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Electronic Energy Pooling in Organic Systems: A Cross-Disciplinary Tutorial Review

Ronald P. Steer

Department of Chemistry
University of Saskatchewan
110 Science Place
Saskatoon, SK
Canada S7N5C9

email: ron.steer@usask.ca

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Abstract:

Electronic energy pooling via excited state (exciton) annihilation, primarily in organic systems, is reviewed in tutorial form. Cross-disciplinary terminologies and references are used and reference is made to the historical origins of the phenomena. Applications in organic photovoltaic and electroluminescent devices are addressed. Particular attention is paid to the kinetics of the processes involved; a standard format for all systems is developed. Within the organic materials framework, all of triplet-triplet, triplet-singlet and singlet-singlet annihilation processes are discussed. Examples from gas, fluid and solid phase systems, including both homo- and hetero-species interactions, are employed. Particular attention is given to triplet-triplet annihilation processes in which product states other than the lowest excited singlet state are formed.

List of Abbreviations (in order of appearance):

DF	delayed fluorescence
TTA	triplet-triplet annihilation
OLED	organic light-emitting diode
IC	internal conversion
ISC	intersystem crossing
IVR	intramolecular vibrational relaxation
R_E	excitation rate
I	light intensity (subscript a, absorbed; subscript ℓ , luminescence; subscript d, delayed)
J	current density
η_e	electric efficiency
SSA	singlet-singlet annihilation
STA	singlet-triplet annihilation
E^*	the electronically excited species participating in the energy pooling process
E^{**}	the electronically excited energy pooled product
η_0	quantum yield of E^* following electronic excitation of E
k_{en}	(or γ_{E^*}) the second order rate constant for excited state-excited state encounter
F_{ep}	the probability of forming one energy pooled product per E^* participating in the initial encounter complex; superscript R, with recycling)
L_{DE^*}	exciton diffusion length
D_{E^*}	exciton diffusion constant
DL	delayed luminescence
DPA	9,10-diphenylanthracene
IQE	internal quantum efficiency
χ_e	exciton production efficiency (subscript p, prompt; subscript d, delayed; superscript R, with recycling)
I_ℓ	luminescence intensity (p, prompt; d, delayed)
ϕ_ℓ	quantum yield of luminescence (p, prompt; d, delayed)
TET	triplet energy transfer
N_{rt}	number of triplet excited states available for recycling per eighteen triplets in the initial encounter pair

Introduction:

The general phenomenon of electronic energy pooling is one outcome, often desirable, of processes referred to in the chemical literature as excited state annihilation (or exciton annihilation or exciton fusion) and non-coherent photon upconversion (or photochemical upconversion). If an interaction between two independently excited species results in the transfer of electronic energy to one from the other, electronic energy is “pooled” in the receiving species. The quantum mechanical basis for understanding these processes began in 1931 when Frenkel¹ defined the result of photon absorption in crystalline solids as an “excitation wave,” later referred to as an exciton. The first description of a “bi-exciton” appears in the late 1950s² and the first reports of bi-excitonic energy pooling phenomena in solids are found in the mid-1960s.³ During the same period, exciton theory was adapted to molecular systems primarily through the seminal work of Davydov, McClure and Kasha.⁴

Experimental evidence of electronic energy pooling phenomena in organic materials has been available since the early 1940s but the mechanism was not understood until the 1960s when P-type (pyrene-type) delayed fluorescence resulting from the annihilation of pairs of polyacene triplet states in solution was first reported.⁵ Anti-Stokes delayed fluorescence (DF) produced upon triplet-triplet annihilation (TTA) following triplet photosensitization, a process resulting in what is now referred to as photon or photochemical upconversion, was reported immediately thereafter.⁶ These observations were paralleled by descriptions of upconverted luminescence resulting from the interaction between pairs of electronically excited singlet dioxygen molecules ($O_2\ ^1\Delta_g$) in the gas phase,⁷ and were extended later in the 1960s when photon upconversion by sensitization in trivalent

lanthanide ion-doped solids was first identified.⁸ In atomic spectroscopy, examples of electronic energy pooling processes were not observed until the advent and application of tunable dye-laser excitation sources in the 1970s.⁹

Several thousand articles in research journals describe these phenomena, which are being exploited in numerous current and potential future applications. The initially electronically excited species may be inorganic, organic or organometallic; atomic, molecular, dendrimeric, polymeric, crystalline or otherwise aggregated; may be dispersed in the gas, liquid or solid phase; and may exist at any temperature at which the system is thermally stable. Much of the present day interest is driven by the potential utility of electronic energy pooling in circumventing the Shockley-Queisser limitation on the efficiencies of single-threshold solar photovoltaic cells,¹⁰⁻¹⁴ in the use of low energy solar photons for the photochemical production of fuels,¹⁵ and in determining the color, brightness and energy conversion efficiency of electroluminescent devices such as organic light-emitting diodes (OLEDs).¹⁶⁻²⁰ Applications in sensors and logic devices have also been proposed.^{21,22}

Although terminologies differ somewhat from discipline to discipline, these diverse energy pooling processes have much in common. The initial electronic excitation is typically accomplished either by the absorption of photons or by exoergic chemical reaction, the latter including charge carrier recombination in electrically activated materials. The participating species can have diverse electronic descriptions; but if stable, electrically neutral organic molecules are involved the ground state is almost always a closed-shell singlet (total electron spin quantum number $S = 0$, with the state labelled S_0). The general phenomenon can be described symbolically by $E^* + E^* \rightarrow E^{**} + E$, that is, a fraction, $0 < f < 1$, of the total thermal

plus electronic excitation energy associated with the interacting pair, $E^* + E^*$, is pooled to produce one more highly electronically excited species (exciton), E^{**} , and one of lower energy, E , often the ground state. The highly excited species may luminesce, producing what has been termed “upconverted delayed emission” if the process is initiated by the absorption of lower energy photons, or it may participate in photochemical reactions to yield a product that would otherwise be inaccessible by the absorption of the lower energy photon. The two excited species participating as reactants in the energy-pooling interaction may be chemically identical (homo-processes) or different (hetero-processes). The energy pooling interaction may occur either between two physically separate species (*e.g.* intermolecular between singly-excited small molecules or inter-chain between singly-excited polymers) or within the same species (*e.g.* intramolecular annihilation in doubly-excited multichromophoric molecules or dendrimers or polymers).

In this review we shall focus only on systems in which at least one step in the overall energy pooling process involves non-coherent electronic energy transfer between two independently excited species. Thus, coherent multi-photon absorption, second harmonic generation and fluorescence upconversion in birefringent crystalline solids, all phenomena that are well-known in laser chemistry and physics, will not be considered. Energy pooling by excited state photon absorption and by thermally activated upconversion will also be excluded, as will a specific form of electronic energy pooling that involves simultaneous double sensitization by three-body resonance energy transfer.^{23,24} Finally, only photostable organic systems in condensed media will be considered in depth; annihilation and upconversion in doped inorganic solids²⁵ and in core-shell nanoparticles²⁶ have been thoroughly reviewed elsewhere.

There is considerable descriptive overlap between the energy-pooling phenomena that will be reviewed and their reverse, exciton fission.²⁷⁻²⁹ Where convenient, the two sets of processes will be compared. Differences in cross-disciplinary nomenclatures will be addressed. Literature citations are often mutually discipline-exclusive despite the fact that the electronic energy pooling phenomena involved are essentially the same. This review will attempt to bridge that gap. Finally, this review has been written at a broadly-based introductory graduate level, giving due attention to historical context as well as current application, but without attempting to be comprehensive.

Nomenclature and conventions:

When describing electronically excited species, researchers in chemistry most frequently use approaches and terminologies that arise primarily from molecular spectroscopy (*e.g.* the use of iterative electronic state notation: S_0 , T_1 , S_1 , etc., and the terms “excited state” and “radical cation or anion”). Those in physics and engineering commonly use approaches and terminology developed via condensed matter physics (*e.g.* use of the terms “exciton” and “polaron”). Whether a species in an electronically excited state would best be described as an exciton depends on the extent to which the excitation energy or promoted electron remains isolated on the initially excited moiety. If the electronically excited species are small photostable molecules in an inert fluid medium, they can diffuse during their lifetime thereby increasing their spatial range. However, the excitation energy will continue to reside on each specific excited species until that species either spontaneously decays or interacts with another active component of the medium. In such circumstances, a

single molecular spectroscopic state descriptor (spin state, symmetry species, etc.) for the excited species is completely appropriate.

On the other hand, if the excited entity is in a condensed medium and is polychromophoric or is non-covalently aggregated with other species capable of electronic communication (or during its lifetime becomes so non-covalently aggregated), then the excitation energy often can be viewed as being shared among electronically interacting moieties. In such circumstances it is appropriate to consider the electronically excited entity as an exciton or bound electron-hole pair. The spatial extent to which the excitation energy or charge is shared among near-identical aggregated moieties then becomes important, and is determined by a variety of correlated factors including the aggregate's composition, structure and morphology. If the electron and hole, though mobile, remain paired – for example following one-electron HOMO to LUMO excitation in a crystalline solid – then it is termed a neutral Frenkel exciton. In solids, such a bound electron-hole pair may be able to diffuse by electron transfer among identical species (or can be trapped), but exhibits no significant charge separation during its lifetime. However, if localized electronic excitation results in subsequent charge separation by electron and/or hole migration to adjacent species then the result is often called a Wannier-Mott or charge transfer exciton that has ionic character. Figure 1 is a cartoon that describes the difference.

(a) Frenkel Exciton Binding energy *ca.* 1 eVRadius *ca.* 1 nm**(b) Wannier-Mott Exciton**Binding energy *ca.* 10 meV,Radius *ca.* 10 nm

Figure 1: 2-D cartoon illustrating the differences between a Frenkel exciton (a) and a Wannier-Mott exciton (b) in a crystalline or otherwise ordered solid matrix.

In suitable organic solids (in the many-body interaction limit) both neutral and charge transfer states can form band structures characteristic of semiconductors. Full charge separation can occur under the influence of electric fields; the resulting charge carriers are often called polarons. Polarons can also be formed by electron (P^-) and/or hole (P^+) injection from electrodes into a semiconductor and/or charge injection layers coupled to them. Charge recombination, *i.e.* P^+P^- neutralization, will result in the formation of more locally electronically excited species (excitons) that may luminesce (*vide infra*).

Understanding the behaviour of charged species at the “interphase” region is important in describing quantitatively the energetics of charge injection in electroluminescent devices and of charge separation in photovoltaics. Here we adopt the IUPAC Electrochemistry Commission’s nomenclature and conventions as described in reference 30. The conventions adopted in these recommendations allow the unambiguous

placement of energies associated with electrode work function and electron affinity, semiconductor Fermi levels, molecular ground and excited states, and standard electrochemical potentials, all relative to vacuum, which is assigned an energy $E = 0$.

Finally, luminescence in organic systems is classified as either fluorescence (a radiative transition involving no change in electron spin multiplicity) or phosphorescence (a radiative transition in which the change in electron spin multiplicity is non-zero). All luminescence resulting from electronic energy pooling, as described above, may be classified as delayed luminescence, distinguishing it from prompt luminescence that arises from the immediate radiative relaxation of a directly excited species that has not acquired additional energy by interspecies energy transfer. Intramolecular radiationless relaxation between states of the same electron spin multiplicity is termed internal conversion (IC) whereas intramolecular radiationless relaxation between states of differing electron spin multiplicity is called intersystem crossing (ISC). These processes are illustrated pictorially in the Jablonski diagram of Figure 2. The structures of all molecular species referred to in the text are given in Scheme 1.

