ChemComm

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Journal:	*ChemComm*
Manuscript ID	CC-FEA-02-2018-001553.R2
Article Type:	Feature Article

ROYAL SOCIETY OF CHEMISTRY

Chem Commun

FEATURE ARTICLE

New Perspectives for Triplet-Triplet Annihilation Based Photon Upconversion Using All-Organic Energy Donor & Acceptor Chromophores†

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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It is recognized that metal organic complexes that serve as sensitizers can present various degrees of challenges viz. synthesis and stability for photonic applications such as triplet-triplet annihilation based photon upconversion (TTA-PUC). Presently, researchers, including our group, are turning their attention toward purely organic triplet sensitizers, which can be handled more easily for photon management science. In this review, we surveyed recently developed all-organic chromophoric systems that were devised and used for TTA-PUC research. Knowing that TTA-PUC research has mainly been focused on the design and synthesis of the triplet sensitizers, we detailed the underlying photophysics and thermodynamics that served as the starting point for the synthesis of the purely organic chromophores in question. Accordingly, this review details triplet sensitizers that operate on i) spin-orbit coupling or heavy atom effect, ii) Baird-type aromaticity and antiaromaticiy, iii) open-shell characteristics or doublet excited state and iv) thermally activated delayed fluorescence.

1. Introduction

Organic materials have the potential to revolutionize modern photonic technologies that require lightweight and flexible components whose electronic and physical properties can be tuned to absorb, modulate and transmit broadband radiation.[1] With synthetic ingenuity, one can easily functionalize or modify the structure of conventional organic chromophores to harvest low-energy radiation and transform these photons into useful energy for applications ranging from photovoltaics (PV) to photocatalytic water splitting. The conversion of low-energy photons to useful or high-energy radiation, which occurs via an anti-Stokes photophysical process, is also known as photon upconversion (PUC). PUC has been demonstrated to be an elegant photophysical process that can be exploited to improve the efficiency of single junction PV in order to overcome the predicted conversion limit of 33%.[2-11] The limitation of single junction PV to harvest and convert the entire solar spectrum into electricity emanates from the narrow bandgap energetic of photonic materials that are utilized as ingredients during the fabrication of these devices. Thus, PUC can provide means to tune the spectral distribution of sub-bandgap solar radiation to match the wavelength range in which PV devices (especially organic PV) operate.[12-17] The modulation of sub-bandgap photons for PV applications presents a unique opportunity to engineer upconverting materials that can be nicely integrated into these devices or used as ingredients in the fabrication of next generation PV to achieve maximum efficiencies.

Of all anti-Stokes photon management techniques reported in recent years, triplet-triplet annihilation based PUC (TTA-PUC) is regarded as one of the most promising processes; this is because the molecular chromophores, which are employed to achieve TTA-PUC, are readily accessible. Mechanistically, TTA-PUC is a bi-molecular non-linear process involving a light-harvesting triplet chromophore that is used to sensitize a luminescent scaffold (energy acceptor or annihilator) via a thermodynamically favoured Dexter-type energy transfer route.

$$\mathbf{D} + \mathbf{h\nu} \rightarrow {}^{1}\mathbf{D}^{*} \rightarrow {}^{3}\mathbf{D}^{*} \qquad \text{(Eq. 1)}$$

$${}^{3}\mathbf{D}^{*} + \mathbf{A} \rightarrow {}^{3}\mathbf{A}^{*} + \mathbf{D} \qquad \text{(Eq. 2)}$$

$$2 \times {}^{3}\mathbf{A}^{*} \rightarrow {}^{1}\mathbf{A}^{*} + \mathbf{A} \rightarrow \mathbf{h\nu'} + 2 \times \mathbf{A} \qquad \text{(Eq. 3)}$$

From a photophysical point of view, the triplet energy donor (**D**) must have a narrow singlet-triplet gap allowing to quickly form triplet excitons (^{3}**D***) via intersystem crossing (ISC) upon absorption of low-energy photons (Eq. 1). Eq. 2 shows the subsequent triplet energy transfer (TET) to the energy accepting chromophore (**A**), which by itself cannot undergo singlet→triplet ISC. Since ISC is seemingly forbidden for the **A** chromophore, upon formation, the triplet excitons (^{3}**A***) would self-quench or undergo annihilation to produce singlet ground

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†Electronic Supplementary Information (ESI) available: Synthetic procedures and compounds characterization; phosphorescence decay traces and intensity-dependent photoluminescence data; methods and techniques and information of instrumentation. See DOI: 10.1039/x0xx00000x

