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An energetics perspective on why there are so few triplet-triplet annihilation emitters†

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The efficiency of solar cells may be increased by utilizing photons with energies below the band gap of the absorber. This may be enabled by upconversion of low energy photons into high energy photons via triplet-triplet annihilation (TTA) in organic chromophores. The quantum yield of TTA is often low due to competing processes. The singlet pathway, where a high energy photon is emitted, is one of three possible outcomes of an encounter between two triplet excitons. The quintet pathway is often too high in energy to be accessible, leaving the triplet pathway as the main competing process. Using many-body perturbation theory in the GW approximation and the Bethe-Salpeter equation, we calculate the energy release in both the singlet and triplet pathways for 59 chromophores of different chemical families. We find that in most cases the triplet pathway is open and has a larger energy release than the singlet pathway. Thus, the energetics perspective explains why there are so few TTA emitters and why the quantum yield of TTA is typically low. That said, our results also indicate that the performance of emitters from known chemical families may be improved by chemical modifications, such as functionalization with side groups, and that new chemical families could be explored to discover more TTA emitters.

1 Introduction

Solar cells suffer from an inherent limitation that photons with energy below the band gap of the absorber, known as the absorption threshold, cannot be harvested[1]. The loss of photons with sub-band-gap energies may be mitigated by optical upconversion (UC)[2,3] of two or more low energy photons into one high energy photon, which can be absorbed by the solar cell. In organics, UC can be achieved through triplet-triplet annihilation (TTA)[3–8], where two low energy triplet excitons are converted into one higher energy singlet exciton. Compared to other UC mechanisms[3,9,10], TTA-UC has the advantage of upconverting incoherent light at low intensities, such as sunlight[2,6,11].

The reactant triplet excitons cannot be created directly by optical absorption because it is spin-forbidden. Therefore, TTA-UC requires a combination of two chromophores. The first is a triplet sensitizer, which absorbs incident photons and converts them into triplet states. The second is a triplet emitter, which undergoes TTA. The sensitizer may be either organic or inorganic[8,12,13]. TTA emitters are organic chromophores, usually polycyclic aromatic hydrocarbons (PAHs)[2,5,8,13,14]. TTA-UC involves a sequence of five processes, illustrated in Figure 1. The process begins with a sensitizer in the ground state, $S_0(S)$, which absorbs a sub-band-gap photon, $h\upsilon_{in}$, to generate a singlet exciton, $S_1(S)$:

$$S_0(S) + h\upsilon_{in} \rightarrow S_1(S) \quad (1)$$

The singlet exciton subsequently relaxes to the lowest energy triplet state of the sensitizer, $T_1(S)$, via inter-system crossing

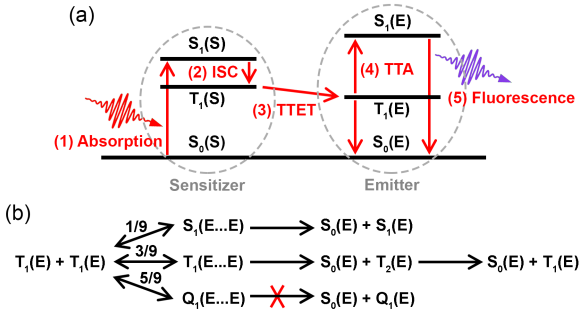

Fig. 1 (a) Schematic of the five processes involved in TTA-UC. (b) The singlet, triplet, and quintet pathways of an emitter triplet encounter complex with their spin-statistical probabilities. The quintet pathway is often closed because the quintet state is too high in energy to be accessible.

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(ISC):

$$S_1(S) \rightarrow T_1(S) \quad (2)$$

The third step is triplet-triplet energy transfer (TTET), where triplet excitons are transferred from the sensitizer to the emitter, $T_1(E)$, through a Dexter process:[5,15,16]

$$T_1(S) \rightarrow T_1(E) \quad (3)$$

Next, TTA takes place in the emitter. Two triplet excitons on different molecules combine to produce one molecule in the lowest singlet excitation state, $S_1(E)$, leaving the other molecule in its ground state, $S_0(E)$:

$$T_1(E) + T_1(E) \rightarrow S_0(E) + S_1(E) \quad (4)$$

Finally, an upconverted photon, $h\upsilon_{out}$, is emitted when an emitter singlet decays radiatively:

$$S_1(E) \rightarrow S_0(E) + h\upsilon_{out} \quad (5)$$

Overall, two sub-band-gap photons, $h\upsilon_{in}$, are upconverted into one higher energy photon, $h\upsilon_{out}$.

