ABSTRACT: Singlet fission (SF) is a two-step process in which a singlet splits into two triplets throughout the so-called correlated triplet-pair (1TT) state. Intramolecular SF (iSF) materials, in particular, have attracted growing interest as they can be easily implemented in single-junction solar cells and boost their power conversion efficiency. Still, the potential of iSF materials such as polymers and oligomers for photovoltaic applications has been partially hindered by their ability to go beyond the 1TT intermediate and generate free triplets, whose mechanism remains poorly understood. In this work, the main aspects governing the 1TT dissociation in donor–acceptor copolymers and the key features that optimize this process are exposed. First, we show that both thermodynamics and kinetics play a crucial role in the intramolecular triplet-pair separation and second, we uncover the inherent flexibility of the donor unit as the fundamental ingredient to optimize them simultaneously. Overall, these results provide a better understanding of the intramolecular 1TT dissociation process and establish a new paradigm for the development of novel iSF active materials.

INTRODUCTION

Singlet fission (SF) is the photophysical phenomenon in which a singlet state is converted into two independent triplets. This occurs via the so-called correlated triplet-pair state (1TT), which belongs to the singlet state manifold and thus can be accessed through a spin-allowed reaction. Once the 1TT state is formed, it dissociates into two triplet excitons to complete the process (eq 1).

\[ S_1 \rightarrow ^1\text{TT} \rightarrow 2T_1 \]  

Materials exhibiting SF have received significant interest for applications in photovoltaics because of their potential to overcome the thermodynamic Shockey–Queisser 33% limit of single-junction solar cells and boost their power conversion efficiency up to 45%.4−6 The challenge of finding SF materials comes from designing chromophores that fulfill not only the energetics \( E(S_1) \geq 2E(T_1) \) but also undergo fast singlet splitting and triplet-pair dissociation rates. Anthracene7 and tetracene8 were the first molecular crystals in which SF was identified. Since then, extensive experimental7−14 and theoretical15−19 work on acene derivatives has significantly pushed the understanding of the SF process. However, the poor photostability of these systems and their limitations for practical implementations has urged the search for more diverse SF-active materials.20−22 In this context, other families of SF materials such as carotenoids23 and conjugated polymers24,25 have been considered, although so far to a much less extent. The one-dimensional sequence of chromophores in extended polymers opens the possibility of iSF through their characteristic lowest singlet excited state of a multieexciton character.26−28 This feature, together with their high tunability and easy processability, makes conjugated polymers particularly attractive for the development of novel iSF materials. In particular, Busby et al. proposed a push–pull donor–acceptor (D−A) copolymer framework to obtain highly efficient iSF.29 In this strategy, optical absorption promotes D-to-A charge transfer (CT) sideways that drives the formation of two low-lying spatially separated triplets localized in the acceptor units (Figure 1). Remarkable triplet quantum yields up to 170% were reported for poly(benzothiophene-alt-thiophene-1,1-dioxide) (BDT-TDO) polymer chains in solution as well as for similar D−A copolymers following the same approach.24,30,31 Still, only very few conjugated polymers fulfill the criteria for iSF, namely, energetics and coupling...
coplanar copolymers was identified.33,34 A comprehensive structure accelerated design strategies to the 5TT state), which is traditionally associated with better

Figure 1. Schematic representation of the iSF steps in D–A copolymers. First, UV–vis light absorption promotes S₀ to S₁, characterized by strong D–to–A CT sideways. Second, S₁ decays via a spin-allowed process toward the triplet-pair state ¹TT, localized in adjacent A. Third, the ¹TT state spatially dissociates and become two independent T₁ triplets.

requirements. Indeed, a fundamental trade-off between the ability to display D–to–A CT S₁ and acceptor-local T₁ in coplanar copolymers was identified, evidencing the need for accelerated design strategies to find promising SF candidates.35,36 A comprehensive structure–property analysis of D–A copolymers allowed us to recognize the role of dihedral torsion in modulating and pushing the CT and local character of the excitations beyond the limit of the coplanar approach.32,35 On the one side, a larger CT resulted in larger S₁/¹TT electronic coupling in a series of modified TDO-based copolymers, promoting fast S₁-to–¹TT dynamics.28 On the other side, localized T₁ in the acceptor reduces the ¹TT binding energy (evaluated as the vertical energy difference with the ¹TT state), which is traditionally associated with better triplet–triplet dissociation rates.36

