenes. In **QP**, a change from 0.90 to 1.15 eV was calculated for the T₁ state upon bending from 0.0 to 167.3°. These observations suggest a finer tuning of $E(T_1)$ in **QP**. The process is expected to be the least endoergic in the series, comparable to tetracene. $E(T_2)$ increases upon bending, but the $E(T_2) - 2E(T_1)$ value becomes slightly more negative when increasing the bend angle (Figure S24 and Table S8).

The reader will observe that most of the bent pyrenacenes do not fulfil the aforementioned inclusive inequality of $E(S_1) \ge 2E(T_1)$. This means that SF should not proceed rapidly at room temperature for these compounds; however, the guiding design principle $E(S_1) \ge 2E(T_1)$ only takes into account the enthalpic side of SF. It ignores the entropic driving force of multiple-exciton creation from a single excited state, which can couple endoergic (i.e., endothermic) SF to an overall exergonic process.^{8a} In practice, materials that do undergo rapid, exoergic (i.e., exothermic) SF suffer from two significant disadvantages: (1) the low triplet energy does not lend itself well to integration with classical semiconductors and (2) exothermic systems suffer from the potential energy loss from poor utilization of the photon energy.²⁵ It has been proposed that slightly endothermic SF is more suitable for application in photovoltaic devices²⁶ with endothermicities as high as 0.2 eV still displaying high efficiencies.²⁷ In fact, the highest possible theoretical efficiencies of singlet-fission-based solar cells are predicted to be those based on endothermic SF.8a

To compare pyrenacenes with rylene diimides and to validate computationally the trend observed by Nuckolls and coworkers in bent **PDIs**, ^{12b,15a} we also calculated the energies of the S₀, T₁ and S₁ states of flat and bent naphthalene diimide (**NDI**), **PDI** and **TDI** using the same level of theory as for the pyrenacene family. As expected (Figure 3), bending the structures of **NDI**, **PDI** and **TDI** has the opposite effect on the energies of the T₁ and S₁ states compared to pyrenacenes (Table S10). $E(T_1)$ of **PDI** and **TDI** can be lowered down to 0.53 and 0.47 eV by bending the structure to 177.3° and 148.5°, respectively. Therefore, only small angles appear to be effective in **PDI** (66.72°), as observed by Nuckolls et al., to match $E_g(Si)$, while larger angles or higher analogs seems to exhibit low $E(T_1)$ values, below $E_g(Si)$. Therefore, even though SF has recently been observed in **QDI**, its low $E(T_1)$ restricts its use in Si-based solar cells.¹⁴ Overall, the relationship between the bend angle and the excited-state energies in pyrenacenes seems to be more favorable for the implementation into solar-cell devices than those of rylene dimindes.

Conclusions

A theoretical analysis of the excited-state energies was performed for a series of flat and bent pyrenacenes, ranging from pyrene to quateropyrene. The results show a trend of increasing T₁-state energy with increasing bend angle. Remarkably, the inverse trend is observed in rylene diimides. For pyrenacenes, this opens up an attractive possibility. Since flat **PDI** displays *E*(T₁) of 1.4 eV, bending beyond angles reached by Nuckolls et al. will further lower $E(T_1)$ below E_g of typical semiconductors. In contrast, the pyrenacene series offers tunability of practical use because careful control of the bend angle could increase $E(T_1)$ to and above $E_g(Si)$. These results suggest that bending pyrenacenes could be a viable strategy to match the energy of the T_1 state with the energy gap of various semiconductors, such as silicon, GaAs, perovskites or TMDCs, for the development of single-junction solar cells capitalizing on SF. In addition, bending pyrenacenes might have a favorable effect on the crystal packing. where the formation of excimers is suppressed, boosting the singlet-fission process.

It is worth noting that not only are the structures discussed here synthetically feasible, more bent teropyrenophanes than those proposed here have already been isolated as bench-stable solids.^{16b,c} Bent peropyrenes and quateropyrenes, which cannot be synthesized by Bodwell's methodology, are among the predicted best materials found in this study. Thus, the results identify a need to find viable synthetic paths that offer precise control of the bend angle for these members of the pyrenacenes, as has been accomplished for pyrene²⁸ and teropyrene.^{16b,c}

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Supporting Information

Supporting Information for this article is available online at https://doi.org/10.1055/a-1939-6110.

Conflict of Interest

The authors declare no conflict of interest.

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- (21) "Lost in translation": In older literature, the pyrenacene series is often referred to as the ropyrene family. The prefixes affixed to the ropyrenes followed those of the rylenes. Thus, the third member of the ropyrenes should be terropyrene, modeled after terrylene. With the first synthesis of terropyrene by Misumi in 1975,²⁹ however, the spelling in this publication, teropyrene, was quickly adopted and has become the accepted spelling. The authors have chosen to adopt the post-Misumi spelling and thus the first four members of the pyrenacene series are listed as pyrene, peropyrene, teropyrene and quateropyrene.
- (22) The Gaussian 16 software package (Revision A.03) was used for geometry optimizations and estimation of the relative energies of the compounds studied. The S₀ and T₁ energies were calculated using density functional theory (DFT) methods, while the S₁ and T₂ energies were computed using time-dependent DFT (TD-DFT). All reported final energies represent the sum of the electronic energy and zero-point vibrational energy correction. For both DFT and TD-DFT calculations, the Becke three-parameter exchange function in combination with the Lee-Yang-Parr correlation functional (B3LYP) was used, since it was proven to give good results in estimating excited-state geometries.³⁰ The Ahlrichs' polarized valence triple- ζ basis set def2-TZVP was used

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for these optimizations. The D3 version of Grimme's dispersion with Becke-Johnson damping (GD3BJ) was applied. The geometries of the different structures were optimized and confirmed to be minima by analyzing their vibrational frequencies. Flat structures were constrained to the D_{2h} symmetry, while bent counterparts to the C_{2y} symmetry. To optimize and calculate the energies of the bent counterparts, we applied the following procedure: 1) terminal carbon atoms were connected through an oligo(methylene) bridge (Figure 2, bottom left) and the geometries of the bridged structures were optimized using semiempirical methods (AM1). When experimental X-ray diffraction structures were available, these geometries were used as the starting point. 2) The oligo(methylene) chain was removed and replaced by hydrogen atoms at the terminal carbon atoms, and the coordinates of the terminal carbon atoms were frozen. 3) Geometry optimization of the S₀ state using DFT (B3LYP/def2 TZVP/GD3BJ). 4) Using the S_0 geometry as a starting point, the geometries of the T₁, S₁ and T₂ states were optimized. Their energies are therefore estimated based on an adiabatic process. Gaussian 16, Revision A.03, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.;

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Short Communication