

Triplet-triplet annihilation photon-upconversion in hydrophilic media with biorelevant cholesteryl triplet energy acceptors

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ABSTRACT

We report two new biorelevant cholesteryl-based triplet energy acceptors, derivatives of DPA or 9,10-diphenylanthracene (C-DPA and C₂-DPA). Using two different triplet sensitizers: QDN ($E_T \approx 1.67$ eV in PEG200) and PdTPP ($E_T \approx 1.78$ eV in PEG200), we were able to achieve both endothermic (with QDN) and exothermic (with PdTPP) triplet sensitization of DPA, C-DPA and C₂-DPA in hydrophilic PEG200 media. While the maximum rate of triplet energy transfer (TET) was achieved with PdTPP and DPA ($k_{TET} = 4.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$), for the cholesteryl-based acceptors, we found that the kinetic of the TET process was dependent upon the concentration of the acceptor. For PdTPP/C-DPA pair, the rate of the dynamic triplet energy quenching was $k_{TET} = 1.9 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$; however, at higher concentrations of the quencher, the system reached a stationary state due to formation of self-assembled sub-domains of C-DPA that likely slowed the TET process. It was also found that this aggregation of C-DPA in PEG200 led to a 3.5 folds increase in the I_{th} compared to 133 mW cm² for DPA. Subsequently, we estimated the Φ_{UC} for these donor/acceptor pairs: QDN/DPA, PdTPP/DPA, and PdTPP/C-DPA. With respect to the estimated threshold intensity (I_{th}), we found that the quantum yields of TTA-UC were $2 \leq \Phi_{UC} \leq 12\%$.

1. Introduction

Triplet-triplet annihilation photon-upconversion (TTA-UC) is an elegant photophysical process that allows to amplify photon energy for applications at the interface of solar energy conversion, optoelectronic science, and bio-imaging. [1–7] It has been well-documented that TTA-UC is a bi-molecular process, where the triplet energy donor/sensitizer absorbs low-energy light and the triplet energy acceptor emits higher-energy photons. [8,9] Under this condition, TTA-UC has been shown to be a promising process vis-à-vis bio-imaging applications, where low-energy light is amplified and the resulting emission could be tailored for *in vivo* photo-excitation of biological markers [10] or even achieve photochemical/biochemical transformations. [11,12] In this scenario, TTA-UC chromophoric systems can be systematically functionalized with biocompatible/biorelevant groups such as cholesteryl in order to facilitate the integration of the modified donor/acceptor dyes into biological environments. In addition, the derivatized dyes could be used to study the underlying photo-kinetics and efficiency of the processes

involved in TTA-UC in lipids and membranes. To study TTA-UC in lipids and membranes, it is also important to mimic the relevant conditions *viz.* viscosity, hydro-philicity/phobicity, and polarity of biological environments. A recent strategy in this regard proposed to achieve the TTA-UC processes in PEG200, which is a hydrophilic polymeric liquid that mimics cell membrane structures and intracellular conditions. [13–16] With this in mind, we are hereby reporting two new cholesteryl-based 9,10-diphenylanthracene (DPA) derivatives (C-DPA and C₂-DPA) (Scheme 1) which we used as triplet energy acceptors for TTA-UC in PEG200. The present study also aimed at deciphering the effect of the biorelevant cholesteryl group on donor-acceptor interactions and the resulting TTA-UC process.

Recently, a new family of triplet sensitizers: quinoidal naphthyl thioamides (QDN) (Scheme 1) were reported by our group. [17] QDN are structurally compatible with over-the-counter acceptors/fluorescent polyaromatic hydrocarbons such as perylene [18,19] and 9,10-diphenylanthracene (DPA) which are routinely employed for TTA-UC processes. We had previously established that the triplet energy of QDN ($E_T \approx 1.77$

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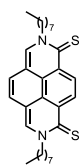
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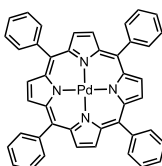
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A) Donors / Sensitizers