The loss of spin coherence between the triplets and the triplet-pair separation process are crucial steps for the successful implementation of SF copolymer materials in solar cell devices.37,38 In this context, theoretical frameworks have been recently developed to model triplet-pair dissociation in acene-based molecular crystals.39,40 Still, the triplet-pair dissociation process in D–A copolymers remains unexplored. In this work, we show that considering the ¹TT binding energy is not enough to anticipate favorable intramolecular triplet–triplet dissociation rates in D–A copolymers. For a series of extended prototypes (Figure 2), we evaluate the TT, 2T₁, and intermediate structures and uncover that not only the ¹TT dissociation thermodynamics but also the intramolecular triplet transport kinetics play an important role in the triplet-pair separation process. We discuss whether it is possible and how to optimize both features simultaneously and propose a simple model based on sequential T₁ potentials to rationalize and predict their behavior.

Figure 2. Left: nine D–A copolymers considered for extended (5A and 4A) models. Right: library of donors and acceptors of the database of 100 A–D–A trimers (2A model) considered, extracted from ref 32. R groups include H, Me, OMe, and COOMe, and X groups include H, F, Cl, CN, and OH. Acronyms: thiophene-1,1-dioxide (TDO), diketopyrrolopyrrole (DPP), benzo[b]thiadiazole (BT), 2,2-bithiazole (bTz), benzodithiophene (BDT), phenylene (Phen), thieno[3,2]thiophene (TT), ethylenedioxythiophene (EDOT), carbazole (Cbz), thiophene-vinyl-thiophene (TVT), cyclopentadithiophene (CPDT), naphthalene (Naph).

METHODS

Initial structures of the D–A copolymers were obtained from the SMILES-to-xyz transformation given by Openbabel with the MMFF94 force field.31 Geometry optimization of the ground state singlet, T₁, TT, and 2T₁ electronic states was performed on top with the obo97X-D functional and 6-31g(d) basis set using Gaussian 09 (D.01).42 The TT and 2T₁ geometries were obtained for the quintuplet spin state with unrestricted DFT. Three different extended models were considered: 5-acceptors (5A) model with sequence A–D–A–D–A–D–A–D–A, 4-acceptors (4A) model with sequence A–D–A–D–A–D–A, and 2-acceptors (2A) model with sequence A–D–A. Transition state (or intermediate) geometries of the TT → 2T₁ reaction were obtained with the SA model starting from the linear interpolation between the A–D–T₁–D–A–D–A–D–A (TT) and A–D–T₁–D–A–D–A–D–A (2T₁) geometries. Transition state (or intermediate) geometries of the T₁ → T₁ reaction were obtained with the 4A (2A) model starting from the linear interpolation between the A–D–T₁–D–A–D–A–D–A (TT) and A–D–A–D–A–D–A–D–A (2T₁) geometries. Frequency computations confirmed the nature of the critical points as minimum or transition states of the potential energy surface.

