Tetracene Dimers: A Platform for Intramolecular Down- and Up-conversion

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ABSTRACT: Photon energy conversion can be accomplished in many different ways, including the two opposing manners, down-conversion (i.e., singlet fission, SF) and up-conversion (i.e., triplet-triplet annihilation up-conversion, TTA-UC). Both processes have the potential to help overcome the detailed balance limit of single-junction solar cells. Tetracene, in which the energies of the lowest singlet excited state and twice the triplet excited state are comparable, exhibits both down- and up-conversion. Here, we have designed meta-diethynylphenylene- and 1,3-diethynyladamantyl-linked tetracene dimers, which feature different electronic coupling, to characterize the interplay between intramolecular SF (intra-SF) and intramolecular TTA-UC (intra-TTA-UC) via steady-state and time-resolved absorption and fluorescence spectroscopy. Furthermore, we have used Pd-phthalocyanine as a sensitizer to enable intra-TTA-UC in the two dimers via indirect photoexcitation in the near-infrared part of the solar spectrum. The work is rounded off by temperature-dependent measurements, which outline key aspects of how thermal effects impact intra-SF and intra-TTA-UC in the different dimers.
**Introduction**

Solar energy is essential if an ever-increasing demand for energy is to be satisfied. While abundant, the solar radiation reaching the earth’s surface covers a broad range of energies, from high-energy ultraviolet, through the visible region, to low-energy infrared. Efficient solar energy capture and conversion are, therefore, challenging. For photons with energies well-above the bandgap of the absorbing material, excess energy is lost predominantly as heat. In contrast, photons with energies below the optical bandgap are not absorbed at all. Therefore, single-junction solar cells are limited to a maximum performance of 33% known as the detailed balance limit. Both down- and up-conversion have the potential to increase solar-energy conversion efficiencies beyond current limitations.

Singlet fission (SF), a down-conversion process, describes the splitting of one excited exciton into a pair of triplet excitons after the absorption of a high-energy photon. SF is spin-allowed and fast, as the correlated triplet pair $|T_1 \text{T}_1\rangle$ is of overall singlet multiplicity. To date, several SF mechanisms have been reported, and, in general, these studies describe either an incoherent or coherent process for SF.

Considering the incoherent scenario, one differentiates between a direct and a two-step mechanism. If coupling between $(S_0 S_0)$ and $|T_1 \text{T}_1\rangle$ is strong, $|T_1 \text{T}_1\rangle$ will evolve directly from $(S_0 S_0)$. In the two-step mechanism, SF proceeds via an intermediate state that mediates the coupling between $(S_0 S_0)$ and $|T_1 \text{T}_1\rangle$. The intermediate is usually a charge transfer (CT) state, and depending on the relative energy of the CT state with respect to $(S_0 S_0)$ and $|T_1 \text{T}_1\rangle$, it acts as either a real (observable) intermediate or as a virtual state. This case is often referred to the superexchange mechanism. If the energy of the CT state drops significantly below that of $(S_0 S_0)$ or $|T_1 \text{T}_1\rangle$ it is likely to be a trap, and, in turn, the formation of $|T_1 \text{T}_1\rangle$ does not occur as direct recovery of the ground state dominates.

When turning to the coherent scenario, a superposition of $(S_0 S_0)$, $|T_1 \text{T}_1\rangle$, and the CT state is formed upon photoexcitation. Strong mixing between all three states is realized if the energetic differences are small. The composition of the coherent superposition changes as a function of time, and different products evolve as a result of dephasing. Such products range from exciters to symmetry-breaking charge-separated states and $|T_1 \text{T}_1\rangle$.

SF would not be complete without the decoherence of $|T_1 \text{T}_1\rangle$, which generates two independent triplet excited states $(T_1 + T_1)$. Decoherence requires a weakening of the coupling between the two triplet excited states in $|T_1 \text{T}_1\rangle$. En-route towards $(T_1 + T_1)$ the quintet form of the correlated triplet pair $|T^2 \text{T}_1\rangle$ is the key intermediate. Time-resolved electron paramagnetic resonance (TREPR) is essential to corroborate the involvement of $|T^2 \text{T}_1\rangle$. Comprehension of the decoherence is linked to the $|T^2 \text{T}_1\rangle$ energy gap. However, electronic interactions between the two triplet excited states in $|T^2 \text{T}_1\rangle$ are weaker than in $|T_1 \text{T}_1\rangle$. This energy difference defines the binding energy, which needs to be overcome for the transformation of $|T(T_1 T_1)\rangle$ to $(T_1 + T_1)$.

In the strong coupling regime, exchange interactions are large and suppress $|T(T_1 T_1)\rangle-|T(T_1 T_1)\rangle$ mixing. Consequently, the two triplet excited states remain bound. In the weak coupling regime, mixing of $|T(T_1 T_1)\rangle-|T(T_1 T_1)\rangle$ is feasible, and electronic coupling takes place, albeit both triplet excited states will remain spin-entangled. Eventually, decoherence to produce $(T_1 + T_1)$ is achieved via diffusion of the triplet excited states, interaction with the environment, or nuclear rearrangement.

The thermodynamic requirement for SF necessitates that the energy of the first singlet excited state $(S_1)$ must exceed, or at least approximate, twice that of the first triplet excited state $(T_1)$. Exothermic SF, such as observed in pentacene, is typically fast and efficient, while the energy barrier for triplet-triplet annihilation up-conversion (TTA-UC), the reverse process, renders the fusion of the resulting triplet excitons to produce $(S_2 S_0)$ unfavorable. Such an exoergic process comes, however, at the expense of thermal losses that lead to overall inefficient solar energy conversion. Furthermore, low triplet excited state energies complicate use in, for example, photovoltaics. Conversely, materials that feature isoelectronic or slightly endergonic SF, such as tetracene, are suitable for emerging applications.

Notably, if SF is isoelectronic, dissociation of the correlated triplet pair into free triplet excited states may be hindered by thermally activated triplet-triplet annihilation up-conversion (TTA-UC), a competitive process that yields a higher-lying singlet excited state.

TTA-UC is the reverse process to SF and involves the fusion of two low-energy triplet excited states to produce one high-energy singlet excited state. For TTA-UC to occur, the energy of the singlet excited state of the annihilator must be lower than twice the energy of the triplet excited state. Based on this parameter, polycyclic aromatic hydrocarbons, including anthracene, tetracene, perylene, and their derivatives have been explored as annihilators in combination with triplet sensitizers that undergo photoexcitation at long wavelengths. TTA-UC is typically a diffusion-controlled, bimolecular process, and photo-sensitized TTA-UC measurements are typically conducted in the high-concentration regime. Seminal work on TTA-UC using dimeric and oligomeric annihilators confirms that intramolecular TTA-UC (intra-TTA-UC) helps to circumvent the need for high concentrations. On the other hand, a definitive scheme describing the process of intra-TTA-UC and how it affects the efficiency of TTA-UC is still lacking.