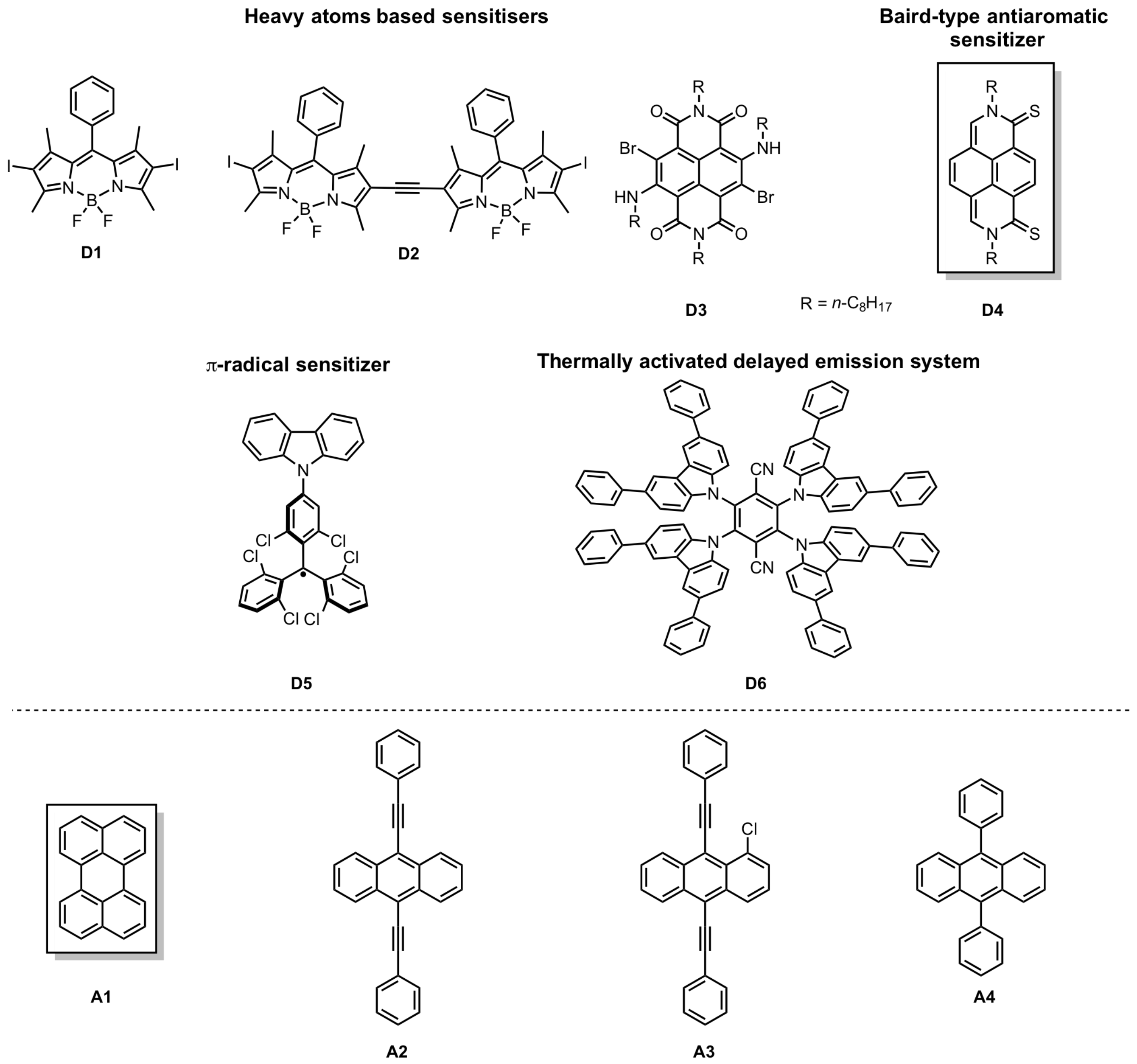


Figure 1. Molecular structures of model organic triplet sensitizers **D1**–**D5** and corresponding triplet energy PAH acceptors **A1**–**A4**, which have successfully used for TTA-PUC. Due to their structural similarity, we believe that **D4** and **A1** are compatible structures that can be tailored for single component TTA-PUC research.

states (**A**) and other ^{1}**A*** excitons in "hot states". The latter species will then relax to the lowest singlet excited state followed by luminescence to produce photons that are higher in energy than the input/absorbed radiation (Eq. 3).[3,18,19]

Fluorophores such as polycyclic aromatic hydrocarbons (PAHs) are well documented to have a large singlet-triplet gap (or forbidden ISC); but these chromophores exhibit excellent fluorescence emission and are routinely employed as the annihilators. Since PAH chromophores are readily available chromophores, research targeting TTA-PUC has so far been devoted for the development of the triplet sensitizers that exhibit moderate to high structural complexities and stability at ambient conditions. A particular focus has been on: i) transition metal complexes sensitizers that function via metal-to-ligand charge transfer processes[14,17,20-23], ii) n,π* organic chromophores[24-26] and hybrid organic-inorganic complexes, iii) heavy atom based π,π* scaffolds.[25,27]. Very recently, our group also has added a new flavor to the library of TTA-PUC materials by introducing novel purely organic Baird-type antiaromatic[28] photosensitizers.[29,30]

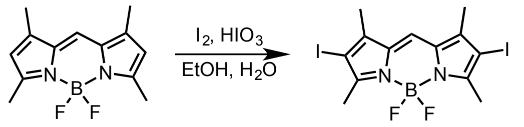
While transition metal complexes or organometallic triplet sensitizers (e.g. Pt(II), Ir(II) and Pd(II) porphyrinoids), which have been used for TTA-PUC research, produced the best quantum efficiency of PUC reported thus far,[14,17,20-26,31,32] these dyes do suffer from photophysical dychotomies such as low extinction coefficient for the long-wavelength S$_0$→MLCT transitions.[33] In this picture, various groups in the area of TTA-PUC have also introduced triplet bichromophores, where the presence of additional PAH scaffold(s) would ensure greater absorption of visible photons. For the present contribution, we will only concentrate on purely organic triplet sensitizers, as these molecular systems can be easily functionalized or derivatized to match the structural features of the energy acceptor PAHs. Complementary contributions that covers TTA-PUC investigations involving transition metal complexes and their derivatives have been recently disseminated in the literature.[3,33,34]

Purely organic light-harvesting triplet sensitizers can be easily synthesized and/or derivatized; but, the ones that absorb visible-to-near infrared are scarce. In addition, the design and synthesis of novel organic triplet chromophores requires considerable knowledge of the underlying photophysical mechanisms and thermodynamics of the TTA-PUC process. The pioneering research in this regard involves heavy atoms (bromine and iodine) substituted boron dipyrromethene (BODIPY) and naphthalene diimide (NDI) dyes which have been intensively researched by Zhao and co-workers.[25,27,34,35] Other contributions vis-à-vis all-organic chromophores for PUC research include π-radical carbazole derivatives reported by Liu and co-workers[36] and thermally activated delayed fluorescence chromophores. Very recently, we introduced a new concept of TTA-PUC that makes use of structurally compatible/complementary polycyclic chromophores, where the light-harvesting sensitizer exhibits Baird antiaromaticity.[28]

Herein, we survey purely organic triplet sensitizers which have been developed in recent years for PUC. We will review i) heavy atom based organic dyes[25,27,34,35], ii) Baird-type aromatic triplet chromophores[30], iii) organic π-radicals[36] and iv) thermally activated delayed chromophores[37,38]. Our discussion will detail the very best of each chromophoric system in question. To avoid redundancy and repetition, derivatized chromophores from these dyes will not be discussed in this report. Moreover, we will unveil a new direction involving single component **D**–**A** bichromophoric systems for TTA-PUC research from our group.