In order for TTA-UC to be a downhill process, the energies of the excited states involved must meet several requirements, as illustrated in Figure 1(a). The singlet and triplet energy levels of the sensitizer should be nested between those of the emitter, $s_1(S) < s_1(E)$ and $t_1(S) > t_1(E)$. The former is necessary for the upconversion from low energy singlets in the sensitizer into high energy singlets in the emitter. The latter enables TTET from the sensitizer to the emitter. Consequently, unavoidable energy losses are incurred in the ISC, TTET, and TTA steps. The energy loss in ISC, $s_1(S) - t_1(S)$, is typically a few hundred meV[11]. The energy loss in TTET, $t_1(S) - t_1(E)$, may be minimized by an appropriate choice of sensitizer and emitter pair with similar triplet energies. The energy loss in TTA is:

$$E_{TTA,S}^{loss} = 2t_1(E) - s_1(E) \quad (6)$$

A small and positive $E_{TTA,S}^{loss}$ is necessary because it provides the thermodynamic driving force for TTA.

In addition to the aforementioned energy losses, a major efficiency bottleneck for TTA-UC is that the quantum yield (QY) of the TTA step is limited by competing processes.[12,13,17]. If there were no competing processes, the upconversion of two emitter triplets into one emitter singlet via TTA would have a QY of 50%. However, the singlet pathway is only one of three possible pathways, as shown in Figure 1(b). When two emitter triplets interact in absence of an external magnetic field, nine different encounter complexes may be formed with equal probabilities. According to the Clebsch-Gordan series, these nine encounter pairs are one singlet, three triplets, and five quintets. In the triplet pathway, an encounter complex converts into one emitter in the ground state and one emitter in a higher excited triplet state, usually the second triplet excited state, $T_2(E)$. According to Kasha's rule,[18] this highly excited triplet rapidly internally decays into the lowest energy triplet, $T_1(E)$, leading to a loss of half of the initial triplet excitons in this pathway. The encounter complex with a multiplicity of 5, $Q_1(E...E)$, can only dissociate back into two emitter triplets because the emitter quintet state $Q_1(E)$ is usually much higher in energy than the complex $Q_1(E...E)$ and thus often inaccessible.[4,17,19,20] If the singlet and triplet pathways are open, $T_2(E)$ decays to $T_1(E)$ in the triplet pathway, and the quintet pathway is closed, the statistical limit of TTA QY is:

$$\frac{25\% \times 1}{25\% \times 2 + 75\% \times (2-1)} = 20\% \quad (7)$$

where 25% and 75% are the probabilities of the singlet and triplet pathways when the quintet pathway is closed. The numerator is the number of singlets generated in the singlet pathway and the denominator is the number of triplets consumed in the singlet and triplet pathways. In some of the literature, two triplets upconverting into one singlet is regarded as a QY of 100% instead of 50% and the resulting QY limit is double (40%)[21]. Owing to losses in the other steps of the TTA-UC mechanism, the overall QY measured in experiments is often only a few percent,[5,22,23] much smaller than the limit given by Eq. 7.

Interestingly, the QY of TTA in rubrene has been reported to surpass 20% in some experiments[4,21], indicating that the weight of the singlet pathway could exceed the spin statistical limit of 25%. Similar to the energy release in the singlet pathway in Equation 6, the energy release in the triplet pathway is defined as:

$$E_{TTA,T}^{loss} = 2t_1(E) - t_2(E) \quad (8)$$

where $t_2(E)$ is the energy of the second triplet excitation in the emitter. Rubrene in toluene has been found to have a small positive $E_{TTA,S}^{loss}$ and a small negative $E_{TTA,T}^{loss}$, making the singlet pathway more favorable than the triplet pathway[21,24]. The energy release in the singlet and triplet pathways, $E_{TTA,S}^{loss}$ and $E_{TTA,T}^{loss}$, thermodynamically drive TTA and determine the relative weights of singlet and triplet pathways together with the spin statistical factors. Thus, in an ideal TTA emitter, $E_{TTA,S}^{loss}$ should be a small positive value and $E_{TTA,T}^{loss}$ should be negative with a large absolute value, such that only the singlet pathway is open with a small energy loss. These energetic criteria can inform the search for more efficient TTA emitters.

Here, we use many-body perturbation theory (MBPT) within the GW approximation and the Bethe–Salpeter equation (BSE)[25–29] to calculate the TTA energetics for a set of 59 molecules, shown in Figure 2 (chemical names are provided in the ESI†). The set comprises experimentally observed TTA emitters (indicated in blue in Figure 2)[5,8,13,14,30,31], some polycyclic aromatic hydrocarbons (PAHs), and some commercially available organic photovoltaic molecules of different chemical families. For most species studied here, the energy release in the triplet pathway is found to be larger than the energy release in the singlet pathway. This explains why there are so few TTA emitters and why the QY is often lower than the 20% spin statistical limit. Although efficient TTA emitters are rare, our results hint at exciting possibilities for enhancing TTA performance and discovering new TTA emitters. We find that within a chemical family side-group functionalization can significantly affect the TTA energetics. This indicates that the QY of TTA emitters from known