Intramolecular SF (intra-SF) in molecular dimers and oligomers is at the forefront of recent investigations of this process. For dimers, the fate of $|T(T_1 T_1)\rangle$ is governed by the electronic coupling between the two chromophores. Control over the coupling is realized by different spacer motifs. In strongly coupled dimers, $|T(T_1 T_1)\rangle-|T(T_1 T_1)\rangle$ mixing is impossible and $|T(T_1 T_1)\rangle$ deactivates via fast TTA. In contrast, weakly coupled dimers allow for $|T(T_1 T_1)\rangle-|T(T_1 T_1)\rangle$ mixing and subsequent decoherence to produce $(T_1 + T_1)$ (an essential event for effective SF). Considering that the initial product of intra-SF, namely $|T(T_1 T_1)\rangle$, bears two coupled triplet excited states, $|T(T_1 T_1)\rangle$ is a promising starting point to...
investigate intra-TTA-UC. Thus, fine-tuning of the electronic coupling by means of different spacer motifs allows for investigating the interplay between the intertwined processes of SF and TTA-UC. Importantly, this becomes imperative in the design of advanced materials.

Acenes — such as anthracene, tetracene, pentacene - and their derivatives are widely used as building blocks to probe multiexcitonic processes like SF and TTA-UC. In anthracene and pentacene, the energy of $S_1$ is lower or higher than twice the energy of $T_1$, respectively, which renders them suitable for the individual investigation of either TTA-UC or SF, respectively. In contrast, the $S_1$ energy of tetracene is close to twice the energy of $T_1$, and both SF and TTA-UC are thermodynamically feasible. Previous investigations have documented that tetracene is indeed capable of undergoing inter- and intramolecular SF46,47,63,64,65,66 and TTA-UC55,56,57,66. To the best of our knowledge, however, studies regarding the interplay between SF and TTA-UC remain rare. To unravel the interplay between SF and TTA-UC, rigidly linked tetracene dimers are a promising platform as they allow for the control of electronic coupling by synthetic design.55,64,67,66,69

In analogy to our previous work on intra-SF in pentacene dimers,34,67,70 we designed two covalently linked tetracene dimers that are rigidly bridged by either a cross-conjugated meto-diethylphenylene (mPhTc) or a non-conjugated 1,3-diethynyladamantyl spacer (mAdTc). Importantly, the through-bond electronic coupling is dictated by the spacer, while the geometrical and spatial arrangements remain nearly identical. Intra-SF and intra-TTA-UC are unequivocally demonstrated for mPhTc and mAdTc through a combination of steady-state and time-resolved measurements. Using Pd(II)1,4,8,11,15,18,22,25-octabutoxyphthalocyanine (PdPc) as the photosensitizer, we find that both mPhTc and mAdTc give rise to more efficient TTA-UC than the corresponding monomers PhTc and AdTc, confirming the intramolecular nature of TTA-UC. In particular, mPhTc shows the highest UC efficiency regardless of the concentration. Our results underpin the significance of inter-chromophore electronic coupling in intra-SF and intra-TTA-UC as we highlight the opposing dependencies of intra-SF and intra-TTA-UC on the inter-chromophore coupling and provide a crucial guideline for designing molecules that feature either efficient dissociation of $^1$(T:T) or efficient up-conversion from $^3$(T:T) via TTA-UC.

**Results and Discussion**

**Synthesis** The cross-conjugated and non-conjugated tetracene dimers mPhTc and mAdTc and the corresponding tetracene monomers PhTc and AdTc were synthesized through a stepwise substitution of 5,12-naphthacenequinone by adapting protocols used to form tetracene71 and pentacene dimers (Scheme 1). Briefly, addition of lithiated trispropylsilylethylene ($i$Pr3Si-C≡C-Li) to a suspension of 5,12-naphthacenequinone in dry tetrahydrofuran (THF) at −78 °C followed by in situ trapping of the resulting alkoxide with Mel affords the common building block. Nucleophilic addition of a lithiated mono- or diyne to ketone 1, followed by SnCl4-mediated reductive aromatization produced the desired products. The products were purified by column chromatography and isolated in acceptable to good yield as scarlet solids. The structures of PhTc and mPhTc are confirmed by X-ray crystallography (Supporting Information).

**Intramolecular Electronic Coupling** The four tetracene derivatives were probed by quantum chemical calculations and steady-state absorption spectroscopy in different solvents to characterize the impact of the spacer on intramolecular interactions in the ground state. We used two different configuration interaction (CI) expansions to investigate different aspects of the systems. AM1 UNO-CIS calculations (Supporting Information) are the most suited for calculating energies of excited states, but only give information on singlet and triplet states because they only include single excitations from the ground state. They show that $S_1$ (2.457 eV, 504.7 nm) in AdTc becomes $S'$ and $S''$ (2.424 and 2.486 eV, 511.4 and 498.7 nm) in mAdTc. $S'$ and $S''$ are separated by 0.062 eV in mAdTc, compared to 0.128 eV in mPhTc because of stronger electronic coupling between the tetracene moieties in mPhTc.73 AM1-CISD

![Scheme 1. Synthesis of tetracene dimers mPhTc and mAdTc as well as the corresponding monomers PhTc and AdTc.](image)
calculations (Supporting Information) were used to investigate coupling between the various (T1;T1) states of different multiplicity because the extra doubly excited states used in the calculation allow for states of higher multiplicity to be observed than in the CIS calculations. However, these doubly excited states stabilize the ground state strongly and lead to calculated excitation energies that are too high. Nonetheless, energy differences between the states of interest are reliable. For AM1-CISD, the dependence of coupling on the spacer was demonstrated by calculating the splitting between different spin multiplicities of (T1;T1), namely, \( ^1(T_1;T_1), ^3(T_1;T_1) \), and \( ^5(T_1;T_1) \). In mAdTc, these three states all occur at the same energy (4.022 eV), which is 0.34 and 0.27 eV above the strongly absorbing \( ^1 \) (3.680 eV at AM1-CISD) and \( ^2 \) (3.752 eV at AM1-CISD) states, respectively. In contrast, the calculated excitation energies in mPhTc are 4.065, 4.066, and 4.108 eV for the \( ^1(T_1;T_1), ^3(T_1;T_1) \), and \( ^5(T_1;T_1) \) states, respectively.