Figure 2: Illustration of the intramolecular relaxation processes of electronically excited polyatomic molecules, using zinc porphyrin as a model. I.C. internal conversion; I.S.C. intersystem crossing; I.V.R. intramolecular vibrational relaxation; $h\nu_f$ fluorescence; $h\nu_p$ phosphorescence. The Soret ($S_0 - S_2$) and Q ($S_0 - S_1$) band absorptions are also illustrated. In condensed media I.V.R. can also refer to intermolecular vibrational relaxation

Scheme 1

Excitation and the fate of the initially formed electronically excited species:

Electronic excited states (excitons) of organic materials are most commonly produced by photon absorption in the uv-visible-nir regions of the spectrum or by exoergic chemical reactions (including charge recombination) in which the reaction coordinates lead to an elevated potential surface of a bound product. In photoexcited systems, the initial rate of excitation, R_E , equals I_a , the absorbed light intensity, for this review quoted in units of moles of photons (einsteins in non-IUPAC sanctioned terminology) per unit volume (usually dm^{-3}) per second. In electroluminescent devices the number of electron-hole (polaron) pairs produced per unit volume (usually cm^{-3}) per second is $J/(ed)$, where J is the current density in A/cm^2 , e is the elementary charge, and d is the thickness of the exciton formation zone in cm. The overall rate of exciton formation, expressed as number per cm^3 per s, is then $R_E = \eta_e J/(ed)$. The proportionality constant, η_e , is called the electric efficiency, which expresses the fraction of the total number of initially created polaron pairs that survive to produce excitons of all possible types ($0 \leq \eta_e \leq 1$; *vide infra*). Excitation by either route often leads to radiative decay of the initially-excited electronic species in the form of prompt fluorescence or phosphorescence. Subsequent processes can lead to delayed luminescence by electronic energy pooling.

In photoluminescent organic systems, the ground state of the emitter is almost always a singlet, S_0 , and the excited state (exciton) initially-formed on photon absorption in formally spin-allowed transitions will also be a singlet, S_n $n \geq 1$. If $n > 1$, then rapid IC to the lowest excited singlet state, S_1 , is most frequently the only important fate of this species, although there are significant exceptions (*vide infra*). Thereafter, several parallel physical processes

can return the excited singlet system to its ground state: (i) fluorescence, with the prompt emission of photons of lower energy than those used to excite the system (*i.e.*, Stokes shifted), (ii) radiationless IC directly to the ground state, (iii) radiationless ISC to the triplet manifold, yielding (perhaps by more than one step if T_n , $n > 1$, is formed initially) the lowest triplet state (or triplet exciton), T_1 . This species is sometimes detected by the appearance of its phosphorescence, but otherwise decays by a second ISC step to S_0 , (iv) quenching to the ground state by other species present in the material, sometimes via the formation of excimers, exciplexes or larger excited aggregates, and (v) annihilation by interactions with other excited species, processes that can lead to delayed luminescence of an electronically excited annihilation (energy-pooled) product. Of course photochemical products can also result from any of these post-photon absorption steps and these products may be either desirable (*e.g.* solar fuel devices) or undesirable (*e.g.* photovoltaic cells and OLEDs).

In electroluminescent devices such as OLEDs, polaron recombination in the emissive layer results in the formation of both singlet and triplet excitons of the organic emitter. Organic polarons are fermions with net electron spin quantum number $S = \frac{1}{2}$. If they diffuse and interact in an uncorrelated manner, fermion spin statistics require that the singlet and triplet exciton products of polaron encounter-pair charge recombination will be formed in the ratio of 1:3. If this were the only process taking place, this spin statistical restriction would place an upper limit of 25% on the internal quantum efficiency of an OLED employing fluorescent emitters. However recent research suggests that for several reasons, including energy pooling (*i.e.*, exciton annihilation), this 25% limit is frequently broken in both small molecule and polymer-based fluorescent OLEDs (*vide infra*). The radiative and radiationless processes resulting from polaron recombination are completely analogous to those that

occur in photo-excited systems. In an OLED, prompt fluorescence will be produced by the singlet excited product of polaron recombination and prompt phosphorescence will be produced by the initially formed triplet product. Delayed luminescence can result from subsequent annihilation of the initially-formed excitons.

Characteristics of the interacting, energy pooling species:

The key competing kinetic processes affecting homo-species energy pooling interactions can be represented in the simplest overall terms by:

where E^* is the electronically excited energy pooling reactant species, $(E^* \cdots E^*)$ is the encounter complex, and E^{**} is the energy-pooled product. Here, k_{ep} is the second order rate constant of the *overall* energy pooling process, and k_{1E^*} is the *sum* of the rate constants for all parallel kinetically first order and pseudo-first order processes by which E^* can decay (*i.e.*, the $1/e$ lifetime of E^* in the absence of annihilation is $\tau_{E^*} = 1/k_{1E^*}$). The energy pooling process must be preceded by species diffusion or electronic energy migration (of some sort) to bring about interaction between the two independently excited moieties. Three conditions must therefore be met if electronic energy pooling is to compete successfully with parallel kinetic first or pseudo-first order processes by which the species relax. (i) The participating excited moieties must have an intrinsic lifetime in the medium that is long enough to allow the second-order diffusional interaction to occur. That is, k_{1E^*} should be small. (ii) The excited species must be produced at a sufficient rate and in a small enough volume to yield a number

density (molar concentration) large enough to allow a second order process to compete. That is, R_E should be large. (iii) The rate constant of the overall energy pooling process, k_{ep} , must be large enough to generate the energy-pooled product in significant yield. Condition (iii) is determined by the exciton diffusion rate and the propensity for the encounter complex to form the desired energy-pooled product and is an absolute requirement for efficient energy pooling. However, conditions (i) and (ii) can offset one another. A large number density produced by a large R_E can offset an excited species lifetime that might otherwise be too short and *vice versa*.

Frequently, the first of these requirements is met when the electronic transition of the excited species back to its ground state is forbidden in some way, *e.g.* when it involves a relaxation process in which the change in total electron spin is non-zero. In organic systems with closed-shell ground states, this requirement is most readily met when the diffusing species is in its lowest triplet state, T_1 . Although $T_1 - S_0$ ISC is electron spin forbidden, its rate nevertheless increases (often exponentially) with decreasing $T_1 - S_0$ electronic energy spacing as the electronic coupling and Franck-Condon factors for vibronic interaction increase. Consequently polyatomic organic species with triplet energies lower than *ca.* 1 eV are often too short-lived to produce efficient yields of energy-pooled product at competing rates. Heavy-atom containing species exhibit enhanced spin-orbit coupling and are therefore useful in promoting rapid ISC from S_1 to T_1 , particularly when the $S_1 - T_1$ energy spacing is small. Indeed, heavy atom-containing emitters such as platinum or palladium octaethylporphyrin³¹ and organo-iridium complexes³² can be used in phosphorescent OLEDs. However, an enhanced rate of neither radiative nor radiationless relaxation from T_1 to the ground state is desirable if a long-lived triplet is required for energy pooling. In addition to

the above, the spacing between T_1 and S_1 should be more than several multiples of $k_B T$ to prevent triplet loss by thermally activated back-intersystem crossing, $T_1 \rightarrow S_1$, and subsequent spin-allowed decay of S_1 . (Note, however, the case of fluorescent OLEDs in which a modest $S_1 - T_1$ energy spacing and appropriate molecular design may produce an enhanced delayed fluorescence yield by thermally activated intersystem crossing from the initially-formed triplet excitons.^{33,34}) Thus, long-lived organic and organometallic triplets used for electronic energy pooling will most often be found among photostable, alternant, polycyclic, aromatic molecules, their derivatives and polymers, containing only elements of relatively low atomic mass.

The properties of the upconverted (energy-pooled) product state, E^{**} , must also be considered. For example, the most energy-efficient homomolecular TTA processes, $2 T_1 \rightarrow S_n$ ($n \geq 1$) + S_0 , will occur when the upconverted singlet product, S_n , has an energy, $E(S_n)$, that is not much lower than $2E(T_1)$. If the object of the annihilation process is to maximize the upconverted fluorescence intensity, then S_n will almost always need to be S_1 , a photochemically stable state with a nanosecond lifetime and a fluorescence quantum yield approaching unity when photo-excited directly. Singlet energy pooling product states S_n ($n > 1$) may be accessible on energy conservation grounds. However, with very few exceptions in organic systems such states exhibit rapid radiationless decay and therefore have very short lifetimes and small fluorescence quantum yields. If $E(S_1) > 2 E(T_1)$, an appropriately designed system can offer the possibility of singlet fission when excited directly to S_1 ,^{27,28} but the energy-pooling TTA process in such a case would need to be thermally activated, leading to relatively low efficiency.

The types of annihilation processes and the identity of the energy-pooled product:

The complexity of non-coherent electronic excited state-excited state interactions is well-illustrated by the nominally simple encounter between two excited atoms or between two electronically excited small molecules in the gas phase. Many examples of electronic energy pooling in excited atoms are now known, but the system $\text{Ca}(4s4p\ ^3P_1) + \text{Ca}(4s4p\ ^3P_1) \rightarrow \text{Ca}(4s4p\ ^1P_1) + \text{Ca}(4s^2\ ^1S_0)$ is perhaps most fully understood. Parks and Leone^{35,36} used polarized pulsed lasers and magnetic fields to control the electromagnetic orientation of the colliding excited atoms and then observed the final state alignment of the electronically excited singlet product, $\text{Ca}(^1P_1)$, by measuring its polarized fluorescence. The efficiency of the energy pooling process was found to be strongly dependent on the relative initial state alignment of the interacting atoms, with alignment of the final state directed predominantly along the relative velocity vector of the collision but only weakly correlated with the initial state alignment. This simple two-body system, however, is characterized by 39 independent parameters, of which only 18 could be assessed in these detailed experiments.

The complexities of electronic energy pooling in small molecules are also revealing. For example consider $2\ \text{O}_2(a^1\Delta_g) \rightleftharpoons [(\text{O}_2)_2]^{**} \rightarrow \text{O}_2(b^1\Sigma) + \text{O}_2(X^3\Sigma)$ in which a full nonadiabatic wave packet calculation³⁷ indicates that six states are needed to account for the electronic degeneracy of the tetraatomic dimer; four singlets that correspond to the $\text{O}_2(a^1\Delta_g) + \text{O}_2(a^1\Delta_g)$ dissociation limit and two triplets that correspond to the forward $\text{O}_2(b^1\Sigma) + \text{O}_2(X^3\Sigma)$ energy pooling dissociation limit that involves a change of total electron spin. From a state-to-state perspective, four singlet to triplet processes contribute to the net energy pooling cross section (which is also strongly dependent on collision energy), but one of them is dominant.

Although such detail is masked in polyatomic molecular and condensed matter organic systems, the characteristic dominance of a single energy-pooling process along a given spin-conservative channel is often retained irrespective of system complexity. In the above atom and diatomic molecule energy-pooling cases, total energy and momentum conservation require that the products take up any electronic energy mismatch between reactants and products in their translational degrees of freedom or, in the case of small molecules, in translational and a few vibrational and rotational degrees of freedom. In polyatomic molecules, particularly in condensed media, the large density of vibrational states (phonon states in solids) available to the products often provides a continuum for energy and momentum conservation. In principle, this situation then makes available all possible product electronic states that meet energy and spin conservation requirements. Nevertheless, even when several different excited product states of a given electron spin multiplicity are accessible on energy conservation grounds, it frequently occurs that only one of them will be preferentially populated (*vide infra*).