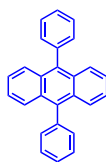


QDN

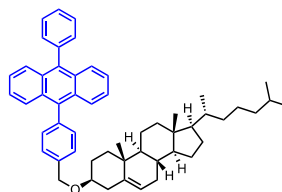


PdTPP

B) Acceptors / Annihilators



DPA



C-DPA

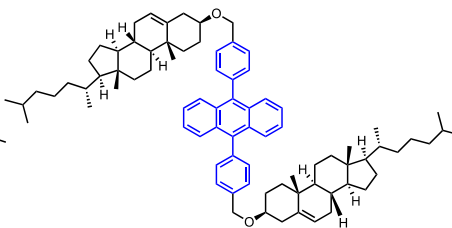
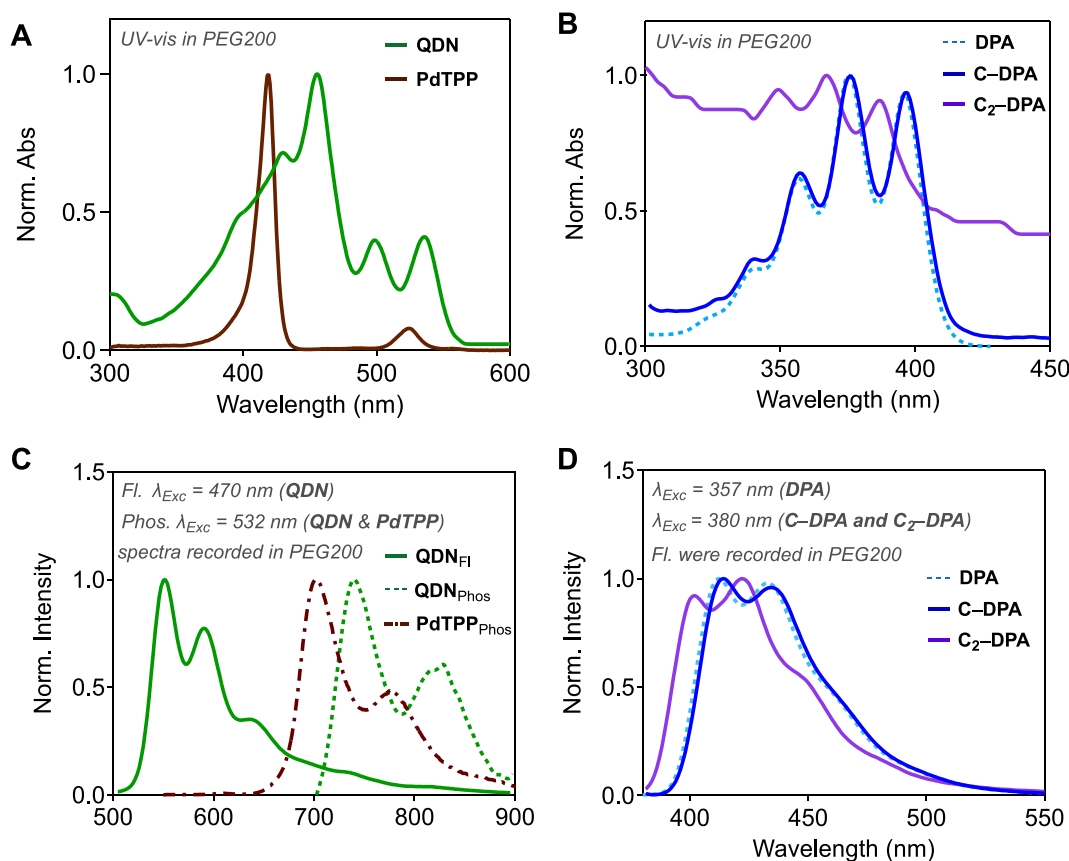
C₂-DPAScheme 1. Chemical structures of sensitizers (QDN and PdTPP) and annihilators (DPA, C-DPA, and C₂-DPA).