\( ^1(T_1;T_1) \) in mPhTc is 0.39 and 0.26 eV higher in energy than \( ^1 \) (3.679 eV at AM1-CISD) and \( ^2 \) (3.806 eV at AM1-CISD), respectively. The splitting between \( ^1(T_1;T_1) \) and \( ^3(T_1;T_1) \) is 0.04 eV in mPhTc, confirming the hypothesis that inter-chromophore coupling is stronger in mPhTc than in mAdTc. This is entirely consistent with the cross-conjugated \( \pi \)-system linking the chromophores in mPhTc with coupling caused by electronic delocalization, compared to the “insulating” alkane-like path in mAdTc.

Note that AM1 UNO-CIS calculations have proven to be very reliable for excitation energies in general, and that AM1-CISD successfully treats the splitting of “equivalent” singlet, triplet, and quintet states, so that we expect the results to be reliable.

At first glance, similar steady-state absorption spectra are found for all four derivatives in both toluene and benzonitrile (Figures 1 and S11 and Table S2). In particular, high-energy (300–400 nm) transitions to populate higher singlet excited states go hand-in-hand with low-energy transitions (450–600 nm) to populate the first singlet excited state. Distinct vibrational fine structure involving the transitions 0-0, 0-1, 0-2, etc., is observed in the region of 450–600 nm. In toluene, for example, AdTc displays absorption maxima at 464, 496, and 533 nm. The absorption features of PhTc are shifted bathochromically by 0.047 eV in comparison to AdTc and show slightly higher extinction coefficients as a result of extended \( \pi \)-conjugation and better electronic delocalization. More significant differences are observed when comparing the steady-state absorption spectra of the dimers mAdTc and mPhTc. The spectrum of mAdTc represents a linear sum of two AdTc monomers, both in terms of absorption maxima and extinction coefficients. For mPhTc, the absorption maxima are further redshifted than for PhTc and the spectrum does not represent the linear sum of two PhTc monomers. To be precise, the intensity ratios of the vibronic peaks \( I_{0-0}/I_{0-1} \) are 1.58 and 1.41 for mPhTc and PhTc, respectively in toluene. These observations confirm that the intramolecular electronic coupling is appreciably stronger in mPhTc than in mAdTc.

Intramolecular Down-conversion Femtosecond and nanosecond transient absorption spectroscopy (fs-TAS and ns-TAS) have been performed based on photoexcitation at 480 nm. The singlet excited state \( (S_1) \) of the monomer PhTc in toluene forms immediately after photoexcitation and is characterized by a dominant, excited-state absorption (ESA) in the range of 400–500 nm, a sharp ground-state bleaching (GB) overlaid with stimulated emission (SE) from 500–600 nm and a broad ESA in the 800–1400 nm range (Figure 2). Essentially the same features evolve for \( (S_1) \) of monomer AdTc on the fs-TAS timescale (Figure S12).

Raw data from fs-TAS experiments of PhTc and AdTc are best fit by Global Analysis with a sequential kinetic model based on two species (Figures 2 and S12-14). On this basis, we assign these two species as \( (S_1) \) and \( (S_1)_{rel} \), namely \( (S_1) \) before and after relaxation to the minimum of the \( (S_1) \) potential energy surface via structural relaxation and solvent reorganization. In contrast to the spectroscopic features, which are independent of solvent polarity, the lifetime of \( (S_1) \), varies as a function of solvent (Table 1). In benzonitrile, the lifetimes are 86.0 ps for PhTc and 207.4 ps for AdTc, while they are dramatically reduced to 2.7 ps for PhTc and 121.5 ps for AdTc in toluene. We rationalize this observation by the greater viscosity of benzonitrile, which slows down structural relaxation and solvent reorganization. The differences between PhTc and AdTc stem from the lower structural flexibility of PhTc due to \( \pi \)-conjugation. Once formed, \( (S_1)_{rel} \) decays predominantly via fluorescence with a quantum yield of around 70% for both monomers (vide infra). As the timescale of fs-TAS is insufficient to cover the full decay dynamics of \( (S_1)_{rel} \) for PhTc and AdTc, we turned to ns-TAS (Figures 3 and S15-S17). In the case of PhTc, \( (S_0) \) is quantitatively reinstated with a lifetime of ca. 10 ns (Table 1), which is in line with time-correlated single-photon counting (TCSPC) measurements (vide infra). In stark contrast, \( (S_1)_{rel} \) deactivation for AdTc is linked to the formation of another state that persists on the timescale of microseconds. This newly formed state is consistent with that generated in triplet-triplet sensitization measurements using N-methylfulleropyrrolidine (N-MFP) as a photosensitizer.
with photoexcitation at 387 nm. (Figures S18 and S20).

Thus, we assign it to the first triplet excited state (T1) of AdTc. In light of the high fluorescence quantum yield (70%), however, it is clear that only a small fraction of (S1)rel is transformed to (T1) via slow spin-forbidden intersystem crossing (ISC).

