



Subscriber access provided by ECU Libraries

# Article

# Varying the inter-pentacene electronic coupling to tune singlet fission

Ilias Papadopoulos, Johannes Zirzlmeier, Constantin Hetzer, Youn Jue Bae, Matthew D. Krzyaniak, Michael R. Wasielewski, Timothy Clark, Rik R. Tykwinski, and Dirk M. Guldi J. Am. Chem. Soc., Just Accepted Manuscript • DOI: 10.1021/jacs.8b09510 • Publication Date (Web): 11 Mar 2019 Downloaded from http://pubs.acs.org on March 11, 2019

# Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.



is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

7

8 9 10

11

12 13

14

15

19

20

21

22

23 24 25

26

27

28

29

30

31

32

33

34 35 36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57

58

59 60

# Varying the inter-pentacene electronic coupling to tune singlet fission

Ilias Papadopoulos,<sup>†</sup> Johannes Zirzlmeier,<sup>†</sup> Constantin Hetzer,<sup>‡</sup> Youn J. Bae,<sup>||</sup> Matthew D. Krzyaniak,<sup>||</sup> Michael R. Wasielewski, Timothy Clark, Rik R. Tykwinski, \*, \\ and Dirk M. Guldi<sup>†,\*</sup>

<sup>†</sup>Department of Chemistry and Pharmacy & Interdisciplinary Center for Molecular Materials, Friedrich-Alexander-Universität Erlangen Nürnberg, Egerlandstraße 3, 91058 Erlangen, Germany

<sup>‡</sup>Department of Chemistry and Pharmacy & Interdisciplinary Center for Molecular Materials, Friedrich-Alexander-

16 Universität Erlangen Nürnberg, Nikolaus-Fiebiger-Strasse 10, 91058 Erlangen, Germany

17 <sup>§</sup>Computer-Chemistry-Center, Department of Chemistry and Pharmacy, Friedrich-Alexander-Universität Erlangen-Nürnberg, 18 Nägelsbachstrasse 25, 91052 Erlangen, Germany

Department of Chemistry and Institute for Sustainability and Energy at Northwestern, Northwestern University, Evanston, Illinois 60208-3113, United State

<sup>11</sup>Present address: Department of Chemistry, University of Alberta, Edmonton, Alberta, T6G 2G2, Canada

KEYWORDS acene oligomers, pentacene, excited states, singlet fission, time-resolved spectroscopy

ABSTRACT: We have designed and used four different spacers, denoted A-D, to connect two pentacenes and probed the impact of intramolecular forces on the modulation of pentacene-pentacene interactions and, in turn, on the key steps in singlet fission (SF), that is, the  ${}^{1}(S_{1}S_{0})$  to  ${}^{1}(T_{1}T_{1})$  as well as  ${}^{1}(T_{1}T_{1})$  to  ${}^{5}(T_{1}T_{1})$  transition by means of transient absorption and electron paramagnetic resonance measurements. In terms of  ${}^{1}(S_{1}S_{0})$  to  ${}^{1}(T_{1}T_{1})$  transition, a super-exchange mechanism, that is, coupling to a higher-lying CT state to generate a virtual intermediate, enables rapid SF in A–D. Sizeable electronic coupling in A and B opens, on one hand, an additional pathway, that is, population of a real intermediate, and changes, on the other hand, the mechanism to that of hopping. In turn, A and B feature much higher  ${}^{1}(T_{1}T_{1})$  quantum yields than C and D with a maximum value of 162% for A. In terms of  $^{1}(T_{1}T_{1})$  to  $^{5}(T_{1}T_{1})$  transition, the sizeable electronic coupling in A and B is counterproductive and, in turn, C and D give rise to higher  ${}^{5}(T_{1}T_{1})$  to  $(T_{1}+T_{1})$  quantum yields than **A** and **B** with a maximum value of 85% for **D**.

## INTRODUCTION

Singlet fission (SF) was first reported in 1965 in the context of photophysical and magnetic observations in crystalline anthracene and tetracene.<sup>[1-3]</sup> These observations were confirmed subsequently and their interpretation refined, leading to comprehensive reviews to the present day.[4-8]

SF is a process in which a singlet excited state is converted into two triplet excited states; often referred to as a correlated triplet pair.<sup>[9]</sup> The two resulting triplets possess a net spin of zero, rendering SF a spin-allowed, fast transition, in stark contrast to the spin-forbidden, slow intersystem crossing (ISC).<sup>[10]</sup> Such a multiple exciton generation (MEG),<sup>[9, 11]</sup> allows highly efficient solar cells to be engineered that potentially exceed the Shockley-Queisser performance limit.<sup>[12]</sup> This represents a fundamental advantage over materials that generate only one electron-hole pair for each absorbed photon. The relationship between the band gap and the output voltage is crucial.<sup>[13]</sup> Any excess energy provided by the absorbed photons results in wasted thermal energy.<sup>[12, 13]</sup> SF can increase the performance limit to approximately 45%, significantly higher than the Shockley-Queisser limit of approximately 32%.<sup>[14]</sup> Several recent studies have demonstrated remarkable progress in the construction of SFbased solar cells.[11, 15-17]



Figure 1. Chemical structures of the investigated pentacene dimers (A, B, C, and D).

There are several requirements for efficient SF: On the one hand, the photoexcited chromophore must interact and share its energy with a neighboring ground-state chromophore. Overall, the SF efficiency is closely associated with the electronic coupling between the chromophores, which is governed by factors such as proximity, overlap, crystal packing, etc.<sup>[18, 19]</sup> Controlling the configurations of the chromophores is essential for fine-tuning their coupling in the ACS Paragon Plus Environment

solid state.<sup>[20, 21]</sup> Early investigations of SF were carried out exclusively in the solid state.<sup>[20]</sup> Friend and coworkers only recently demonstrated SF in room-temperature solution.[10] This required highly concentrated solutions of pentacene derivatives in order to obtain SF, even though the chromophores lack the close, ordered orientations found in crystals.<sup>[10]</sup> Some thermodynamic requirements must also be met for SF. First, the energy of the lowest-lying singletexcited state must exceed twice the energy of two triplet excited states  $(S_1 \ge 2T_1)$ . To avoid the formation of higher triplet states as a product of triplet-triplet annihilation, the energy of the higher triplet states should significantly exceed twice the energy of the lowest-lying triplet state  $(T_2 \ge 2T_1)$ .<sup>[20,</sup> <sup>22</sup>] Recent investigations have shown that tetracene, pentacene, hexacene, and their derivatives are promising molecular building blocks for molecular SF materials, with pentacene and its derivatives representing the prototypical SF material that fulfills all of the criteria described above.<sup>[23, 24]</sup>

1

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57

58

59

60

The molecular mechanism of SF has been discussed controversially.<sup>[25, 26]</sup> The central questions concern the electronic states, their coupling, and their effective nuclear dynamics.<sup>[27-36]</sup> Two contrasting SF mechanisms have emerged; a direct, one-step, and an indirect, two-step mechanism. The former proceeds from the initially populated singlet-excited state into a correlated triplet-pair state (<sup>1</sup>(TT)), also referred to as a multiexcitonic state, which has overall singlet character. The correlated triplet pair then dissociates into two separated triplet excited states.[37] In the indirect, two-step mechanism, SF is mediated by an intermediate charge-transfer (CT) state. The two triplets, likewise, separate into two individual triplet excited states.<sup>[20, 28-30]</sup> Furthermore CT states, both as a virtual or real state, can play a decisive role in the SF mechanism.<sup>[38-41]</sup> Overall, these discussions demonstrate the complexity of SF and underline the necessity of an improved mechanistic understanding of SF.

The electron spin-spin interactions, a component of the electronic coupling, dictate the efficiency for ling lived triplets through SF. The spin-spin interactions comprise the intratriplet zero field splitting, the inter-triplet exchange interaction  $(J_{SO})$  and dipolar coupling (D). The exchange interactions depend exponentially on the distance between the two spincorrelated triplet states and the nature of the intervening spacer or medium.<sup>[35]</sup> Dipolar coupling, on the other hand, depend inversely on the cube of the distance.[42] The energy splitting and subsequent mixing between the  ${}^{1}(T_{1}T_{1})$  and  ${}^{5}(T_{1}T_{1})$  states depends on all three spin-spin interactions, though in SF dimers the splitting tends to be dominated by  $J_{SQ}$ ;<sup>[27-36]</sup> the stronger  $J_{SO}$  is, the higher is the <sup>5</sup>(T<sub>1</sub>T<sub>1</sub>) energy relative to that of  ${}^{1}(T_{1}T_{1})$ . If the two pentacenes interact too strongly,  $J_{SO}$  will be large such that the  ${}^{1}(T_{1}T_{1})$  state initially formed may not mix with  ${}^{5}(T_{1}T_{1})$ . The ultimate goal will be to dissect contributions from D and  $J_{SQ}$  in order to understand and tune the coupling.