Non-collinear spin-flip TDDFT44 (with the obo97X-D functional) and restricted active space spin-flip RAS-2SF45 computations, both with 6-31g(d), were performed on top of the optimized TT and 2T₁ 5A model geometries (A–D–T₁–D–T₁–D–A–D–A and A–D–T₁–D–A–D–T₁–D–A) to determine the ¹TT–³TT–¹TT vertical energy splitting and the ¹¹TT → 2T₁ reaction energies using Q-Chem 5.1.46 Extended computational details, including basis set and functional benchmarking, can be found in Sections S1–S4 of the Supporting Information.
and 2T1 geometries was computed in the singlet, triplet, and Section S5). To do so, the relative energy between the TT of the BDT-TDO coplanar prototype was evaluated (Figure 3 and S5.1). This anticipates that intrachain triplet transport is a crucial step in the triplet–triplet dissociation reaction of ISF in D–A copolymers. The same analysis was performed for the BDT-DPP non-coplanar prototype (Figure 2 and Section S6). This D–A copolymer displays a significant dihedral torsion (~60°) between the donor and acceptor units due to the steric repulsion between their functional groups and, as a consequence, reduces the 1TT–2T1 splitting down to ~0 eV. In agreement with this result, the computed TT-to-2T1 reaction energies of the extended chain are close to 0 eV regardless of the spin state (Table S6.1). The dissociation barrier, however, increases up to ~0.5 eV for the minimum energy intermediate that connects both structures (Figure S6.1). Therefore, while the 1TT dissociation thermodynamics of BDT-DPP is more favorable than that of BDT-TDO, the triplet dissociation kinetics would slow down. Indeed, the electronic entropy of the 1TT → 2T1 process is ~0.3 eV, and thus, barriers or dissociation energies above this value would promote triplet-pair trapping. This indicates that solely reducing the TT binding energy is not enough to improve TT dissociation rates and that the triplet transfer barrier needs to be also minimized. In this context, similar conclusions were reported for intermolecular TT dissociation in acene-based molecular crystals, for which TT exchange interactions (splitting) and triplet–triplet energy transfer (t) need to be optimized simultaneously to achieve successful triplet-pair separation. It is therefore necessary to determine how to optimize these two features simultaneously in D–A copolymers. We address this question by evaluating the TT dissociation energy and triplet transfer kinetics of a series of extended and minimal D–A prototypes. First, to establish whether a systematic correlation between the TT splitting and the intramolecular TT-to-2T1 reaction encounters along the copolymer chain assuming long T1 lifetimes, leading to an effective equilibrium between 2T1, TT, and S1 states. Analysis of the spin density of the TT, intermediate, and 2T1 structures shows that the dissociation is mainly characterized by the energy transfer of one T1 from one acceptor to another passing throughout a donor unit (Figures 3 and S5.1). This anticipates that intrachain triplet transport is a crucial step in the triplet–triplet dissociation reaction of ISF in D–A copolymers.

### RESULTS AND DISCUSSION

The TT binding energy is considered the minimal energy required for the separation of the triplet-pair and is usually evaluated as the ΔVT-TT vertical energy difference, as it is related to the degree of electronic configuration mixing of the TT states. On the one side, the mixing of the 5TT state is limited because the other quintuplet configurations are much higher in energy; thus, it is used as a proxy of two non-interacting triplets (2T1). On the other side, electronic interaction between the triplets becomes large in 1TT when other singlet configurations significantly contribute to stabilize its energy. This is usually the case in extended conjugated systems such as polymers where the characteristic low-lying multi-excitonic singlet is strongly mixed with the lowest mono-electronic transition of the same symmetry. In a previous work, we showed how the TT binding energy can be reduced in A–D–A trimers by means of inducing dihedral torsion between the D and A molecular building blocks, therefore potentially accelerating the triplet-pair dissociation rates in agreement with the model established for SF dimers. Still, it is unknown whether this model applies to extended D–A copolymers and more importantly which features control the intrachain triplet-pair dissociation process in these systems. To address this question, the triplet–triplet dissociation scenario of the BDT-TDO coplanar prototype was evaluated (Figure 3 and Section S5). To do so, the relative energy between the TT and 2T1 geometries was computed in the singlet, triplet, and quintuplet states as well as the minimum energy barrier between the two structures. Both 5TT and 1TT spin states result in non-zero dissociation energies. In the case of 1TT the dissociation energy to 2T1 is negative (~0.18 eV), indicating repulsive interaction between the triplets, while for 5TT, the dissociation energy is positive (~0.13 eV), indicating attraction. Near zero dissociation energy is obtained for 3TT (~0.03 eV). Remarkably, the three spin states display similar barrier energies whose value (~0.3 eV) is significantly larger than the 1TT → 2T1 reaction energy, thus indicating that the kinetics would control the rate of the TT dissociation process over the thermodynamics. Note that the 2T1 → TT process is also possible. There will be inevitable triplet–triplet re-
energy exists, these values were computed for nine D–A extended copolymers based on TDO and DPP acceptors (Figure 2). These hold inherently low triplet energies and have been identified as promising building blocks for SF.29,32,34,35,50,51 The results show that 1TT-to-2T1 reaction energies follow opposite trends with respect to the vertical 3TT–1TT splitting in a way that larger splitting results in less favorable 1TT-to-2T1 thermodynamics (Figure 4a) in agreement with the literature.36,47 Thus, TT splitting can be used as the reference of TT dissociation energies.