In almost all organic systems the only electronic states of species either entering or leaving a homo-type energy pooling interaction that need be considered are triplets and excited singlets that lie relatively low in the electronic manifold of valence states. Singlet and triplet excited electronic states, S_n ($n > 1$) and T_n ($n > 1$), higher in energy than twice that of either T_1 or S_1 need not be considered for illustration purposes. Within this restricted set of relatively low-lying valence states, all combinations of singlet-singlet (SSA), singlet-triplet (STA) and triplet-triplet (TTA) annihilation (with consequent energy pooling) are well-known. The interactions may involve two excitons of the same molecular identity (homo-

type) or of different identity (hetero-type), but when hetero-type interactions are involved charge transfer product states must also be considered.

Although S_1 is the most frequently desired energy-pooling product, if the application involves electron or electronic energy transfer from the excited singlet product of annihilation to an acceptor, then other higher energy singlet states, S_n ($n > 1$) with shorter lifetimes and smaller fluorescence quantum yields, could be useful (*vide infra*). If maximizing the energy efficiency of the annihilation process is critical, then the desired product singlet should have an electronic energy not much smaller than the sum of the electronic energies of the two interacting excited species.

So, if several different excited singlet product states are accessible on energy conservation grounds, which is formed and with what efficiency? This depends on the nature of the energy-pooling interaction (SSA, STA or TTA; homo- or hetero-; inter-species or intra-species). Each case will be discussed in sequence following a general discussion of the kinetics of these systems, with particular attention on the formation of the encounter complex and the generic energy-pooled excited product(s) derived from it.

Kinetics of electronic energy-pooling processes:

Ultimately, the overall efficiency of any electronic energy pooling interaction is determined by the kinetics of the competing processes involved in forming the encounter complex from E^* and the fraction of the encounter complexes that yield the desired energy-pooled species, E^{**} . The kinetic mechanisms at play are well understood, and those associated with homo-TTA particularly have recently been thoroughly reviewed.^{13,17} There remain some inconsistencies in defining the rate constants, particularly for processes that are second

order in a single reactant, and a self-consistent rendering of the kinetics that can be generally applied to energy pooling processes is presented here. The kinetic models for electronic energy-pooling systems were developed in the early work of Birks,³⁸ were adapted by Weisman and coworkers for annihilation processes in the fullerenes,³⁹⁻⁴¹ and were liberally applied to processes in optoelectronic devices in the early 2000s.^{13,14,16,17}

The two sets of competing kinetic processes previously represented by generic rate equations are now written in greater detail. To illustrate, consider either pulsed or continuous photon excitation forming E^* at a rate $\eta_0 R_E$, where η_0 is the quantum efficiency by which E^* is formed following initial excitation of E , which is photostable. The kinetically first order (and pseudo-first order) processes for the loss of E^* and the associated rate constants are then:

The second order electronic energy pooling process producing E^{**} is then represented, for a homo-species encounter, as:

In the absence of annihilation (and quenching by other transients), the lifetime of the excited species, E^* , is given by:

$$\tau_{E^*} = 1/(k_r + k_{nr} + k_{sq}[E] + k_{et}[Q]) = 1/k_{1E^*}$$

(Here we use $[X]$ to represent molar concentrations of species X and employ molar units for the second order rate constants. An equivalent representation uses number densities, n_X in cm^{-3} , with second order rate constants in molecular units, $\text{cm}^3 \text{s}^{-1}$.) We assume a model in which the concentrations of E^* are spatially uniform although this is never fully achieved experimentally.

The quantity $k_{1E^*} = 1/\tau_{E^*}$ is the sum of the first order and pseudo-first order rate constants for all parallel processes by which E^* can decay back to the ground state. If the concentrations of E and Q are much greater than those of E^* throughout the considered time-span and annihilation is minimal, then any self-quenching and energy transfer processes will be kinetically pseudo-first order and E^* can be expected to decay exponentially following pulsed excitation, *i.e.*,

$$[E^*]_t = [E^*]_0 \exp(-k_{1E^*}t) = [E^*]_0 \exp(-t/\tau_{E^*})$$

The value of k_{1E^*} can then be obtained by following the temporal decay of E^* using either transient emission or transient absorption methods. Since k_{1E^*} is a function of the concentrations of E and Q , the second order quenching rate constants can be obtained by measuring τ_{E^*} as a function of either $[E]$ or $[Q]$ while maintaining pseudo-first order conditions, using low excitation rates, and keeping all other conditions constant. These data are then subject to a Stern-Volmer analysis, as shown in Figure 3a, where the slope of the linear $1/\tau_{E^*}$ vs. $[Q]$ plot gives k_{et} directly and the intercept at $[Q] = 0$ gives $1/(\tau_{E^*})_{Q=0}$, the inverse of the lifetime of E^* in the absence of the one particular quencher, Q . The value of k_{et}

will then reflect both the rate of mutual diffusion of the $E^* + Q$ pair in the medium and the propensity for the energy transfer process. Alternatively, in luminescent systems, the relative quantum yields (or relative intensities) of photo-excited luminescence of E^* can be measured under steady state illumination conditions as a function of $[Q]$, as shown in Figure 3b, and the slope equated to $k_{et}(\tau_{E^*})_{Q=0}$.

Figure 3: The formats of Stern-Volmer plots for luminescence quenching. (a) when luminescence lifetimes, τ , are measured, and (b) when luminescence quantum yields, ϕ , are measured.

If τ_{E^*} can be measured in the absence of quenching by a system component, *i.e.* at $[Q] = 0$, and with $[E]$ small enough that τ_{E^*} is independent of $[E]$, then obtaining the values of τ_{E^*} and $\phi_{\ell E^*}$, the quantum yield of luminescence of E^* , under these circumstances will yield the rate constants k_r and k_{nr} for the first order relaxation of E^* via $k_r = \{\phi_{\ell E^*}/(\tau_{E^*})\}_{Q=0, E \rightarrow 0}$ and $k_{nr} = \{(1 - \phi_{\ell E^*})/(\tau_{E^*})\}_{Q=0, E \rightarrow 0}$. Note that in this scheme k_{nr} will represent the *sum* of the rate constants of all parallel intra-species first order processes by which E^* can relax non-radiatively. So if E^* is an excited singlet state $k_{nr} = k_{ic} + k_{isc}$ whereas if E^* is the lowest triplet state $k_{nr} = k_{isc} + k_{bisc}$. Here k_{bisc} represents the rate constant for thermally activated back-intersystem crossing and is related to the $S_1 - T_1$ energy spacing via $k_{bisc} = (k^0)_{bisc} \exp\{-\Delta E(S_1 - T_1)/(k_B T)\}$.

Two different conventions have been used previously to write the rate equations for second order homo-annihilation processes, depending on how the stoichiometry of the reaction is accounted for. Here we use the convention $+d[E^{**}]/dt = -\frac{1}{2} d[E^*]/dt$ for the limiting case of a homo-annihilation process that proceeds 100% to completion after forming the encounter complex. In the general case $k_{ep} = F_{ep}k_{en}$ where k_{en} represents the second order rate constant for $E^* + E^*$ pairwise encounters, and we incorporate the stoichiometric factor of $\frac{1}{2}$ into F_{ep} , the probability of forming one energy pooled product per E^* participating in the initial encounter complex. Theoretical maximum values of F_{ep} then depend not only on stoichiometry, but also on electron spin statistics, electronic energy levels of the system in the encounter complex and the mechanism of the energy pooling process, including the rate of dissociation of $(E \cdots E)^{**}$. Note particularly that, unlike some treatments of the kinetics,¹³ here the rate of formation of the forward energy-pooled product relative to the rate of

dissociation of $(E\cdots E)^{**}$ is also incorporated into F_{ep} . For homo-TTA in particular the overall efficiency of formation of the energy-pooled product may need to include the recycling of triplet states from failed triplet-triplet encounters; this process will be dealt with separately (*vide infra*).

In fluid media k_{en} will be the second order rate constant for the mutual diffusion-enabled interaction of the two excited species that form the encounter complex; its value will be determined by the viscosity and temperature of the medium, the diffusion coefficients of the interacting species and, importantly, the mechanism of the interaction leading to energy pooling. Thus TTA will involve short-range, "collisional" interaction whereas TSA and SSA will involve interactions over substantially larger distances. In amorphous, crystalline, nanoparticulate and polymeric media, the mechanism of the energy pooling interaction will again be important in determining the magnitude of k_{en} . However, in these media the process is most frequently described in terms of exciton diffusion, where – using molecular units – the exciton diffusion length, $L_{DE^*} = (D_{E^*}\tau_{E^*})^{1/2}$, is a key parameter. For homo-annihilation processes of this nature D_{E^*} is the exciton diffusion constant in $\text{cm}^2 \text{s}^{-1}$ appropriate to the medium in which E^* is produced and is often given by $D_{E^*} = \gamma_{E^*}/(8\pi a_0)$, where a_0 is the average inter-exciton distance at annihilation. The constant γ_{E^*} (in $\text{cm}^3 \text{s}^{-1}$) has the same significance as the kinetic second order rate constant ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$) for the bimolecular excited state (biexcitonic) encounter, k_{en} , in solution. In solids, L_{DE^*} thus depends upon both D_{E^*} and the lifetime of the exciton, which is in turn determined in part by the structure and composition of the medium. In addition to its intrinsic modes of decay (intra-species radiative and non-radiative relaxation), E^* therefore has a lifetime that is influenced by quenching due to the

components of these media and by trapping in defects. Thus L_{DE^*} and the exciton encounter rate are determined in large measure by the structure, composition, degree of crystallinity and the purity of the solid.

Using these conventions and writing the rate equations for E^* consumption and E^{**} production based on the above kinetic mechanism then yields the following:

$$\frac{d[E^*]}{dt} = \eta_0 R_E - k_{1E^*}[E^*] - k_{ep}[E^*]^2 \quad (1)$$

$$\frac{d[E^{**}]}{dt} = k_{ep}[E^*]^2 - k_{1E^{**}}[E^{**}] \quad (2)$$

Here $\eta_0 R_E$ is the rate of excitation yielding E^* , and is equal to $\eta_0 I_a$ in photoluminescent systems where η_0 is the fractional yield of E^* produced from the photon-absorbing ground state species. Thus for direct excitation to S_1 , η_0 equals 1 if $E^* \equiv S_1$ and equals η_{isc} if $E^* \equiv T_1$. In electroluminescent systems $\eta_0 R_E = (\chi_{e,p})(\eta_e)/(ed)$. Here $\eta_0 = \chi_{e,p}$ is the fractional yield of excitons of a given electron spin produced via the initial (prompt) polaron recombination, and is distinguished from $\chi_{e,d}$, the fractional yield of excitons of the same electron spin produced via the delayed exciton annihilation process. Thus, $\eta_0 = \chi_{e,p}$ has a maximum value of either 0.25 if singlet excitons are produced or 0.75 for triplets. The lifetime of the energy-pooled product under the conditions prevailing during annihilation is $\tau_{E^{**}} = 1/k_{1E^{**}}$, and the lifetime of the energy-pooling reactant in the absence of annihilation is $\tau_{E^*} = 1/k_{1E^*}$ as defined above. Note that this definition of k_{1E^*} excludes hetero-annihilation that can sometimes be found in triplet sensitized photo-excited systems.¹³

We now write analytical solutions to these differential rate equations for the case of continuous and pulsed excitation. For continuous excitation, steady state conditions apply so that both (1) and (2) can be set equal to zero and (1) becomes:

$$\eta_0 R_E = k_{1E^*}[E^*] + k_{ep}[E^*]^2 \quad (1a)$$

Because the lifetime of E^* is normally orders of magnitude longer than that of E^{**} , the steady state approximation for eq. 2 can be used to obtain the time-averaged concentration of excited, energy-pooled species:

$$[E^{**}] = \frac{k_{ep}}{k_{1E^{**}}}[E^*]^2 \quad (3)$$

We can then analyze these expressions for two extremes; very low excitation rates in which $k_{1E^*} \gg k_{ep}[E^*]$ and very high excitation rates in which $k_{1E^*} \ll k_{ep}[E^*]$, called the weak and strong annihilation limits respectively.