Motivated by recent results, we decided to use pentacene dimers to investigate SF in solution. The role of crystal packing for SF in crystalline films is fulfilled by the molecular spacer. Both the structure and topology (rigidity, distance, etc.) and the electronic coupling (interactions between the two photoactive termini) are important in determining the performance of the spacers. An important feature of pentacene-spacer-pentacene conjugates is the possibility of introducing a systematic alteration of separation, orientation, and overlap without affecting the electronic nature of the termini.<sup>[24, 38, 43-49]</sup>

Past work has focused mainly on through-bond interactions to control the electronic coupling between two pentacenes and, in turn, the rate of SF. Simply put, the electronic coupling drives not only the spin-allowed  ${}^{1}(S_{1}S_{0})$  to  ${}^{1}(T_{1}T_{1})$  SF, but also the mixing between  ${}^{1}(T_{1}T_{1})$  and  ${}^{5}(T_{1}T_{1})$  and the ability to dissociate into  $(T_1 + T_1)$ . The two steps are intimately linked to each other and require a fine balance: The molecular spacer should provide sufficient electronic coupling between the pentacenes to render SF facile, while at the same time keeping the coupling sufficiently weak to allow spin decoherence. For example, in rigid,  $\pi$ -bonded phenylene-spacers, the electronic coupling is off balance and triplet-triplet annihilation is faster decoherence.<sup>[50]</sup> than In rigid. σ-bonded adamantyl/bicyclooctane spacers, the coupling is balanced and decoherence is faster than triplet-triplet annihilation.[35] Notably is, however, the rotational and vibrational flexibility, which does not affect the relative distance.<sup>[51-53]</sup> The electronic coupling in even longer rigid,  $\sigma$ -bonded spacers than adamantyl/bicyclooctane will likely be off balance and, in turn, SF will not be competitive with the efficient intersystem crossing/fluorescence.



**Figure 2.** Schematic outline of pentacene dimers based on flexible linkers that prevent through-bond coupling while allowing through-space interactions.

The impact of through-space coupling remains, for the most part, unexplored.<sup>[40, 54, 55]</sup> Considering the distance dependencies on the electronic coupling, we expect significantly altered outcomes for "through-bond" and for "through-space" driven SF processes. To this end, studying different linkers as a means to change the electronic coupling enables to dissect the impact on both short-range  $J_{SQ}$  and longrange D and helps to distinguish between them. We therefore explored the use of the four "flexible" spacers **A–D** (Figure 1) to tether the two pentacenes (Figure 2). It is important that the length of the flexible spacers renders a possible through-bond electronic coupling negligible. Because SF in the linked pentacene dimers is intra- rather than intermolecular, bottlenecks such as diffusional encounter, etc. are eliminated.

A central question relating to molecular structure is to investigate intramolecular forces, by which pentacenes organize in solution into ordered structures without an external input. Are additional forces, such as specific, local interactions among, for example, solubilizing head groups, needed in the structural self-ordering of pentacenes? Ultimately, this will affect the electronic communication and the question arises whether the effective attractions are strong enough to enable the through-space interactions required for the  ${}^{1}(S_{1}S_{0})$  to  ${}^{1}(T_{1}T_{1})$  transition and still allow the  ${}^{1}(T_{1}T_{1})$  to  ${}^{5}(T_{1}T_{1})$ decoherence, which are intrinsic spin-vibronic interactions that couple vibrations with spin and/or hyperfine interactions with nuclear spins. Importantly, we expect the quantum yields for the dissociation of  ${}^{5}(T_{1}T_{1})$  into  $(T_{1}+T_{1})$  to scale with the pentacene-pentacene electronic coupling.



Scheme 1. Assembly of pentacene dimers A–D.

#### SYNTHESIS

Using a handful of readily available building blocks 1-3, dimeric pentacenes A-D were assembled with a variety of flexible spacers (Scheme 1). Dimers A and B were obtained via desymmetrization of 6,13-pentacenequinone (1) followed by stepwise nucleophilic acetylide addition<sup>[56]</sup> and SnCl<sub>2</sub>mediated reductive aromatization.<sup>[57]</sup> Dimers A and B were obtained in 43% and 46% yield (from 1), respectively (see SI for synthetic details). Toward dimer C, ketone 2 is formed directly from 6,13-pentacenequinone (1) in a single step.<sup>[58]</sup> A four-step sequence of nucleophilic addition, desilvlation, homo-coupling under Hay conditions, and reductive aromatization reactions gave C in 41% yield (from 2). Finally, 6.13-pentacenequinone can be converted to divne 3 in two steps, and dimer **D** (Scheme 1) was formed in two steps via a sequence of Sonogashira coupling and reductive aromatization (Supporting Information). From divne 3, D was obtained in 50% overall yield (from 3).

Dimers A–D are nicely soluble in common organic solvents (>6 mg/mL), including CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, THF, and toluene. Dimers **B–D** are stable toward air and moisture under normal laboratory conditions, but slowly decompose over several days when exposed to light and oxygen. In the case of dimer **A**, however, decomposition can be rapid (< 1 day) when stored in solution under normal laboratory conditions.

#### THEORY

Initial force-field and AM1 semiempirical molecular orbital (MO) geometry optimizations revealed both extended (*trans-*) conformations and several folded (*gauche-*) conformations as minima. These minima were subsequently optimized using density-functional theory (DFT) with the B3LYP hybrid functional, Grimme's D3 dispersion correction and the 6-31G(d) basis set (details and results are given in the Supporting Information, Table S10).

Judging the coupling in such complex systems is difficult because factors such as contact between the substituents and hyperconjugation through the bridge affect both orbital and state energies. Thus, the most reliable measure that we found was the splitting between the first two singlet-excited states calculated using AM1-CI with only four active orbitals (HOMO and HOMO-1, LUMO and LUMO+1) in order to reduce the model to a simple frontier-orbital picture for the ACS Paragon two pentacene chromophores. The splitting decreases in the order  $\mathbf{A} > \mathbf{B} > \mathbf{D} > \mathbf{C}$  with 1420, 758, 678, and 492 cm<sup>-1</sup>, respectively, in the most stable folded conformations found. This order changes when the bridges are removed and replaced by a single acetylenic hydrogen with splittings of 290, 742, 661, and 476 cm<sup>-1</sup> for  $\mathbf{A}$ ,  $\mathbf{B}$ ,  $\mathbf{D}$  and  $\mathbf{C}$ , respectively, and when the R<sub>3</sub>Si groups were also replaced by hydrogens (250, 718, 226, and 444 cm<sup>-1</sup>). Thus, compound  $\mathbf{A}$  is unique among those studied in that the bridge provides significant hyperconjugative coupling due to the presence of C-C bonds approximately perpendicular to the ring plane. This is evident from the bridge contribution to the HOMO, shown in Figure 3.



**Figure 3.** The HOMO of **A**, showing the conjugation through the bridge, the inter-pentacene stacking in **B** and the contact between the pentacenes and the trialkylsilyl groups of the adjacent pentacene moiety in **D**.

The calculated splitting in **B** remains constant, regardless of whether the bridge and substituents are present, suggesting that this compound has the best through-space inter-pentacene coupling. Of the two remaining compounds, **D** is interesting because its coupling decreases strongly when the trialkylsilyl substituents are removed, suggesting that in this case coupling is transmitted by the bulky substituents.

1) in order to The calculations suggest that **B** has the inherently best stacking geometry for through-space coupling, whereas **A** is ACS Paragon Plus Environment

Journal of the American Chemical Society

75000

60000

45000

30000

15000

350 400 450

1.0

0.8

0.6

0.4

0.2

0.0-

600

ormalized intensity [a.u.]

500

550 600 650 700 750 800 850

700

650

λ [nm]

extinction coefficient (M<sup>-1</sup>cm<sup>-1</sup>

#### PHOTOPHYSICAL CHARACTERIZATION

Steady-state characterization; Ground, reduced, oxidized, and excited states. To gather insight into pentacene-pentacene interactions, we first directed our attention to results of ground-state measurements. At first glance, similar absorption spectra were found for all four pentacene dimers: Features in the high-energy (350 to 500 nm) range as well as in the low-energy (500 to 750 nm) range were detected. Of great spectroscopic importance is the low-energy range, in which the vibrational progression associated with the lowest singlet excited state including the 0-\*0, 0-\*1, etc. transitions evolves. Relative to what is seen for A-C, the long wavelength, fundamental 0-\*0 transition is red-shifted by 20 nm for **D**. It is the extended conjugation in **D** relative to A-C, rather than any other electronic effects, which causes the overall red-shift. A closer look reveals, however, significant differences in, for example, the extinction coefficients: The values for the long wavelength 0-\*0 transition range from as large as 48,000  $M^{-1}$  cm<sup>-1</sup> in **D** to as small as 11,500  $M^{-1}$  cm<sup>-1</sup> in A. We use the extinction coefficient of 24,500 M<sup>-1</sup> cm<sup>-1</sup>, which was determined for **TIPSPc** (Figure 4 – black line), as a reference. Values of less than 49,000 M<sup>-1</sup> cm<sup>-1</sup>, twice the reference value, are taken as evidence for electronic interactions between the two pentacenes.<sup>[58]</sup> In other words, the TIPSPc values are only reached in D, suggesting minimum electronic coupling. Overall, the extinction coefficients follow the splitting between the first two singlet-excited states determined in the theoretical section - vide supra. The respective absorption spectra of TIPSPc and dimers A-D are illustrated in Figure 4.[60]

Independent of the conclusions drawn from the above experiments, we postulate that the interactions between the two pentacenes must be weak, even in the different *gauche*-conformers. Complementary electrochemical investigations only showed subtle changes: In, for example, **D**, the first one-electron oxidation and the first one-electron reduction are found at +0.33 and -1.39 V versus Fc/Fc<sup>+</sup>, respectively, compared with +0.40 and -1.45 V for the corresponding one-electron oxidation and reduction of **TIPSPc**, respectively. The measured values are also close to those determined for **C** (+0.29 and -1.57 V), **B** (+0.37 and -1.44 V), and **A** (+0.41 and -1.44 V) (Supporting Information, Figure S2, Table S2).

