Singlet fission in pentacene dimers

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Singlet fission (SF) has the potential to supersede the traditional solar energy conversion scheme by means of boosting the photon-to-current conversion efficiencies beyond the 30% Shockley–Queisser limit. Here, we show unambiguous and compelling evidence for unprecedented intramolecular SF within regioisomeric pentacene dimers in room-temperature solutions, with observed triplet quantum yields reaching as high as $156 \pm 5\%$. Whereas previous studies have shown that the collision of a photoexcited chromophore with a ground-state chromophore can give rise to SF, here we demonstrate that the proximity and sufficient coupling through bond or space in pentacene dimers is enough to induce intramolecular SF where two triplets are generated on one molecule.

acene oligomers | excited states | singlet fission | multireference perturbation theory | time-resolved spectroscopy

Singlet fission (SF) is a spin-allowed process to convert one singlet excited state into two triplet excited states, namely a correlated triplet pair (1). The ability to effectively implement SF processes in solar cells could allow for more efficient harvesting of high-energy photons from the solar spectrum and allow for the design of solar cells to circumvent the Shockley–Queisser performance limit (2). Indeed, several recent studies have demonstrated remarkably efficient solar cell devices based on SF (3–6).

One requirement that needs to be met to achieve SF is that the photoexcited chromophore in its singlet excited state must share its energy with a neighboring ground-state chromophore. As such, the potential of coupled chromophores to afford two triplet excited states via SF has been elucidated in, for example, a tetracene dimer with an SF yield of around 3% (3, 7). Additionally, past experiments in single-crystal, polycrystalline, and amorphous solids of pentacene have documented that the efficiency of SF relates to the electronic coupling between these two chromophores (8, 9). Hence, molecular ordering in terms of crystal packing, that is, proximity, distances, orbital overlap, etc., is decisive with respect to gaining full control over and to fine-tuning interchromophoric interactions in the solid state (10, 11). Of equal importance are the thermodynamic requirements, namely that the energy of the lowest-lying singlet absorbing state must match or exceed the energy of two triplet excited states ($S_1 \geq 2T_1$) (11). In light of both aspects, hydrocarbons such as acenes—tetracene, pentacene, hexacene—and their derivatives are at the forefront of investigations toward a sound understanding and development of molecular building blocks for SF. In tetracenes, the singlet- and triplet-pair energy levels are nearly degenerate ($S_1 = 2T_1$), leaving no or little standard enthalpy of reaction for SF (12). In solution, the latter is, however, offset by sizable entropy rendering the process rather slow and, thus, inefficient (13). In addition, the low SF yield relates to the dimer geometry. Its nature hinders electronic coupling through space, leaving only through-bond coupling effective. The latter is, however, insufficient to enhance the SF rate (7, 14). In stark contrast, the relaxed triplet excited state in pentacenes has significantly less than half the energy of the singlet excited state. In turn, the thermodynamic SF requirement, that is ($S_1 \geq 2T_1$), is fulfilled for pentacenes rendering this process exothermic and unidirectional (13). Finally, from SF in hexacenes two triplet

excited states plus a certain amount of phonons are derived as the main relaxation products. In other words, the dissipated heat leads to a decrease in SF yields and rates (15).

In terms of exploiting SF for improving device performances, e.g., hybrid solar cells, it is necessary to efficiently dissociate correlated triplet pairs as they are formed, to overcome triplet–triplet annihilation (5, 16). Rapid injection of electrons into fullerenes, perylene diimides, colloidal nanocrystals, semiconductor substrates, etc. suggests a viable strategy. If successful, two charge carriers might be produced per absorbed photon and the photocurrents of the device can reach external quantum efficiencies of more than 100% (5, 17, 18).