(i) In the weak annihilation limit with continuous excitation, $\eta_0 R_E = k_{1E^*}[E^*]$. Then, using

$I_{DL,weak} = k_{rE^{**}}[E^{**}]$, and $\phi_{lE^{**}} = k_{rE^{**}}/k_{1E^{**}}$ we obtain:

$$I_{DL,weak} = \frac{k_{rE^{**}}k_{ep}}{k_{1E^{**}}}[E^*]^2 = \frac{\phi_{lE^{**}}k_{ep}(\eta_0 R_E)^2}{(k_{1E^*})^2} = \phi_{lE^{**}}\tau_{E^*}^2 F_{ep} k_{en}(\eta_0 R_E)^2 \quad (4)$$

from which it may be seen that the delayed luminescence intensity depends quadratically on the excitation rate.

(ii) In the strong annihilation limit, $\eta_0 R_E = k_{ep}[E^*]^2$, so that

$$I_{DL,strong} = k_{rE^{**}}[E^{**}] = \frac{k_{rE^{**}}k_{ep}}{k_{1E^{**}}}[E^*]^2 = (\phi_{lE^{**}})_{strong}\eta_0 R_E \quad (5)$$

and the delayed luminescence intensity is a linear function of the continuous excitation rate. It is important to note that $(\phi_{lE^{**}})_{\text{strong}}$ in (5) refers to the quantum yield of luminescence of the energy-pooled product, E^{**} , measured under the conditions of strong excitation, a quantity that frequently will not be equal to the luminescence quantum yield of E^{**} obtained under conditions of direct, low-intensity excitation in dilute media (*vide infra*).

The strong excitation limit is only attained when R_E is large enough that an overwhelming proportion of E^* decay by annihilation. Although an upper limit of $I_{DL,\text{strong}}$ is often reached at sufficiently high R_E , the mathematical limit in which all E^* decay *via* annihilation is extraordinarily difficult to achieve in practice in fluid systems where excitons annihilate by inter-species interaction. However, pairs of long-lived triplets confined in solid structures such as MOFs⁴² or in single polymer chains⁴³ where exciton diffusion within the structure is rapid relative to exciton decay may exhibit relatively high TTA efficiencies even at very low excitation rates (*e.g.*, in photovoltaic devices when R_E is comparable to unfocussed solar illumination rates).

For δ -pulse excitation in which the concentration of E^* at $t = 0$ is $[E^*]_0$, the time evolution of E^* is given by:

$$[E^*]_t = [E^*]_0 \frac{\exp(-k_{1E^*}t)}{1 + \frac{[E^*]_0 k_{ep}}{k_{1E^*}} [1 - \exp(-k_{1E^*}t)]} \quad (6)$$

In the weak annihilation limit, at low $[E^*]_0$, resulting for example from low power pulsed excitation, $k_{ep}[E^*]_0 \ll k_{1E^*}$ and E^* exhibits first order decay kinetics with a lifetime

approaching $\tau_{1E^*} = 1/k_{1E^*}$. The decay of the delayed luminescence intensity of E^{**} following δ -pulse excitation of E is then given by:

$$I_{DL,weak}(t) = k_{rE^{**}}[E^{**}]_t = \frac{k_{rE^{**}}k_{ep}}{k_{1E^{**}}}[E^*]_t^2 = \phi_{lE^{**}}k_{ep}[E^*]_t^2 \quad (7)$$

Substituting (6) into (7) and again applying the weak annihilation approximation, it may be seen that the delayed luminescence intensity of E^{**} also exhibits a quadratic dependence on $[E^*]_0$ and decays at twice the rate of E^* , i.e., $(\tau_{E^{**}}) = (\tau_{E^*})/2$. An example, involving homo-annihilation of a thione triplet, producing delayed fluorescence from the S_2 state is given in Figure 4.⁴⁴

Figure 4: Kinetic first order decay of triplet (T_1) phosphorescence, I_P , at two different laser excitation powers (a, b), and of delayed (S_2) fluorescence, I_{DF} , for benzopyranthione in an inert perfluoroalkane solvent, showing that $2\tau_{DF} = \tau_P$ in the weak annihilation limit. Reproduced from reference 44.

The crossover from the weak to the strong annihilation regimes is particularly important in photon upconversion systems under continuous excitation. Experimental photon energy upconversion efficiencies are maximized in this region and there has been a concerted effort to find systems in which this crossover region coincides with unfocussed solar photon excitation rates. The threshold absorbed excitation rate, $\eta_0 R_{E,th} = \eta_0 I_{a,th}$, for this crossover region has been shown by Monguzzi, *et al.*⁴⁵ to be related to the annihilation kinetic parameters, here expressed in molar units, by:

$$\eta_0 R_{E,th} = \eta_0 I_{a,th} = \frac{(k_{1E^*})^2}{k_{ep}} = \frac{(k_{1E^*})^2}{F_{ep} k_{en}} \quad (8)$$

where the notation and conventions are those employed previously. Thus the lowest threshold intensities are found when the reactant energy-pooling species is produced with the highest efficiency (η_0 approaches 1) and exhibits the longest lifetime (smallest value of k_{1E^*}), and when the second order energy-pooling rate constant is largest. Clearly, only long-lived triplet states and efficient TTA energy pooling will meet these conditions at excitation intensities associated with unfocussed solar radiation. Figure 5 illustrates the strong, crossover and weak annihilation regions using the PdOEP-sensitized photon upconversion of 9,10-diphenylanthracene (DPA) in fluid solution as an example.⁴⁵

Figure 5: Double logarithmic plot of the upconverted S_1 fluorescence intensity of DPA (blue) as a function of incident photon flux resulting from the absorption and triplet sensitization by PdOEP excited at 532 nm in fluid solution at room temperature. The red data points are the phosphorescence of PdOEP in the absence of DPA. The green lines represent the AM1.5 solar flux centered at 532 nm taken with 1, 10 and 100 nm bandwidths. The values of m are the slopes, showing the crossover from the weak to the strong excitation regions. Reproduced with permission.⁴⁵ Copyright American Physical Society 2012.

Values for $k_{ep} = F_{ep}k_{en}$ or $k_{ep} = \chi_{e,d} \gamma_{E^*}$

The only kinetics parameter remaining to be discussed is the second order rate constant for energy pooling, k_{ep} . In this review, k_{ep} (in either molar or molecular units) is factored into a product of the second order exciton encounter rate constant, k_{en} or γ_{E^*} , and the probability that the encounter complex, once formed, will yield a specific energy-pooled

product, F_{ep} or $\chi_{e,d}$. Distinct from some other approaches,^{13,42,46} we define F_{ep} as the probability *per electronically excited reactant* that one specific energy-pooled product will be formed, thereby taking into account the stoichiometry of the process and the quantization of electronic photo-excitation. This places the efficiencies of energy pooling on a common basis of per absorbed photon from photoexcitation or per exciton formed from pairwise polaron neutralization.

(i) *Energy-pooling efficiencies and spin statistics:*

The overall efficiency of electronic energy pooling is often a major concern in the operation of devices in which exciton annihilation is either a required process or is an auxiliary tool (or problem). In OLEDs the external quantum efficiency of electroluminescence, $EQE = \eta_{oc}(IQE)$, is a product of the internal quantum efficiency, IQE , and the output coupling efficiency, $\eta_{oc} = (\text{number of photons detectable outside the device})/(\text{number of photons produced within the device})$, often taken to be *ca.* 0.2. For both fluorescent and phosphorescent devices, the internal quantum efficiency is expressed as:

$$IQE = \eta_e \chi_e \phi_\ell = \eta_e (\chi_{e,p} + \chi_{e,d}) \phi_\ell \quad (9)$$

The electric efficiency is $\eta_e = (\text{total number of excitons produced by polaron neutralization})/(\text{total number of polaron pairs injected})$. Its value is largely determined by the polaron migration rate (hence also by the applied voltage) and the polaron quenching rate. The exciton production efficiency is $\chi_e = (\text{total number of excitons of a given electron spin})/(\text{total number of excitons created})$, and is determined by considering both prompt and delayed processes so that $\chi_e = \chi_{e,p} + \chi_{e,d}$. The probability of obtaining an exciton product species of given electron spin multiplicity per polaron recombination event is $\chi_{e,p}$, which we

define as the efficiency of the prompt excitation process. Thus the spin-statistically determined values of $\chi_{e,p}$ are $\chi_{e,p,S} = 0.25$ and $\chi_{e,p,T} = 0.75$ for the singlet and triplet products respectively.

Thereafter, exciton annihilation events can either increase the electroluminescence IQE or reduce it at high device driving currents (observed as intensity “roll-off”).²⁰ The probability per energy pooling encounter of obtaining an exciton of the same spin multiplicity as that produced in the prompt polaron annihilation process is $\chi_{e,d}$, the delayed efficiency. The quantity $\chi_{e,d}$ is thus completely analogous to F_{ep} in photoexcited systems. The quantity ϕ_ℓ is the quantum yield of luminescence (either fluorescence or phosphorescence) of the exciton product as if it had been directly one-photon-excited under the conditions prevalent in the operating device, as described above.

The quantum yield of directly photoexcited, prompt luminescence for an emitter, $\phi_{\ell,p}$, is a simple ratio of [the number of (moles of) photons emitted per unit time per unit volume]/[the number of (moles of) photons absorbed per unit time per unit volume], *i.e.*, $\phi_{\ell,p} = I_{\ell,p}/I_a$. However, the quantum yield of delayed luminescence in photoexcited systems, $\phi_{\ell,d}$, is determined exclusively via electronic excited state energy pooling (thermally activated processes are excluded here), and is preferably calculated using the expression:

$$\phi_{\ell,d} = I_{\ell,d} / R_E = I_{\ell,d} / I_a = \eta_o F_{ep} \phi_{\ell,E^{**}} \quad (10)$$

Again, η_o is the quantum efficiency of production of the desired electronically excited species, E^* , that participates as the reactant in the energy pooling process. For direct excitation $\eta_o = 1$ if the energy-pooling reactant species is identical to the singlet electronic species produced

initially by photon absorption, as in SSA. Otherwise, η_o will equal η_{isc} if the desired excited species is the lowest triplet state formed by intramolecular intersystem crossing following initial excitation to an excited singlet state. If the energy-pooling reactant species is obtained by triplet photosensitization then η_o will equal η_{isc} of the absorbing donor multiplied by the fractional efficiency of triplet-triplet energy transfer, TET, from donor to acceptor, *i.e.*, $\eta_o = \eta_{isc} \eta_{TET}$. The interpretation of $\phi_{lE^{**}}$ in eq. 10 is as described in the above section on kinetics.