The spectroscopic evidence in the excited state is stronger. steady-state fluorescence spectra In the following photoexcitation at 610 nm, the short-wavelength, fundamental \*0-0 transitions are red-shifted relative to the longwavelength, fundamental 0-\*0 transitions in the absorption spectra. Regardless of the solvent polarity, the fluorescence spectrum of **D** is fine-structured, similar to the fine-structured fluorescence found for TIPSPc with overall fluorescence quantum yields of 39.9%, 26.4%, and 20.0% in toluene, THF, and benzonitrile, respectively. Also, the relatively high fluorescence quantum yields for D of 17.7%, 13.3%, and 9.9% in toluene, THF, and benzonitrile, respectively, are in sound agreement with the characteristics of TIPSPc. Dimers A, B, and C fluoresce less strongly, with quantum yields in benzonitrile of 2.0%, 2.8%, and 3.5%, respectively. In contrast to **D**, however, the fluorescence spectra of A–D lack any fine structure. Mutual pentacene-pentacene interactions, which are operative in A-C, govern the featureless, quenched

fluorescence. The fact that only **D** exhibits fluorescence similar to that seen for **TIPSPc** is due to the weakest electronic coupling within the series of pentacene dimers A-D. Overall, the quantum yield trend follows the findings based on absorption spectroscopy and modeling. The respective fluorescence spectra of **TIPSPc** and dimers A-D are illustrated in Figure 4.



750

800

850

900

Time-resolved characterization; Singlet- and Tripletexcited states. In time-resolved fluorescence measurements with an excitation wavelength of 610 nm, we found a major, short-lived and a minor, long-lived component in the 650 to 700 nm range. The major lifetimes are  $4.88 \pm 0.01$  ns for **D**,  $3.20 \pm 0.04$  ns for C,  $1.90 \pm 0.03$  ns for B, and  $1.38 \pm 0.02$  ns for A in benzonitrile and corroborate the trends described in the steady-state measurements. The major lifetimes in toluene are very similar:  $6.11 \pm 0.01$  ns for **D**,  $3.48 \pm 0.04$  ns for **C**,  $1.97 \pm 0.03$  ns for **B**, and  $1.41 \pm 0.02$  ns for **A**. Minor, longlived components of  $7.8 \pm 0.06$  ns in, for example, benzonitrile reflect the presence of a trans-conformer in A-C except D, in which the *trans*-conformation coexists with the corresponding gauche-conformer. In toluene and benzonitrile, the gauche-totrans ratio is quantitatively identical at 50:50 for **D**. 83:17 for C, 86:14 for B, and 90:10 for A.<sup>[61]</sup> All ratios remained unchanged in methyl-cyclohexane and cyano-cyclohexane as non-aromatic analogs of toluene and benzonitrile, respectively. The lifetimes of the short-lived components in A and B, however, change with values in the range from 4 to 5 ns (Supporting Information, Figure S1, Table S1). From the aforementioned trend we conclude that aromatic solvents augment the electronic coupling when through-space/through solvent interactions are operative. Notably, only the gaucheconformers, for which theory predicts a higher preference,

56

57

58

59

60

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27 28

29

30

31

32

33 34

35

36

37

38

39

40 41

42

43

44

45

46

47 48

49

50

51 52

53

54

55

56

57

58 59

60

seem to contribute to SF. The *trans*-conformers are SFinactive and, in turn, governed by a slow and inefficient triplet formation *via* intersystem crossing – *vide infra*.

To establish the triplet excited-state features of A-D, (0 - $1.0 \times 10^{-4}$  M) we turned to triplet-triplet energy-transfer experiments using N-methylfulleropyrrolidine (N-MFP, 8.0 x 10-5 M, Figure 5) as triplet sensitizer using 480 nm photoexcitation (800 nJ).<sup>[50, 58]</sup> We started with N-MFP solutions of 8 x 10<sup>-5</sup> M and added varying concentrations of A–D in the range from  $1.0 \times 10^{-5}$  to  $1.0 \times 10^{-4}$  M. In the absence of A-D, only the long-lived triplet excited-state features of N-MFP are recorded with maxima at 421, 442, and 690 nm. In the presence of A–D, these maxima are, however, replaced on the longer timescales by differential absorption changes that include both a 510 nm maximum and 605 and 648 nm minima. The underlying features are assigned to the triplet excited-state fingerprints of  ${}^{3}(T_{1}S_{0})$ , that is, a single triplet excited state on one of two pentacences in the pentacene dimers. Pseudo first-order analyses confirmed that the underlying triplet-triplet energy-transfer dynamics are diffusion-controlled: 5.0 x 109 M<sup>-1</sup>s<sup>-1</sup>. The singlet ground state extinction coefficients, derived from N-MFP sensitization, are 19,000, 23,000, 31,000, and 55,000 M<sup>-1</sup> cm<sup>-1</sup> for A, B, C, and **D**, respectively, at the 450 nm maximum. The correlation of these extinction coefficients with those determined from steady-state spectroscopy for the corresponding ground states is noteworthy. The triplet excited-state extinction coefficients at the 510 nm maximum, are 85,390, 86,080, 109,010, and 116,350 M<sup>-1</sup> cm<sup>-1</sup> for A, B, C, and D, respectively. (Supporting Information, Figure S3-S18).



**Figure 5.** Chemical structures of **TIPSPc** and *N*-methylfulleropyrrolidine (*N*-**MFP**).

Time-resolved characterization; Singlet fission. In pumpprobe experiments on the femto-, pico-, and nanosecond timescales, 610 nm excitation is followed by the instantaneous formation of the singlet-excited state  $(S_1S_0)$ . Here, maxima at 458 and 1250 nm and a minimum at 652 nm assist in the spectroscopic assignment (Figure 6, top-left). For A-D, these pure singlet excited-state features transform into a new intermediate state within 20 ps. This transformation is most evident when analyzing the feature at 1250 nm, which shows a hypsochromic shift and broadening. In line with previous this intermediate state relates to solvent work,<sup>[59]</sup> reorganization, caused by differences in the dipole moments between the ground and excited states: It is denoted as  $(S_1S_0)_{SOLV}$  and the driving forces stem from reducing the solvation energy of the excited state.

 $(S_1S_0)_{SOLV}$  is metastable, and at the end of its transformation, the same triplet excited-state features are discernable that evolved in triplet-triplet energy-transfer experiments for A–D



**Figure 6.** Top-Left: Differential femtosecond transient absorption spectra ( $\lambda_{ex} = 610 \text{ nm}$ , 400 nJ) of **A** (4 x 10<sup>-5</sup> M) in benzonitrile with time delays between 0 and 7500 ps; Top-Right: Respective time absorption profiles at the given wavelengths; Bottom-Left: Deconvoluted femtosecond transient absorption spectra of the singlet excited (S<sub>1</sub>S<sub>0</sub>) (black), the intermediate state (S<sub>1</sub>S<sub>0</sub>)<sub>SOLV</sub> (red), the intermediate state (S<sub>1</sub>S<sub>0</sub>)<sub>(T1T1)</sub><sup>CT</sup> (blue), and the singlet correlated triplet state <sup>1</sup>(T<sub>1</sub>T<sub>1</sub>) (green) of **A** as obtained by target analysis, using the proposed kinetic model, in benzonitrile; Bottom-Right: Respective population kinetics.

– vide supra. Most notable are maxima at 478, 510, 860, and 980 nm and a minimum at 648 nm (Figure 6, top-left). The overall singlet to triplet excited-state conversion is accompanied at, for example, the 648 nm minimum by an increase of the ground-state bleaching by roughly 15% (Figure 6: Top-right – blue dots), suggesting that  ${}^{1}(T_{1}T_{1})$ , in which two triplet excited states are located on the same pentacene dimer, is formed rather than  ${}^{3}(T_{1}S_{0})$ .

1

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29 30

31

32

33

34

35 36 37

38 39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57

58

59

60

Next, multi-wavelength and target analyses were used to determine the underlying lifetimes. Two different kinetic models were applied to fit contributions from the SF active *gauche*-conformers. In the case of **C** and **D**, a purely sequential kinetic model was used, in which  $(S_1S_0)$  deactivates *via* the solvent-stabilized  $(S_1S_0)_{SOLV}$  to afford  ${}^1(T_1T_1)$  with rate constants of 1.1 x 10<sup>11</sup> and 2.0 x 10<sup>8</sup> s<sup>-1</sup>, respectively. Implicit in this kinetic model is a super-exchange mechanism, in which an energetically higher-lying CT-state serves as a virtual intermediate between  $(S_1S_0)_{SOLV}$  and  ${}^1(T_1T_1) - vide$  infra. (CT)<sub>virtual</sub> is displayed in the fs-TAS for **C** and **D** shown in Figures S20–S21.<sup>[62]</sup>

Fitting the data for **A** and **B** required a minor modification of the kinetic model. Details regarding the kinetic models are given in Figure 7. Initially,  $(S_1S_0)$  transforms into the same  $(S_1S_0)_{SOLV}$  intermediate, which is implemented in the kinetic model for **C** and **D** – *vide supra*. In contrast to **C** and **D**,  $(S_1S_0)_{SOLV}$  deactivates in **A** and **B** in a parallel fashion to yield  ${}^1(T_1T_1)$ .  ${}^1(T_1T_1)$  is formed, on one hand, directly (one-step), *via* a super-exchange mechanism as described for **C** and **D**, and, on the other hand, indirectly (two-step), *via* an observable intermediate state.<sup>[63, 64]</sup>



Figure 7. Top: Kinetic model used to fit the transient absorption data for C and D; Bottom: Kinetic model used to fit the transient absorption data for A and B.