The picture is quite different for covalent dimers mPhTc2 and mAdTc2. For both dimers, three rather than two species are required to fit the fs-TAS data by means of Global Analysis employing a sequential kinetic model (Figures 4, S21-S23). The characteristics of the first and second species are assigned as singlet excited states before (S1;S0) and after relaxation (S1;S0)rel, respectively, consistent with (S1) and (S1)rel as observed for monomers PhTc and AdTc. ESAs between 400–500 and 600–1400 nm next to GSB in the range of 500–600 nm corroborate this assignment.76 The lifetime of (S1;S0)rel depends on both spacer and solvent (Table 1). For mPhTc2, the lifetimes of (S1;S0)rel are 46.9 ps in benzonitrile and 80.0 ps in toluene, respectively, while they are significantly longer for mAdTc2 with 369.1 ps and 886.6 ps in benzonitrile and toluene, respectively. The third species is characterized by attenuated broad singlet ESAs in the range of 600–1400 nm along with triplet ESAs at 523 nm for mPhTc2 and 502 nm for mAdTc2 (vide infra). The fact that the triplet-excited state signatures appear within hundreds of picoseconds indicates that population of the triplet excited-state occurs via fast spin-allowed intra-SF rather than slow spin-forbidden intersystem crossing (ISC).
Figure 2. Global Analysis of the fs-TAS raw data for PhTc following photoexcitation at 480 nm in argon-saturated toluene at room temperature. a) Heat map of fs-TAS raw data obtained from pump-probe experiments with time delays up to 5500 ps. b) Differential absorption spectra at various time delays. Insert: Time absorption profiles as well as corresponding fits of selected wavelengths (see the figure legend for details). c) Relative populations of the respective species with colors correlating with the evolution associated spectra (EAS). d) EAS of the deconvoluted species: the first species is the singlet excited state \( \left(S_1\right) \) (grey), and the second species is the relaxed singlet excited \( \left(S_1\right)_{rel} \) (red); note that \( \left(S_1\right)_{rel} \) cannot be completely deconvoluted on this timescale.
The fate of \((S,S_0)_{[T1T1]}^{CT}\) was determined in ns-TAS measurements. Global Analysis based on a sequential kinetic model with three species fits the ns-TAS raw data of both \(\text{mPhTc}_2\) and \(\text{mAdTc}_2\). (Figures 5 and S25–S27). Importantly, the third fs-TAS species and the first ns-TAS species are both the intermediate state \((S,S_0)_{[T1T1]}^{CT}\). The lifetime of \((S,S_0)_{[T1T1]}^{CT}\) is ca. 10 ns and is barely affected by solvent polarity and spacer (Table 1). The second and third species share the same spectral signatures, that is ESA at 502 nm along with GSB at 535 nm for \(\text{mPhTc}_2\), and ESA at 523 nm as well as GSB at 550 nm for \(\text{mAdTc}_2\) in toluene. To establish their identity, triplet-triplet sensitization measurements were performed, using \(N\)-methylfulleropyrrolidine (\(N\)-MFP) as the photosensitizer, with photoexcitation at 387 nm (Figures S1B, S2B, and S29). The spectral similarities between the sensitized \((T)\) and the spectroscopic signatures of both the second and third species in the ns-TAS are striking. We conclude that two different triplet excited states are formed for both \(\text{mPhTc}_2\) and \(\text{mAdTc}_2\). The lifetimes of the two different triplet species are 66.5 ns and 51.1 µs in toluene for \(\text{mPhTc}_2\) and 73.7 ns and 90.0 µs for \(\text{mAdTc}_2\). The fact that the triplet ESAs of both dimers decay bi-exponentially, instead of mono-exponentially as seen for the monomer \(\text{AdTc}\), is further evidence that a different mechanism, namely intra-SF, is responsible for the triplet excited-state population of \(\text{mPhTc}_2\) and \(\text{mAdTc}_2\). Thus, we assign the second species to the correlated triplet pair \((T,T_i)\), which has been formed directly from \((S,S_0)_{[T1T1]}^{CT}\) via fast spin-allowed intra-SF. To be precise, formation of \((T,T_i)\) occurs upon dephasing of \((S,S_0)_{[T1T1]}^{CT}\), induced by nuclear rearrangement or solvent relaxation. The third species, whose lifetime is fully consistent with any microsecond-lived free \((T_i)\), as observed for \(\text{AdTc}\), is ascribed to uncorrelated triplet excited state \((T_i + T_i)\) that is from decoherence of \((T_i,T_i)\).
Notably, the final step of intra-SF, that is \((T_1T_1')\) decoherence to produce two independent triplet excited states \((T_1+T_1')\), is observed in both strongly coupled \textit{mPhTc}\textsubscript{2} and weakly coupled \textit{mAdTc}\textsubscript{2}. The quintet form of \((T_1T_1')\), namely \((T_1T_1')\), is an intermediate along the dissociation of \((T_1T_1')\) in dimeric systems.\textsuperscript{12,18,34,35} The deconvolution of \((T_1T_1')\) and \((T_1T_1')\) failed as both states are indistinguishable by means optical spectroscopy. Thus, we refer to \((T_1T_1')\) rather than \((T_1T_1')\) or \((T_1T_1')\).\textsuperscript{18} The short lifetime of \((T_1T_1')\), especially for \textit{mPhTc}\textsubscript{2}, suggests that TTA is active. As a matter of fact, TTA represents a competitive deactivation pathway to the decoherence of \((T_1T_1')\).\textsuperscript{46,77}
Figure 4. Global Analysis of the fs-TAS raw data for mPhTc2 following photoexcitation at 480 nm in argon-saturated toluene at room temperature. a) Heat map of fs-TAS raw data obtained from pump-probe experiments with time delays up to 5500 ps. b) Differential absorption spectra at various time delays. Insert: Time absorption profiles as well as corresponding fits of selected wavelengths (see the figure legend for details). c) Relative populations of the respective species with colors correlating with the evolution associated spectra (EAS). d) EAS of the deconvoluted species: the first species is the singlet excited state (S1S0) (grey), the second species is the relaxed singlet excited state (S1S0)rel (red), and the third species is the intermediate state (S1S0)CT (blue); note that (S1S0)CT is not completely deconvoluted on this timescale.

Triplet quantum yields (ΦT) for mPhTc2 and mAdTc2 have been approximated by means of singlet oxygen quantum yields (Φo) (Supporting Information and Table 1). The (T1) energy of tetracene (1.21 eV) is higher than those of pentacene and molecular oxygen with ca. 0.8 and 0.98 eV, respectively. Hence, diffusive triplet-triplet energy transfer (TTEnT) from tetracene and O2 is thermodynamically feasible. For both mPhTc2 and mAdTc2, all values of Φo exceed 100%, which is an unambiguous indication for intra-SF. Values of Φo are as high as 170% for mAdTc2 and 128% for mPhTc2 in toluene. It is noted that a faster intramolecular TTA impacts Φo. In particular, stronger electronic coupling in mPhTc2 favors (T1:T1) deactivation via TTA prior to any collision with O2. Consequently, lower Φo values evolve for mPhTc2 than for mAdTc2. Furthermore, Φo values for both dimers are higher in toluene than in more polar benzonitrile. We rationalize this trend by considering two aspects. On one hand, the lower viscosity of toluene relative to benzonitrile allows for better diffusion and, therefore, more efficient sensitization of singlet oxygen. On the other hand, CT states are well known to be stabilized in polar solvents like benzonitrile. Changing the energy of the CT state will change the composition of (S1S0)CT. Efficient mixing requires that the involved states are close in energy. SF is, however, slightly endothermic in tetracene. As such, it is likely that a lower-energy CT state will mix preferably with (S1S0)CT rather than with (T1:T1). In other words, the contribution of (T1:T1) to (S1S0)CT will be lower in a more polar solvent. The consequence of reduced mixing of (T1:T1) to the coherent superposition will hamper intra-SF and, in turn, reduce Φo in more polar solvents. A dependence of Φo on solvent polarity is taken as further evidence for the participation of a CT state in intra-SF.