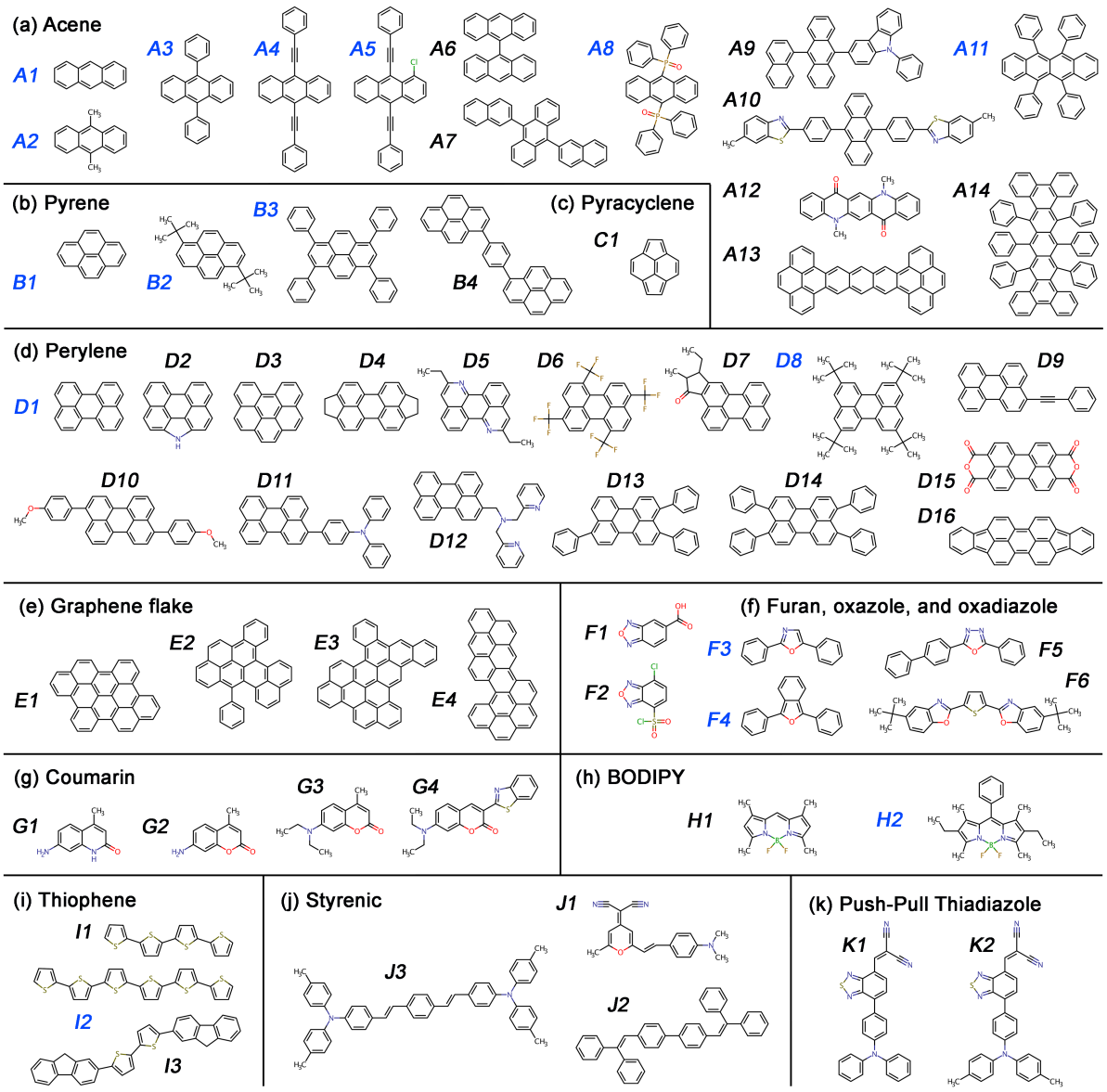

Fig. 2 The set of 59 molecules studied here, arranged by chemical families. Experimentally observed TTA emitters[5,8,13,14,30–32] are indicated in blue.