We hypothesize that the intermediate state is a superimposition of  $(S_1S_0)_{SOLV}$  and  ${}^{1}(T_1T_1)$  mixed with CT characteristics. Recently, many different variations in terms of relative ratios between the respective characteristics have been summed into a single term,  $(S_1S_0)_{(T1T1)}^{CT,[40, 41]}$  Figures 6 and S19 depict the fs-TAS, the time absorption profiles, the deconvoluted species associated spectra (SAS), and the population kinetics<sup>[65]</sup> from Glotaran target analysis for A and **B**, respectively. SAS (Figure 6, bottom-left) reveal features of  $(S_1S_0)_{SOLV}$  and  ${}^{1}(T_1T_1)$ , especially in the near-infrared (NIR) ACS Paragon Plus

region. As a matter of fact, the population of  $(S_1S_0)_{(T1T1)}^{CT}$  is accompanied by blue-shifted  $(S_1S_0)_{SOLV}$  at around 1215 nm, and the rise of the 865 and 980 nm characteristics, albeit of much lower intensity, of  ${}^1(T_1T_1)$ .

Please note that the pure  $(S_1S_0)_{SOLV}$  lacks the features at 860 and 980 nm, while the pure  ${}^1(T_1T_1)$  state lacks the maximum at 1215 nm. To clarify the spectroscopic differences throughout the  $(S_1S_0)_{SOLV}$ -to- $(S_1S_0)_{(T1T1)}^{CT}$  transition further, we inspected the decay associated spectra (DAS) of **A** – Figure 8. By virtue of the fact that the 860 and 980 nm markers point "downwards" we infer that they will be present throughout the transition toward  $(S_1S_0)_{(T1T1)}^{CT}$ . The same considerations are applicable for the 1215 nm marker. It is only during the transition toward pure  ${}^1(T_1T_1)$  that the 1215 nm marker disappears. For **B**–**D**, the DAS are essentially identical – Figure S22.<sup>[66]</sup>

Independent proof for the existence of  $(S_1S_0)_{(T|T1)}^{CT}$  came from fs-TAS measurements in toluene. When using a solvent of lower polarity, appreciable changes in the fs-TAS are in line with this expectation. To this end, for  $(S_1S_0)_{(T|T1)}^{CT}$  the 1215 nm maximum, which relates to  $(S_1S_0)_{SOLV}$ , is still discernable and so are the maxima at 860 and 980 nm, with both refer to  ${}^1(T_1T_1)$ . But, unlike our analysis in benzonitrile, the maximum at 511 nm, which relates to triplet excited states, is sharper and more prominent in toluene (fs-TAS, DAS and rate constants of **A** and **B** are illustrated in Figures S23–S25 and Table S6). In short, contributions from  ${}^1(T_1T_1)$  in  $(S_1S_0)_{(T1T1)}^{CT}$  increase in toluene at the expense of contributions from CT, which seemingly is playing only a minor role.



**Figure 8.** Normalized decay associated spectra of **A** as obtained by target analysis of the deconvoluted femtosecond transient absorption spectra in benzonitrile. The figure legend refers to the respective transitions. Please note that the  ${}^{1}(T_{1}T_{1})$ -to- ${}^{5}(T_{1}T_{1})$ transition is not fully resolvable on the fs-TAS timescale.

The modus operandi in **A** and **B** is likely to be hopping. Interesting is the fact that the dominance of the direct (onestep) over the indirect (two-step) pathway is linked to the electronic coupling. For example, in **C** and **D** the relative ratios for the indirect (two-step) and direct (one-step) pathways are 0% to 100%. In **A** and **B**, the ratios are 45% to 55% and 65% to 35%, respectively, which demonstrates the importance of the indirect pathway. In toluene, the ratios change to 70% to 30% for **A** and 80% to 20% for **B**, again due to a larger contribution from  ${}^{1}(T_{1}T_{1})$  in  $(S_{1}S_{0})_{(T1T1)}^{CT}$ . Moreover, the relative ratio impacts the  ${}^{1}(T_{1}T_{1})$  quantum yields: The lowest quantum yields of 50% were found for **D**, followed by 84% for **C**, 142% for **B**, and 162% for **A** in Environment

benzonitrile. In short, the electronic coupling and the  ${}^{1}(T_{1}T_{1})$  quantum yields compare remarkably well.<sup>[67]</sup> ("Methods" section and Supporting Information, Figure S43 and Table S9).<sup>[35, 38, 39]</sup>

Time-resolved characterization; Spin decoherence. Pump-probe experiments on the nano- and microsecond timescales shed light on the fate of  ${}^{1}(T_{1}T_{1})$  in A–D. With the exception of the early time delays, at which the  ${}^{1}(T_{1}T_{1})$  growth is still found, at any given time delay between 1 ns and 100 µs, the differential absorption spectra resemble those of  ${}^{1}(T_{1}T_{1})$ . Multi-wavelength analyses suggest, however, that the  ${}^{1}(T_{1}T_{1})$ decays are multiphasic and feature three different components. Here, target analyses using our recently published kinetic model are decisive.<sup>[35]</sup> In the case of C and D, we modified the kinetic model by adding the parallel decay of the SF-inactive trans-conformer next to the decay of the SF-active gaucheconformer; the relative ratios are based on the steady-state fluorescence experiments - vide supra - Figures S27 and S28).<sup>[68]</sup> In terms of the trans-conformer, only the slow intersystem crossing to afford  ${}^{3}(T_{1}S_{0})$  and the subsequent recovery are discerned. In terms of the gauche-conformers, starting with  ${}^{1}(T_{1}T_{1})$ , the recovery of the ground state (S<sub>0</sub>S<sub>0</sub>) proceeds via the sequential population of a correlated and an uncorrelated pair of triplet excited states,  ${}^{5}(T_{1}T_{1})$  and  $(T_{1}+T_{1})$ , respectively. Dimer **D** gives the lowest  ${}^{5}(T_{1}T_{1})$  quantum yields

(45%), followed by **A** (40%), **B** (53%), and then **C** (67%). Overall, **C** seems to have the optimum electronic coupling to assist in the highest  ${}^{5}(T_{1}T_{1})$  quantum yield. Relative to **C**, in **A** and **B** the  ${}^{5}(T_{1}T_{1})$  state is raised in energy and, in turn, the  ${}^{5}(T_{1}T_{1})$  quantum yields are lower. Notably, the  ${}^{5}(T_{1}T_{1})$  energy increase relative to  ${}^{1}(T_{1}T_{1})$  depends on the electronic coupling, which is higher in **A** and **B** than in **C**. The low  ${}^{5}(T_{1}T_{1})$ quantum yield in **D**, in turn, might be correlated to its unique mode in coupling, which is mediated by the Si-Si contacts as described by modeling.

Finally, the  ${}^{5}(T_{1}T_{1})$ -to- $(T_{1}+T_{1})$  transformation makes the highest  $(T_{1}+T_{1})$  quantum yields possible in the case of **D** with a value of 85%, whereas **A**–**B** feature yields of about 45%. Considering that we found the weakest electronic coupling among the **A**–**D** series for **D**, the two pentacenes are fairly decoupled. As such, the subsequent decoherence of  ${}^{5}(T_{1}T_{1})$  to afford the corresponding uncorrelated  $(T_{1}+T_{1})$  is most strongly favored. Likewise, we consider that the different mode in coupling, the extended conjugation of the spacer, and the lack of competing deactivations play a role in forming  $(T_{1}+T_{1})$  in such high quantum yields. The ns-TAS, time absorption profiles, deconvoluted nanosecond transient absorption spectra, and population kinetics derived from target analysis for **A** are illustrated in Figure 9 and for **B**–**D** in Figures S26–S28, respectively.



**Figure 9.** Top-Left: Differential nanosecond transient absorption spectra ( $\lambda_{ex} = 610 \text{ nm}$ , 400 nJ) of the **A** (4 x 10<sup>-5</sup> M) in benzonitrile with time delays between 0 and 400 µs; Top-Right: Respective time absorption profiles at the given wavelengths; Bottom-Left: Deconvoluted nanosecond transient absorption spectra of the intermediate state  $(S_1S_0)_{(T_1T_1)}^{CT}$  (black), the singlet correlated triplet state  ${}^{1}(T_1T_1)$  (red), the quintet correlated triplet state  ${}^{5}(T_1T_1)$  (blue), and the uncorrelated triplet excited state  $(T_1+T_1)$  (green) of **A** as obtained by target analysis, using the proposed kinetic model, in benzonitrile. Bottom-Right: Respective population kinetics. Please note that the NIR is not shown due to the low intensity in ns-TAS.

Our recent investigations<sup>[35]</sup> have shown the impact of modulating through-bond electronic communication regarding the  ${}^{1}(T_{1}T_{1})$ -to- ${}^{5}(T_{1}T_{1})$  and  ${}^{5}(T_{1}T_{1})$ -to- $(T_{1}+T_{1})$  transformations. By keeping the pentacene-pentacene distances in a series of

conjugated and non-conjugated pentacene dimers constant, vastly different  $J_{SQ}$ s were realized. Large values of  $J_{SQ}$  disable any of the aforementioned transformations in the earlier cases and activate the ground-state recovery. Small values of  $J_{SQ}$ 

enable both transformations in the latter cases and groundstate recovery is negligible. In the current investigation, we demonstrate that in the case of weak electronic couplings, where  $J_{SQ}$  is insignificant, through-space electronic communication by means of *D* plays a decisive role. Spin decoherence requires both weak  $J_{SQ}$  and weak *D*. In **D**, the weakest *D* results in the slowest  ${}^{1}(T_{1}T_{1})$ -to- ${}^{5}(T_{1}T_{1})$  and  ${}^{5}(T_{1}T_{1})$ -to- ${}^{(T_{1}+T_{1})}$  transformations with rate constants of 3.1 x  $10^{6}$  and 1.1 x  $10^{6}$  s<sup>-1</sup>, respectively.

1

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57

58

59

60

In **A**, which features the strongest electronic coupling in the series of **A**–**D**, triplet-triplet annihilation is facilitated with rate constants as high as 9.0 x  $10^7$  and 1.4 x  $10^7$  s<sup>-1</sup>, for the respective transformations. The fact that the fluorescence deactivation of **A** and **B** in non-aromatic methyl-cyclohexane and cyano-cyclohexane is notably slower than in aromatic toluene and benzonitrile points to the mediating effects of the aromatic solvents at facilitating an electronic coupling sufficient to have both  $J_{SQ}$  and D operative.