Fig. 1. UV – vis profiles of (A) QDN and PdTPP and (B) DPA, C-DPA, and C₂-DPA in PEG200. (C) Emission profiles of QDN and PdTPP and (D) DPA, C-DPA, and C₂-DPA recorded in PEG200 with samples O.D. = 0.2; at the excitation wavelength 532 nm for QDN and PdTPP, 357 nm for DPA, 380 nm for C-DPA and C₂-DPA.

eV, in 77 K EtOH:DCM glassy matrix) is suitable for an exothermic energy transfer to perylene ($E_T \approx 1.53$ eV); however, it was unexpected that QDN could be used to sensitize DPA ($E_T \approx 1.78$ eV) [20] in deoxygenated PEG200, since its measured E_T value at room temperature in that medium was estimated at 1.67 eV, far below the triplet energy of DPA. It is worth noting that, in order to maintain the deoxygenated state of all of our photo-samples, 30 mM of oleic acid was added to the

PEG200 material (oleic acid was used as an oxygen scavenger). Triplet sensitization study of DPA using QDN and/or another conventional sensitizer 5,10,15,20-TetraPhenylPorphyrinato Palladium(II) (PdTPP) with $E_T \approx 1.78$ eV [20] revealed that both endothermic QDN $\rightarrow$ DPA and exothermic PdTPP $\rightarrow$ DPA TET could be achieved in biorelevant PEG200 media. Armed with these exciting findings, we furthered the TTA-UC studies with the new cholesteryl-based triplet energy acceptors C-DPA

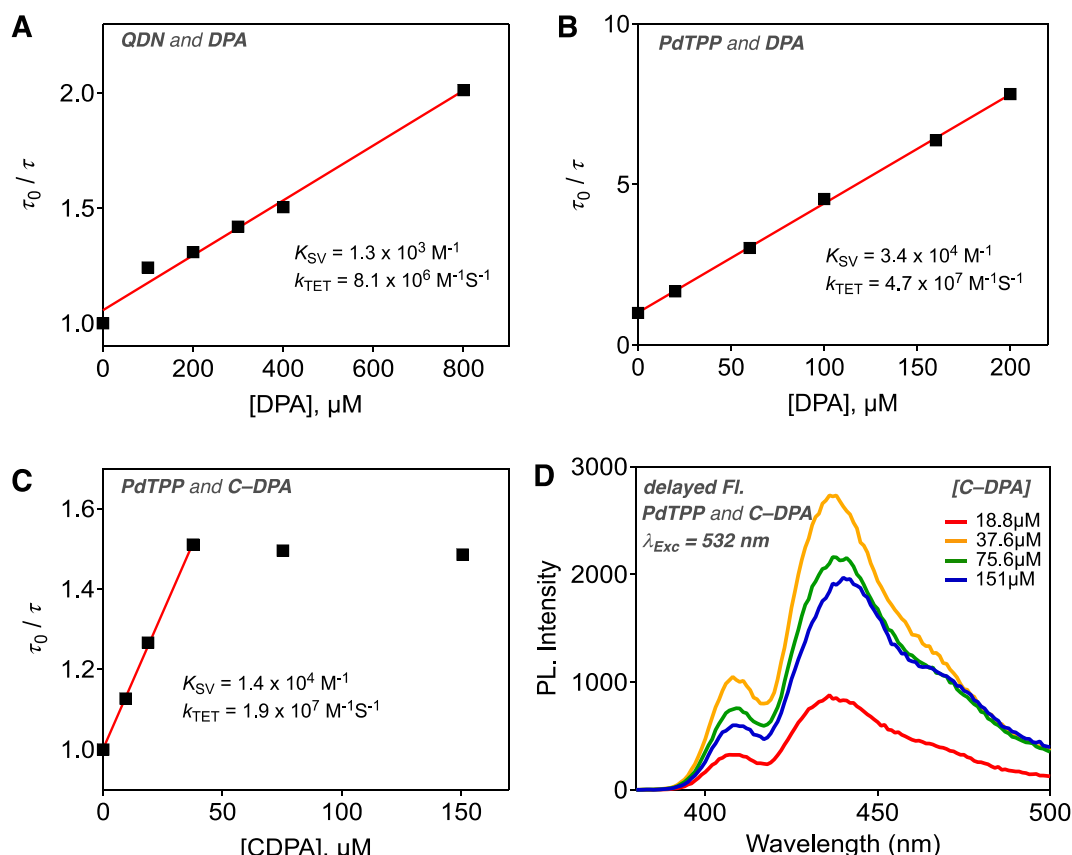


Fig. 2. Stern – Volmer plots of (A) QDN and DPA (B) PdTPP and DPA (C) PdTPP and C-DPA in PEG200 with the resulting Stern – Volmer constants (K_{SV}) and TET rate constants (k_{TET}). (D) Intensity-dependent delayed emission of C-DPA in deoxygenated PEG200 using PdTPP as the sensitizer and excitation wavelength of 532 nm. Note: The phosphorescence samples were recorded in deoxygenated PEG200 in the presence of 30 mM of oleic acid.

and C₂-DPA. Expectedly, the cholesteryl unit would not only enhance interactions of the hydrophobic donor•••acceptor in the hydrophilic PEG200 medium, but also induce the formation of self-assembled sub-domains at higher concentrations of the donor/acceptor chromophoric systems.