2. BODIPY dyes triplet sensitizers (D1 & D2)

BODIPY are well-known fluorophores with narrow Stokes shift and high quantum yield often approaching unity irrespective of the property of the medium.[27,35,39] These properties render the BODIPY scaffolds as excellent chromophores that can be easily modified to harvest visible photons as well as diminishing the spin allowed $S_1 \rightarrow S_0$ radiative transition to favor $S_1 \rightarrow T_1$ pathway through spin-orbit coupling process. As early as 2005, Nagano and co-workers successfully modified the structure of BODIPY with heavy atoms such as iodine to afford a triplet sensitizer, which they used to produce singlet oxygen ($^1O2$) (Scheme 1).[40] They also reported that the iodinated BODIPY (**2I-BDP**) exhibits comparable visible light absorptivity (λ_{max} = 502 nm) with the native scaffold; but, **2I-BDP** showed superior photo-activity and -stability than conventional sensitizers such as Rose Bengal. Moreover, due to the strong spin-coupling, the quantum yield (Φ_F) for $S_1 \rightarrow S_0$ transition was found to drop from 0.7 for **BDP** to 0.02 for **2I-BDP** inferring that the lowest T_1 state was efficiently populated at a faster rate due to the internal heavy atom effect.



BDP **2I-BDP**

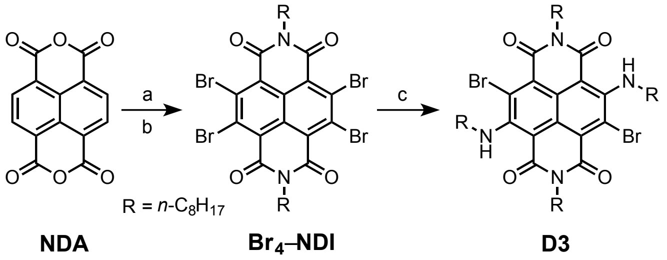
Scheme 1. Synthesis of heavy atom containing BODIPY dyes reported by Nagono and co-workers.[40]

Following this seminal contribution that allowed for tuning the photophysical properties of BODIPY using heavy atoms, Zhao and co-workers adopted similar strategies to create a library of iodinated BODIPY photosensitizers, which they used as light-harvesting triplet energy donors to achieve TTA-PUC.[25,34,35,41] From this investigation, it was found that *bis*-iodinated BODIPY **D1** exhibits a greater spectral red-shift ca. 20 nm compared to the mono-iodinated analogue. Notably, the Φ_F of **D1** from their investigation is similar to the value reported by Nagano and co-workers (*vide infra*). Moreover, they demonstrated that **D1** phosphorescence band is located near 750 nm, which is close to the triplet level of the annihilator perylene **A1** ($E_T \approx 35$ kcal/mol). In addition to the phosphorescence data from **D1**, evidence of the corresponding triplet transient was proved by nanosecond time-resolved pump-probe spectroscopy showing that upon laser pulsed excitation at 532 nm, a transient absorption band appears between 580 and 800 nm with a time constant of 57.1 µs, which was attributed to the lifetime of the triplet transient (**^{3}D1***).

The **D1**$\rightarrow$**A1** TET process was then monitored via transient absorption experiments, where perylene T_1 emerged near 495 nm. Also, the TTA-PUC phenomenon was verified by measuring the excitation intensity dependence of the delayed fluorescence from **A1**, which gave a quantum yield Φ_{PUC} = 5.4%. Interestingly, this photon dynamics exhibits a linear relationship with the power density of the incident 532 nm light most likely indicating a highly populated triplet excited state of **D1** and efficient **D1**$\rightarrow$**A1** TET process.[42] Furthermore, the structure of **D1** was modified to afford the dimeric system **D2** which has a maximum absorption at 618 nm allowing for the upconversion of red radiation to blue photons using **A3** as an emitter/annihilator. From the same report, it was demonstrated that iodinated BODIPY chromophores could be tailored for practical applications, as the TTA-PUC process was also investigated in polymer matrices of analogous structures of **D1**/ **D2** in the presence of **A1** or **A2**.

Importantly, one of the highlights from the work involving iodinated BODIPY dyes is that the quenching rates of their triplet states or transients by **A1** or **A2** are comparable to, or even exceed, the values reported so far with transition metal complexes which have been used for TTA-PUC research.[20-22,26,43] While these photo-dynamics and -kinetics can be attributed to the long-lived T_1 state of the sensitizers, the small size of the BODIPY scaffolds was found to be conducive to enhancing molecular diffusion and hence producing greater interaction with the annihilators molecular units.