Spin dephasing in  ${}^{1}(T_{1}T_{1})$  and  ${}^{5}(T_{1}T_{1})$  is fundamentally slow and, as such, competes with triplet-triplet annihilation. Considering, for example, **D** and comparing its  ${}^{1}(T_{1}T_{1})$ lifetime of 147 ns with those seen in electronically decoupled, non-conjugated pentacene dimers with 90 ns (NC).<sup>[35]</sup> we postulate, as mentioned earlier, that it is close to the intrinsic limit in **D**. Still, efficient formation of  ${}^{5}(T_{1}T_{1})$  seems to necessitate – like the formation of  ${}^{1}(T_{1}T_{1})$  – sizeable electronic spin dipole-dipole interactions. When comparing the  ${}^{5}(T_{1}T_{1})$ lifetimes of 835 ns for **D** and 175 ns for NC, a similar conclusion is reached.<sup>[35]</sup> A closer look at the overall  $(T_1+T_1)$ quantum yields reveals the benefits of using non-conjugated spacers: The electronic coupling is significantly attenuated and allows the population of  $(T_1+T_1)$ . The respective rate constants and quantum yields for A-D are summarized in Figure S43 and Tables S4-S5.

**Time-resolved electron paramagnetic resonance (trEPR) spectroscopy:**  ${}^{5}(T_{1}T_{1})$  **state validation.** To validate the presence of  ${}^{5}(T_{1}T_{1})$ , time-resolved Electron Paramagnetic Resonance (trEPR) spectroscopy was performed on **A** and **D**. In frozen 2-methyltetrahydrofuran (MeTHF) at 85 K, both **A** (Figure 10 and S44) and **D** (Figure S46) possess similar features.<sup>[69]</sup> Upon freezing the solution of, for example, **A** a distribution of different orientations goes hand-in-hand with a distribution of  $J_{SQ}$ . However, the width of the quintet and triplet features, which show a ~12 mT broad feature centered at g = 2 and one at 40 mT, respectively, matches well with the previously measured pentacene dimer **NC**.<sup>[35]</sup>

Fitting the transient spectra required three exponentials, where the first species relates to the formation of  ${}^{5}(T_{1}T_{1})$ followed by the bi-exponential decay of  ${}^{5}(T_{1}T_{1})$  and  $(T_{1}+T_{1})$ . The quintet feature is most evident in the first and second species with sharp emissive and absorptive features at 340 and 352 mT, respectively. In contrast, the triplet features dominate the third species. The dynamics observed in trEPR matches well with those observed in low temperature transient absorption measurements:  ${}^{1}(T_{1}T_{1})$  lifetime is 222.2 ns and  $^{5}(T_{1}T_{1})$  lifetime is 1.89 µs. In trEPR, the lifetime of  $^{1}(T_{1}T_{1})$ corresponds to the rise of the signal, which is 100 ns and that of  ${}^{5}(T_{1}T_{1})$  is 510 ns. Notable is the decay of  $(T_{1}+T_{1})$ , which is beyond the time window of our trEPR experiments of 3000 ns. In addition, simulations were performed on A to further support the assignment of the triplet excited state, as well as, to demonstrate the effect on the quintet spectrum as one pentacene unit is rotated about the y axis of its zero field tensor from 60-90 degrees (Figure S45).



Figure 10. TrEPR spectra of dimer A in MeTHF at 85 K ran at X-band.

Temperature and viscosity dependent studies. On one hand, we lowered the temperature from 298 to 80 K and, on the other hand, we increased the viscosity by using different ratios of MeTHF and paraffin from 10/0 (v/v) to 1/9 (v/v). We, again, opted for **A** and **D**. With respect to steady-state fluorescence, both assays led to a reinstatement of the vibrational fine structure for **A**, shown in Figure 11, and a sharpening of the structure for **D**, shown in Figure S31. Inspection of the time-resolved fluorescence measurements of **A** and **D** revealed that both the short- and the long-lived components of the *gauche*- and *trans*-conformations, respectively, increased upon a temperature decrease and viscosity increase, as seen in Figures 12 and S32, and Table S7, respectively.



**Figure 11.** Top: Normalized temperature dependent fluorescence spectra ( $\lambda_{ex} = 610$  nm) for **A** (4 x 10<sup>-5</sup> M) at 298 (black), 220 (red), 150 (blue), and 80 K (green) in 2-Methyltetrahydrofuran (MeTHF). Bottom: Normalized viscosity dependent fluorescence spectra for **A** in MeTHF/paraffin mixtures of 10/0 (v/v) (black), 5/5 (v/v) (red), and 1/9 (v/v) (blue).

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55 56

57

58

59

60



**Figure 12.** Top: Temperature dependent fluorescence time profiles ( $\lambda_{ex} = 610 \text{ nm}$ ) of **A** (4.0 x 10<sup>-5</sup> M) at 298 (black), 220 (red), 150 (blue), and 80 K (green) in argon saturated MeTHF. Bottom: Viscosity dependent fluorescence time profiles (excitation at 610 nm) of **A** (4.0 x 10<sup>-5</sup> M) in argon saturated MeTHF/paraffin mixtures of 10/0 (v/v) (black), 5/5 (v/v) (red), and 1/9 (v/v) (blue).

Steady state and time-resolved fluorescence measurements underpin the fact that SF is influenced by through-space interactions and electronic coupling, which relate to the relative geometry of the pentacenes. Small variations in distances cannot be ruled out. In **A**, lower temperatures/higher viscosities restrict the overall geometry, which leads to a decreased electronic coupling and, in an extreme scenario, to behavior similar to that found for **D**. The electronic coupling in **D**, which is the weakest among the **A–D** series, affords only subtle changes upon changing temperature and viscosity.

Changes were also observable in the fs- and ns-TAS measurements, as Figures 13, 14, S32–S42, and Table S8 demonstrate. For example, as the temperature is lowered stepby-step, the lifetimes and yields of  ${}^{1}(T_{1}T_{1})$ ,  ${}^{5}(T_{1}T_{1})$ , and  $(T_{1}+T_{1})$  decrease. Interestingly, at temperatures below 150 K a mechanistic change is noted for **A**: The direct, superexchange mechanism – top part of Figure 7 – takes over like in the scenario established for **C** and **D** at higher temperature, that is, all the way to room temperature.

The outcome of lowering the temperature for **D** is different: SF is completely deactivated. Instead a conventional intersystem crossing dominates the slow excited state deactivation and, in turn, the inefficient triplet excited state formation.<sup>[70]</sup> In a 1/9 (v/v) MeTHF/paraffin mixture, the same mechanistic crossover from the indirect to the direct mechanism occurs for **A**. Once again, the cause relates to electronic couplings and geometric effects. For **D**, SF is not completely deactivated under these conditions, but the overall yields are less than 18%.

#### CONCLUSION

In summary, we have designed four pentacene dimers, in which four different spacers were introduced to modulate intramolecular forces and, in turn, pentacene-pentacene interactions. Emphasis was placed on probing the impact on the  $^{1}(S_{1}S_{0})$ -to- $^{1}(T_{1}T_{1})$  transition, the  $^{1}(T_{1}T_{1})$ -to- $^{5}(T_{1}T_{1})$ decoherence, as well as the  $(T_1+T_1)$  formation. All of the aforementioned intermediates were spectroscopical characterized by transient absorption and/or electron paramagnetic resonance measurements in a wide temperature range, that is, from 298 to 77 K, in a wide solvent polarity range, that is, from toluene to benzonitrile, and in a wide solvent viscosity range, that is, from pure MeTHF to a 1/9 (v/v) MeTHF/paraffin mixture. Fluorescence spectroscopy, namely steady-state and time-resolved, and molecular modeling rounded off our mechanistic investigations.



**Figure 13.** Top row – left to right: Differential femtosecond transient absorption spectra ( $\lambda_{ex} = 610$  nm, 400 nJ) of **A** (4.0 x 10<sup>-5</sup> M) in MeTHF with time delays between 0 and 7 500 ps at 80 K; Respective time absorption profiles of the triplet excited state at 500 nm at given temperatures; Deconvoluted femtosecond transient absorption spectra of the singlet excited (S<sub>1</sub>S<sub>0</sub>) (black) and the intermediate state (S<sub>1</sub>S<sub>0</sub>)<sub>SOLV</sub> (red) of **A**, as obtained by global analysis using a sequential model, in MeTHF at 80 K; Respective population kinetics. Bottom row – left to right: Differential femtosecond transient absorption spectra ( $\lambda_{ex} = 610$  nm, 400 nJ) of **A** (4.0 x 10<sup>-5</sup> M) in a 1/9 (v/v) MeTHF/paraffin mixture with time delays between 0 and 7500 ps; Respective time absorption profiles of the triplet excited state at 500 nm at given ratios; Deconvoluted femtosecond transient absorption spectra of the singlet excited (S<sub>1</sub>S<sub>0</sub>) (black) and the intermediate state (S<sub>1</sub>S<sub>0</sub>)<sub>SOLV</sub> (red) of **A**, as obtained by global analysis using a sequential model, in a 1/9 (v/v) MeTHF/paraffin mixture; Respective femtosecond transient absorption spectra of the singlet excited (S<sub>1</sub>S<sub>0</sub>) (black) and the intermediate state (S<sub>1</sub>S<sub>0</sub>)<sub>SOLV</sub> (red) of **A**, as obtained by global analysis using a sequential model, in a 1/9 (v/v) MeTHF/paraffin mixture; Respective population kinetics. The respective spectra for <sup>1</sup>(T<sub>1</sub>T<sub>1</sub>) are not shown because global analysis hampers the complete deconvolution.