Second, to characterize the triplet-pair dissociation kinetics of these systems, the minimum energy path of the triplet energy transfer process was evaluated from one acceptor to another throughout the donor (i.e., between A–D–T1–D–A–D–A and A–D–A–D–T1–D–A) and compared to that of the TT-to-2T1 dissociation barrier. The results show that the TT-to-2T1 barrier mostly originates from the energy transfer of an isolated triplet (Section S7), and thus the latter can be used to predict the TT dissociation barrier. For the nine extended D–A copolymers, the correlation between their TT splitting and their triplet transfer barrier shows an unfortunate inversely direct trend in which the cases with the smallest (largest) TT splitting result in the largest (smallest) barriers (Figure 4b). This points to the need for larger-scale sampling of D–A combinations to uncover whether it is indeed possible to find systems in the optimal region, namely, with small TT splitting and triplet transfer barriers, and, thus, to minimize both simultaneously. We took advantage of the 2994 database of D–A dimers previously reported22 to extract 100 candidates that fulfill the requirements for iSF38 (Figure 2 and Section S8). For those systems, the TT vertical splitting and triplet energy barrier of their minimal A–D–A model were evaluated. The minimal model slightly overestimates the TT splitting and underestimates the triplet transport barriers but is able to capture the trends of the extended model (Figure S8.1). The results show that the 100 systems spread all over the bottom-left diagonal of the property space but only few have small TT splitting and triplet transfer barriers simultaneously (Figure 4c). Interestingly, the BDT-TDO copolymer prototype lies on the edge of the ~0.3 eV limit. Analysis of the chemical composition of the systems in the optimal region reveals that these have bithiophene (or TVT in one case) as the donor. In the absence of these two donors, the inversely direct trend between the TT splitting and the triplet transfer barrier is recovered (Figure S8.2). The particularity of these two donors is that they hold inherent flexibility to display coplanar and non-coplanar conformations around the central bond (depending on the electronic state), while the rest are based on conjugated fused rings without this possibility (Figure 2). This inherent flexibility comes from the fact that they are based on two or more covalently bound units with a small rotational barrier. This allows to modulate their coplanarity differently for the TT state minimum, in which the central bond is formally a single bond, and the T1 transition state structure, in which the central bond acquires a double bond character (Scheme 1). The non-coplanarity of the TT minimum reduces the triplet–triplet interaction and thus the TT binding energy, while the coplanarity of the T1 intermediate (or transition state) tends to reduce the energy barrier.7,52 For that reason, rigid donors can only minimize one while penalizing the other, (or hold the perfect balance as BDT-TDO) depending on their optimal D–A dihedral. Remarkably, this provides an important extra functionality to the donor unit beyond assisting the S1-to-1TT step of the iSF process, which is to drive the 1TT dissociation reaction via intrachain triplet energy transfer. Note that intrachain triplet energy transfer would be also possible in polymer thin films.53,54 This will, however, depend on unpredictable intermolecular arrangements beyond a molecule-based design approach for iSF. In the following, we analyze which features

Figure 4. (a) Correlation between 3TT–1TT vertical splitting and 1TT-to-2T1 dissociation energy of the nine D–A copolymers evaluated with the SA model. (b) Correlation between 3TT–1TT splitting and transition state (ts) or intermediate energy barrier associated with the intramolecular energy transfer of a triplet from one acceptor to another, evaluated with the 4A model. The star indicates the optimal region to find systems with a small TT binding energy and triplet transport barrier. (c) Same correlation as in (b) evaluated with the 2A model for a database of 100 A–D–A trimers extracted from ref 32, color-coded with the donor unit. The BDT-TDO and the best candidate are pinpointed and the structure shown. Colored guidelines highlight the trends.

Scheme 1

Noncoplanar TT

Coplanar T1 ts
control the triplet energy transfer barrier throughout the donor and, therefore, the efficiency of the intrachain triplet exciton transport.

Triplet energy transfer is usually described as a bilateral Dexter-type process and is mainly controlled by electronic coupling and inter- (or intra-)molecular distance. Within a Marcus-like potential energy surface perspective, the relative difference between the T1 of the donor and the acceptor (labeled Δ), and the coupling between the two, which is partially modulated by the dihedral. The effect of increasing Δ is shown in (b) and of decreasing the distance in (c). Note that the nature of the middle point as an intermediate or transition state would depend on each case.