2. Results & discussion

The synthetic procedures for all precursors of C-DPA and C₂-DPA are extensively described in the [Supporting Information](#) (Scheme S1). C-DPA and C₂-DPA were synthesized following Suzuki coupling reaction conditions, where cholesteryl 4-bromobenzyl ether (Br-PhCH₂-O-Chol) was reacted with 10-phenyl-9-anthracene boronic acid for C-DPA and 9,10-anthracenediboronic acid bis(pinacol) ester for C₂-DPA ([Supporting Information](#), Scheme S1-S5). C-DPA and C₂-DPA were successfully characterized by NMR ([Supporting Information](#), Figure S1-S8), thermogravimetry ([Supporting Information](#), Figure S15), and single-crystal XRD ([Supporting Information](#), Figure S16).

UV-vis absorption profiles of C-DPA and C₂-DPA, recorded in PEG200, revealed the same transitions features that are seen in the spectrum of parent DPA ([Fig. 1B](#)). The absorption features of C-DPA was precisely the same as parent DPA, which is not surprising. However, the spectrum of C₂-DPA exhibits a slight hypsochromic-shift compared to C-DPA or DPA. The positive offset in the spectrum of C₂-DPA is suggestive of self- or H-aggregation, which could be problematic for an efficient donor•••acceptor interaction in PEG200. Importantly the positive spectral shift was not observed in the absorption spectrum of C₂-DPA in DCM solution ([Supporting information](#), Figure S11). Similarly, the steady-state emission profiles of C-DPA and C₂-DPA depict the typical vibronic bands of DPA with no apparent/trivial spectral shift.

With this result, we ascertain that the cholesteryl unit has little impact on the optoelectronic transitions of the new acceptors ([Fig. 1D](#)). Nevertheless, the emission spectra recorded in PEG200 are slightly red-shifted presumably due to aggregation or the hydrophilic PEG200 medium. ([Supporting information](#), Figure S9-S11).

Next, we performed Stern-Volmer (S-V) quenching experiments, using conventional triplet energy acceptors e.g. DPA, to establish the best sensitizer (QDN vs. PdTPP) for efficient TET with both C-DPA and C₂-DPA. The quenching experiment was monitored by recording the phosphorescence of the two sensitizers in the presence of the acceptor/annihilator(s) with varying concentrations. The quenching data was analyzed following equations (1) and (2). [21]

$$K_{SV} = K_q \tau_0. \quad (1)$$

Where K_q is the quenching rate constant, τ_0 is the intrinsic phosphorescence lifetime of the sensitizer, and K_{SV} is the Stern-Volmer constant.

For dynamic quenching mechanism, [22] we presumed that

$$\frac{\tau_0}{\tau} - 1 = K_q \tau_0 [Q] \quad (2)$$

Where τ is the phosphorescence lifetime of the sensitizer in the presence of the acceptor/annihilator(s), and $[Q]$ is the concentration of acceptor/annihilator(s).

[Fig. 2](#) shows the S-V plots with respect to the concentration of annihilator/quencher. The slope of the S-V plot is determined as $K_{SV} = K_q \tau_0$ (Eq. (1)). Next, the rate of triplet energy transfer (k_{TET}) was computed from the following equation:

$$k_{TET} = \frac{K_{SV}}{\tau_0} \quad (3)$$

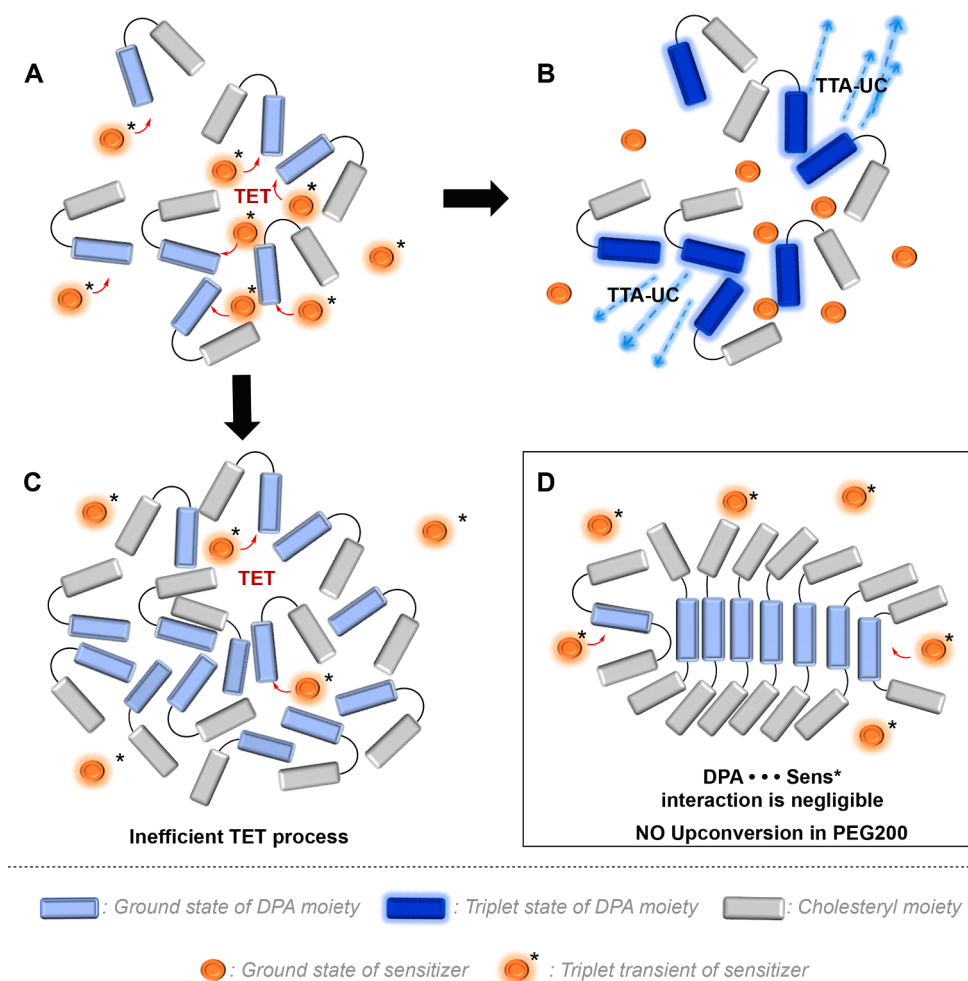


Fig. 3. A cartoon depicting the energy flow and mechanism of TTA-UC. Proposed aggregation features of (A) C-DPA with low & medium concentration, (C) C-DPA with high concentration, and (D) C₂-DPA in PEG200. (B) Proposed TTA-UC in C-DPA; the sensitizer represents PdTPP or QDN.

τ_0 for QDN was 160 μ s, and that of PdTPP was 720 μ s (both values were measured in PEG200). We then established that for DPA, the TET rate constant $k_{\text{TET}} = 8.1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for QDN and $k_{\text{TET}} = 4.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for PdTPP (Fig. 2A & 2B). As one can see, the k_{TET} for QDN $\rightarrow$ DPA revealed an endothermic energy transfer with $\Delta E_{\text{T}} = -0.046 \text{ eV}$ at least, whereas PdTPP $\rightarrow$ DPA TET with $\Delta E_{\text{T}} = -0.01 \text{ eV}$ is an exothermic process (assuming a rate of diffusion $k_{\text{diff}} = 5 \times 10^7$ in PEG200). [13,14] These values indicate that for an efficient TET, the later sensitizer is the preferred triplet energy donor for both C-DPA and C₂-DPA. The S-V quenching experiments are summarized in Fig. 2. While the phosphorescence quenching with DPA depicts the expected dynamic quenching behavior, the quenching study with C-DPA reached a stationary state after certain threshold concentration of the quencher. For example, as shown in Fig. 2C, at low/medium concentration of C-DPA, the $k_{\text{TET}} = 1.9 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for PdTPP $\rightarrow$ C-DPA in the dynamic regime was three times smaller than that of PdTPP $\rightarrow$ DPA suggesting hindered intermolecular interactions/collisions due to the presence of the cholesteryl moieties that may be shielding the DPA core. In this picture, we also hypothesized that at micellar concentration of 39 μ M, there is a possibility of back DPA $\rightarrow$ PdTPP energy transfer via the FRET mechanism.