ACS Paragon Plus Environment



**Figure 14.** Top row – left to right: Differential nanosecond transient absorption spectra ( $\lambda_{ex} = 610$  nm, 400 nJ) of **A** (4.0 x 10<sup>-5</sup> M) in MeTHF with time delays between 0 and 400 µs at 80 K; Respective time absorption profiles of the triplet excited state at 500 nm at given temperatures; Deconvoluted nanosecond transient absorption spectra of the singlet correlated triplet state <sup>1</sup>(T<sub>1</sub>T<sub>1</sub>) (black), the quintet correlated triplet state <sup>5</sup>(T<sub>1</sub>T<sub>1</sub>) (red), and the uncorrelated triplet excited state (T<sub>1</sub>+T<sub>1</sub>) (blue) of **A**, as obtained by global analysis using a sequential model, in MeTHF at 80 K; Respective population kinetics. Bottom row – left to right: Differential nanosecond transient absorption spectra ( $\lambda_{ex} = 610$  nm, 400 nJ) of **A** (4.0 x 10<sup>-5</sup> M) in a 1/9 (v/v) MeTHF/paraffin mixture with time delays between 0 and 400 µs; Respective time absorption profiles of the triplet excited state at 500 nm at given ratios; Deconvoluted nanosecond transient absorption spectra of the singlet correlated triplet state <sup>1</sup>(T<sub>1</sub>T<sub>1</sub>) (black), the quintet correlated triplet state  $(\lambda_{ex} = 610$  nm, 400 nJ) of **A** (4.0 x 10<sup>-5</sup> M) in a 1/9 (v/v) MeTHF/paraffin mixture with time delays between 0 and 400 µs; Respective time absorption profiles of the triplet excited state at 500 nm at given ratios; Deconvoluted nanosecond transient absorption spectra of the singlet correlated triplet state <sup>1</sup>(T<sub>1</sub>T<sub>1</sub>) (black), the quintet correlated triplet state <sup>5</sup>(T<sub>1</sub>T<sub>1</sub>) (red), and the uncorrelated triplet excited state (T<sub>1</sub>+T<sub>1</sub>) (blue) of **A**, as obtained by global analysis using a sequential model, in a 1/9 (v/v) MeTHF/paraffin mixture; Respective population kinetics. The respective spectra for (S<sub>1</sub>S<sub>0</sub>)<sub>(T1T1)</sub><sup>CT</sup> are not shown because global analysis hampers the complete deconvolution. Please note that the NIR is not shown due to the low intensity in ns-TAS

In the context of the  ${}^{1}(S_{1}S_{0})$ -to- ${}^{1}(T_{1}T_{1})$  transition, a superexchange mechanism, that is, coupling to a higher-lying CT state to generate a virtual intermediate, enables rapid SF in **A**– **D**. Sizeable electronic coupling in **A** and **B** opens, however, an additional pathway, that is, population of a real intermediate, which is a superimposition of  $(S_{1}S_{0})_{SOLV}$  and  ${}^{1}(T_{1}T_{1})$  mixed with CT characteristics:  $((S_{1}S_{0})_{(T1T1)}^{CT})$ . In turn, **A** and **B** feature much higher  ${}^{1}(T_{1}T_{1})$  quantum yields than **C** and **D**, which reach up to 162%. In the context of the  ${}^{1}(T_{1}T_{1})$ -to- ${}^{5}(T_{1}T_{1})$  decoherence, sizeable electronic coupling as seen in **A** and **B** is counterproductive and, in turn, **D** features the highest  $(T_{1}+T_{1})$  quantum yields with a value of 85%.

#### METHODS

**Photoluminescence spectroscopy.** Steady-state fluorescence spectra were carried out at a FluoroMax3 spectrometer from Horiba in the visible detection range (RT). The data was recorded using the FluorEssence software from Horiba Jobin Yvon. Fluorescence lifetimes were determined by the time correlated single photon counting (TCSPC) technique using a FluoroLog3 emission spectrometer (Horiba JobinYvon) equipped with an R3809U-58 MCP (Hamamatsu) and a SuperK Extreme high-power supercontinuum fiber laser EXW-6 (NKT) exciting at 610 nm (150 ps fwhm).

Transient Absorption Spectroscopy. Femtosecond transient absorption (TA) experiments were carried out with an amplified Ti:Sapphire CPA-2110 fs laser system (Clark MXR: output 775 nm, 1 kHz, 150 fs pulse width) using transient absorption pump/probe detection systems (Helios and Eos, Ultrafast Systems) with argon purged solutions. The 480 and 610 nm excitation wavelengths, with energies of 800 and 400 nJ, respectively, were generated with a noncolinear optical parametric amplifier (NOPA, Clark MXR). Cryostat supported measurements at 298, 220, 150, and 80 K were conducted using an Optistat DN2 cryostat from Oxford Instruments. Viscosity dependent measurements were performed using 2-methyltetrahydrofuran (MeTHF, SIGMA-ALDRICH, anhydrous,  $\geq$ 99%) and paraffin (SIGMA-ALDRICH, for IR spectroscopy) mixtures of 10/0, 5/5, and 1/9 (v/v). Data evaluation of the fs- and ns-TAS data has been conducted by means of multiwavelength and Glotaran global and target analysis. Global analysis was performed on the TA data sets using a sequential model. Global target analysis was performed on the TA data sets using the proposed kinetic models. The analytic solution to the coupled differential equations that describe the kinetic model is convoluted with a Gaussian instrument response function. After the least-squares fitting has converged, the raw data matrix is deconvoluted using the specific solution to the kinetic model and parameters from the fit to obtain the species-associated spectra and their populations as a function of time.

Transient Electron Paramagnetic Resonance Spectroscopy. Dimer A and D were dissolved in MeTHF to achieve an optical density of 0.5 in 2 mm cuvette at 660 nm (ca. 10<sup>-4</sup> M). To dry quartz tubes (2.40 mm o.d.  $\times$  2.00 mm i.d.), this solution was loaded, degassed with three freeze-pump-thaw cycles, and flamesealed under vacuum (<10<sup>-4</sup> torr). Samples were placed in a split ring resonator (Bruker ER4118X-MS3) with a grated window for optical excitation. The samples were photoexcited with 7 ns, 3.0 mJ, 640 nm and 660 nm pulses for dimer A and D, respectively, generated by an optical parametric oscillator (Spectra-Physics Basi-scan), pumped with the output of a frequency-tripled Nd:YAG laser (Spectra-Physics Quanta-Ray Pro 350). A commercial X-band (ca. 9.5 GHz) Bruker Elexsys E680-X/W EPR spectrometer was utilized for all EPR measurements. The temperature was maintained at 85 K by an Oxford Instruments CF935 continuous flow cryostat using liquid N<sub>2</sub>. Data was collected in quadrature with Xepr software which stores the nominally orthogonal x- and y-axis channels as real and imaginary numbers, respectively.

**Triplet Yield Determination.** The TQY determination was performed by using the normalization of the spectra at the ground state bleaching using Glotaran target analysis and the ratio of

60

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57 58 59

60

singlet and triplet excited state molar extinction coefficients and absorptions, as found in literature.<sup>[35, 38, 39]</sup> In short, this approach is based on certain assumptions: (1) the singlet excited state is delocalized over the entire molecule, thus bleaching both pentacene units; (2) a single triplet excited state likewise bleaches ground-state singlet transition; (3) the entire no overlying/additional features are located at the ground-state bleaching area from roughly 600 to 700 nm, which allows one to normalize the triplet excited state spectra relative to the singlet excited state ones; and (4) that two triplet excited states on the dimer lead to a bleaching twice that of a single one. By combining these criteria and the kinetic model in a Glotaran target analysis. one is able to determine the efficiency and rate constant of each transition. In the context of the TQY, all transitions prior to the formation of  ${}^{1}(T_{1}T_{1})$  contribute to its overall yield. Details, regarding the efficiencies and rate constants, are illustrated in the Supporting Information, Figure S43 and Table S4, S5, and S9.

# ASSOCIATED CONTENT

**Supporting Information**. (I) Listing of the general experimental methods; (II) text and schemes describing the synthetic routes; (III) figures and tables illustrating the results from time-resolved fluorescence, electrochemical, femto/nanosecond transient absorption, time-resolved electron paramagnetic resonance spectroscopy, temperature and viscosity dependent measurements; (IV) text and table depicting the calculation details; (V) details describing time-resolved electron paramagnetic resonance spectroscopy data; (VI) twenty-two NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

# AUTHOR INFORMATION

#### **Corresponding Author**

\*dirk.guldi@fau.de

#### Author Contributions

The manuscript was written through contributions of all authors. / All authors have given approval to the final version of the manuscript.

#### Funding Sources

Emerging Fields initiative (EFI)

Cluster of Excellence Engineering of Advanced Materials (EAM) Solar Technologies go Hybrid (SolTech)

Natural Sciences and Engineering Research Council of Canada (NSERC)

## ACKNOWLEDGMENTS

Funding is gratefully acknowledged from the Emerging Fields initiative (EFI) "Singlet Fission" supported by FAU, as well as the Cluster of Excellence Engineering of Advanced Materials (EAM), "Solar Technologies go Hybrid" – an initiative of the Bavarian State Ministry for Science, Research and Art, and the Natural Sciences and Engineering Research Council of Canada (NSERC). This work was supported by the U.S. Department of Energy, Office of Science, and Office of Basic Energy Sciences under Award DE-FG02-99ER14999 (Y.J.B., M.D.K., M.R.W., experiments).