Figure 5. Schematic representation of the potential energy profile for intramolecular triplet energy transfer between two acceptors separated by a donor (A−D−A). The blue potentials represent the T1 state of the acceptors and the red potential the T1 state of the donor. The three main features that control the magnitude of the barrier are indicated in (a) the distance between the acceptors, the relative difference between T1 of the donor and the acceptor (labeled Δ), and the coupling between the two, which is partially modulated by the dihedral. The effect of increasing Δ is shown in (b) and of decreasing the distance in (c). Note that the nature of the middle point as an intermediate or transition state would depend on each case.

Figure 6. Correlation between the T1(D)−T1(A) difference (eV), the acceptor−acceptor distance in Å (which corresponds to the donor length), and the intramolecular triplet transfer barrier (eV) obtained for the 100 A−D−A studied trimers. The molecular structure of an example of each region is shown on the right with the same color.

CONCLUSIONS

In this work, we exposed the importance of considering triplet exciton transport kinetics, besides TT thermodynamics, to optimize TT dissociation rates in extended D−A copolymers for iSF. Our analysis revealed that optimal values for both features can only be achieved when using flexible donors that have at least one rotatable sigma bond leading to a coplanar and a non-coplanar conformation such as bithiophene or TVT, whereas using non-flexible (fused-rings) donors can minimize one while penalizing the other. Using a simple model based on sequential T1 potentials, we discussed the main aspects...
governing the triplet exciton transport kinetics in A−D−A systems, namely, the acceptor–acceptor distance, the relative energy difference between T1(A) and T1(D), and the degree of coplanarity of the A−D−A chain. Together with the energetic, coupling, and separation requirements previously identified, these additional features can be easily computed and implemented in large-scale high-throughput screening protocols to accelerate the discovery of more efficient D−A copolymer candidates for iSF and, thus, to expand the very limited library of reported systems as of now.

### ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chemmater.2c00367.

MS-RASPT2, SF-TDDFT, and RAS-2SF benchmarking; TT dissociation profile of BDT-TDO and BDT-DPP; comparison of TT-to-2T1 and T1-to-T1 barriers; and 100 A−D−A trimer results. All computations reported in this work can be found at [https://archive.materialscloud.org](https://archive.materialscloud.org) (PDF)

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#### Notes

The authors declare no competing financial interest.

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### REFERENCES

(1) Smith, M. B.; Michl, J. Singlet Fission. Chem. Rev. 2010, 110, 6891−6936.

(2) Smith, M. B.; Michl, J. Recent Advances in Singlet Fission. Annu. Rev. Phys. Chem. 2013, 64, 361−386.

(3) Miyata, K.; Conrad-Burton, F. S.; Geyer, F. L.; Zhu, X.-Y. Triplet Pair States in Singlet Fission. Chem. Rev. 2019, 119, 4261−4292.

(4) Einzinger, M.; Wu, T.; Kompalla, J. F.; Smith, H. L.; Perkinson, C. F.; Nienhaus, L.; Wiegold, S.; Congreve, D. N.; Kahn, A.; Bawendi, M. G.; et al. Sensitization of Silicon by Singlet Exciton Fission in Tetracene. Nature 2019, 571, 90−94.

(5) Futscher, M. H.; Rao, A.; Ehrler, B. The Potential of Singlet Fission Photon Multipliers as an Alternative to Silicon-Based Tandem Solar Cells. ACS Energy Lett. 2018, 3, 2587−2592.

(6) Pazos-Outón, L. M.; Lee, J. M.; Futscher, M. H.; Kirch, A.; Tabachnyk, M.; Friend, R. H.; Ehler, B. A Silicon−Singlet Fission Tandem Solar Cell Exceeding 100% External Quantum Efficiency with High Spectral Stability. ACS Energy Lett. 2017, 2, 476−480.

(7) Singh, S.; Stoicheff, B. P. Double-Photon Excitation of Fluorescence in Anthracene Single Crystals. J. Chem. Phys. 1963, 38, 2032−2033.

(8) Swenberg, C. E.; Stacy, W. T. Bimolecular Radiationless Transitions in Crystalline Tetracene. Chem. Phys. Lett. 1968, 2, 327−328.