3. NDI triplet sensitizers (D3)



Scheme 2. Synthesis of photosensitizer **D3**: a) Dibromoisocyanuric acid, oleum (20% SO_3), 25 °C, 3 h; b) *n*-octylamine, acetic acid, 90 °C, 30 min, N_2, then PBr_3, dry toluene, reflux, 12 h; c) *n*-octylamine, dry dimethylformamide, 135 °C, 6 h.[27]

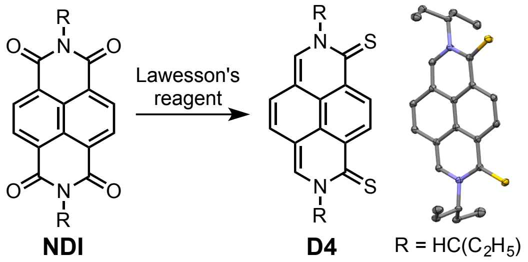
The structural similarity of poly-heterocyclic aromatics such as naphthalene and perylene diimides (NDI and PDI respectively) with their PAH counterparts should be beneficial for TTA-PUC. As we discussed in the introduction, the **D**→**A** TET is a Dexter process (vide supra) that requires a very short intermolecular distance (typically less than 10 Å) between the interacting chromophores leading to efficient overlap of the **D** and **A** molecular wavefunctions. Electron deficient NDI and its congeners can form intrinsic π-π supramolecular donor-acceptor systems with PAHs (electron rich) due to the similarity and complementarity of their molecular backbone.[44,45] However, the NDI scaffold is electron deficient, rendering its interaction with PAHs to result in π-acid•••π-base complexes rather than **D•••A** or **^{3}D*•••A**. NDI has been used in various photonics research efforts, it is well-documented to exhibit weak fluorescence (with short excited state lifetime).[46]

From all of the above, it seems that the photophysical properties of this chromophore are not useful for PUC research. As noted in the previous section, with synthetic ingenuity, the photophysics of fluorophore dyes can be altered or manipulated after subtle functionalization of the scaffold of interest (with/using molecular synthons) leading to efficient population of their corresponding lowest triplet state.[47-51] Similar with BODIPY dyes, Zhao and co-workers synthesized bromine containing NDIs, which they used as photosensitizers for TTA-UC (Scheme 2).[27,52-54]

Sensitizer **D3** was prepared starting from naphthalene dianhydride (**NDA**).[27] The presence of electron-donating N-octyl amino groups on the backbone of **D3** allowed to red-shift its absorption that ends near 560 nm as well as "balancing" its π-acidity as encountered in native NDIs. On the other hand, the presence of bromine heavy atoms will certainly exert strong spin-orbit coupling that should be crucial to access the triplet state of this chromophore. However, the authors were not able to fully resolve the phosphorescence profile of **D3**; and evidence of its triplet state was rationalized using the pump-probe absorption method. Upon laser excitation (λ_{Exc} = 532 nm) of a toluene solution of **D3**, its triplet transient (^{3}**D3***) absorption bands were observed at 339 nm, 469nm and between 550-800 nm with a lifetime of 51.7 µs. The authors noted that this transient was readily quenched in aerated media inferring a likely triplet species. Furthermore, **D3** was successfully used to sensitize **A1** to produce a bluish emission using a 532 nm laser as the excitation source.

4. BAIRD-type aromatic quinoidal naphthalene triplet sensitizers (D4)

It has been recently demonstrated that heavy atom-free thionated NDIs (e.g. exchanging the carbonyl oxygen with sulfur atom) can also absorb visible photons and can easily perform ultra-fast ISC to produce triplet species.[55] Unpublished complementary investigations involving thionated NDIs from our group indicate that these heavy atom-free chromophores exhibit non-radiative triplet→S_0 ISC with a decay kinetic faster than the phosphorescence lifetime of a typical triplet chromophore for TTA-PUC. We later found that thionated NDIs are not suitable for TTA-PUC. So far, triplet NDIs containing heavy atoms seems to be the stepping stone to devise novel all-organic light-harvesting poly-heterocyclic aromatic triplet sensitizers that are structurally similar/complementary to PAH annihilators. In the case of **D3**, we hypothesize that the N-octyl amino groups and the bromine atoms on the π-core of NDI may become too cumbersome thus hampering the **D3•••A1** interaction affecting the efficiency of the **D3**→**A1** TET process even through the energy transfer is dominated by molecular collision. It is worth noting that the structural complementarity of this class of chromophores would be conducive to devise novel organic materials for solid-state PUC. Thus, to preserve the structural integrity of the sensitizer **NDI** backbone, we opted instead to tune the aromaticity of this chromophore to afford novel photosensitizers such as naphthoquinodimethane **D4** whose structure exhibits "broken symmetry and aromaticity" (Scheme 3).[29] **D4** was specifically designed to exhibit ground state Baird-type 4n π-electrons aromaticity[28]; we expected this property to be reversed in the excited state to produce metastable Baird anti-aromatic triplet species upon photoexcitation according to Baird's rule of excited state aromaticity.



Scheme 3. Lawesson reagent mediated reductive desulfurization of NDI to afford photosensitizer **D4**.[29]. The XRD crystal structures of the donor and acceptor chromophores are also shown.

The UV-vis absorption and emission profiles of **D4** shown in Figure 2 clearly indicate that this chromophore can harvest visible photons up to ca. 570 nm. Remarkably, the steady state emission of the sensitizer resembles the one of parent NDI[29], but this emission band with Φ_F = 0.002 is significantly overlapping with the ground state absorption. The low quantum yield of the $S_1 \rightarrow S_0$ is indicative of a highly competitive ISC to form triplet ^{3}**D4*** species. Further photoluminescence studies revealed that the $T_1 \rightarrow S_0$ emission band is centered at ca. 725 nm (λ_{onset} = 700 nm) with a lifetime of τ_P = 395 µs recorded in 1:1 EtOH:DCM. As elaborated earlier, for efficient TET, it is desirable to produce long-lived triplet states of the light-harvesting sensitizer. A value of 395 µs for Baird-type aromatic **D4** chromophore is compelling vis-a-vis NDI derivatives. As a matter of fact, NDIs (containing heavy atom Br) used for TTA-PUC exhibit shorter triplet radiative decay lifetimes in the range of 50 µs (*vide supra*).[27]

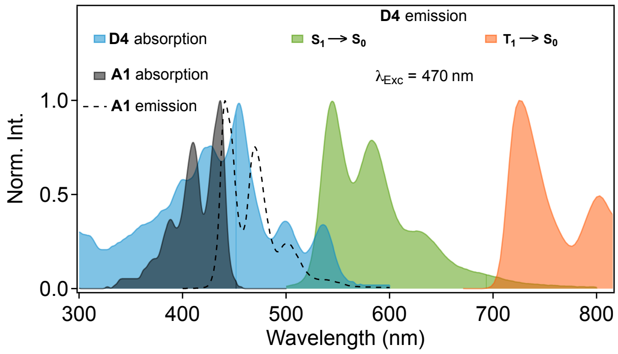


Figure 2. Normalized absorption and emission spectra of **D4** and **A1** in 1:1 EtOH:DCM. The phosphorescence ($T_1 \rightarrow S_0$) of **D4** was recorded 100 µs after pulsed excitation in EtOH:DCM glass at 77 K. Adapted with permission from Ref. 30. Copyright 2017 American Chemical Society.