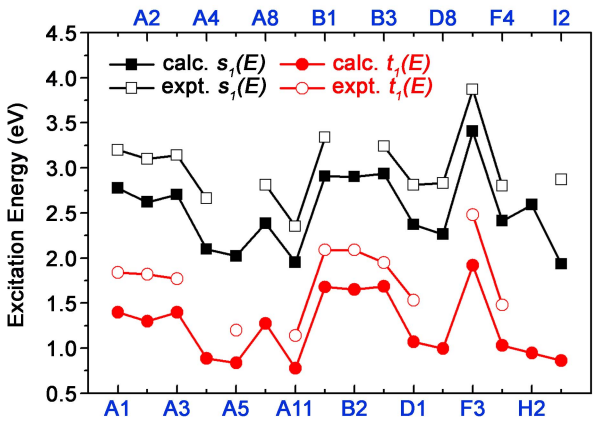

Fig. 3 The lowest singlet (black) and triplet (red) excitation energies of 16 experimentally observed TTA emitters, calculated with G_0W_0+BSE@PBE (solid), compared to experimental values extracted from absorption spectra in solution (hollow)[12,14,41–62].

chemical families may be optimized by chemical modification. Moreover, we identify several chemical families beyond the well-known anthracene and perylene derivatives, that could be further explored in search of new TTA emitters.

2 Methods

All calculations were conducted using the all-electron numerical atom-centered orbital code, FHI-aims[33,34]. Geometry optimizations were performed using density functional theory (DFT) with the generalized gradient approximation of Perdew, Burke, and Ernzerhof (PBE)[35] coupled to the Tkatchenko-Scheffler (TS) pairwise dispersion method[36] and tight tier-2 basis sets[33]. Non-self-consistent G_0W_0 and BSE calculations were performed using augmented tier-2 basis sets[37]. PBE was used as the DFT starting point, denoted as G_0W_0+BSE@PBE. A detailed account of the GW implementation in FHI-aims is provided in Refs.[38,39]. Briefly, the self-energy is first calculated on the imaginary frequency axis and then analytically continued to the real frequency axis. A 16-parameter Pade approximation was used in the analytical continuation[38,40]. Using the GW quasiparticle energies, BSE calculations were performed to obtain the singlet and triplet excitation energies.[37] All chromophores studied here are in the feasible size range for GW+BSE calculations with converged basis sets.

3 Results and discussion

We begin by assessing the performance of G_0W_0+BSE@PBE. Figure 3 shows a comparison of calculated singlet and triplet excitation energies to experimental data for known TTA emitters. We note that the experiments were conducted at finite temperature and in different solvents, which may contribute to discrepancies between the measured and calculated values. Overall, G_0W_0+BSE@PBE results are in qualitative agreement with experiment and the trends among different species are captured correctly. However, G_0W_0+BSE@PBE systematically underestimates both $s_1(E)$ and $t_1(E)$ by about 0.4 to 0.5 eV. This may be attributed to the underestimation of the fundamental gap due to overscreening by the PBE functional, which is not fully corrected by non-self-consistent G_0W_0.[63] The error in the quasiparticle gap further propagates to the BSE calculation, leading to underestimated singlet and triplet excitation energies. Although using a hybrid functional starting point or performing partial self-consistency in the GW step may improve the quantitative agreement of GW+BSE with higher-level wave-function methods,[29,64,65] the accuracy of G_0W_0+BSE@PBE has been found to be adequate for predicting qualitative trends among different molecules.[29,64,66] One outlier in Figure 3 is **I2** α-sexithiophene (α-6T), whose singlet excitation energy is underestimated by 0.94 eV. This may be attributed to two reasons. First, the absorption spectra of α-oligothiophenes have a strong dependence on temperature, such that at room temperature they are significantly blue shifted compared to low temperature measurements[62]. The experimental value for **I2** α-6T shown in Figure 3 was measured at room temperature[62]. Second, α-oligothiophenes have conformational degrees of freedom due to rotation of the σ bonds between thiophene moieties. In solution, σ bond rotation decreases the π conjugation length of α-6T, increasing the observed transition energies[61]. The performance of G_0W_0+BSE@PBE for $t_2(E)$ could not be benchmarked, owing to lack of experimental data. For higher singlet excited states, the errors of GW+BSE are similar to the errors for the lowest singlet excitation, based on the agreement between the shapes of computed and measured absorption spectra for different materials.[28,67–70] Considering this, and the similar underestimation of $s_1(E)$ and $t_1(E)$, it is reasonable to assume that higher triplet excitation energies, such as $t_2(E)$, are also underestimated similarly by about 0.4 to 0.5 eV. Therefore, we consider the qualitative trends in $E^{loss}_{TTA,S}$ and $E^{loss}_{TTA,T}$ calculated with G_0W_0+BSE@PBE to be sufficiently reliable to compare between different materials.