From the S-V quenching studies, we deduced that the maximum TET and possibly upconversion process could be achieved at [C-DPA] = 39 μ M with 34% quenching efficiency rate (without any aggregation of the acceptor). We attributed the plateau of the S-V curved beyond [C-DPA] = 39 μ M to the aggregation of C-DPA units to form self-assembled sub-

domains or phase-separation of C-DPA, which was visible to the naked eye, indicating that the critical micellar concentration of the cholesteryl-based DPA is around 39 μ M. Accordingly, we postulated that the cholesteryl moieties of C-DPA might form a barrier preventing effective interactions of the sensitizer with the core DPA of the acceptor (Fig. 3A, 3B, and 3C). Results for the S-V quenching studies with C₂-DPA are described in the Supporting information, Figure S12; with this acceptor, it was deemed unnecessary to carry out subsequent investigation with C₂-DPA, as no TTA-UC was detected using both QDN and PdTPP (Fig. 3D).

Fig. 4 shows the double logarithmic plots of the upconverted emission intensity with respect to the 532 nm excitation power density. All three donor-acceptor pairs display the typical low-to-high power density regimes transition [23–26]: from quadratic (slope = 2) to linear (slope = 1) intensity dependence, which is a clear indication of the expected TTA process [13]. The power density threshold (I_{th}), [27] where the intensity of the TTA process becomes the dominant deactivation channel for an annihilator triplet state, and the quantum yield of the upconversion process is equal to half of its maximum. From Fig. 4, we found that I_{th} are 1790, 133, and 490 mW/cm^2 for QDN/DPA, PdTPP/DPA, and PdTPP/C-DPA, respectively. We also hypothesize that the intrinsic radiative and non-radiative decays of the sensitizer could be predominant at low power densities. Under this consideration, at power densities above the I_{th} , the TTA process was prevalently approaching a maximum delayed fluorescence driven by the TTA-UC process. Also, the high I_{th} for QDN/DPA suggests a less efficient (endothermic) energy