A provocative debate has been ignited about the mechanism of SF at the molecular level (19, 20). Controversy exists around the electronic states that are involved in the process, the coupling among them, and the effective nuclear dynamics (14, 21–27). Two contrasting SF mechanisms have been traditionally postulated—the direct and the two-step mechanism. These mechanisms differ in the number and nature of the electronic states that are involved in the SF process. For the direct mechanism, the nonradiative relaxation of the initially populated bright state proceeds via a correlated triplet pair state of singlet character—sometimes called multiexcitonic (ME) state—which then dissociates into two separated triplet excited states (28). For the two-step mechanism, the relaxation of the bright state occurs via an intermediate charge transfer (CT) state to the ME state. As in the direct mechanism, the ME state eventually allows the two triplet excited states involved to separate and undergo separate spin relaxation (11, 21–23). Recent works have, however, challenged these traditional viewpoints on the SF mechanism and several new models have been proposed. In particular, it has been suggested (13, 29, 30) that the initial excitation produces a coherent superposition of the lowest-lying absorbing state and the ME state, with the latter splitting into two separated triplet states after

Significance

In the present work, we show compelling evidence for the unprecedented intramolecular singlet fission at room temperature and in dilute solutions within a set of three different regioisomeric pentacene dimers. Pump–probe experiments, which were complemented by theoretical calculations using high-level ab initio multireference perturbation theory methods, corroborate triplet quantum yields as high as $156 \pm 5\%$. To this end, electronic couplings between the two pentacenes in the dimers, by virtue of through-bond or through-space interactions, are decisive in tuning the rates of singlet fission.

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Fig. 1. (Upper) Synthesis of pentacene dimers **o-2**, **m-2**, and **p-2**. (Lower) SF mechanism.

spectra. All of these observations are in excellent agreement with previously reported singlet and triplet excited-state absorptions of TPC in solution (31). When using singlet molar extinction coefficients of $8.3 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ at the 447-nm maximum, in combination with triplet molar extinction coefficients of $1.45 \times 10^5 \text{ M}^{-1}\text{cm}^{-1}$ at the 498-nm maximum, the computed TPC triplet quantum yield is 16%. For this analysis, ground-state extinction coefficients of $3.3 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ at the 641-nm minimum and $1.6 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ at the 587-nm minimum were used.

Next, the three pentacene regioisomers **o-2**, **m-2**, and **p-2** were examined in solvents of varied polarity (i.e., toluene, THF, and benzonitrile) with photoexcitation at either 610 or 656 nm as shown in Fig. 2 as well as *SI Appendix, Figs. S19, and S20*, respectively, and the same low photon flux described for TPC—vide

supra. The *meta*-isomer (**m-2**) was examined in benzonitrile and at time delays as short as 0.5 ps singlet excited-state features are discernible in the form of maxima at 456, 510, 582, and 670 nm. In contrast with the slow intersystem crossing seen for TPC, these singlet excited-state features are rapidly replaced by strong absorptions, which are concentration independent in the range from 1.0×10^{-5} to $1.0 \times 10^{-4} \text{ M}$ and, thus, strictly unimolecular. These strong absorptions, which appear at time delays of around 200 ps, bear great resemblance with that of the triplet excited state of **m-2**. In particular, maxima at 477, 510, 855, and 972 are complemented by minima at 610 and 664 nm and are a perfect match to the photosensitized triplet excited-state spectra of the dimer **m-2** (vide infra).

Fig. 2. SF in pentacene dimer *m-2*. (Upper Left) Chemical structure. (Upper Right) Differential absorption spectra (visible and near-infrared) of the spectra shown in the lower right with time delays of 2.0 ps (black) and 190.0 ps (gray). (Lower Left) Time absorption profiles of the spectra shown in the lower right at 456 nm (black), 510 nm (red), 582 nm (orange), and 664 nm (gray) illustrating the dynamics of the singlet excited-state formation followed by the singlet to triplet transformation in the form of SF, and triplet–triplet annihilation. (Lower Right) Differential absorption changes (visible and near-infrared) obtained upon femtosecond pump–probe experiments (610 nm) of *m-2* (3.5×10^{-5} M) in argon-saturated benzonitrile at room temperature with several time delays between 0 and 5,500 ps.