Finally, the yields for the dissociation of (T1:T1) to afford uncorrelated triplet excited states (T1 + T1) have been determined (Tables 1 and S3). This analysis was aided by the fact that the GSB and triplet ESA related extinction
coefficients remain constant throughout the dissociation process. Therefore, the dissociation yield can be calculated using the ratio between the ΔOD values of the EAS of \((T_1,T_1)\) and \((T_1 + T_1)\). The dissociation yield \((\Phi_{\text{Diss}})\) for \(m\text{AdTc}_2\) in benzonitrile (46%) is 10-times greater than that for \(m\text{PhTc}_2\) (4.5%). It is noted that high values of \(\Phi_{\text{Diss}}\) were found in pentacene dimers with a 1,3-diethynyladamantyl spacer, while dimers with a 1,3-diethynylphenylene spacer fail to produce significant amounts of \((T_1 + T_1)\).\(^{34,70}\) In line with quantum chemical calculations, weak electronic coupling in \(m\text{AdTc}_2\) favors \(1(T_1T_1)\)-\(5(T_1T_1)\) spin-mixing and allows for dissociation of \((T_1T_1)\) to form \((T_1 + T_1)\). Stronger inter-tetracene coupling in \(m\text{PhTc}_2\) lifts the degeneracy of \(1(T_1T_1)\) and \(5(T_1T_1)\) and, therefore, inhibits \(1(T_1T_1)\)-\(5(T_1T_1)\) mixing. Consequently, \((T_1T_1)\) dissociation is very unlikely in \(m\text{PhTc}_2\).
Figure 5. Global Analysis of the ns-TAS raw data for mPhTc following photoexcitation at 480 nm in argon-saturated toluene at room temperature. a) Heat map of ns-TAS raw data obtained from pump-probe experiments with time delays up to 350 µs. b) Differential absorption spectra at various time delays. Insert: Time absorption profiles as well as corresponding fits of selected wavelengths (see the figure legend for details). c) Relative populations of the respective species with colors correlating with the evolution associated spectra (EAS). d) EAS of the deconvoluted species: the first species is the intermediate state \((S_1S_0)_{\text{CT}}\) (blue), the second species is the correlated triplet pair \((T_1T_1)\) (green), and the third species represents two uncorrelated triplet excited states \((T_1 + T_1)\) (violet).
Table 1. Lifetimes (τ) and dissociation quantum yields (Φ_{Diss}) obtained from Global Analysis of fs- and ns-TAS, as well as singlet oxygen quantum yields (Φ_{Δ}) of AdTc, PhTc, mAdTc₂, and mPhTc₂ in toluene (Tol) and benzonitrile (BN).

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<tr>
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</tr>
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<tr>
<td></td>
<td>Tol</td>
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^a Φ_{Δ} is determined using C₆₀ in toluene as reference. An error margin of ±10% is implicit in the determination of Φ_{Δ}.

^b Φ_{Diss} = ΔOD((T₁ + T₁))/ΔOD((T₁;T₁)), where ΔOD refers to the ΔOD values of the ground state bleaching minimum of the evolution associated spectrum of the respective species. An error margin of ±10% is implicit in the determination of Φ_{Diss}. 
Photosensitized Up-conversion In the next step, we probed AdTc, PhTc, mAdTc2, mPhTc2 as annihilators in the context of photosensitized TTA-UC. To this end, we used a photosensitizer that generates (T1) of the annihilator via TTEnT following low-energy excitation of the photosensitizer. Subsequently, two annihilators in their triplet excited states collide and undergo TTA-UC. The net result is one annihilator (S1) and one annihilator (S1) that fluoresces with higher energy. (Figure S32). As such, the efficiency of TTA-UC (Φ(TTA)) is given by

\[ \Phi_{TTA} = 1/f \Phi_{ISC} \Phi_{TTEnT} \Phi_{TTA} \]

where \( \Phi_{ISC} \), \( \Phi_{TTEnT} \), and \( \Phi_{TTA} \) are the efficiencies of ISC of the photosensitizer, TTEnT from the photosensitizer to the annihilator, and TTA of the annihilator, respectively, while \( f \) is the fluorescence quantum yield of the annihilator.49.79 The parameter \( f \) is the spin statistical factor, which relates to the probability that \( (S_1) \) is formed upon TTA, and \( 1/2 \) is due to the fact that one high-energy photon is emitted upon absorption of two low-energy photons during TTA-UC.

Firstly, we examine the emission properties of the tetracene derivatives. The fluorescence spectra of the monomers and dimers upon photoexcitation at 480 nm are mirror images of the ground-state absorptions (Figure S33). The vibrational fine structure shows maxima at 535, 580, and 625 nm for both AdTc and mAdTc2 in toluene. These are redshifted to 550, 592, and 641 nm for PhTc and to 555, 597, and 643 nm for mPhTc2 as a result of extended π-conjugation. Under ambient conditions, PhTc and AdTc fluoresce strongly with quantum yields in the range of 70%, regardless of solvent polarity (Table S4). In contrast the fluorescence quantum yields of mPhTc2 and mAdTc2 are quenched to 6.9 and 15.6% in toluene, respectively, and to 21.3 and 19.6% in benzonitrile, respectively.

Secondly, the TTEnT dynamics were studied (Supporting Information). We used PdPc as triplet photosensitizer due to its near unity ISC efficiency, its high molar extinction coefficient of \( 1.8 \times 10^5 \) M\(^{-1}\)cm\(^{-1}\) at 730 nm, and the minimal spectral overlap between its absorption in the range of 600 to 800 nm and the tetracene fluorescence between 500 to 650 nm (Figure S35). Upon photoexcitation of PdPc at 730 nm in toluene, efficient intermolecular TTEnT (inter-TTEnT) from PdPc to the tetracene annihilators is confirmed via Stern-Volmer analyses, and the underlying inter-TTEnT rate constants are determined (k\(_{TTEnT}\)).