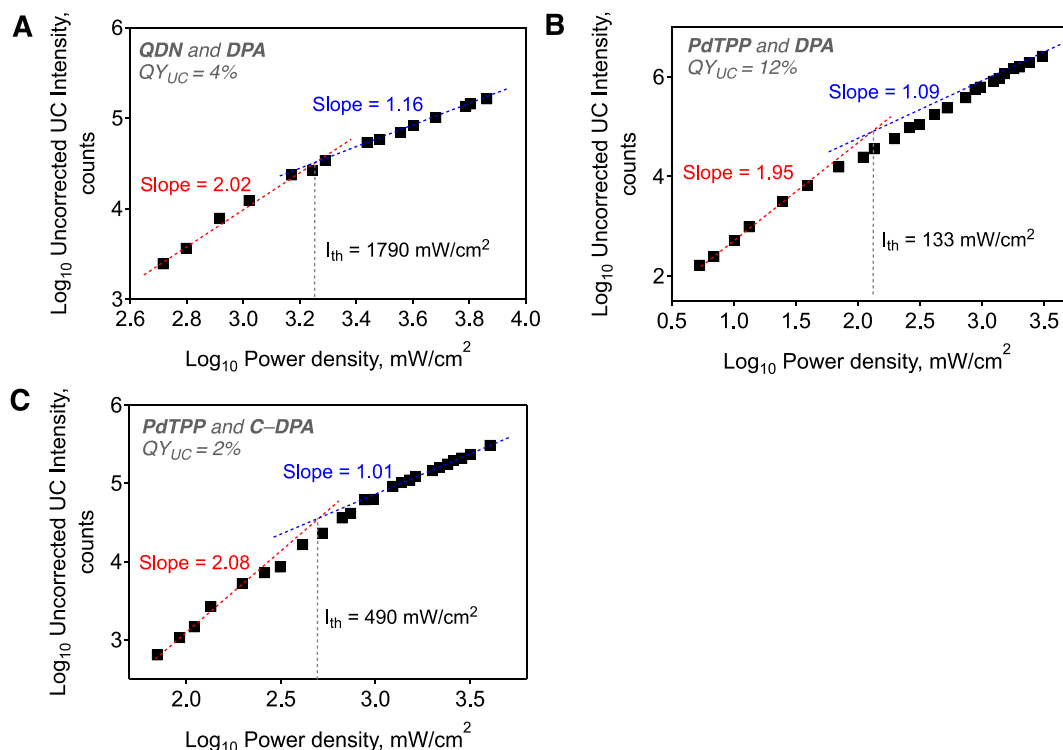


Fig. 4. Double logarithmic plot of the upconverted emission for (A) QDN and DPA (B) PdTPP and DPA (C) PdTPP and C-DPA as a function of power density of the 532 nm Nd:YAG laser.

transfer [14] as revealed earlier from the S-V quenching results. For the PdTPP/DPA pair, the threshold intensity is substantially lower than that of QDN/DPA. This observation/result is also in good agreement with the relatively high k_{TET} from the S-V quenching study (Fig. 2A and 2B).

Furthermore, we measured the quantum yield of TTA-UC (QY_{UC}) of the three pairs of donor-acceptor using equation (4) and rhodamine 6G [28] as photon counter standard.

$$QY_{UC} = QY_{std} \times \left(\frac{A_{std}}{A_{UC}} \right) \times \left(\frac{I_{UC}}{I_{std}} \right) \times \left(\frac{\eta_{UC}}{\eta_{std}} \right)^2 \quad (4)$$

Where QY represents the quantum yield, A is absorbance (O.D.) at the excitation wavelength. I denotes the integrated photoluminescence, and η is the refractive index of the solvent.

$_{std}$ stands for the standard (here, rhodamine 6G) sample, and $_{UC}$ denotes the upconversion sample. We then estimated that the QY_{UC} for (QDN/DPA) is 2% (4% after correcting for inner filter effect), 6% (12%) for (PdTPP/DPA), and 1% (2%) for (PdTPP/C-DPA).

3. Conclusions

In summary, this study aims at providing additional molecular tools to the upconversion community wherein over-the-counter annihilators, such as DPA, have been functionalized with cholesteryl tag(s) to afford C-DPA and C₂-DPA. In the present work, we successfully employed both DPA and C-DPA to achieve TTA-UC in biorelevant hydrophilic and viscous polymeric liquid PEG200 media. Moreover, this study offers insight on the behavior of these modified annihilators in terms of donor-acceptor interactions and the resulting effect on the upconversion process. Using Stern-Volmer quenching experiments, we found that the rate of PdTPP → C-DPA TET is three times lower than that of PdTPP → DPA. This reduced k_{TET} value was hypothesized to originate from the shielding effect of the cholesteryl unit. Beyond a certain concentration threshold, C-DPA formed self-assembled sub-domains in the PEG200 medium, which was observed by a plateau in the TET efficiency. This finding was further consolidated by investigating the upconversion

efficiency of C-DPA upon increasing its concentration. While the cholesteryl units may be beneficial in terms of incorporating dye molecules into lipid bilayers, micelles, and hydrogels and also provide some shielding to molecular oxygen to perform TTA-UC in biological media, we discovered that this substituent may hamper effective donor-acceptor interactions due to reduced molecular mobility and formation of hydrophobic sub-domains that are inaccessible to the triplet energy donor. This effect is also manifested by the absence of TTA-UC using C₂-DPA as the acceptor. Nevertheless, we successfully achieved TTA-UC with three pairs of donor/acceptor systems QDN/DPA, PdTPP/DPA, and PdTPP/C-DPA with QY_{UC} values of 2% (4%), 6% (12%), and 1% (2%), respectively. The present study brings new insight into molecular engineering and function of modified biorelevant dyes in order to achieve TTA-UC in biological environments.

4. Associated Content

4.1. Data Availability

The data that support the findings of this study are available from the corresponding author upon reasonable request. In addition, details of the synthetic procedures for all precursor of C-DPA and C₂-DPA: ¹H and ¹³C NMR spectra, additional UV-vis absorption spectra, emission spectra, this material is available free of charge via the Internet at Elsevier.com.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jphotochem.2021.113412>.

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