We note that an alternative approach to calculating singlet and triplet excitation energies is time-dependent density functional theory (TDDFT), which has been used by others to study TTA emitters.[46,71,72] The performance of TDDFT depends strongly on the choice of exchange-correlation functional. Several benchmarks have shown that the performance of GW+BSE and TDDFT is comparable, with GW+BSE having a slight advantage for Rydberg and charge-transfer like excitations.[29,64,66,73,74]

Figure 4 shows the calculated $E^{loss}_{TTA,T}$ as a function of $E^{loss}_{TTA,S}$ for all molecules studied here (tabulated values are provided in the ESI†). Experimentally observed TTA emitters are indicated in blue. Based on the positions of some known TTA emitters on this chart, we define criteria to evaluate new candidates. In rubrene (**A11**), TTA is experimentally known to be approximately isoergic.[21] Therefore, we consider the G_0W_0+BSE@PBE $E^{loss}_{TTA,S}$ of rubrene, which is -0.40 eV due to the underestimation of the method, to be the lower bound for the singlet pathway of TTA to be open. Molecules with $E^{loss}_{TTA,S}$ smaller than rubrene may be more likely to undergo singlet fission (SF), the reverse process of TTA. This is indicated by the left dashed vertical line in Figure 4. Of the 16 experimentally observed TTA emitters studied here, only a boron-dipyrromethene (BODIPY) derivative (**H2**)[30] has a $E^{loss}_{TTA,S}$ smaller than rubrene, indicating that TTA in this molecule may be endoergic. This criterion is also verified by representative experimentally observed and/or computationally

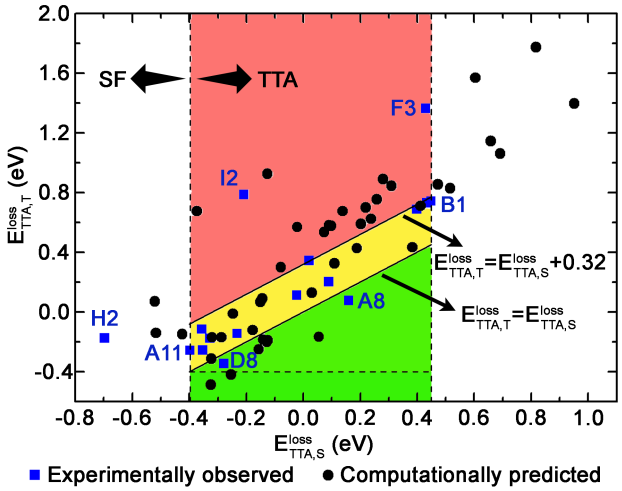

Fig. 4 The energy loss in the triplet pathway, $E^{loss}_{TTA,T}$, vs. the energy loss in the singlet pathway, $E^{loss}_{TTA,S}$, obtained from G_0W_0+BSE@PBE calculations. Experimentally observed TTA emitters are represented by blue squares and computationally predicted materials are represented by black circles. The optimal region for TTA from the energetics perspective is colored in green. The region where most experimentally observed emitters are concentrated is colored in yellow.

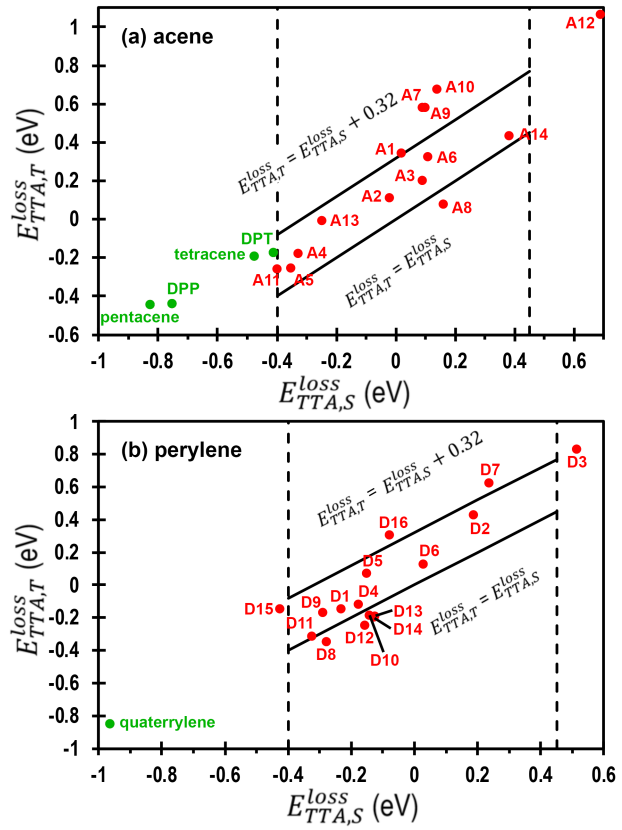

Fig. 5 The energy loss in the triplet pathway, $E^{loss}_{TTA,T}$, vs. the energy loss in the singlet pathway, $E^{loss}_{TTA,S}$, obtained from G_0W_0+BSE@PBE calculations for the (a) acene and (b) perylene families. The labels correspond to Figure 2. The SF chromophores, tetracene, pentacene, DPT, DPP, and quaterrylene, are shown for comparison.

predicted SF chromophores, shown in Figure 5. Tetracene, pentacene, diphenyltetracene (DPT), diphenylpentacene (DPP), and quaterrylene[68,75] are located to the left of the dashed vertical line at -0.4 eV. The largest calculated $E^{loss}_{TTA,S}$ of the 16 experimentally observed emitters is 0.45 eV for **B1** pyrene. Therefore, we consider this as the upper bound, above which molecules may not be efficient TTA emitters because the energy loss would be too high. This is indicated by the right vertical dashed line in Figure 4.