Considering (T1) energies of 1.13 and 1.21 eV for PdPc and tetracene, respectively, inter-TTEnT is endergonic by -0.08 eV. All k\(_{TTEnT}\) values are within the same range of \( 10^5 \) M\(^{-1}\)s\(^{-1}\) (Figure S36 and Table S5). We next sought to establish TTA-UC as the subsequent step to TTEnT via photoexcitation of PdPc at 730 nm and recording the up-converted fluorescence from the tetracene derivatives annihilators in the range of 500–650 nm. PdPc and annihilator concentrations were held constant at 4.5 × 10\(^{-5}\) and 2.5 × 10\(^{-4}\) M, respectively. The power-law dependence of the integrated up-converted fluorescence intensity versus the incident photon power is the hallmark of TTA-UC.79.80 At low incident power densities, some PdPc triplet excited states will not collide with an annihilation partner, but will decay non-radiatively. Under these conditions, the integrated up-converted fluorescence shows a quadratic dependence on the incident power density. At high incident power densities TTA-UC becomes dominant, and the dependence of up-converted fluorescence becomes linear. Importantly, the typical evolution from a quadratic to a linear power density dependence is observed for all up-conversion systems (Figure 6a) as the power is increased step-by-step, indicating that TTA-UC occurs. The crossing point, namely the power density threshold (I\(_{th}\)), is a key parameter for TTA-UC. At power densities above I\(_{th}\), where the integrated up-converted fluorescence depends linearly on the power density, the TTA-UC efficiency reaches its maximum and remains constant. Therefore, low I\(_{th}\) values are desirable for effective utilization. The I\(_{th}\) values of PhTc and AdTc are 23.0 and 33.3 W/cm\(^2\) respectively, while values as low as 9.5 and 16.0 W/cm\(^2\) are realized using mPhTc2 and mAdTc2, respectively. As mPhTc2 outperforms mAdTc2, we optimized I\(_{th}\) further by increasing the concentration of mPhTc2. As shown in Figure S37, an I\(_{th}\) value of 3.8 W/cm\(^2\) is derived when increasing the mPhTc2 concentration to 3.5 × 10\(^{-4}\) M. Finally, at a concentration of 4.5 × 10\(^{-4}\), I\(_{th}\) for mPhTc2 is, in fact, too low to be experimentally observed.

Finally, we unraveled respective contributions from intra-TTA-UC and intermolecular TTA-UC (inter-TTA-UC).

The incident photon power densities were kept constant at 70.0 W/cm\(^2\), and the integrated fluorescence was calculated at variable concentrations of the dimeric acene annihilator in the presence of a constant concentration of PdPc (4 × 10\(^{-5}\) M, Figure 6b). Quantitatively, the integrated up-converted fluorescence is higher for the dimers than for the monomers across the entire concentration range. Overall, mPhTc2 gives rise to the highest integrated up-converted fluorescence. Strikingly, the up-converted fluorescence of mPhTc2 is detectable at concentrations as low as 1 × 10\(^{-6}\) M, where for the other tetracene derivatives no up-converted fluorescence was discernable.
Figure 6. a) Power density dependence of the integrated up-converted emission of AdTc, PhTc, mAdTc₂, and mPhTc₂ (2.5 × 10⁻⁵ M) with PdPc (4 × 10⁻⁵ M) in toluene; dashed lines show the power density thresholds. b) Log-log plots of integrated up-converted fluorescence as a function of the varied concentration of annihilators at a constant concentration of PdPc (4 × 10⁻⁵ M). Inset: Picture of the up-converted mPhTc₂ fluorescence via photoexcitation of PdPc at 730 nm.

To derive subtle details of TTA-UC, we determined the relative TTA-UC fluorescence quantum yields using a TIPSTc/PdPc system as a standard (ΦUC,F,STD) [TIPSTc = 5.12-bis(trisopropylsilyl)ethyl]tetracene, supporting information and Table 2). At annihilator concentrations as low as 1.0 × 10⁻⁵ M, where diffusion-controlled inter-TTA-UC is limited, ΦUC,F is about 14 times larger for mPhTc₂ (0.031%) than for PhTc (0.0021%). Considering, however, that Φₜ for mPhTc₂ is much lower than for PhTc (Table 2), a 14-fold increase can only be rationalized through intra- TTA-UC contributions, which dominate over inter-TTA-UC contributions. Interestingly, ΦUC,F of mAdTc₂ (0.0086%) at the same concentration is only around 9 times higher than that of AdTc (0.0010%). As such, intra-TTA-UC is more effective in mPhTc₂ than in mAdTc₂. Stronger inter-tetracene electronic coupling in mPhTc₂, which stems from the π-conjugated spacer, lowers the energy of △(T₁T₂) relative to that of [3/5(T₁T₂)]. Thus, formation of △(T₁T₂) is preferred and goes hand-in-hand with a larger spin statistical factor f and, therefore, higher ΦUC,F for mPhTc₂.

Turning to higher concentrations of the annihilator (2.5 × 10⁻⁴ M), the differences in ΦUC,F between the dimers and the corresponding monomers are rather subtle with ΦUC,F-ratios of around 3 for both pairs, mPhTc₂ (1.611%) and PhTc (0.444%) as well as mAdTc₂ (0.992%) and AdTc (0.345%). Two conclusions should be drawn at this stage. First, at high concentrations the dominance of intra- TTA-UC is lost as inter- TTA-UC becomes increasingly significant. Second, the nature of the spacer becomes less important at a point in which inter- TTA-UC contributions to the overall ΦUC,F are significant. Overall, the superior TTA-UC performance of mPhTc₂ in the high concentration regime likely results from the synergy between inter- and intra- TTA.

Intramolecular Up-conversion We further elaborate on intra- TTA-UC in mPhTc₂ and mAdTc₂ by performing steady-state and time-resolved fluorescence spectroscopy under direct excitation at 480 nm. For both dimers, the absence of O₂ leads to an increase in fluorescence intensity especially for mPhTc₂ in toluene (Figure S34). This effect is less pronounced in the monomers. To be precise, Φₜ values for both dimers increase to ca. 30% in toluene and benzonitrile in the absence of O₂ (Table S4). Among both dimers, fluorescence for mPhTc₂ in toluene is the most sensitive to O₂, as Φₜ increases significantly by a factor of 4 compared to a factor of 2 for mAdTc₂ in toluene. Therefore, we conclude that intramolecular rather than intermolecular interactions, namely intra- TTA-UC, must be operative in the excited state decay of the dimers.