## REFERENCES

(1) Swenberg, C. E.; Tracy, W. T., Bimolecular radiationless transitions in crystalline tetracene. *Chem. Phys. Lett.* **1968**, *2*, 327.

(2) Geacintov, N.; Pope, M.; Vogel, F., Effect of magnetic field on the fluorescence of tetracene crystals: exciton fission. *Phys. Rev. Lett.* **1969**, *22*, 593.

(3) Singh, S.; Jones, W. J.; Siebrand, W.; Stoicheff, B. P.; Schneider, W. G., Laser generation of excitons and fluorescence in anthracene crystals. *J. Chem. Phys. Rev.* **1965**, *42*, 330.

(4) Johnson, R. C.; Merrifield, R. E., Effects of fields on the mutual annihilation of triplet excitons in anthracene crystals. *Phys. Rev. B* **1970**, *1*, 896.

(5) Suna, A., Kinematics of exciton-exciton annihilation in molecular crystals. *Phys. Rev. B* **1970**, *1*, 1716.

(6) Swenberg, C.E.; Geacintov, N. E., *Exciton interactions in organic solids*; Wiley: New York, **1973**.

(7) Merrifield, R. E., Magnetic effects on triplet exciton interactions. *Pure Appl. Chem.* **1971**, *27*, 481.

(8) Rao, A.; Friend, R. H., Harnessing singlet exciton fission to break the Shockley-Queisser limit. *Nature Reviews Materials* **2017**, *2*, 17063.

(9) Smith, M. B.; Michl, J., Singlet fission. Chem. Rev. 2010, 110, 6891.

(10) Walker, B. J.; Musser, A. J.; Beljonne, D.; Friend, R. H., Singlet exciton fission in solution. *Nat. Chem.* **2013**, *5*, 1019.

(11) Lee, J.; Jadhav, P.; Baldo, M. A., High efficiency organic multilayer photodetectors based on singlet exciton fission. *Appl. Phys. Lett.* **2009**, *95*, 033301.

(12) Shockley, W.; Queisser, H. J., Detailed balance limit of efficiency of p-n junction solar cells. J. Appl. Phys. **1961**, *32*, 510.

(13) Congreve, D. N.; Lee, J.; Thompson, N. J.; Hontz, E.; Yost, S. R.; Reusswig, P. D.; Bahlke, M. E.; Reineke, S.; Van Voorhis, T.; Baldo, M. A., External Quantum Efficiency Above 100% in a Singlet-Exciton-Fission–Based Organic Photovoltaic Cell. *Science* **2013**, *340*, 334.

(14) Hanna, M. C.; Nozik, A. J., Solar conversion efficiency of photovoltaic and photoelectrolysis cells with carrier multiplication absorbers. *J. Appl. Phys.* **2006**, *100*, 074510.

(15) Ehrler, B.; Musselman, K. P.; Böhm, M. L.; Friend, R. H.; Greenham, N. C., Hybrid pentacene/asilicon solar cells utilizing multiple carrier generation via singlet exciton fission. *Appl. Phys. Lett.* **2012**, *101*, 153507.

(16) Reusswig, P.D.; Congreve, D. N.; Thompson, N. J.; Baldo, M. A., Enhanced external quantum efficiency in an organic photovoltaic cell via singlet fission exciton sensitizer. *Appl. Phys. Lett.* **2012**, *101*, 113304.

(17) Jadhav, P. J.; Brown, P. R.; Thompson, N.; Wunsch, B.; Mohanty, A.; Yost, S. R.; Hontz, E.; Van Voorhis, T.; Bawendi, M. G.; Bulović, V.; Baldo, M. A., Triplet exciton dissociation in singlet exciton fission photovoltaics. *Adv. Mater.* **2012**, *24*, 6169.

(18) Johnson, J. C.; Reilly, T. H., III; Kanarr, A. C.; Van De Lagemaat, J., The ultrafast photophysics of pentacene coupled to surface plasmon active nanohole films. *J. Phys. Chem. C* **2009**, *113*, 6871.

(19) Marciniak, H.; Pugliesi, I.; Nickel, B.; Lochbrunner, S., Ultrafast singlet and triplet dynamics in microcrystalline pentacene films. *Phys. Rev. B* **2009**, *79*, 235318.

(20) Yost, S. R.; Lee, J.; Wilson, M. W. B.; Wu, T.; McMahon, D. P.; Parkhurst, R. R.; Thompson, N. J.; Congreve, D. N.; Rao, A.; Johnson, K.; Sfeir, M. Y.; Bawendi, M. G.; Swager, T. M.; Friend, R. H.; Baldo, M. A.; Van Voorhis, T., A transferable model for singlet-fission kinetics. *Nat. Chem.* **2014**, *6*, 492.

(21) Wilson, M. W. B.; Rao, A.; Clark, J.; Kumar, R. S. S.; Brida, D.; Cerullo, G.; Friend, R. H., Ultrafast Dynamics of Exciton Fission in Polycrystalline Pentacene. *J. Am. Chem. Soc.* **2011**, *133*, 11830.

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

(23) Chan, W.L.; Ligges, M.; Zhu, X. Y., The energy barrier in singlet fission can be overcome through coherent coupling and entropic gain. *Nat. Chem.* **2012**, *4*, 840.

(24) Hetzer, C.; Guldi, D. M.; Tykwinski, R. R., Pentacene Dimers as a critical tool for the investigation of intramolecular singlet fission. *Chem. Eur. J.* **2018**, *24*, 8245.

(25) Zimmerman, P. M.; Musgrave, C. B.; Head-Gordon, M., A

correlated electron view of singlet fission. Acc. Chem. Res. 2013, 46, 1339.

1

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57 58 59

60

(26) Johnson, J. C.; Nozik, A. J.; Michl, J., The role of chromophore coupling in singlet fission. *Acc. Chem. Res.* **2013**, *46*, 1290.

(27) Berkelbach, T. C.; Hybertsen, M. S.; Reichman, D. R., Microscopic theory of singlet exciton fission. II. Application to pentacene dimers and the role of superexchange. *J. Chem. Phys.* **2013**, *138*, 114103.

(28) Feng, X.; Luzanov, A. V.; Krylov, A. I., Fission of entangled spins: An electronic structure perspective. *J. Phys. Chem. Lett.* **2013**, *4*, 3845.

(29) Parker, S. M.; Seideman, T.; Ratner, M. A.; Shiozaki, T., Model Hamiltonian analysis of singlet fission from first principles. *J. Phys. Chem. C* **2014**, *118*, 12700.

(30) Piland, G. B.; Burdett, J. J.; Dillon, R. J.; Bardeen, C. J., Singlet fission: From coherences to kinetics. *J. Phys. Chem. Lett.* **2014**, *5*, 2312.

(31) Teichen, P. E.; Eaves, J. D., A microscopic model of singlet fission. J. Phys. Chem. B 2012, 116, 1473.

(32) Zeng, T.; Hoffmann, R.; Ananth, N., The low-lying electronic states of pentacene and their roles in singlet fission. *J. Am. Chem. Soc.* **2014**, *136*, 5755.

(33) Zimmerman, P. M.; Bell, F.; Casanova, D.; Head-Gordon, M., Mechanism for singlet fission in pentacene and tetracene: From single exciton to two triplets. *J. Am. Chem. Soc.* **2011**, *133*, 19944.

(34) Berkelbach, T. C.; Hybertsen, M. S.; Reichman, D. R., Microscopic theory of singlet exciton fission. I. General formulation. *J. Chem. Phys.* **2013**, *138*, 114102.

(35) Basel, B.; Zirzlmeier, J.; Hetzer, C.; Phelan, B.; Krzyaniak, M.; Reddy, R.; Coto, P. B.; Horwitz, N.; Young, R.; White, F.; Hampel, F.; Clark, T.; Thoss, M.; Tykwinski, R. R.; Wasielewski, M.; Guldi, D. M., Unified Model for Singlet Fission within a Non-conjugated Covalent Pentacene Dimer. *Nat. Commun.* **2017**, *8*, 15171.

(36) Tayebjee, M. J. Y.; Sanders, S. N.; Kumarasamy, E.; Campos L. M.; Sfeir, M. Y.; McCamey, D. R., Quintet multiexciton dynamics in singlet fission. *Nature Physics* **2017**, *13*, 182.

(37) Chan, W. L.; Ligges, M.; Jailaubekov, A.; Kaake, L.; Miaja-Avila, L.; Zhu, X. Y., Observing the multiexciton state in singlet fission and ensuing ultrafast multielectron transfer. *Science* **2011**, *334*, 1541.

(38) Lukman, S.; Chen, K.; Hodgkiss, J. M.; Turban, D. H. P.; Hine, N. D. M.; Dong, S.; Wu, J.; Greenham, N. C.; Musser, A. J., Tuning the role of charge-transfer states in intramolecular singlet exciton fission through side-group engineering. *Nat. Commun.* **2016**, 7, 13622.

(39) Lukman, S.; Musser, A. J.; Chen, K.; Athanasopoulos, S.; Yong, C. K.; Zeng, Z.; Ye, Qu.; Chi, C.; Hodgkiss, J. M.; Wu, J.; Friend, R. H.; Greenham, N. C., Tuneable Singlet Exciton Fission and Triplet–Triplet Annihilation in an Orthogonal Pentacene Dimer. *Adv. Funct. Mater.* **2015**, *25*, 5452.

(40) Margulies, E. A.; Miller, C. E.; Wu, Y.; Ma, L.; Schatz, G. C.; Young, R. M.; Wasielewski, M. R., Enabling singlet fission by controlling intramolecular charge transfer in  $\pi$ -stacked covalent terrylenediimide dimers. *Nature Chemistry* **2016**, *8*, 1120.