Knowing that the lowest triplet level of **D4** is located at ca. 40.8 kcal/mol above its ground state, it is intuitive to use an energy accepting chromophore whose triplet energy is below that value. Thus, we selected **A1** as the annihilator for its high fluorescence quantum yield (Φ_F = 0.75), photo– and thermal–stability as well as being structurally complementary to the sensitizer.

To ascertain the kinetics of the TET process, we performed quenching experiments that provided insights about the dynamics and rate of molecular collision. We had hypothesized that due to the complementarity of their molecular backbone, when both **D4** and **A1** are placed in any matrix, it is likely they form π-π supramolecular assemblies. In this picture, it will seem impossible to unravel the kinetics of the TET process. As illustrated in Figure 3a, a solution matrix containing 1:1 molar ratio of both **D4** and **A1** show complete quenching of the phosphorescence of the sensitizer. This result most likely indicates a perfect overlap of the molecular wavefunction of the two chromophores. Even when **D4** and **A1** are placed in a rigid matrix, the quenching experiments show that the two chromophores do interact strongly (or are pre-organized) in the rigidified matrix in a such a way that the TET still exhibits a fast kinetics (Figure 3b).[29,30]

The enclosure of Figure 3a depicts the expected bimolecular dynamics/interactions between **D4** and **A1**; but, this cartoon does not provide any information regarding the kinetics of the **D4**→**A1** TET process. Thus, we performed further transient absorption studies to unravel the nature and kinetics of the two interacting chromophores in the excited state. After a laser excitation at 520 nm, the triplet transient spectrum of **D4** recorded in deaerated THF appeared near 400 nm and between 500 and 800 nm. It is worth noting that this transient with lifetime of more than 1.4 µs was readily quenched by molecular oxygen. In the presence of **A1**, excited state kinetics of ^{3}**D4*** was one order of magnitude reduced to 0.17 µs whereas the triplet transient of the annihilator (^{3}**A1***) appeared near 690 nm with a lifetime of 0.2 µs suggesting an efficient **D4**→**A1** TET to produce metastable ^{3}**A1*** species, which undergo a rapid TTA ($k_{TTA} < 5\text{x}10^6$ s^{-1}).[29,30] From the transient absorption experiment, we were able to deconvolute the delayed fluorescence of **A1** near 465 nm with a lifetime of 5.8 µs, a value that is three order of magnitude faster than the kinetics of its prompt emission. Figure 3c illustrates the delayed or upconverted bluish emission from **A1** using a 532 nm commercial laser. Unfortunately, it appears that the upconverted bluish emission exhibits a low quantum yield of 0.16%. We further ascertained that the low value for Φ_{PUC} most likely transpires from reabsorption of the emitted blue photons by the sensitizer. Another reason for the low value of Φ_{PUC} could be attributed to ^{1}**(A1)***→**D4** back energy transfer via FRET mechanism. This observation is consistent with the overlap of the absorption band of **D4** with the emission of **A1** (Figure 2).

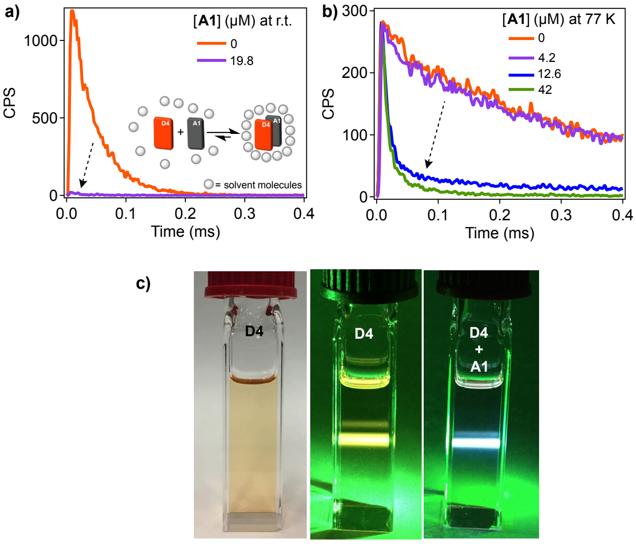


Figure 3. Phosphorescence (monitored at 725 nm) decay traces of **D4** (conc. = 1.71x10^{-5} M) in the presence of **A1** at a) room temperature in deaerated 1:1 EtOH:DCM (Inset: Graphical illustration of intermolecular or bi-molecular interaction of **D4** and **A1** in solution or condensed matrices) and b) at 77 K in 1:1 EtOH:DCM glassy matrix. c) Photograph of photoluminescence of **D4** (left) and **A1**upconverted photoluminescence in deaerated THF (right) using a 532 nm commercial laser (30-40 mW/cm^2). Adapted with permission from Ref. 30. Copyright 2017 American Chemical Society.

Since it is customary to assess the non-linearity of the TTA-PUC process, we performed intensity-dependent photoluminescence experiments, where the upconverted emission of **A1** was recorded even with power density as low as 45 mW/cm^2 (Figure 4). This result demonstrates that **D4** and **A1** constitute an example of pair of chromophores that can be implemented to transform non-coherent radiation of power < 1 sun for tangible applications.