A particularly striking effect observed for *m-2* during the accelerated triplet excited-state formation is the long wavelength blue shift, from 670 to 664 nm, that is accompanied by a $155 \pm 10\%$ intensification of the transient bleaching. This effect is notable upon 610-nm excitation rather than 656-nm excitation. If the ground-state absorption depletion in this spectral region were quantitative for the singlet excited state, this infers more than one triplet excited state is formed per dimer. Nevertheless, the triplet excited state is surprisingly short-lived and decays with concentration-independent kinetics. The only plausible *modus operandi* is based on intramolecular triplet–triplet annihilation governed by the unique scenario that more than one triplet excited state is localized on each dimer. Multiwavelength analyses attest that the triplet excited-state formation is biexponential in benzonitrile, and it features two distinct steps with CT (τ_{CT}) and SF (τ_{SF}) lifetimes of 16.4 ± 1.9 and 63.0 ± 6.3 ps, respectively. From the study of solvent dependence *vide infra*, we postulate the involvement of an additional state that possesses an intramolecular CT character and mediates the transition to the ME state (either directly or virtually). A closer look at the transient absorption spectra taken at delay times of 80–300 ps reveals a 445-nm shoulder, which is likely to stem from the CT state (SI Appendix, Fig. S21). Once formed, the triplet excited-state decay is monoexponential for *m-2*, with a rather short triplet–triplet annihilation lifetime (τ_{TTA}) of 2.2 ± 0.1 ns.

Turning our attention to the *para*- and *ortho*-isomers (*p-2* and *o-2*), their singlet excited-state features are discernible immediately after photoexcitation in benzonitrile. For *p-2*, these are maxima at 462 and 1,117 nm and a minimum at 686 nm (SI Appendix, Fig. S19). The features of the singlet state of *p-2*, however, transform even faster than in *m-2* into the triplet excited-state maxima at 475 and 508 nm as well as its minimum at 670 nm. From multiwavelength analyses we derive lifetimes for the growth and decay of the triplet excited state as 2.7 ± 1.0 and 17.3 ± 1.3 ps, respectively. It is likely that the dramatic difference in behavior in *p-2* versus *m-2* kinetics derives from enhanced through-bond electronic coupling in the ground state of the *para*-isomer as a means to impact both SF and triplet–triplet annihilation (32, 33). As such, the electronic coupling matrix elements as the decisive factor to govern CT are larger in *p-2* than in *m-2* (32). For *o-2*, the 472- and 507-nm

fingerprints for the singlet and triplet excited states, respectively, evolve in pump–probe experiments. Here, in contrast with *p-2* and *m-2*, strong through-space couplings between the two pentacene moieties affect the triplet excited-state kinetics—both in terms of formation and decay—and deconvolution results in upper values of 0.5 ± 0.2 ps and 12.0 ± 0.3 ps, for formation and decay, respectively. The short-lived nature of the triplet excited states in *p-2* and *o-2* hampers a meaningful triplet excited-state quantum yield determination. The latter is corroborated in the geometry-optimized structures (SI Appendix, Fig. S27), which reveal, on one hand, the coplanarity between the two pentacenes in *p-2* and *m-2*, and, on the other hand, only sizable through-space couplings in *o-2*.

Triplet Quantum Yield and SF Yield Determination. Using the differential absorption changes at 610 and 664 nm for *m-2*, for which ground-state extinction coefficients of 2.8×10^4 and 5.3×10^4 M $^{-1}$ ·cm $^{-1}$ have been determined, the singlet and triplet molar extinction coefficients are calculated as 7.9×10^4 and 1.4×10^5 M $^{-1}$ ·cm $^{-1}$, respectively. In recent studies, it was hypothesized that the bleaching at 610 nm is elusive for the triplet excited state, whereas that the bleaching at 664 nm serves as an internal standard to calibrate the singlet excited state (31). Because the *meta*-dimer *m-2* has only very weak ground-state absorption at 456 nm, the observed amplitude of differential absorption at 456 nm and 0.5 ps relates entirely to the singlet excited-state concentration formed after excitation. In doing so, differential absorption changes of 0.028 a.u. at 456 nm and 0.0726 a.u. at 510 nm were converted into a triplet quantum yield ($\Phi_{Triplet}$) of $145 \pm 10\%$. This high triplet quantum yield along with its ultrafast formation provides strong evidence that the triplet excited state for *m-2* forms by intramolecular SF between the two pentacenes. The triplet quantum yield for *p-2* was determined by extrapolation to time zero as 130%.