(41) Chen, M.; Bae, Y. J.; Mauck, C. M.; Mandal, A.; Young, R. M.; Wasielewski, M. R., Singlet Fission in Covalent Terrylenediimide Dimers: Probing the Nature of the Multiexciton State Using Femtosecond Mid-Infrared Spectroscopy. J. Am. Chem. Soc. 2018, 140, 9184.

(42) Kaplan, I. G., Intermolecular Interactions: Physical Picture, Computational Methods and Model Potentials; Wiley: Chichster, London, **2006**.

(43) 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.

(44) Yamakado, T.; Takahashi, S.; Watanabe, K.; Matsumoto, Y.; Osuka, A.; Saito, S., Conformational Planarization versus Singlet Fission: Distinct Excited-State Dynamics of Cyclooctatetraene-Fused Acene Dimers. *Angew. Chem. Int. Ed.* **2018**, *57*, 5438. (45) Sanders, S. N.; Kumarasamy, E.; Pun, A. B.; Trinh, M. T.; Choi, B.; Xia, J.; Taffet, E. J.; Low, J. Z.; Miller, J. R.; Roy, X.; Zhu, X.-Y.; Steigerwald, M. L.; Sfeir, M. Y.; Campos, L. M., Quantitative Intramolecular Singlet Fission in Bipentacenes. *J. Am. Chem. Soc.* **2015**, *137*, 8965.

(46) Kumarasamy, E.; Sanders, S. N.; Tayebjee, M. J. Y.; Asadpoordarvish, A.; Hele, T. J. H.; Fuemmeler, E. G.; Pun, A. B.; Yablon, L. M.; Low, J. Z.; Paley, D. W.; Dean, J. C.; Choi, B.; Scholes, G. D.; Steigerwald, M. L.; Ananth, N.; McCamey, D. R.; Sfeir, M. Y.; Campos, L. M., Tuning Singlet Fission in  $\pi$ -Bridge- $\pi$ Chromophores. J. Am. Chem. Soc. **2017**, 139, 12488.

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

(48) Fuemmeler, E. G.; Sanders, S. N.; Pun, A. B.; Kumarasamy, E.; Zeng, T.; Miyata, K.; Steigerwald, M. L.; Zhu, X.-Y.; Sfeir, M. Y.; Campos, L. M.; Ananth, N., A Direct Mechanism of Ultrafast Intramolecular Singlet Fission in Pentacene Dimers. *ACS Cent. Sci.* **2016**, *2*, 316.

(49) Cook, R. E.; Phelan, B. T.; Kamire, R. J.; Majewski, M. B.; Young, R. M.; Wasielewski, M. R., Excimer Formation and Symmetry-Breaking Charge Transfer in Cofacial Perylene Dimers. *J. Phys. Chem. A* **2017**, *121*, 1607.

(50) Zirzlmeier, J.; Lehnherr, D.; Coto, P. B.; Chernick, E. T.; Casillas, R.; Basel, B. S.; Thoss, M.; Tykwinski, R. R.; Guldi, D. M., Singlet fission in pentacene dimers. *Proc. Natl. Acad. Sci.* **2015**, *112*, 5325.

(51) Tamura, H.; Huix-Rotllant, M.; Burghardt, I.; Olivier, Y.; Beljonne, D., First-Principles Quantum Dynamics of Singlet Fission: Coherent versus Thermally Activated Mechanisms Governed by Molecular  $\pi$  Stacking. *Phys. Rev. Lett.* **2015**, *115*, 107401.

(52) Alguire, E. C.; Subotnik, J. E.; Damrauer, N. H., Exploring Non-Condon Effects in a Covalent Tetracene Dimer: How Important Are Vibrations in Determining the Electronic Coupling for Singlet Fission? *J. Phys. Chem. A* **2015**, *119*, 299.

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

(54) Korovina, N. V.; Das, S.; Nett, Z.; Feng, X.; Joy, J.; Haiges, R.; Krylov, A. I.; Bradforth, S. E.; Thompson, M. E., Singlet Fission in a Covalently Linked Cofacial Alkynyltetracene Dimer. *J. Am. Chem. Soc.* **2016**, *138*, 617.

(55) Lubert-Perquel, D.; Salvadori, E.; Dyson, M.; Stavrinou, P. N.; Montis, R.; Nagashima, H.; Kobori, Y.; Heutz, S.; Kay, C. W. M., Identifying triplet pathways in dilute pentacene films. *Nat. Commun.* **2018**, *9*, 4222.

(56) Lehnherr, D.; Murray, A. H.; McDonald, R.; Tykwinski, R. R., A modular synthetic approach to conjugated pentacene di-, tri-, and tetramers. *Angew. Chem. Int. Ed.* **2010**, *49*, 6190.

(57) Marshall, J. L.; Lehnherr, D.; Lindner, B. D.; Tykwinski, R. R., Reductive Aromatization/Dearomatizationand Elimination Reactions to Access Conjugated Polycyclic Hydrocarbons, Heteroacenes, and Cumulenes. *ChemPlusChem* **2017**, *82*, 967.

(58) Zirzlmeier, J.; Casillas, R.; Reddy, S. R.; Coto, P. B.; Lehnherr, D.; Chernick, E. T.; Papadopoulos, I.; Thoss, M.; Tykwinski, R. R.; Guldi, D. M., Solution-based intramolecular singlet fission in cross-conjugated pentacene dimers. *Nanoscale* **2016**, *8*, 10113.

(59) Basel, B. S.; Zirzlmeier, J.; Hetzer, C.; Reddy, S. R.; Phelan, B. T.; Krzyaniak, M. D.; Volland, M. K.; Coto, P. B.; Young, R. M.; Clark, T.; Thoss, M.; Tykwinski, R. R.; Wasielewski, M. R.; Guldi, D. M., Evidence for Charge-Transfer Mediation in the Primary Events of Singlet Fission in a Weakly Coupled Pentacene Dimer. *Chem* **2018**, *4*, 1092.

(60) Overall, the electronic coupling is even in A and B too weak to support appreciable Davydov splitting in the absorption spectra.

(61) The *gauche*-to-*trans* ratios in **A-D** were determined by using the respective fluorescence quantum yields and by relating these

exclusively to the *trans* conformers. Notable is use of the fluorescence quantum yield of **TIPSPc** with 20% in benzonitrile. This approach is justified by the different rates of singlet excited state deactivation in the non-to-poorly fluorescent *gauche* conformers relative to the strongly fluorescent *trans* conformers.

(62) In the TAS of **D** a small bleach corresponding to stimulated emission ( $\approx$ 750 nm) can be seen. We attribute the weak coupling and the resulting high fluroescence quantum yield and slow (S1S<sub>0</sub>)<sub>SOLV</sub> deactivation, compared to the remaining dimers, to be the cause. This bleach shows no additional kintecs, etc..

(63) Please note that despite the competitive pathways, which govern the parallel  ${}^{1}(T_{1}T_{1})$  population in **A** and **B**, the overall  $(S_{1}S_{0})_{SOLV}$  deactivation is appreciably faster than in **C** and **D**.

(64) We have performed target analysis, without any kind of normalization on the GSB, with three species rather with four species for dimers **A** and **B**; eliminating one species. A complete deconvolution to a pure singlet and triplet excited state was, however, not realized:  $(S_1S_0)_{SOLV}$ , for example, carries triplet signature, on one hand, and the  ${}^1(T_1T_1)$  features singlet character, on the other hand. In addition "artifacts" (downwards pointing peaks at roughly 510 nm) arose, further signalizing that deconvolution was not realized. Furthermore, we performed target analysis, using three and four species, but with a sequential and parallel deactivation pathway, in both cases. Again, no meaningful deconvolution was obtained. Further details are locasted in the Supporting Information in Figure S29 and S30.

(65) The population kinetics illustrates the overall population of the each species at a given time. Rates, efficiency, and nature (linear or parallel fashion) for their population and depopulation are also considered. This explains why the population of  ${}^{1}(T_{1}T_{1})$  in **A** (Figure 6, bottom-right) and **B** (Supporting Information, Figure S19, bottom-right) extends to the kinetics of  $(S_{1}S_{0})_{SOLV}$  and  $(S_{1}S_{0})_{(T1T1)}^{CT}$ , as both species contribute parallel to its formation.

(66) Decay associated spectra (DAS), in general, show the rise or decay of signals, which are followed by the transition from one species to another and, therefore, are able to illustrate the differences at every wavelength. Features that are pointing upwards convey that the following species has less or no features. Features pointing downwards mean that additional features will appear in the next species.

(67)  ${}^{1}(T_{1}T_{1})$  quantum yield determination was based on the normalization of the spectra at the ground state bleaching using Glotaran target analysis, on one hand, and the ratio of singlet and triplet excited state molar extinction coefficients and absorptions, on the other hand.

(68) We have performed target analyses of the ns-TAS data, that is, starting with about a 1 nanosecond time delay, using the gauche-to-trans ratios determined in steady-state experiments – vide supra. This selection is based on the fact that the intersystem crossing/fluorescence dynamics in the trans-conformer are on the order of tens of nanoseconds. Of great relevance is the fact that we have obtained very good fits of the ns-TAS experiments, which are shown in the supporting information (Figures S27 and S28), in cases that the strongly fluorescent trans conformer is present in more than 10%. In contrast, 10% or less of the trans conformer leads to unreasonable fitting results.

(69) The weaker electronic coupling in  $\mathbf{D}$  led to an overall lower quality of the spectra, hence shifting our focus on  $\mathbf{A}$ .

(70) The possible formation of aggregates of **D** at low temperatures might explain why  ${}^{5}(T_{1}T_{1})$  was detected in trEPR measurements, albeit with lower quality, while in ns-TAS measurements only a small amount of triplet excited state via intersystem crossing is detected.