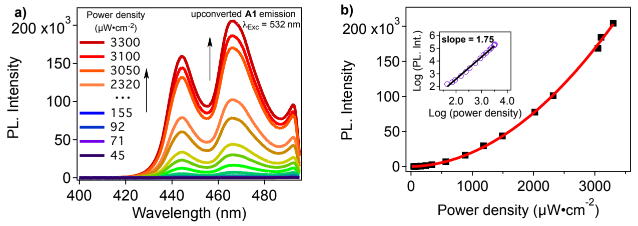
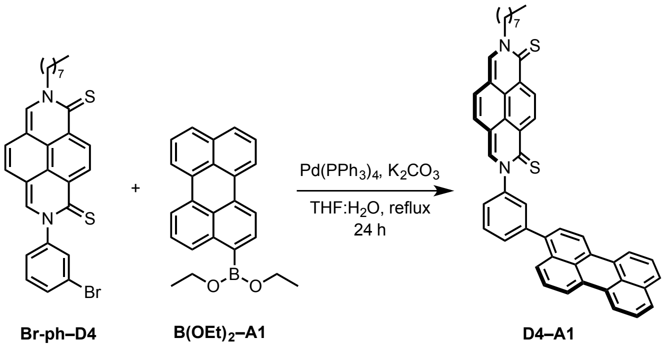


Figure 4. a) Intensity-dependent upconverted emission of **A1** in the presence of **D4** excited at 532 nm ([**D4**] = 7.04x10^{-5} M; [**A1**] = 21.12x10^{-5} M) in deaerated THF; a 500 nm shortpass filter was used to discard the overlapping emission from **D4** as well as cutting off the incident radiation. b) Best quadratic fit (x^2) of the PL intensity at 465 nm. Inset: Double logarithmic plot PL intensity vs. power density of the incident light producing a linear fit with slope = 1.75. Adapted with permission from Ref. 30. Copyright 2017 American Chemical Society.



Scheme 4. Synthesis of dyad **D4–A1** via Suzuki coupling. The detailed synthesis of starting materials **Br-ph–D4** and **B(OEt)$_2$–A1** can be retrieved in the Supplementary Information.

Although we hypothesized earlier that **D4** and **A1** may be engaged in supramolecular π-π interacting, we did not establish a clear picture for the mode of interaction viz. face-to-face or edge-to-face. To clarify the bi-molecular dynamics described in Figure 3a (inset), we synthesized a bichromophoric system, featuring both **D4** and **A1** chromophores (Scheme 4 & Supplementary Information). Dyad **D4–A1** was cleverly designed to enforce through-bond electronic couplings between **D4** and **A1** moieties. Furthermore, we expect strong interactions between the **A1** moiety of the dyad and free **A1** chromophore in the matrix via the well-documented perylene π-π interaction.

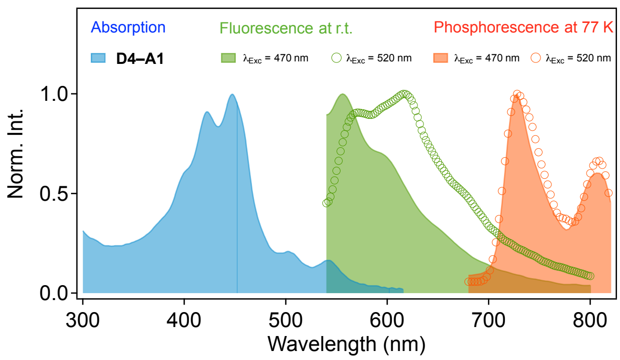


Figure 5. Normalized absorption and emission spectra of **D4–A1** in 1:1 EtOH:DCM.

As depicted in Figure 5, the UV-vis absorption profile of **D4–A1** exhibits the typical π,π* transitions seen in both **D4** and **A1** chromophores with a slight red-shift up to ca. 600 nm. Also, the steady state emission of this system, excited at both 470 and 520 nm, seems to be the convoluted emission bands of the two chromophoric moieties. Remarkably, the phosphorescence band looks unchanged suggesting no possible intramolecular **D4**→**A1** TET. But, we suspected a partial delocalization of the triplet state to the **A1** moiety, as the fitting of the phosphorescence decay trace produced two components (29 µs and 275 µs) kinetics (Figure S1, Supplementary Information).

Knowing that a Stern-Volmer quenching experiment would not reveal much of the type of dynamics and kinetics we should expect when **A1** is mixed with dyad **D4–A1**, we employed transient absorption methods to evaluate the photo-dynamics and -kinetics as illustrated in Figure 6.

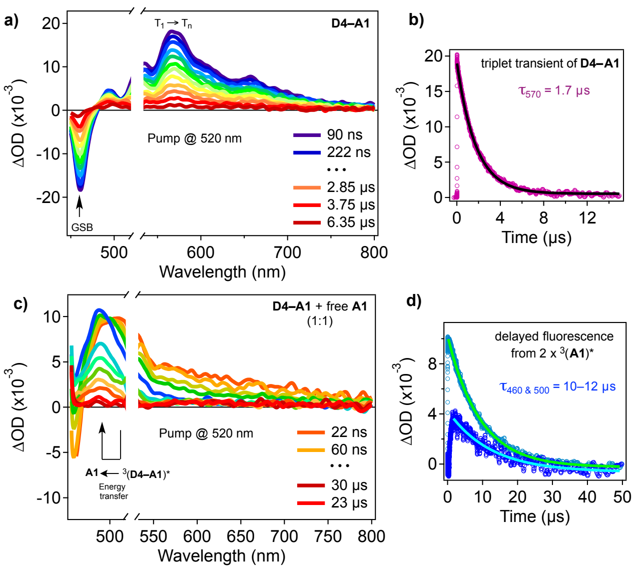


Figure 6. a) Nanosecond time-resolved transient absorption spectra for **D4–A1**; b) Decay kinetics for ^{3}(**D4–A1**)*; c) Nanosecond time-resolved transient absorption spectra for **D4–A1** in the presence of free **A1** (O.D. = 0.33, λ_{Exc} = 520 nm, 1 µJ) in deaerated THF; d) Decay trace monitored at 465 and 500 nm depicting the kinetics of **A1** delay fluorescence in deaerated THF.