For an ideal TTA emitter, the energy release in the triplet pathway, $E^{loss}_{TTA,T}$, should be as low as possible, preferably negative or at the very least smaller than the energy release in the singlet channel, $E^{loss}_{TTA,S}$, to hinder the triplet channel. This is indicated by the green area under the line $E^{loss}_{TTA,T} = E^{loss}_{TTA,S}$ in Figure 4. Under the assumption that the second triplet excitation energy $t_2(E)$ is underestimated similarly to $s_1(E)$ and $t_1(E)$, we expect the triplet pathway to be endoergic and therefore closed if $E^{loss}_{TTA,T}$ is smaller than about -0.40 eV. This is indicated by the horizontal dashed line in Figure 4. None of the experimentally observed TTA emitters studied here are found in this optimal region, where only the singlet pathway is exoergic. Although the triplet pathway of rubrene (**A11**) in toluene has been reported to be slightly endoergic (by about 74 meV),[21,24] its calculated $E^{loss}_{TTA,T}$ is not in the optimal region, possibly because solvent and temperature effects are not considered in the calculation of an isolated rubrene molecule. Of the experimentally observed emitters, there are only two molecules whose $E^{loss}_{TTA,T}$ is slightly smaller than $E^{loss}_{TTA,S}$, 9,10-bis(diphenylphosphoryl)anthracene (BDPPA, **A8**) and 2,5,8,11-tetra-tert-butylperylene (TTBP, **D8**). Most of the experimentally observed TTA emitters (11 out of 16) are concentrated in the region where $E^{loss}_{TTA,T}$ is larger than $E^{loss}_{TTA,S}$ by up to 0.32 eV, colored in yellow in Figure 4. Only α-6T (**I2**) and 2,5-diphenyloxaxole (PPO, **F3**) have $E^{loss}_{TTA,T}$ significantly larger than their $E^{loss}_{TTA,S}$ (red region in Figure 4), indicating that they might not be efficient TTA emitters. This is consistent with experiments. TTA in **I2** α-6T has been observed only in thin films[31], whose excitation energies are different than isolated molecules. TTA has been reported for PPO (**F3**) dissolved in benzene, albeit with a very low QY of 0.58%.[76] In search of more potential TTA emitters, we used G_0W_0+BSE@PBE to investigate 43 additional chromophores from various chemical families, shown in Figure 2. The results are represented by black circles in Figure 4. Of these chromophores, 7 fall in the most promising green region and 12 fall in the less efficient yellow region. The overall picture that emerges from figure 4 explains in terms of energetics why there are so few TTA emitters and why the QY of most emitters is low.

Figures 5 and 6 show a breakdown of the chromophores studied here by chemical families. Many of the known TTA emitters belong to the acene family, shown in Figure 5(a), including rubrene and several anthracene derivatives. Of the acene derivatives studied here, molecules **A1** to **A10** have an anthracene backbone. All anthracene derivatives have $E^{loss}_{TTA,S}$ in the range we consider as promising for TTA. **A8** has a $E^{loss}_{TTA,T}$ slightly smaller than its $E^{loss}_{TTA,S}$. Six anthracene derivatives are between the $E^{loss}_{TTA,T} = E^{loss}_{TTA,S}$ and $E^{loss}_{TTA,T} = E^{loss}_{TTA,S} + 0.32$ eV lines. For three of the anthracene derivatives, **A7**, **A9**, and **A10**, $E^{loss}_{TTA,T}$ is more

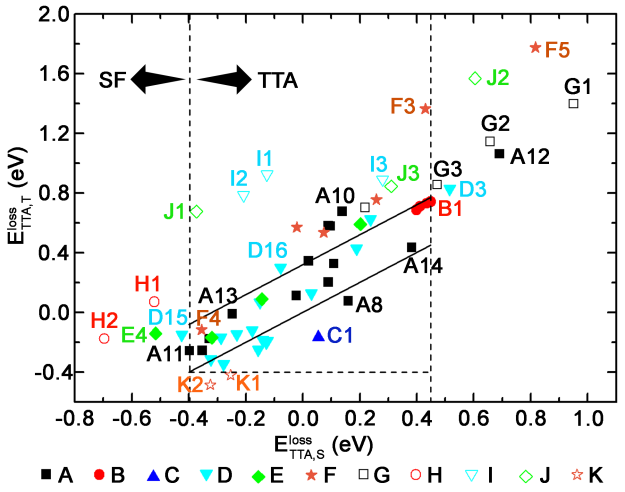

Fig. 6 The energy loss in the triplet pathway, $E^{loss}_{TTA,T}$, vs. the energy loss in the singlet pathway, $E^{loss}_{TTA,S}$, obtained from G_0W_0+BSE@PBE calculations, with a breakdown by chemical families. The labels correspond to Figure 2.