(9) Sanders, S. N.; Kumarasamy, E.; Pun, A. B.; Steigerwald, M. L.; Sfeir, M. Y.; Campos, L. M. Intramolecular Singlet Fission in Oligoacene Heterodimers. Angew. Chem., Int. Ed. 2016, 55, 3373−3377.

(10) Felter, K. M.; Grozema, F. C. Singlet Fission in Crystalline Organic Materials: Recent Insights and Future Directions. J. Phys. Chem. Lett. 2019, 10, 7208−7214.

(11) Mora-Fuentes, J. P.; Papadopoulos, I.; Thiel, D.; Alvarez-Boto, R.; Cortizo-Lacalle, D.; Clark, T.; Melle-Franco, M.; Guldi, D. M.; Mateo-Alonso, A. Singlet Fission in Pyrene-Fused Azaacene Dimers. Angew. Chem., Int. Ed. 2020, 59, 1113−1117.

(12) Schnedermann, C.; Alvertis, A. M.; Wende, T.; Lukman, S.; Feng, J.; Schröder, F. A. Y. N.; Turban, D. H. P.; Wu, J.; Hine, N. D. M.; Greenham, N. C.; Chin, A. W.; Rao, A.; Kukura, P.; Musser, A. J. A molecular movie of ultrafast singlet fission. Nat. Commun. 2019, 10, 4207.

(13) Pun, A. B.; Asadpoordarvish, A.; Kumarasamy, E.; Tayebjee, M. J. Y.; Niesner, D.; McCamey, D. R.; Sanders, S. N.; Campos, L. M.; Sfeir, M. Y. Ultra-fast intramolecular singlet fission to persistent multie excitons by molecular design. Nat. Chem. 2019, 11, 821−828.

(14) Johnson, J. C. Open questions on the photophysics of ultrafast singlet fission. Commun. Chem. 2021, 4, 85.

(15) Casanova, D. Theoretical Modeling of Singlet Fission. Chem. Rev. 2018, 118, 7164−7207.

(16) Korovina, N. V.; Joy, J.; Feng, X.; Feltenberger, C.; Krylov, A. I.; Bradford, S. E.; Thompson, M. E. Linker-Dependent Singlet Fission in Tetracene Dimers. J. Am. Chem. Soc. 2018, 140, 10179−10190.

(17) Japahuge, A.; Zeng, T. Theoretical Studies of Singlet Fission: Searching for Materials and Exploring Mechanisms. ChemPlusChem 2018, 83, 146−182.

(18) Reddy, S. R.; Coto, P. B.; Thoss, M. Intramolecular Singlet Fission: Insights from Quantum Dynamical Simulations. J. Phys. Chem. Lett. 2018, 9, 5979−5986.

(19) Yablon, L. M.; Sanders, S. N.; Miyazaki, K.; Kumarasamy, E.; He, G.; Choi, B.; Ananth, N.; Sfeir, M. Y.; Campos, L. M. Singlet fission and triplet pair recombination in bipentacenes with a twist. Mater. Horiz. 2022, 9, 462−470.

(20) Ullrich, T.; Munz, D.; Guldi, D. M. Unconventional singlet fission materials. Chem. Soc. Rev. 2021, 50, 3485−3518.

(21) Padula, D.; Omar, O. H.; Nematiaram, T.; Troisi, A. Singlet fission molecules among known compounds: finding a few needles in a haystack. Energy Environ. Sci. 2019, 12, 2412.

(22) López-Carballeira, D.; Polcar, T. A new protocol for the identification of singlet fission sensitizers through computational screening. J. Comput. Chem. 2021, 42, 2241−2249.

(23) Musser, A. J.; Mauiri, M.; Brida, D.; Cerullo, G.; Friend, R. H.; Clark, J. The Nature of Singlet Exciton Fission in Carotenoid Aggregates. J. Am. Chem. Soc. 2015, 137, 5130−5139.

(24) Hu, J.; Xu, K.; Shen, L.; Wu, Q.; He, G.; Wang, J.-Y.; Pei, J.; Xia, J.; Sfeir, M. Y. New insights into the design of conjugated polymers for intramolecular singlet fission. Nat. Commun. 2018, 9, 2999.