We found that the transient absorption spectrum of the dyad (Figure 6a) is similar to the one of **D4** alone in the presence of **A1**.[30] Expectedly, the lifetime of the triplet transient ^{3}(**D4–A1**)* was measured for τ_{570} = 1.7 µs. This time constant is close to the one we had obtained before with free **D4** + **A1**.[30] However, upon addition of free species of the annihilator, the transient spectrum between 500 and 800 nm quickly disappeared with a time constant of τ_{570} = 0.3 µs and a new band between 460 and 500 nm emerged indicating a likely energy transfer to free **A1** species to form the corresponding ^{3}**A1*** transients, which underwent self-quenching to produce the delayed emission as shown in Figures 6c & 6d. Although the kinetics data is in agreement with our previous observations and our expectations, we found that the energy transfer process exhibited a different dynamic. From this experiment, we established that free **A1** must be strongly associating with

Table 1: key photophysical data for organic donor (**D**) chromophores compared to data from a metal complex sensitizer.

Entry	Sensitizers	λ_{abs}^{max} (nm)/ ε ($M^{-1}cm^{-1}$)	τ_T (μs)[b]	E_T (kcal mol^{-1})	Light Upconversion	(Φ_{PUC}) / Acceptor	References
1	**D1**	529 / 89000	57.1	34.6	Green→Blue	5.4% / **A1**	[25]
2	**D2**	618 / 89500	47.0	32.9	Red→Blue	1.7% / **A3**	[25]
3	**D3**	526 / 15000	51.7	–	Green→Blue	18.5% / **A1**	[27]
4	**D4**	452 / 13164	1.5	40.8	Green→Blue	0.16% / **A1**	[30]
5	**D5**	600 / NA	–[c]	41.9[d]	Red→Blue & Red→cyan	0.25% / **A2** or **A4**	[36]
6	**D6**	400-550[a]	–	50.9	Green→Blue	0.28% / **A2**	[38]
7	**PtTPBP**[e]	411 (Soret) & 611 (Q-band)	41.5[f]	40.8	Red→Blue	0.65%/ **A1**	[60]

[a] Recorded in thin film; [b] Triplet state lifetime measured by nanosecond pump-probe method; [c] 27 ns; [d] Doublet excited state; [e] PtTPBP = platinum(II) tetraphenyltetrabenzoporphyrin; [f] value measured at room temperature.

the perylene moiety of the dyad otherwise no change would have been noticed in the transient absorption profile. We have also hypothesized that the strong **A1**(free)•••**A1**(dyad) interaction is still a dynamic process. This dynamic is translated in to the growing band centered at 500 nm (Figure 6c) suggesting a probable TTA of free ^{3}**A1*** species.

We then demonstrated that the interesting molecular photo-dynamics involving dyad **D4–A1** and free **A1** species should lead to the typical non-linear photophysical process as expected for TTA-PUC. Using 1:1 and 1:2 molar ratios of **D4–A1** sensitizer to free annihilator **A1**, we were able to realize the PUC phenomenon, which was visually quantified and qualitatively ascertained by incident green light intensity dependent photoluminescence of **A1** (Figure S2, Supplementary Information).

5. Organic π-radical sensitizers (D5)

A disregarded limitation of TTET based PUC is the energy loss during $S_1 \rightarrow T_1$ ISC; yet, this small energy loss may seem detrimental for the ever-growing attempt to utilize low-energy incident light to achieve maximum PUC efficiency. In this picture, several research groups have proposed novel transition metal complexes triplet sensitizer to bypass the $S_1 \rightarrow T_1$ route and directly populate the T_1 state via $S_0 \rightarrow T_1$.[56,57] Alternatively, the group of Liu has recently proposed to utilize organic π-radical dye (4-*N*-carbazolyl-2,6-dichlorophenyl)bis(2,4,6-trichlorophenyl)methyl (**D5**) that exhibit a much reduced excited state energetics thanks to its doublet state. Accordingly, the excited doublet state of **D5** was shown to be lower in energy than the lowest singlet excited state. Unlike conventional S→T chromophores, **D5** can easily perform Doublet→Triplet energy transfer (DTET) to annihilator **A4** by dissipating only a very small amount of the excited state energy.[36] In this picture, the mechanism of donor-acceptor energy transfer is similar to the well-documented Dexter energy transfer channel using the existing or traditional triplet sensitizers (Eq. 1-3) as illustrated in Figure 7a.

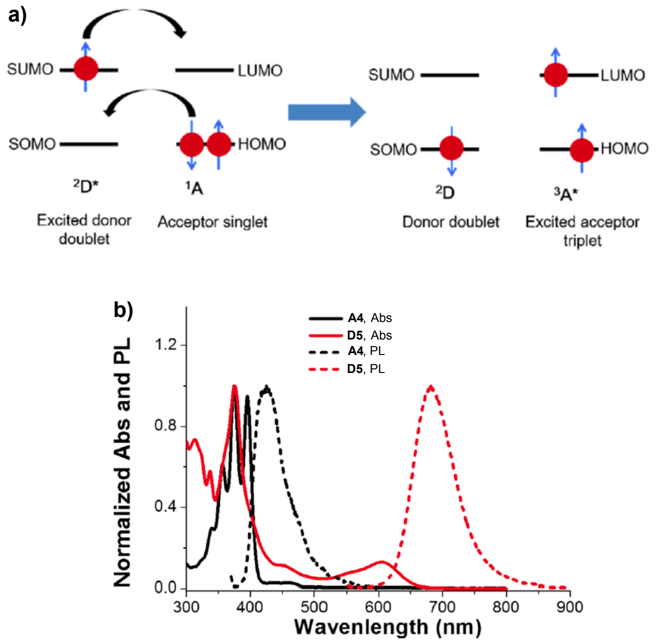


Figure 7. a) Schematic representation of Dexter-like doublet-triplet energy transfer. b) Normalized absorption and emission spectra of **D5** (0.1 mM; λ_{Exc} = 530 nm) and **A4** (0.1 mM; λ_{Exc} = 375 nm) in toluene. Adapted with permission from Ref. 36. Copyright 2017 American Chemical Society.