The quantity F_{ep} is thus defined in a manner similar to $\chi_{e,d}$ in electro-excited systems. For both electroluminescent and upconverting photoluminescent devices, the actual values of IQE (via $\chi_{e,d}$) and $\phi_{l,d}$ (via F_{ep}) achieved are determined by the theoretical maximum values applicable to the system under investigation and by a variety of processes that tend to prevent these maxima from being realized. The theoretical maxima provide the limiting values of $\chi_{e,d}$ and $\phi_{l,d}$ and are determined by (i) the energy-pooling model used for the system under study, and (ii) the electronic characteristics of the energy pooling species. The kinetics of the energy pooling interaction determine the actual values obtained. Prominent among the competing processes that lower efficiencies are quenching effects in which either a potentially luminescent energy-pooled species or its precursor(s) is deactivated prior to radiative decay. When energy pooling is involved, the nature of the excited state (exciton) transport process is often critical. Accordingly, there can be a big difference in efficiency between inter-species and intra-species transport processes leading to interaction, as for example, inter-chain vs. intra-chain energy pooling in electronically excited polymers.⁴³ Both F_{ep} and $\chi_{e,d}$ take on values that are also determined by the extent of recycling (if any) of

electronically excited species remaining after (or produced in) the initial annihilation events (*vide infra*).

In photon upconversion systems, some authors⁴⁷ have used $\phi_{e,d} = 2\eta_o F_{ep} \phi_{eE^{**}}$ to allow for the fact that two photons must be absorbed to produce one excited state energy-pooling encounter. However, this usage places the values of $\phi_{e,d}$ for photon-excited systems and the $\chi_{e,d}$ part of the IQE for electroluminescent systems on different absolute scales. Quantum efficiencies of electroluminescent devices are determined on a “per created electron-hole pair” basis. As recently noted by Gray, *et al.*,¹² it then seems preferable to set the equivalent quantum efficiency in photoluminescent devices on a similar “per absorbed photon” basis, *i.e.* $\phi_{e,d} = \eta_o F_{ep} \phi_{eE^{**}}$, as is the usual case for the determination of prompt luminescence quantum yields.

We now consider all homo- and hetero- TTA, STA and SSA energy pooling interactions within a common framework and examine the F_{ep} (or $\chi_{e,d}$) probabilities first.

Triplet-triplet annihilation (TTA):

(i) *Homomolecular-triplet-triplet annihilation (Homo-TTA; $E^* = T_1$):* Energy transfer resulting from this type of interaction is frequently modeled by a short-range Dexter electron exchange process.⁴⁹ In the usual description, the two interacting quantum-mechanically uncorrelated triplet states (triplet excitons) will produce an encounter complex with nine electron spin states that exhibits no net charge transfer character. (Note, however, a recent more detailed theoretical description of the annihilation encounter pair state.⁵⁰)

In addition to dissociating to separated triplet reactants, the encounter complex could in principle proceed to net products along three possible spin-conservative paths;

Only one of the nine spin states of the encounter complex correlates with the singlet product states, $S_n + S_0$; three correlate with the excited triplet product state, T_n ; five correlate with a quintet product state, Q_1 . If the two triplets entering the encounter complex have uncorrelated spins and all nine spin states were to lead to energy-accessible products with equal probability, the singlet excited product could be formed, statistically, at a maximum of only 1 of every 9 potential energy-pooling encounters, or 1 energy-pooled excited singlet product per 18 electronically excited triplet reactants. Thus, ignoring recycling of triplets, the maximum singlet exciton production efficiency per triplet exciton, $(F_{ep,S})_{\max} = (\chi_{e,d,S})_{\max}$, would be $1/18 = 0.0556$. However, for most known homo-TTA cases in organic systems⁵¹ the quintet product is energetically inaccessible, *i.e.* $E(Q_1 + S_0) \gg 2 E(T_1)$, and interaction along this coordinate will be unproductive. If only the singlet and triplet channels are energetically accessible, only one in every four pairwise triplet encounters can yield singlets, and the maximum singlet exciton production efficiency per triplet exciton will then be $(F_{ep,S})_{\max} = (\chi_{e,d,S})_{\max} = 0.125$, ignoring recycling.

The efficiency of the homo-TTA channel leading to the triplet product is also influenced by the energies of the possible product triplet states. Usually the excited triplet

product of energy pooling, T_n , has an energy $E(T_n) < 2 E(T_1)$, and will rapidly and quantitatively relax by radiationless IC within the triplet manifold to T_1 . This channel therefore results in both a net loss of triplet states and energy wastage. In a very few cases T_n may be relatively long-lived (*e.g.* a metal-centered $^3(d, d)$ state of a heavy atom metalloporphyrin)⁵² or may contribute indirectly to delayed fluorescence via rapid decay from T_n to S_1 or to an intermediate intramolecular charge transfer state.⁵³ Moreover, in some other rather rare cases such as perylene⁵⁴ the two lowest energy triplet states, T_1 and T_2 , have energies $E(T_2 + S_0) > 2 E(T_1) \leq E(S_1 + S_0)$, so that energy pooling along the triplet product coordinate can only occur by thermal activation. In the latter situation only the S_1 singlet product channel (equation 11b) will be accessible on energy grounds (since the quintet channel is also inaccessible). In this special case the spin statistical factor applicable to each homo-TTA interaction will be 1 and the maximum yield of excited singlet states (singlet excitons) per interacting triplet, $(F_{ep,S})_{\max} = (\chi_{e,d,S})_{\max}$, will equal 0.5 (irrespective of the number of repeated triplet-triplet encounters via recycling, *vide infra*). Note, however, that the relative energies of the S_1 and T_2 states are somewhat medium-dependent and can invert, as for example with 9,10-diphenylanthracene in solvents of different polarity.⁵⁵

These annihilation-augmented maximum theoretical efficiencies were first discussed by Kondakov^{48,56} and later by Monkman⁵⁷ to account quantitatively for enhanced IQEs in OLEDs. Thus for a fluorescent OLED operating on singlet excitons formed initially by polaron recombination and subsequently only by single TTA encounters (*i.e.*, ignoring recycling and thermally activated delayed fluorescence), $\chi_e \equiv \chi_S = (\chi_{e,p,S} + \chi_{e,p,T}\chi_{e,d,S})$ and the theoretical maximum IQE is obtained from

$$IQE_{\max} = (\eta_e \chi_S \phi_{i,S})_{\max} = (\eta_e (\chi_{e,p,S} + \chi_{e,p,T}\chi_{e,d,S}) \phi_{i,S})_{\max} \quad (12)$$

with $\eta_e = 1$ and $(\chi_{e,p,S} + \chi_{e,p,T})_{\max} = (0.25 + 0.75) = 1$. Then, if $(\chi_{e,d,S})_{\max} = 0.5$, $\text{IQE}_{\max} = 1 \times (0.25 + 0.75 \times 0.5) \times 1 = 0.625$; if $(\chi_{e,d,S})_{\max} = 0.125$, $\text{IQE}_{\max} = 0.344$; if $(\chi_{e,d,S})_{\max} = 0.0556$, $\text{IQE}_{\max} = 0.292$; and if $(\chi_{e,d,S})_{\max} = 0$, the classical limit with no triplet annihilation is obtained, yielding $\text{IQE}_{\max} = 0.25$.

However, for many cases of homo-TTA, the overall maximum probability that fluorescent excited species will be produced by excited state (exciton) annihilation can be augmented by the recycling of excited states from: (i) failed encounters (*e.g.* along the unattainable quintet coordinate), (ii) encounters that produce excited triplet states (*e.g.* $T_n \rightarrow T_1$ along the triplet product channel), and (iii) possibly from intersystem crossing of the desired S_1 product to T_1 . Thus a given triplet species, during its lifetime, may undergo several sequential triplet-triplet encounters, each contributing to the overall probability of energy-pooling to give the excited singlet product and therefore influencing the values of $\chi_{e,d}$ and F_{ep} .

We introduce the superscript R to indicate when recycling is included in the calculation of the maximum theoretical efficiencies for these annihilation processes. The maximum values of $\chi_{e,d}^R$ and F_{ep}^R are thus obtained for triplets of infinite lifetime that continue to find each other by diffusion and annihilate until their population is insignificantly small. Formally, the maximum yields of the excited singlet product of homo-TTA with recycling, $(F_{ep}^R)_{\max} = (\chi_{e,d,S}^R)_{\max}$, may be obtained from:

$$(F_{ep}^R)_{\max} = (\chi_{e,d,S}^R)_{\max} = \sum_{n=0}^{n=\infty} \frac{(N_{rt})^n}{(N_t)^{(n+1)}} = \frac{1}{N_t - N_{rt}} \quad (13)$$

where n is the number of repeats in the cycles of annihilation (*i.e.*, $n = 0$ if only the initial pairwise interaction is considered). N_{rt} is the maximum number of triplet excited states

available for recycling per eighteen triplets in the initial encounter pairs (*i.e.*, $N_t = 18$ for 9 pairwise triplet encounters). In fluorescent OLEDs, the luminescent materials are chosen so that $\phi_{\ell}E^*E^*$ of the product excited singlet is as close as possible to 1, and the yield of triplets formed by $S_1 - T_1$ intersystem crossing is near zero. Thus, in fluorescent OLEDs for the case in which there is no recycling and all of the quintet, triplet and singlet product states are accessible, $n = 0$, and $(\chi_{e,d,S}^R)_{max} = 0.0556$, the classical limit. (For this case we set $N_{rt} = 0$ and define $0^0 = 1$.)

With recycling $N_{rt} = 13$ for the case in which TTA along the quintet channel returns two T_1 and along the triplet channel yields one energy-pooled triplet, resulting in $(\chi_{e,d,S}^R)_{max} = 0.200$. Figure 6, adapted from references 20 and 46, visually represents the case of $(\chi_{e,p,T} \chi_{e,d,S}^R)_{max} = (0.75 \times 0.2) = 0.15$ in OLEDs. If TTA

Figure 6: Processes involved in annihilation events in OLEDs. Reproduced from reference 20 with permission. Copyright Wiley-VCH. Panel (b) represents the case in which recycling following TTA leads to a maximum efficiency of $(\chi_{e,p,T}\chi_{e,d,S}^R)_{max} = 0.15$ and an overall singlet production efficiency of 0.40.

along the quintet channel produces one triplet (by ISC) plus S_0 and along the triplet channel produces one energy-pooled triplet plus S_0 , then for 9 pairs of triplets in the encounter complexes, $N_{rt} = 8$ and $(\chi_{e,d,S}^R)_{max} = 0.100$. In working fluorescent OLEDs the observed values of χ_S and IQE will be always be less than these theoretical maxima.

(Note that an oft-quoted article by Friend and coworkers⁴⁶ defines f as the fraction of triplet-triplet exciton pairwise encounters that initially yield singlet S_1 states in fluorescent OLEDs when quintet energy-pooled products are excluded. With recycling, the expression for the sum used to obtain the value of f_∞ (eq. 2a in ref. 46, which is the equivalent of $(\chi_{e,p,T}\chi_{e,d,S}^R)_{max}$ in this review) is mathematically incorrect, although the number provided for the sum is correct. In ref. 46, Eq. 2a should read

$$f_\infty = f \sum_{n=1}^{n=\infty} \left(\frac{1-f}{2}\right)^n = f \frac{1-f}{1+f}$$

leading to the correct value of $f_\infty = 0.15$ for $f = 0.25$; the sum in Eq. 2a as written in ref. 46 gives an incorrect value of $f_\infty = 0.20$.)