(25) Musser, A. J.; Al-Hashimi, M.; Heeney, M.; Clark, J. Heavy-atom effects on intramolecular singlet fission in a conjugated polymer. J. Chem. Phys. 2019, 151, 044902.

(26) Aryanpour, K.; Dutta, T.; Huynh, U. N. V.; Vardeny, Z. V.; Mazumdar, S. Theory of Primary Photoexcitations in Donor-Acceptor Copolymers. Phys. Rev. Lett. 2015, 115, 267401.
Intramolecular Singlet Fission Mechanism in Donor-Acceptor J. Phys. Chem. Lett.

Doubled Triplet Excitons through Intramolecular Singlet Fission. J. Phys. Chem. Lett.

Free-triplet generation with improved efficiency in tetracene Y.; Ma, H.; Fang, W.; Yao, Y.; Sang, H.; Wang, X.; Li, X.; Xiao, M.

Fission: A DMRG Study. Z. Naturforsch. Chem. 2021, 76, 400.

Singlet Fission Requirements in Donor-Acceptor Copolymers. Corminboeuf, C. Identifying the Trade-off between Intramolecular Splitting of Triplet Pairs in Singlet Fission. Phys. Chem. Chem. Phys.

Triplet-Triplet Exchange and Triplet-Triplet Energy Transfer in Polyenes and Related Molecules. J. Phys. Chem. C 2014, 118, 5188–5195.

Molecular Design Strategy for High-Yield and Long-Lived Individual Doubled Triplet Excitons through Intramolecular Singlet Fission. ACS Energy Lett. 2022, 7, 390–400.

Free-triplet generation with improved efficiency in tetracene oligomers through spatially separated triplet pair states. Nat. Chem. 2021, 13, 559–567.

Overlap-Driven Splitting of Triplet Pairs in Singlet Fission. J. Am. Chem. Soc. 2020, 142, 20040–20047.

Revealing the Contest between Triplet-Triplet Exchange and Triplet-Triplet Energy Transfer Coupling in Correlated Triplet Pair States in Singlet Fission. J. Phys. Chem. Lett. 2021, 12, 10505–10514.

Babel: An open chemical toolbox. J. Cheminf. 2011, 3, 33.

Long-range corrected hybrid density functionals with damped atom-atom dispersion corrections. Phys. Chem. Chem. Phys. 2008, 10, 6615–6620.

Gaussian 09, Revision D.01; Gaussian, Inc.: Wallingford, CT, 2009.

Spin-flip time-dependent density functional theory using non-collinear kernels: theory, implementation, and benchmarks. J. Chem. Phys. 2012, 136, 204103.

Efficient implementation of restricted active space configuration interaction with the hole and particle approximation. J. Comput. Chem. 2013, 34, 720.

Advances in molecular quantum chemistry contained in the Q-Chem 4 program package. Mol. Phys. 2015, 113, 184–215.

From Ground-State to Excited-State Electronic Structures of Donor-Acceptor Copolymers: A Quantum-Chemical Approach to Optical Phenomena. J. Phys. Chem. Lett. 2013, 4, 3845–3852.

On the origin of a low-lying forbidden transition in polyenes and related molecules. Chem. Phys. Lett. 1972, 14, 305–309.

Overlap-Driven Singlet Fission in Diketopyrrolopyrrole Dimers: A Mediating Charge Transfer versus a Trapping Symmetry-Breaking Charge Separation. Adv. Energy Mater. 2020, 10, 2001496.

Evaluation of Fused Aromatic-Substituted Diketopyrrolopyrrole Derivatives for Singlet Fission Sensitizers. J. Phys. Chem. A 2020, 124, 5331–5340.

Spatial separation of triplet excitons drives endothermic singlet fission. Nat. Chem. 2020, 12, 391–398.

Controlling Long-Lived Triplet Generation from Intramolecular Singlet Fission in the Solid State. J. Phys. Chem. Lett. 2017, 8, 6086–6091.

Exciton Diffusion in Conjugated Polymers: From Fundamental Understanding to Improvement in Photovoltaic Conversion Efficiency. J. Phys. Chem. Lett. 2015, 6, 3417–3428.

A theory of sensitized luminescence in solids. J. Chem. Phys. 1953, 21, 836–850.

Electron transfer reactions in chemistry. Theory and experiment. Rev. Mod. Phys. 1993, 65, 599–610.