In addition to characterizing **D5** using UV-vis and emission spectroscopy methods, the authors have also performed complementary experiments such as EPR to ascertain the open-shell characteristics of this doublet sensitizer. The UV-Vis profile of **D5**, shown in Figure 7a indicates, that red photons (up to ca. 660 nm) can be readily absorbed by this dye. Accordingly, the authors demonstrated that **D5** was used to harvest red photons and sensitize **A4**, which then generated blue light with a Φ_{PUC} = 0.25% using an incident source that operates at ca. 300

mW/cm^2. In this investigation, the authors attributed the low quantum yield of upconversion to the modest efficiency of the DTET process (Φ_{DTET} = 69%), which seems to be affected also by the relatively short lifetime of the doublet exciton ($\tau_{\mathbf{D5}}$ = 27 ns).

6. Thermally Activated Delayed Fluorescence (TADF) sensitizers (D6)

Like in the case of the DTET sensitizer **D5**, the same rationale with regard to the small energy loss during ISC has led to employ TADF chromophores for PUC. TADF chromophores exhibit small S_1–T_1 gap and they have been widely used for a number of photonic applications including OLED, where these chromophores can help harvest both singlet and triplet excitons leading to a greater quantum efficiency of the light emitting devices. The continuous search for new organic sensitizers led to survey a few TADF chromophores for PUC research. Baldo and co-workers (among many others) have adopted TADF sensitizers such as **D6** to perform PUC.[38] Very recently, Yang and co-workers have also developed thiadiazole TADF chromophores for PUC research.[37] The photophysical mechanism of PUC involving TADF chromophores is still similar to conventional triplet sensitizers except the S_1–T_1 energetics. Inspired by the outstanding performance of OLED based on **D6**,[58] Baldo and co-workers used this chromophore to sensitize **A4**. Remarkably, the PUC experiment was done in the solid state, where **D6** and **A4** were sequentially deposited layer-by-layer onto a quartz substrate. The solid-state device thus constructed showed a performance of Φ_{PUC} = 0.28% by absorbing green photons to the generate blue emission of **A4**. Furthermore, other groups were able to devise various analogous chromophores to achieve PUC quantum yields as high as 3.9%.[59] However, one of the major issues reported with TADF sensitizers was that these chromophores are susceptible to perform Reverse ISC due to the small S_1–T_1 gap hampering the efficiency of the TET process.

7. Challenges & Perspectives

A major drawback for TTA-PUC using all-organic chromophores is that very often, the absorption and emission bands of the sensitizer and annihilator chromophores overlap in the UV-to-vis spectral range. This photophysical dichotomy usually leads to reabsorption of the upconverted photons by the sensitizer molecules. A likely back energy transfer from excited acceptor species to the donor chromophore could also occur via FRET mechanism. As revealed in Table 1, the analysis of the low values for the Φ_{PUC} (except for Entry 3) clearly conjectures that the excited state of the annihilators is readily quenched presumably via back energy transfer to the sensitizer molecules. In this context, future molecular designs attempting to improve the **D**$\rightarrow$**A** TET kinetics in order to achieve better Φ_{PUC} should also take into account the decoupling of the absorption and emission bands of the interacting donor and acceptor chromophores. Particularly, one can see that the Φ_{PUC} value, using **D4** and **A1**, is significantly low (Table 1, Entry 4). To solve this problem, our group has been working on modifying the structure of sensitizer **D4** using molecular and aromatic synthons in a such a way that the resulting light-harvesting sensitizers exhibit better photophysical properties. Based on our theoretical predictions, we hope to achieve better Φ_{PUC} using Baird-type antiaromatic derivatives of **D4** sensitizer.

8. Conclusions

PUC is an emerging photon management technique that is continuously drawing various degrees of attentions to develop novel light harvesting chromophores. But, it is imperative to systematically assess the underlying photophysical processes governing the PUC phenomenon in order to devise the appropriate molecular tools that meet the required criteria to achieve an efficient quantum yield. Since PUC is a bi-molecular process, which requires a triplet light-harvesting chromophore (donor) and an energy accepting fluorophore or annihilator, it is essential to assure a greater extend of overlap of the molecular wavefunctions of the energy donor and accepting chromophores in order to achieve maximum quantum yield of upconversion. With that in mind, various groups have proposed and used a number of organic sensitizers for TTA-PUC with mixed results. We have also used purely organic and structurally compatible/complementary donor(antiaromatic) and acceptor(aromatic) chromophores that were easy to synthesize and manipulate. Furthermore, we ascertained that the structural features of the chromophores of our interest were conducive to a faster kinetic of the energy transfer process, which infers a stronger donor-acceptor interaction. Building on this achievement, we have been devising analogous purely organic bichromophoric systems featuring a Baird-type antiaromatic moiety (sensitizer) and the energy accepting aromatic fluorophores. We will also be capitalizing on bichromophoric **D4**–**A1** system to devise novel organic photonic materials for PUC research.

Acknowledgements

The authors thank IIT for the generous support to this research. This material is based upon work supported by the National Science Foundation under a CAREER grant N° 1753012 Awarded to AJA. Use of the Center for Nanoscale Materials, an Office of Science user facility, was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

Conflicts of interest

There are no conflicts to declare.

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