For photo-excited systems, using the unscaled expression for $\phi_{\ell,d}$, the maximum upconversion quantum efficiency in producing a fluorescent singlet product is given by $(\phi_{\ell,d})_{max} = (\eta_o F_{ep} \phi_{\ell,E^*E})_{max}$. With triplet recycling conditions similar to those discussed above for OLEDs, if $(F_{ep}^R)_{max}$ is identical to $(\chi_{e,d,S}^R)_{max}$ then $(\phi_{\ell,d})_{max} = 0.5, 0.2$ and 0.0588 for the three cases of $(\chi_{e,d,S}^R)_{max} = 0.5, 0.2$ and 0.0588 respectively.

However unlike OLEDs, in photon upconversion systems employing homo-TTA there may be instances in which the quantum yield of triplet states arising from intersystem

crossing subsequent to energy pooling along the singlet channel is non-zero (*i.e.*, $\phi_T > 0$). This case has been clearly described by Weisman and coworkers.³⁹⁻⁴¹ The entire set of data for assessing the theoretical maximum values of χ_e and F_{ep} under the conditions discussed above is collected in Table 1.

insert Table 1

(ii) *Which singlet product species is formed preferentially via the singlet channel?* It is possible that several excited singlet product states of TTA could be accessible on energetic grounds. In such cases, empirical evidence initially reported primarily by Nickel⁵⁸ indicates that the excited singlet state, S_n , initially populated preferentially on homo-TTA and observed by its delayed fluorescence is the one that (i) exhibits the smallest positive value of $E(S_n) - 2 E(T_1)$ and (ii) has the largest oscillator strength for its radiative decay to the ground state. For structurally rigid species, the preference for a close electronic energy match between the reactant and product species has been rationalized by consideration of the Franck-Condon (vibrational overlap) factors involved in proceeding from the encounter complex to the product.⁵⁹ In organic species containing only low atomic weight atoms, homo-TTA normally occurs via short-range energy transfer and therefore requires species-to-species wavefunction overlap to facilitate electron exchange. The most favorable Franck-Condon factors for structurally rigid, electrically neutral species will thus often be found when the initial products accept rather small amounts of vibrational energy, *i.e.* when the $2E(T_1) - E(S_n)$ energy difference is positive but small. Note in particular that the singlet TTA channel could yield two ground state species on spin conservation grounds, but this would be highly Franck-Condon forbidden and is thus inconsequential. Note also that an early report⁶⁰ of a

preference for $S_1 + S_0$ rather than $S_2 + S_0$ from the TTA of metalloporphyrins (where $2 E(T_1) \approx E(S_2) + E(S_0)$) fails to account for the self-quenching of the S_2 state in the very short-lived product encounter complex.

If highly excited singlet states, S_n ($n > 1$), are formed initially, they most frequently decay quantitatively and very rapidly by IC to the lowest excited singlet state, S_1 . Then, if S_1 is the desired upconverted product, the energy mismatch between $2 T_1$ and $S_1 + S_0$ constitutes a thermal energy loss. However, in a few families of compounds the initially-formed upper electronic singlet products of homo-TTA can have lifetimes long enough to permit efficient electron or inter-species energy transfer and can produce significant upconverted delayed fluorescence. Well-established examples involve azulene and related non-alternant aromatic hydrocarbons, rigid aromatic thiones, and the closed-shell d^0 and d^{10} metalloporphyrins and similar porphyrinoids.⁶¹⁻⁶³

In all three of these exceptional cases, $2 E(T_1) \geq E(S_2)$, and homo-TTA along the singlet spin-conservative channel involves production of a fluorescent second excited singlet state product, S_2 , *i.e.*,

Competition between the rates of $S_2 - S_0$ radiative decay and $S_2 \rightarrow S_1$ radiationless decay then determine the lifetime of the S_2 product and the quantum yield of $S_2 - S_0$ delayed upconverted fluorescence. In these statistical limit⁶⁴ cases, the rate of S_2 radiationless decay is determined

largely by the $S_2 - S_1$ electronic energy gap and by the interstate coupling energy for $S_2 - S_1$ internal conversion in all three systems. Fluoroazulenes, with the largest $S_2 - S_1$ electronic energy spacings (and hence the slowest IC rates on Franck-Condon grounds), have S_2 lifetimes in the nanosecond range and exhibit quantum yields of $S_2 \rightarrow S_0$ fluorescence of up to *ca.* 0.1. Smaller $S_2 - S_1$ electronic energy gaps are found in the d^0 and d^{10} metalloporphyrins such as zinc tetraphenylporphyrin, but they exhibit an almost exact $2 E(T_1) = E(S_2) + E(S_0)$ energy match and the S_2 state is the highly radiative Soret state. Thus, significant fluorescence quantum yields (albeit $< 10^{-3}$) are obtained irrespective of the picosecond lifetimes of the S_2 product states and the potential for self-quenching in the singlet product encounter complex (excimer, *vide infra*). Rigid aromatic thiones such as xanthione have intermediate $S_2 - S_1$ electronic energy gaps, but their $S_2 - S_1$ interstate coupling energies are smaller owing to their weaker $^1(\pi, \pi^*) - ^1(n, \pi^*)$ orbital overlap (compared with $^1(\pi, \pi^*) - ^1(\pi, \pi^*)$ orbital overlap in the previous two cases), leading to S_2 lifetimes of the order of a few tenths of nanoseconds. These upper singlet fluorescence quantum yields are too small to be used in photon upconversion, but the S_2 lifetimes can be long enough for efficient electron or energy transfer to occur.⁶⁵

(iii) *Hetero-triplet-triplet annihilation (Hetero-TTA)*: Early progress in understanding hetero-triplet-triplet interactions arose from research on ground state oxygen quenching of molecular triplet states.⁶⁶ Here, as in all triplet-triplet interactions between species containing only low atomic weight atoms, energy transfers occur at short range by an electron exchange mechanism. However, in the hetero-TTA case the dynamics are complicated by the possibility of net charge transfer within the encounter complex and the fact that either of the interacting excited species could be donor or acceptor in the energy

transfer process. Moreover, the efficiency of hetero-TTA may be severely diminished by means of triplet energy transfer from the species with the higher triplet energy to the ground state of the species with the lower triplet energy. DF from hetero-TTA is therefore rarely seen in steady state (cw) photoexcitation experiments and is usually only observed following relatively intense pulsed laser photoexcitation or with high currents in electroluminescent devices. Hetero-TTA is, however, a potential source of inefficiency in photosensitized photon upconversion, particularly when the triplet states of the sensitizer and the upconverter are both long-lived.

The earliest reports of hetero-TTA for organic molecules in fluid systems were by Nickel and coworkers who were particularly interested in annihilation between an azulene triplet and a second triplet energy donor chosen to produce highly Stokes-shifted fluorescence from the S_2 state of azulene.⁶⁷ The body of Nickel's work in this area⁶⁸ then demonstrates empirically that hetero-TTA along the singlet channel may lead to a population of any energetically accessible excited singlet state of either of the interacting pair. Nevertheless, although propensities for preferential initial formation of one excited singlet product can be deduced from these reports, a full analysis of the photophysical reasons leading to these observations has yet to be developed.

More recently, hetero-TTA has proved to offer interesting promise of improved photon upconversion quantum efficiencies in fluid media. Cao, *et al.*⁶⁹ report significantly enhanced fluorescence yields in a system consisting of a platinum octaethylporphyrin sensitizer with two triplet acceptors, 9,10-diphenylanthracene and 1,3-diphenylisobenzofuran, in deoxygenated dimethylformamide solution compared with the

sum of yields obtained with the same sensitizer and a single acceptor. The enhanced efficiency was attributed to hetero-TTA, but the mechanism of the processes resulting in this synergism was not explored in detail. Hetero-TTA has also been reported in doped crystalline organic solids.⁷⁰

(iv) *What is the nature of the delayed fluorescence following TTA?* TTA along the singlet channel yields a pair of singlet species, one of which is excited and is initially situated at a van der Waals distance from the other. Consequently, the photophysical properties of the excited species and its delayed fluorescence may or may not be similar to those produced by one photon excitation of a single isolated absorber in the same medium. If the excited singlet is relatively long-lived (*e.g.* nanoseconds or longer), if the intermolecular binding energy between it and its S_0 partner is small and if the system is in a fluid medium, then dissociative diffusion will ensure that its DF spectrum and lifetime closely resemble those of the isolated photo-excited species. However, even if the $S_n \cdots S_0$ binding energy is small, the DF spectrum and photophysics of the excited species may be rather different from that of the isolated species if the lifetime of the excited singlet is very short, thereby limiting the extent of dissociative diffusion. Typically, the latter situation results in significantly broader and spectrally displaced bands in the DF spectrum, as is the case, for example, with homo-TTA in the d^0 and d^{10} metalloporphyrins, which produce fluorescing S_2 excited states with picosecond lifetimes when directly excited.^{71,72} An even greater difference between delayed and prompt fluorescence can be seen when the binding energy between the two singlet product species is significant and/or when exciton diffusion is restricted, as is the case in some solid media. Under these circumstances, the initial singlet product of homo-TTA can be described as an excited dimer or excimer. For hetero-TTA under similar conditions, the

complexed excited singlet product is termed an exciplex. The lifetime of an excimer or exciplex is often shorter than that of the excited monomer from which it is derived, and its fluorescence spectrum, if observable, is almost always broad and relatively unstructured as a result of radiative relaxation from a bound to an unbound (or much more weakly bound) potential surface. In fluid media, excimer delayed fluorescence subsequent to homo-TTA has been known for some time; pyrene provides a well-studied example.^{73,74} Methods of distinguishing between excimers radiating immediately in the undissociated encounter complex and those radiating after subsequent association of the excited monomer with ground state molecules have been established.^{75,76}

In OLEDs, excimer fluorescence is commonplace as a result of the association of excitons with ground state species, thereby trapping them and incrementally restricting their mobility. Both excimer and exciplex delayed fluorescence resulting from triplet exciton annihilation have also been reported (although in these cases exciplexes can be formed either directly by hetero-TTA or by homo-TTA followed by energy transfer).⁷⁷ Again, triplet-triplet energy transfer from donors with higher triplet energies to potential acceptors with lower triplet energies may complicate the kinetics in these OLED systems.