than 0.48 eV larger than $E^{loss}_{TTA,S}$. In particular, the $E^{loss}_{TTA,S}$ of **A10** is very close to that of **A8**, however its $E^{loss}_{TTA,T}$ is higher by about 0.60 eV. Pentacene and its derivatives are usually considered as SF chromophores[77], rather than TTA emitters. Interestingly, the pentacene derivative **A12** has a relatively high $E^{loss}_{TTA,S}$, possibly owing to backbone substitutions. **A13**[78,79] and **A14**[80] have acene backbones functionalized with aromatic terminal groups that produce an extended π-system. Both have $E^{loss}_{TTA,S}$ in the range we consider as promising for TTA and are between the $E^{loss}_{TTA,T} = E^{loss}_{TTA,S}$ and $E^{loss}_{TTA,T} = E^{loss}_{TTA,S} + 0.32$ eV lines.

Pyrene (**B1**) and some of its derivatives are known as TTA emitters. All pyrene derivatives studied here (group **B**) lie very close to each other in Figure 6. Of the chromopores studied here, pyracyclene (**C1**) stands out as having the lowest $E^{loss}_{TTA,T}$ relative to its $E^{loss}_{TTA,S}$. However, despite its favorable energetics, pyracyclene (**C1**) is not a good TTA emitter because the lifetime of its lowest triplet state is rather short and radiationless decay of its lowest singlet state is rapid[81]. Synthesis of additional pyrene and pyracyclene derivatives with different chemical modifications could potentially produce chromophores with improved properties.

Another promising chemical family for TTA is perylene derivatives (group **D**), shown in Figure 5(b). Perylene (**D1**) and 2,5,8,11-tetra-tert-butylperylene (**D8**) have been reported to undergo TTA[57]. The QY of TTA in perylene varies from 0.16% to 9.25% in experiments[13,82,83]. Similar to the anthracene derivatives, most perylene derivatives have $E^{loss}_{TTA,S}$ in the promising range for TTA vs. SF. Side group functionalization leads to significant variation in $E^{loss}_{TTA,S}$ vs. $E^{loss}_{TTA,T}$. Most perylene derivatives fall within the region between the $E^{loss}_{TTA,T} = E^{loss}_{TTA,S}$ and $E^{loss}_{TTA,T} = E^{loss}_{TTA,S} + 0.32$ eV lines. Five perylene derivatives, **D8**, **D10**, **D12**, **D13**, and **D14**, lie under the $E^{loss}_{TTA,T} = E^{loss}_{TTA,S}$ line. Notably, all 16 perylene derivatives studied here have known crystal structures, available in the Cambridge Structural Database (CSD). This could be a potential advantage for solid-state implementations of solar cells with TTA-UC[3,4].

Group E contains four large asymmetric PAHs dubbed "graphene flakes". **E1** and its derivatives have been studied for applications in organic field-effect transistors[84]. However, this chemical family has not been considered for TTA to our knowledge. Of these molecules, **E4** has $E^{loss}_{TTA,S}$ below that of rubrene and could potentially undergo SF. **E1**-**E3** could potentially undergo TTA in terms of their $E^{loss}_{TTA,S}$. **E2** and **E3** are within the region between the $E^{loss}_{TTA,T} = E^{loss}_{TTA,S}$ and $E^{loss}_{TTA,T} = E^{loss}_{TTA,S} + 0.32$ eV lines. **E1** lies slightly outside of this region. This indicates that further exploration of this class of molecules may produce additional SF and TTA chromophores.

Group **F** comprises several species characterized by a five-membered ring with one oxygen atom and a varying number of nitrogen atoms. TTA has been experimentally observed in two of them, PPO (**F3**) and 1,3-diphenylisobenzofuran (DPBF, **F4**). As discussed above, the QY of TTA in PPO (**F3**) is very low. The $E^{loss}_{TTA,S}$ of DPBF (**F4**) is very close to that of rubrene, and like rubrene, it has also been reported to undergo SF in its two molecular crystal polymorphs.[85] TTA has been observed in DPBF in deoxygenated dimethylformamide solution with a QY of 4.35%, which was enhanced to 16.0% when combined with 9, 10-diphenylanthracene (DPA, **A3**).[32] None of the other molecules in group **F** seem promising as TTA emitters. With the exception of DPBF (**F4**), all molecules in this group lie above the $E^{loss}_{TTA,T} = E^{loss}_{TTA,S} + 0.32$ eV line. **F5** also has a very large $E^{loss}_{TTA,S}$. Hence, of this group, only benzofuran derivatives may be of interest for further exploration.