In time-correlated single photon counting (TCSPC) experiments, emission from PhTc and AdTc decays mono-exponentially with a lifetime of 10 ns that is independent of solvent polarity in a deoxygenated environment (Figures S38–S40; Tables S6 and 2). In contrast, the emission of mPhTc₂ and mAdTc₂ decays tri-exponentially and lasts for several hundreds of nanoseconds. It features one short and prompt (ps) as well as two long and delayed (ns) components. In toluene, mPhTc₂ shows lifetimes of <200 ps, 9.0 ns, and 58.7 ns with relative amplitudes of 3.2, 9.6, and 87.3%, respectively. For mAdTc₂, the three lifetimes are 810 ps, 11.6 ns, and 59.1 ns and the relative amplitudes are 37.2, 49.5, and 13.3%. The agreement between the lifetimes from TCSPC and those from TAS measurements is solid (vide supra), for example, (S,S₂)₄T₁(T₁T₂) (8.7 ns), and (T₁T₂) (66.5 ns) for mPhTc₂ in toluene in TAS. Notably, the presence of O₂ accelerates the deactivation of all compounds and eliminates the emission from the longest-lived component for the dimers.
O₂-sensitive fluorescence underpins the involvement of a triplet excited state during the radiative decay. In light of the fact that mPhTc₂ and mAdTc₂ undergo intra-SF, we posit that (T₁; T₁) is involved in the delayed fluorescence. Two different scenarios are considered. On one hand, (T₁; T₁) undergoes a direct radiative decay to the electronic ground state (S₀S₀), giving implicit spectral changes in the fluorescence spectrum. On the other hand, since E(S₁) ≤ 2×E(T₁) for tetracene, delayed fluorescence might also originate from (S₁S₁)rel which has been repopulated via TTA-UC. In that case, no spectral changes are expected, over time. To clarify the nature of the delayed fluorescence, time-resolved emission spectroscopy (TRES) is recorded upon photoexcitation at 480 nm in the absence of O₂ (Figures 7 and S41–S43). In line with the TCSPC assays, mPhTc₂ and mAdTc₂ fluoresce well beyond hundreds of nanoseconds and without any discernable spectral changes through the entire timescale. Deconvolution of the TRES raw data by means of a three-species sequential kinetic model yields three spectroscopically identical fluorescence spectra. For example, fluorescence of mPhTc₂ and mAdTc₂ in toluene show maxima at 550 and 535 nm, respectively, throughout the entire deactivation process. This is in agreement with the corresponding steady-state fluorescence spectra.

In short, all three fluorescent components originate from the same state, namely (S₁S₁)rel, and corroborate intra-UC in mPhTc₂ and mAdTc₂. Thus, following direct photoexcitation, the prompt fluorescence comes directly from (S₁S₁)rel while the two delayed fluorescence events result from intramolecular up-converted fluorescence involving (S₁S₁)(T₁T₁)² and (T₁T₁). The relative amplitudes obtained from TCSPC for the emission resulting from up-converted (T₁T₁) are 87.3% for mPhTc₂ and 13.3% for mAdTc₂ in deoxygenated toluene, confirming that mPhTc₂ is more efficient for intramolecular up-conversion due to stronger electronic coupling (Figure S40). Combining our results from steady-state and time-resolved absorption and emission spectroscopy we summarize the deactivation process of the dimers as illustrated in Figure 8.

Table 2. Lifetimes (τ) and relative amplitudes obtained from TCSPC of AdTc, PhTc, mAdTc₂, and mPhTc₂ in O₂-free toluene, as well as up-conversion fluorescence quantum yields (ΦUC-F) using a constant concentration of the PdPc sensitizer (4 × 10⁻⁵ M) and two different concentrations of the AdTc, PhTc, mAdTc₂, and mPhTc₂ annihilators (2.5 × 10⁻⁴ and 1.0 × 10⁻⁵ M) in O₂-free toluene.

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<td>τ₃</td>
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<td>(3.16%)</td>
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</tr>
<tr>
<td>mAdTc₂</td>
<td>810 ps</td>
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<td>(37.17%)</td>
<td>(49.51%)</td>
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a Average values of ΦUC-F and standard deviations are obtained from three different measurements.
b The lifetime is below the resolution limit of our TCSPC setup.
Figure 7. Global Analysis of the TRES raw data for mPhTc$_2$ following photoexcitation at 480 nm in argon-saturated toluene at room temperature. a) Heat map of TRES raw data. b) Emission spectra at various time delays. Insert: Time absorption profiles as well as corresponding fits of selected wavelengths (see the figure legend for details). c) Relative populations of the respective species with colors correlating with the evolution associated spectra (EAS). d) EAS of the deconvoluted species: the first species is the fluorescent relaxed singlet excited state (S$_1$S$_0$)$_{rel}$ (red), the second species is the up-converted fluorescent (S$_1$S$_0$)$_{rel}$ from the intermediate state (S$_1$S$_0$)$_{T1T1}$CT (blue), and the third species is the up-converted fluorescent (S$_1$S$_0$)$_{rel}$ from the correlated triplet pair (T$_1$T$_1$) (green).

Figure 8. Schematic representations of intra-SF (black arrows) and intra-TTA-UC (orange arrows) after 480 nm photoexcitation of mPhTc$_2$ and mAdTc$_2$ in argon-saturated toluene and benzonitrile. The relaxed singlet excited state (S$_1$S$_0$)$_{rel}$ is the sole fluorescent state, and its radiative deactivation is highlighted in yellow. The species are marked by the same colors as the corresponding spectra in TAS and TRES with the singlet excited state (S$_1$S$_0$) in grey, the relaxed singlet excited state (S$_1$S$_0$)$_{rel}$ in red, the intermediate state (S$_1$S$_0$)$_{T1T1}$CT in blue, the correlated triplet pair (T$_1$T$_1$) in green, and the state representing uncorrelated triplet excited states (T$_1$+T$_1$) in violet.

Thermal Effects in Down- and Up-Conversion To better document the interplay between intra-SF and intra-TTA-UC, we studied thermal effects in mPhTc$_2$ and mAdTc$_2$ under direct photoexcitation by means of temperature-dependent steady-state absorption and emission spectroscopy, TCSPC, as well as fs- and ns-TAS. For this purpose, we varied the temperature stepwise from 300 to 80 K. To start, we inspected the thermal effects on the
steady-state absorption spectra in O2-free 2-methyltetrahydrofuran (MeTHF), as shown in Figures S44a and S45a. As the temperature is lowered, the absorptions of both dimers undergo a slight bathochromic shift and feature increased oscillator strengths in addition to sharper vibrational structure. Overall, the shape of the spectra is, however, temperature-independent. At the same time, the fluorescence of both dimers sharpens and shifts bathochromically while maintaining the same overall profile (Figures S44b and S45b). Strikingly, the fluorescence intensity of mAdTc2 increases dramatically with decreasing temperature. To factor out increasing oscillator strength in the absorption spectra upon lowering the temperature, we calibrated the integrated fluorescence by means of dividing it by the optical density at the photoexcitation wavelength.