Singlet-singlet annihilation (SSA):

(i) *Homo-SSA, where $E^* = S_1$* : The singlet-singlet energy pooling process in organic systems can be referred to as singlet-singlet annihilation (SSA) or singlet exciton fusion – the latter term more frequently employed when describing aggregates in condensed media. In the most general terms the process may be written

but excited products with $n > 1$ are always preferred on Franck-Condon grounds. Because excited singlet states (singlet excitons) of polyatomic organic molecules in condensed media are intrinsically short-lived (relative to T_1), this phenomenon is seen only in systems in which the singlet number density is relatively large, as for example with pulsed laser excitation at high peak powers or in OLEDs at high current densities. The SSA process itself is frequently followed by observing the decay of $S_1 - S_0$ fluorescence, which is non-exponential at early times after intense pulsed laser excitation and becomes mono-exponential at longer times as the S_1 number density decreases. Indeed, the first report of SSA in fluid media involved intense pulsed nitrogen laser-excitation of optically thick solutions of anthracene in benzene, where the annihilation processes were deduced from observations of increased deviation of the integrated anthracene fluorescence intensity from linear dependence on absorbed light intensity with increasing laser power.⁷⁸

There are several possible product states in homo-SSA; the formation of one highly excited singlet and one ground singlet state is most likely and is of greatest interest, as in $S_1 + S_1 \rightarrow S_n (n > 1) + S_0$. Unlike TTA events, the forward process is entirely electron spin-allowed and in fluid media its measured second order rate constant can exceed the usual hard-sphere diffusion limit because SSA is essentially a long-range Förster-type of electronic energy transfer. The particular state in the upper singlet manifold populated by SSA is thus determined primarily by the relative magnitudes of the interstate dipole-dipole coupling terms, *i.e.* by the energy matches between the $S_1 - S_0$ and the $S_n (n > 1) - S_1$ pairs of product states, the oscillator strengths of the two transitions, and geometric transition dipole considerations.⁷⁹

Irrespective of the identity of S_n ($n > 1$), its most frequent fate in condensed media is rapid IC to vibrationally hot S_1 followed by thermalization on a ps time scale, so the overall result of SSA in optoelectronic devices is essentially one of energy wasting. Self-ionization or photochemical damage of the excited product is possible if the total electronic excitation energy exceeds the ionization or photochemical threshold of the species in the medium.⁸⁰ In aggregates, triplets have the potential to be formed subsequent to SSA either by singlet fission or, if S_n ($n > 1$) ionizes, by polaron recombination. However, despite some suggestions to the contrary,⁸¹ the direct production of triplets from singlet-singlet energy-pooling encounters will be disfavored due to spin conservation requirements in all but heavy-atom containing systems.⁸² SSA is thus undesirable in most optoelectronic devices, and is one source of “roll-off” in fluorescent OLEDs, *i.e.* a decrease in efficiency at high brightness.²⁰ SSA is also a source of inefficiency in devices designed to perform as organic laser diodes in which annihilation reduces population inversions.

The calculation and interpretation of the maximum yield of S_n ($n > 1$) per interacting singlet exciton in homo-SSA is straightforward and simply represents the stoichiometry of the forward energy pooling process. Thus, $\chi_{e,d,S} = F_{ep} = 0.500$ for SSA. Although the S_n product of SSA relaxes to S_1 , further recycling of this excited singlet usually need not be considered due to its relatively short lifetime.

SSA processes are of no known importance in photo-activated systems exposed to normal steady-state (*e.g.* solar) illumination intensities, but can be used to examine the dynamics of exciton migration and trapping in aggregates, including photosynthetic units,

dendrimers and thin films, by observing their non-exponential fluorescence decay rates following ultrashort laser pulse excitation.⁸³⁻⁸⁷

In a few instances, SSA produces upper singlet states that can easily be detected from their upconverted fluorescence emission. The classic case is that of thiophosgene, Cl_2CS of C_{2v} symmetry, which upon excitation to S_1 in the gas phase undergoes SSA via the process $2 S_1 \rightarrow S_2 + S_0 (v > 0)$.^{88,89} The S_1 state is excited via a nominally electric dipole-forbidden, $^1A_2 \leftarrow ^1A_1$ transition and the molecule is small enough that subsequent ISC to T_1 is slow in the gas phase due to its low density of accepting vibronic states. S_1 is therefore relatively long-lived, with a lifetime of tens of microseconds at low pressures – long enough to undergo bimolecular SSA via diffusional encounters after ns pulsed laser excitation. On the other hand the excited S_2 product is of 1A_1 symmetry and fluoresces from its bound vibrational levels via an electric dipole allowed transition with a quantum yield near unity. The intensity of this delayed, upconverted fluorescence depends on the square of the absorbed excitation light intensity, as required by the second order annihilation process. Note, however, that the same process cannot be observed in condensed media where the lifetime of the S_1 state of thiophosgene is orders of magnitude shorter.⁹⁰ Moreover, there are no reports of measurable upconverted fluorescence intensities produced via SSA in larger polyatomic organic molecules in condensed media; S_1 lifetimes are often too short and S_n ($n > 1$) radiative quantum yields are always too small.

(ii) *Hetero-SSA*: Hetero-SSA, $S_1(D) + S_1(A) \rightarrow S_n (n > 1)(A) + S_0(D)$, is simply another form of electron spin-allowed long-range energy transfer that can be described by the Förster dipole-dipole coupling scheme, except that it is characterized by the interaction of both an excited

donor, D, and an initially excited acceptor, A. Both of the interacting excited singlet species could act as either donor or acceptor. Apart from this, all other aspects of SSA apply, as described above for homo-SSA.

Singlet-triplet energy annihilation (STA):

Heteromolecular singlet-triplet annihilation (hetero-STA) was first observed as a flash of fluorescence upon admitting oxygen to samples of phosphorescing dyes adsorbed on cold silica gel.⁹¹ This observation was later interpreted⁹² as resulting from the energy-pooling transfer of electronic energy from $O_2(^1\Delta_g)$ to an organic triplet, a process that is common when both excited species are produced by photosensitization. The process is $O_2(^1\Delta_g) + T_1 \rightarrow O_2(^3\Sigma_g^-) + S_1$, and delayed fluorescence is observed when the excited singlet product decays radiatively to the ground state. Electronic energy conservation requires that the excited singlet-triplet energy spacing of the organic moiety, $\Delta E(S_1-T_1)$, be less than or equal to *ca.* 1 eV, the $O_2(^1\Delta_g)$ excitation energy. Many experiments indicate that the most efficient energy pooling by this process occurs when these two energy gaps are closely matched, although thermal activation can make up for small deficiencies.⁹³ It is also possible to produce delayed fluorescence from organic molecules such as near-IR absorbing dyes with low-lying triplet states by a double activation process using $O_2(^1\Delta_g)$, *viz.* $O_2(^1\Delta_g) + S_0 \rightarrow O_2(^3\Sigma_g^-) + T_1$ (which may require additional thermal activation to bridge the $T_1 - S_0$ energy spacing), followed by $O_2(^1\Delta_g) + T_1 \rightarrow O_2(^3\Sigma_g^-) + S_1$. This process has been recently investigated by Schmidt and coworkers⁹⁴ for purposes of improving the NIR harvesting ability and energy conversion efficiency of dye-sensitized solar cells.

In this context it is worth noting that it is possible with just one absorbed photon to induce the equivalent of energy pooling in an oxygenated photosensitization system. Consider the following sequence, where D is the donor and A is the acceptor. (i) $D(S_0) + h\nu \rightarrow D(S_1)$; (ii) $D(S_1) + O_2(^3\Sigma_g^-) \rightarrow D(T_1) + O_2(^1\Delta_g)$; (iii) $D(T_1) + A(S_0) \rightarrow D(S_0) + A(T_1)$; (iv) $O_2(^1\Delta_g) + A(T_1) \rightarrow O_2(^3\Sigma_g^-) + A(S_1)$; (v) $A(S_1) \rightarrow A(S_0) + h\nu_{DF}$. This case is admittedly trivial because the energy-pooled emission would not be anti-Stokes shifted. However, in this example the maximum quantum yield of energy-pooled delayed fluorescence could be 1 (for substances with very low-lying $D(T_1)$ and $A(T_1)$ energies), illustrating the preference for avoiding the use of $\phi_{\ell,d} = 2\eta_o F_{ep}\phi_{\ell E^{**}}$.

In purely organic systems, the STA process involves electronic energy pooling within the triplet manifold,

and is fully electron spin allowed. Hence, the preferred mechanism involves long-range Förster dipole-dipole energy transfer, just as in SSA. Now, the identity of the preferred product state, T_n , is determined by how closely the energy differences between the $S_1 - S_0$ and the $T_n (n > 1) - T_1$ states are matched, and by the oscillator strengths of the $S_1 \rightarrow S_0$ and $T_1 \rightarrow T_n$ transitions. Quantitatively determining the oscillator strength of the triplet-triplet transition can be difficult, however.

By far the most common examples of STA in organic materials are now found in aggregated systems, including OLEDs⁹⁵ and polymers employed in photovoltaics.⁹⁶ In OLEDs, large exciton number densities can be produced and it is likely that “roll off” in the

efficiencies of fluorescent OLEDs at high currents will be greater due to STA than that due to SSA because of the longer lifetime of triplet excitons relative to their singlet counterparts. Figure 7 provides typical quantitative data, including that for polaron quenching. Thus enhancement of the IQE in fluorescent OLEDs due to TTA can be offset by STA, which results in singlet exciton loss. In luminescent polymers such as P3HT self-aggregation by chain folding can have the effect of limiting luminescence efficiency via STA even in single polymer chains. STA has also been invoked as the source of inefficiency in dye-sensitized solar cells employing polyene and modified chlorophyll absorber/sensitizers.⁹⁷⁻⁹⁹

Figure 7: Contributions to loss of luminescence intensity ("roll off") as a function of current density in typical OLEDs: (a) fluorescent, (b) phosphorescent. Number densities are n_T (triplet), n_S (singlet), n_P (polaron). Reproduced with permission.²⁰ Copyright Wiley-VCH.

Values of k_{en} :

The values of k_{en} are determined by exciton diffusion rates, an extremely active area of research in which there are many recent reviews¹⁰⁰⁻¹⁰⁴ applicable to both electroluminescent and photovoltaic materials. In principle, it should be possible to estimate the values of the second order, excited state (exciton) encounter rate constants, k_{en} , from diffusion theory

using approaches appropriate to the nature of the medium in which the excitons are created. However, in practice the rates of exciton diffusion are strongly dependent both on the structure of the exciton and on the precise state and configuration of the medium. This is particularly evident in as-prepared solids and thin films where quantitative structure-diffusion length relationships are currently almost non-existent. For a crystalline material, for example, its morphology, degree of crystallinity, the number density of its defects and its inherent anisotropy all need to be taken into consideration in determining an exciton's diffusion length. As a result, the rates of exciton annihilation observed in both crystalline and amorphous solids and in polymer blends will often need to be measured for each set of reproducibly-synthesized samples. For solids, some simplicity can sometimes be achieved by employing 1-dimensional active components such as carbon-nanotubes,¹⁰⁵ or inert 3-dimensional frameworks such as MOFs^{102,106} into which the active components can be dispersed with geometric order.

One can most easily obtain reliable values of k_{en} for excitonic diffusion when considering small molecules in homogeneous fluids. In such media, simple estimates for k_{en} when the excitonic interactions are at short range (*e.g.* TTA) can be obtained from the rate of hard sphere collisions in a continuum of viscosity η . In the "slip" diffusion limit, when η is in SI units of $\text{kg m}^{-1} \text{s}^{-1}$, the rate constant is in units of $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ and the universal gas constant, R , is in units of $\text{J K}^{-1} \text{mol}^{-1}$, the value of the diffusion-controlled encounter rate constant is given by

$$k_{en} = \frac{8000RT}{3\eta} \quad (19)$$

A small molecule TTA process that is diffusion limited in a fluid medium will therefore exhibit a rate that is proportional to T/η with values of k_{en} typically of the order of $10^9 - 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ in solutions of relatively low viscosity. However, such calculations provide only rough estimates and do not account for long-range energy transfer, molecular shape, specific solute-solvent interactions and requirements other than short-range collision.