Taking the ratio from 510/456 nm as an indicator for the respective quantum yield, we note that it increases from toluene ($126 \pm 3\%$) to THF ($132 \pm 2\%$) and to benzonitrile ($145 \pm 10\%$). We surmise from this trend that the mediating step, which dictates the triplet excited-state formation, features CT-type character and this operates through-bond for dimer *m-2*. Such a postulate fits well

pronounced stabilization of the CT states which locates them ~ 0.35 eV above the lowest-lying LE and ME states in **m-2** (*SI Appendix*). Taking into account the experimentally observed solvent dependence of the triplet yield and the kinetics, our results indicate that CT states participate in SF either as virtual states via a superexchange mechanism (14) or directly if nuclear relaxation of the lowest-lying absorbing state facilitates population of the CT state via internal conversion. In addition to the characterization of the excited singlet states, we also have characterized the excited triplet states of **m-2**. The results in *SI Appendix, Table S3* reveal a strong $T_1 \rightarrow T_0$ excitation at 2.43 eV, which corresponds to the pronounced triplet feature at 510 nm observed in the transient absorption spectra (Fig. 3).

Conclusions

In conclusion, we used pump-probe experiments and complementary theoretical calculations using multireference perturbation theory to corroborate for the first time, to our knowledge, intramolecular SF in pentacene dimers. Three regioisomeric pentacene dimers, in which the two pentacenes are linked via a phenylene spacer in *ortho*-, *meta*-, or *para*-position—**o-2**, **m-2**, and **p-2**—feature triplet quantum yields as high as $156 \pm 5\%$ mediated either by through-space or through-bond electronic couplings in the ground- and excited state. As recently hypothesized, mixing between the singlet excited state and the CT state might be helpful in terms of overcoming the activation barrier (14). It is in **m-2** where the right balance between triplet formation and triplet decay optimizes the SF yield. Such an efficient SF reaches well beyond the 3% mark found in tetracene dimers, for which, incidentally, it is the *para*-isomer that revealed the highest SF yields (7). The demonstrated depletion of the ground state, the quantitative analysis of forming more than one triplet excited state per singlet, and the very low concentrations used corroborate the intramolecular nature of SF. Although our studies demonstrated that the singlet excited states in all three different

pentacene dimers are rapidly and efficiently converted to triplet excited states via SF, this is considered only as a preliminary step toward realizing SF enhanced devices. In this context, a sound platform en route toward charge separation with suitable electron acceptors and charge collection at suitable electrodes is forming.

Materials and Methods

The synthesis of **o-2**, **m-2**, and **p-2**, materials, general methods, and computational details are described in *SI Appendix*.

For the photophysical characterization (see *SI Appendix* for details), the samples were placed in fluorometric cuvettes with different pathways and, when necessary, purged with argon. Steady-state UV-vis absorption spectra were acquired at room temperature (RT) using a Perkin Elmer Lambda 2 spectrometer. Steady-state fluorescence spectra were carried out at a FluoroMax3 spectrometer from Horiba in the visible detection range (RT) and at a FluoroLog3 spectrometer from Horiba in the near infrared. Femtosecond (fs) transient absorption 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).

Details of the calculations can be found in the *SI Appendix*. Briefly, the geometries of **o-2**, **m-2**, and **p-2** were optimized using density functional theory. In all systems, *t*-Bu₃Si- groups have been modelled using H₃Si- to ensure computational tractability. For the different systems investigated, vertical excitation energies were calculated at the CASPT2/CASSCF/ANO-SVDZP level of theory (35, 36). In all calculations, an active space of 8 electrons in 8 orbitals (comprising the HOMO-1, HOMO, LUMO, and LUMO+1 orbitals per pentacene unit; see *SI Appendix, Fig. S26*) was used.

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