The four coumarin derivatives studied here (group **G**) are not found to be promising for TTA because their $E^{loss}_{TTA,T}$ is large compared to their $E^{loss}_{TTA,S}$. For **G1** and **G2**, $E^{loss}_{TTA,S}$ is also too large to be efficient TTA emitters. BODIPY derivatives (group **H**) are interesting because some are TTA sensitizers[86], whereas others are emitters[8]. Both BODIPY derivatives studied here, **H1** and **H2**, are more likely to undergo SF than TTA because their $E^{loss}_{TTA,S}$ is smaller than that of rubrene. Other BODIPY derivatives where TTA has been experimentally observed[8] are too large for G_0W_0+BSE@PBE calculations with converged basis sets. This family may be investigated further in the future. For the thiophene derivatives studied here (group **I**), the energy release in the singlet pathway is in the appropriate range for TTA to be favorable. However, the energy release in the triplet pathway is too large for high QY. Group **J** contains organic photovoltaic molecules, comprising six-membered rings connected by single and double carbon-carbon bonds. Of this group, $E^{loss}_{TTA,S}$ of **J1** is close to that of rubrene, $E^{loss}_{TTA,S}$ of **J3** is closer to the higher end of the range considered here as promising for TTA, and $E^{loss}_{TTA,S}$ of **J2** is too high for efficient TTA. For all three chromophores, $E^{loss}_{TTA,T}$ is too large compared to $E^{loss}_{TTA,S}$. Therefore, groups **I** and **J** do not seem promising for TTA. Group **K** contains two push-pull dyes with a triphenylamine donor and a benzothiadiazole acceptor, reminiscent of some of the chromophores used for thermally activated delayed fluorescence (TADF).[87,88] Interestingly, these molecules are the only group located in the optimal region where only singlet pathway is exothermic. This points at a possible new

direction to explore in search of TTA emitters.

Figures 5 and 6 show that within a chemical family, functionalization with side groups and backbone substitutions may significantly change the excited state energetics. This indicates that if a certain chemical family shows promise, the TTA QY may be improved by chemical modifications. Figure 6 also indicates that, in addition to the well known anthracene and perylene derivatives, several of the chemical families studied here may be of interest for further exploration, including pyrene derivatives, pyracyclene derivatives, graphene flakes, benzofuran derivatives, BODIPY derivatives, and push-pull thiadiazoles. It should be noted, however, that even if a chromophore appears promising from the energetics point of view, there are other requirements that a good TTA emitter must meet. High photoluminescence is required from the final singlet state to maximize brightness, and stability and solubility concerns must be addressed as applications are developed.[89–91]

4 Conclusion

In summary, we have performed G_0W_0+BSE@PBE calculations for 59 chromophores of diverse chemical families. Based on the results obtained for 16 known TTA emitters, we defined criteria to evaluate new candidates. A chromophore is considered more likely to undergo TTA than SF if its energy release in the singlet pathway, $E^{loss}_{TTA,S}$, is greater than that of rubrene. The energy loss is considered as too high for efficient TTA if $E^{loss}_{TTA,S}$ is higher than that of pyrene. Ideally, in order for the QY to exceed the spin-statistical limit of 20%, the triplet pathway should be less thermodynamically favorable than the singlet pathway. This means that $E^{loss}_{TTA,T}$ should be as small as possible, preferably negative, and at the very least smaller than $E^{loss}_{TTA,S}$. We find that very few of the chromophores studied here meet the latter criterion. Even for most experimentally known emitters studied here, $E^{loss}_{TTA,T}$ is found to be somewhat higher than $E^{loss}_{TTA,S}$. This explains, in terms of energetics, why there are so few known TTA emitters and why the QY of TTA is typically low.

Although chromophores meeting the energetic requirements for efficient TTA are rare, the chemical compound space is still largely unexplored. Computer simulations may aid the search for new TTA emitters. Our results demonstrate that within a given chemical family the excitation energies vary significantly with side group functionalization and backbone substitution, which may change the energy balance between the singlet pathway and the triplet pathway. Hence, chemical modification is a promising route for optimizing the TTA QY within a chemical family. In addition, our results indicate that some chemical families, beyond the well-known anthracene and perylene derivatives, may be of interest for further exploration. These include pyrene derivatives, pyracyclene derivatives, graphene flakes, benzofuran derivatives, BODIPY derivatives, and push-pull thiadiazoles. We note that even if a compound is identified as promising from the energetics point of view, other considerations may prevent it from being a good TTA emitter. Therefore, the energetic criteria suggested here may be applied in the first stage of materials screening and additional criteria should be developed for further evaluation of the viability of TTA candidates.

Conflicts of interest

There are no conflicts to declare.

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