The calibrated integrated fluorescence of mPhTc2 remains constant as a function of temperature, indicating temperature-independent fluorescence quantum yields of mPhTc2 (Figure S44b insert). In contrast, the calibrated integrated fluorescence of mAdTc2 increases as the temperature is decreased. In particular, the calibrated integrated fluorescence at 80 K is around 3 times greater than at 300 K (Figure S45b insert). Therefore, radiative deactivation of mAdTc2 is more likely to occur at low temperature.

Next, we turned to thermal effects on the radiative deactivation pathways using temperature-dependent TCSPC in O2-free MeTHF (Figures S46 and S47 and Table S7). For mPhTc2, the prompt (S1S0)rel lifetime is below the instrumental time resolution. The lifetime of the second component, that is, (S1S0)VTCT, displays little temperature dependence. The remaining long lifetime, namely that of (T1T1), increases from 50.2 ns at 300 K to 148.0 ns at 80 K with relative amplitudes of 68.5 and 18.8%, respectively. Hence, TTA-UC from (T1T1) contributes less to the overall emission at lower temperatures. Our observations indicate that TTA-UC from (T1T1) is thermally activated for mPhTc2. According to the Arrhenius plot (Figure S48), the activation barrier for intra-TTA-UC in mPhTc2 is around 0.011 ± 0.003 eV.85 Turning to mAdTc2, the lifetime of (S1S0)rel increases from 0.7 ns at 300 K to 3.0 ns at 80 K. Temperature dependence is not noted for the lifetime of (S1S0)VTCT, while that of (T1T1) becomes longer as the temperature is reduced. As a matter of fact, intra-UC from (T1T1) is shut down completely below 160 K, as a biexponential fitting turned out to be sufficient for the TCSPC data. For mAdTc2, the activation barrier by means of Arrhenius analysis is around 0.03 eV.86 Higher fluorescence quantum yields of mAdTc2 at lower temperatures relate to a radiative decay even before (T1T1) is formed.

In the final part of our analysis, thermal effects on intra-SF have been investigated by means of temperature-dependent fs- and ns-TAS in O2-free MeTHF. The raw data is fitted according to the sequential kinetic model shown in Figure S32.87 As Figures S49-52and Tables S8 and S9 illustrate, we detect all key steps of intra-SF across the temperature range from 80 to 300 K for both dimers. The lifetimes of (S1S0)rel, (S1S0)VTCT, and (T1T1) are in sound agreement with the TCSPC results. Notably, the lifetime of (S1S0)rel for mPhTc2 is temperature independent with a constant value of ca. 100 ps (Table S11). For mAdTc2, however, the lifetime of (S1S0)rel increases from ca. 800 ps at 300 K to ca. 2.4 ns at temperatures below 120 K. We assume that the formation of the superposition of (S1S0)rel, the CT state, and (T1T1) requires vibronic coupling of the involved states. The restricted motion of the nuclei at lower temperatures, therefore, slows the generation of the superposition, namely the formation of (S1S0)VTCT. For mPhTc2, however, the stronger electronic coupling reduces the extent of nuclei motion required to generate (S1S0)VTCT. Consequently, the formation of (S1S0)VTCTin mPhTc2 is less sensitive to temperature. Subsequently, (S1S0)VTCT exhibits constant lifetimes of 8–10 ns upon cooling in both dimers. We attribute this to the fact that the dephasing is driven mainly by electronic processes and requires less nuclear motion. Overall, intra-SF for mAdTc2 is temperature dependent, while for mPhTc2 it is temperature independent. To further elaborate on this, we have determined the relative triplet quantum yields (ΦT)88 of mPhTc2 and mAdTc2 by comparing the GSB intensities of the EAS of (S1S0)VTCT and (T1T1) (Table S12). Upon cooling from 300 to 80 K, ΦT of mPhTc2 remains constant at ca. 70–80%. For mAdTc2, a decrease in temperature reduces ΦT from 84% at 300 K to 32% at 80 K, indicating that intra-SF is less efficient at lower temperatures. This finding is in sound agreement with our results from temperature-dependent steady-state and time-resolved emission measurements, namely enhanced radiative deactivation accompanied by the loss of the up-converted emission from (T1T1) of mAdTc2 at low temperatures.

Conclusion

We have explored two tetracene dimers that feature either a 1,3-diethylnyladamantyl (mAdTc2) or a phenylene spacer (mPhTc2) and that are designed to fine-tune the intramolecular coupling between the tetracene chromophores while conserving an identical spatial relationship. Down- and up-conversion have been characterized, especially in comparison with the corresponding monomers PhTc and AdTc. Following photoexcitation, intra-SF operates efficiently in both dimers, with over 100% triplet quantum yields, and is mediated by a superposition of (S1S0), a CT state, and (T1T1). In photosensitized up-conversion measurements with the assistance of PdPc, intra-UC is confirmed in both dimers. The dimer mPhTc2 exhibits a better up-conversion performance due to more efficient intra-TTA that results from stronger inter-tetracene coupling. Independent evidence for intra-UC comes from direct excitation of the tetracene dimers, which leads to delayed up-converted fluorescence from the intermediate state (S1S0)VTCTand the correlated triplet pair (T1T1) alongside prompt (S1S0)rel fluorescence. Inter-tetracene coupling is the decisive factor that governs the fate of (T1T1). On one hand, the more strongly coupled, π-cross-conjugated phylene-linked mPhTc2 favors TTA-UC from (T1T1). On the other hand, the more weakly coupled, non-conjugated 1,3-diethylnyladamantyl spacer of mAdTc2 supports efficient (T1T1) decorrelation, which is vital for efficient intra-SF. To round off the studies on the interplay between intra-SF and intra-UC, temperature-dependent measurements have been carried out under direct
photoexcitation of the dimers. At low temperatures, intra-SF of mAdTe2 is slowed down significantly and consequently, no intra-TTA-UC is observed. However, both intra-TTA-UC and intra-SF of mPhtTe2 are active even at 80 K due to stronger electronic coupling between the two tetracene chromophores. The current work defines our understanding of the potentially competitive processes of down- and up-conversion, providing design principles for chromophores that lead to either efficient TTA-UC or the generation of uncorrelated triplet excited states formed via intra-SF.

ASSOCIATED CONTENT

Supporting Information.

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Notes

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REFERENCES


The Splitting between the (T'T') and (T'T't) in mADTeCs is less than the resolution of the program output.


For mPHT in Benzonitrile, the Slow Solvent Rearrangement of (S1$O$) in Viscous Benzonitrile and the Fast Formation of the Third Species Hammers Clearly Distinguishing between (S1$O$) and (S1$O$)Rel. 2.


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