Estimates for k_{en} in condensed media may also be obtained from Förster theory for long-range, electron spin-allowed, dipole-dipole energy transfers such as SSA and STA,^{107,108} or from Dexter theory¹⁰⁹ for short-range, electron-exchange energy transfers such as TTA and triplet sensitization. These theories, the calculations arising from them, and their application in solid state OLEDs and photovoltaic devices have been reviewed frequently;^{95-98,110} the details need not be repeated here. Briefly, for long-range dipole-dipole energy transfer of the homo-SSA type, where the interacting singlet states are both E^* , one a donor and the other an acceptor, the rate constant $k_{en} \equiv k_{SSA}$ is given by,

$$k_{en} \equiv k_{SSA} = \frac{\phi_{\ell,E^*} \kappa^2}{\tau_{E^*} r_{E^*E^*}^6} \left\{ \frac{9(\ln 10)}{128\pi^5 n^4 N_A} \right\} J_{E^*E^*}(\bar{\nu}) \quad (20)$$

where ϕ_{ℓ,E^*} is the unquenched quantum yield of fluorescence of the donor (E^*), τ_{E^*} is the unquenched experimental lifetime of the excited state of the donor, $r_{E^*E^*}$ is the centre to centre distance between the annihilating excitons, n is the refractive index of the medium, N_A is Avogadro's number, $J_{E^*E^*}(\bar{\nu})$ is the overlap integral and κ^2 is the *orientation factor*, which is often taken to be 2/3 in isotropic media. The overlap integral in wavenumber units is given by:

$$J_{E^*E^*}(\bar{\nu}) = \int f_{E^*}(\bar{\nu}) \varepsilon_{E^*}(\bar{\nu}) (\bar{\nu})^{-4} d\bar{\nu} \quad (21)$$

where $f_{E^*}(\bar{\nu})$ is the normalized emission (fluorescence) spectrum of the donor (E^*), $\varepsilon_{E^*}(\bar{\nu})$ is the $S_1 \rightarrow S_n$ absorption spectrum of the acceptor (E^*), and the integral is over the region of their spectral overlap, with both spectra measured in wavenumbers ($\bar{\nu}$, cm^{-1}). Note that in cases like this where the acceptor is an excited singlet state, its (transient) absorption spectrum and its values of $\varepsilon_{E^*}(\bar{\nu})$ may not be readily available. Note also that simple, direct substitutions for the properties of the acceptor in equations 20 and 21 are all that is needed to permit the calculation of k_{en} for hetero-SSA and for STA. Extensions of Förster's theory to account for coherence, superexchange and other effects have been reviewed by Scholes and Fleming.^{111,112} These considerations are particularly relevant for EET between large molecules where the dimensions of the molecule are similar to the distances over which the energy transfer occurs and the point dipole approximation is no longer valid.

For TTA and triplet sensitization, short-range Dexter type energy transfer theory¹⁰⁹ also allows for the calculation of k_{en} . Thus for homo-TTA, where E^* is T_1 ,

$$k_{en} \equiv k_{TTA} = \frac{2\pi}{\hbar} V_{E^*E^*}^2 J_{E^*E^*}(\bar{\nu}) = K \exp\left\{-\frac{2r_{E^*E^*}}{L}\right\} J_{E^*E^*}(\bar{\nu}) \quad (22)$$

where $V_{E^*E^*}$ is the interspecies interaction potential, $r_{E^*E^*}$ is the centre to centre distance between the two triplets, L is the sum of their van der Waals radii, and K is a constant (that can contain factors of uncertain magnitude). Because of the uncertainties inherent in obtaining exact values of the factors $V_{E^*E^*}$, L and K , equation 22 is better used to obtain relative values of k_{en} .

Finally, we consider the difference in k_{en} between inter-species and intra-species annihilation - a difference that is particularly important when considering exciton annihilation rates in polymers. As in previous cases, the excitons can be generated by either

polaron recombination or photoexcitation and can be detected by either transient absorption or transient emission. In polymers, inter-species annihilation involves inter-chain interactions and can be slow if chain diffusion is required, whereas intra-species annihilation involves the annihilation of two excitons singly deposited in the same chain, a process that can be many orders of magnitude faster. There are two simple ways of photo-exciting a single multi-chromophoric polymer chain twice, but non-coherently; (i) direct, sequential one photon excitation of the active chromophores in a single chain of the polymer itself and, (ii) two-fold sensitization either intermolecularly by an external sensitizer, or intramolecularly if the polymer is directly bonded to one or more sensitizing chromophores. If the two excitation steps produce triplet excitons in high yield, intramolecular (intrachain) TTA can occur, and can be detected if upconverted fluorescence is produced. If the two excitations produce two singlet excitons, intrachain SSA can occur and can be detected by following the power dependence and/or deviation from single exponential decay of the fluorescence (or transient absorption) of the singlets at high power. STA can occur if singlets and triplets are produced in the same system. Using intramolecular TTA to rapidly and efficiently produce singlet excitons capable of charge donation is a particularly attractive way of circumventing the Shockley-Queisser efficiency limitations of single threshold photovoltaic devices.

As an example, consider the rates of interchain vs. intrachain TTA in a $\text{Ru}(\text{bpy})_3^{2+}$ sensitized polymer containing closely-spaced, pendant 9,10-diphenylanthracene (DPA) chromophores.^{43,113} The $\text{Ru}(\text{bpy})_3^{2+}$ derivative is photo-excited in the visible region of the spectrum and, acting as the absorber/sensitizer, can produce a near quantitative yield of triplet DPA excitons by TET. The sensitization can be either intramolecular when the $\text{Ru}(\text{bpy})_3^{2+}$ is synthesized with pendant DPA polymer arms, or intermolecular when the

$\text{Ru}(\text{bpy})_3^{2+}$ sensitizer is incorporated independently into the degassed DPA polymer solution. At low excitation powers interchain TTA of singly sensitized polymers yields upconverted fluorescence from DPA that decays on a 100s of microsecond time scale - as expected when the lifetime of the DPA T_1 state is of the order of $\frac{1}{2}$ millisecond. However, at higher excitation powers with a pulsed laser, an additional, very short-lived component of the upconverted fluorescence is observed due to the sequential two-fold sensitization of single DPA chains, followed by exciton migration leading to intrachain TTA on a subnanosecond time scale.

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Figure Captions:

Figure 1: 2-D cartoon illustrating the differences between a Frenkel exciton (a) and a Wannier-Mott exciton (b) in a crystalline or otherwise ordered solid matrix.

Figure 2: Illustration of the intramolecular relaxation processes of electronically excited polyatomic molecules, using zinc porphyrin as a model. I.C. internal conversion; I.S.C. intersystem crossing; I.V.R. intramolecular vibrational relaxation; $h\nu_f$ fluorescence; $h\nu_p$ phosphorescence. The Soret ($S_0 - S_2$) and Q ($S_0 - S_1$) band absorptions are also illustrated. In condensed media I.V.R. can also refer to intermolecular vibrational relaxation

Figure 3: The formats of Stern-Volmer plots for luminescence quenching. (a) when luminescence lifetimes, τ , are measured, and (b) when luminescence quantum yields, ϕ , are measured.

Figure 4: Kinetic first order decay of triplet (T_1) phosphorescence, I_P , at two different laser excitation powers (a, b), and of delayed (S_2) fluorescence, I_{DF} , for benzopyranthione in an inert perfluoroalkane solvent, showing that $2\tau_{DF} = \tau_P$ in the weak annihilation limit. Reproduced from reference 44.

Figure 5: Double logarithmic plot of the upconverted S_1 fluorescence intensity of DPA (blue) as a function of incident photon flux resulting from the absorption and triplet sensitization by PdOEP excited at 532 nm in fluid solution at room temperature. The red data points are the phosphorescence of PdOEP in the absence of DPA. The green lines represent the AM1.5 solar flux centered at 532 nm taken with 1, 10 and 100 nm bandwidths. The values of m are the slopes, showing the crossover from the weak to the strong excitation regions. Reproduced with permission.⁴⁵ Copyright American Physical Society 2012.

Figure 6: Processes involved in annihilation events in OLEDs. Reproduced from reference 20 with permission. Copyright Wiley-VCH. Panel (b) represents the case in which recycling following TTA leads to a maximum efficiency of $(\chi_{e,p,T}\chi_{e,d,S}^R)_{max} = 0.15$ and an overall singlet production efficiency of 0.40.

Figure 7: Contributions to loss of luminescence intensity (“roll off”) as a function of current density in typical OLEDs: (a) fluorescent, (b) phosphorescent. Number densities are n_T (triplet), n_S (singlet), n_P (polaron). Reproduced with permission.²⁰ Copyright Wiley-VCH.

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Table 1: Theoretical maximum values of χ_e and F_{ep} in electroluminescent and photoluminescent systems with energy pooling and $\eta_{isc} = \eta_{bisc} = 0$.* In electroluminescent systems with recycling, $\chi_S = \chi_{e,p,S} + \chi_{e,p,T}^R \chi_{e,d,S}^R$ and $\chi_T = \chi_{e,p,T} + \chi_{e,p,S}^R \chi_{e,d,T}^R$

excitation type	electroluminescent		photoluminescent
excitation rate, R_E	$R_E = J/(ed)$; $\eta_e = 1$;		$R_E = I_a$; $\eta_0 = 1$
mode of operation	phosphorescent $\chi_{e,p,T} = 0.75$	fluorescent $\chi_{e,p,S} = 0.25$	fluorescent
<u>SYSTEMS</u>			
I. homo-TTA; no recycling			
(i) singlet product; all channels open	-	$\chi_{e,d,S} = 0.0556$ $\chi_S = 0.292$	$F_{ep} = 0.0556$
(ii) singlet product; (a) $E(Q_1) \gg 2E(T_1)$ and $E(T_2) < E(S_1)$	-	$\chi_{e,d,S} = 0.125$ $\chi_S = 0.344$	$F_{ep} = 0.125$
(iii) singlet product; $E(Q_1) \gg 2E(T_1)$ and $E(T_2) > E(S_1)$ and $2E(T_1) > E(S_1)$	-	$\chi_{e,d,S} = 0.500$ $\chi_S = 0.625$	$F_{ep} = 0.500$
(iv) triplet product; $E(Q_1) \gg 2E(T_1)$ and $E(T_2) < E(S_1)$	$\chi_{e,d,T} = 0.375$ $\chi_T = 0.844$	-	-
II. homo-TTA; maximum recycling			
(i) singlet product; all channels open	-	$(\chi_{e,d,S}^R)_{max} = 0.0588$ $(\chi_S)_{max} = 0.294$	$(F_{ep}^R)_{max} = 0.0588$
(ii) singlet product; (a) $E(Q_1) \gg 2E(T_1)$ and $E(T_2) < E(S_1)$	-	$(\chi_{e,d,S}^R)_{max} = 0.200$ $(\chi_S)_{max} = 0.400$	$(F_{ep}^R)_{max} = 0.200$

(b) and $Q_1 \rightarrow T_n$	-	$(\chi_{e,d,S}^R)_{max} = 0.100$ $(\chi_S)_{max} = 0.325$	$(F_{ep}^R)_{max} = 0.100$
(iii) singlet product; $E(Q_1) \gg 2E(T_1)$ and $E(T_2) > E(S_1)$ and $2E(T_1) > E(S_1)$	$(\chi_{e,d,T}^R)_{max} = 0.200$ $(\chi_T)_{max} = 0.800$	$(\chi_{e,d,S}^R)_{max} = 0.500$ $(\chi_S)_{max} = 0.625$	$(F_{ep}^R)_{max} = 0.500$
(iv) triplet product; $E(Q_1) \gg 2E(T_1)$ and $E(T_2) < E(S_1)$		-	-
III. homo-SSA; no recycling	-	$\chi_{e,p,S} = 0.500$	$F_{ep} = 0.500$

* Cases for which $0 < \eta_{isc} < 1$ have been described by Weisman, *et al.*, references 39-41.