Electronic Supplementary Information (ESI)
on
Triplet-triplet annihilation photon upconversion from
diphenylhexatriene and its ring-substituted derivatives solution

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References
1. Synthesis of pico DPH and jul DPH

General
HR-MS data were obtained using a Hitachi M80B spectrometer. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker Avance 400 spectrometer (400 MHz and 100 MHz, respectively) with tetramethysilane (TMS) as internal reference. The spectra are displayed in Figures S1 and S2.

$(E,E,E)$-1,6-Bis[4-(di-2-picolylamino)phenyl]hexa-1,3,5-triene (pico DPH)
To a solid mixture of 4-(di-2-picolylamino)benzaldehyde [1] (1.52 g, 5.0 mmol) and $(E)$-2-butene-1,4-bis(tributylphosphonium chloride) (0.66 g, 1.25 mmol) was added a solution of sodium ethoxide in ethanol (0.83 M, 3 mL) at 45°C under nitrogen atmosphere. After stirring for 2 h, ethanol (9 mL) was added to the reaction mixture. The resulting orange precipitate was filtered off, washed with water (60 mL), and dried. Recrystallization from ethanol. Yield 23 %. Mp 195 °C. HR-MS calcd for C$_{42}$H$_{38}$N$_6$: 626.3158, found 626.3147; $^1$H NMR (CDCl$_3$): $\delta =$ 8.58-8.60 (m, 4H; ring), 7.62 (td, J = 7.7, 1.8 Hz, 4H; ring), 7.16-7.25 (m, 12H; ring), 6.61-6.67 (m, 6H; ring and triene), 6.41 (d, J = 15.2, 2H; triene), 6.36 (dd, J = 6.9, 3.1 Hz, 2H; triene), 4.83 (s, 8H, methylene); $^{13}$C NMR (CDCl$_3$): $\delta =$ 158.6, 149.8, 147.5, 136.9, 132.3, 131.5, 127.5, 127.1, 126.0, 122.1, 120.8, 112.7, 57.3.

$(E,E,E)$-1,6-Bis(5-julolidino)hexa-1,3,5-triene (jul DPH)
To a solid mixture of 9-julolidinecarboxaldehyde (TCI) (1.01 g, 5.0 mmol) and $(E)$-2-butene-1,4-bis(tributylphosphonium chloride) (0.66 g, 1.25 mmol) was added a solution of sodium ethoxide in ethanol (0.5 M, 5 mL) at 45°C under nitrogen atmosphere. After stirring for 2 h, ethanol (9 mL) was added to the reaction mixture. The resulting orange precipitate was filtered off, washed with water (60 mL), and dried. Recrystallization from acetone. Yield 35 %. Mp 206 °C (decomp). HR-MS calcd for C$_{30}$H$_{34}$N$_2$: 422.2722, found 422.2714; $^1$H NMR (CDCl$_3$): $\delta =$ 6.85 (s, 4H; ring), 6.63 (ddd, J = 15.4, 6.9, 3.1 Hz, 2H; triene), 6.354 (d, J = 15.4 Hz, 2H; triene), 6.353 (dd, J = 7.0, 2.9 Hz, 2H; triene), 3.14 (t, J = 5.7 Hz, 8H; methylene), 2.74 (t, J = 6.5 Hz, 8H; methylene), 1.93-1.99 (m, 8H; methylene); $^{13}$C NMR (CDCl$_3$): $\delta =$ 142.4, 131.9, 131.8, 125.4, 125.2, 125.0, 121.4, 50.0, 27.7, 22.1.
2. Quantum chemical calculation
Geometries of all DPH derivatives were optimized at the B3LYP/6-31G(d) level of theory. The geometry optimizations were separately done for singlet ground state (S\(_0\)) and the lowest triplet state (T\(_1\)). The energy level of T\(_1\) from S\(_0\) was calculated as the difference in the total energy of the calculations. The energy levels of the lowest singlet excited state (S\(_1\)) from S\(_0\), i.e., the transition energies, were calculated at the TD-CAM-B3LYP/6-31+G(d) level of theory by using the optimized geometries mentioned above. The use of the Coulomb-attenuating method (CAM) [2] improved the underestimation of the transition energies. The diffuse orbital was augmented to the basis set in the CAM-B3LYP calculation. The obtained results of S\(_1\) transition energy reproduced the experimental result with good accuracy (0.14 eV or less, mostly within 0.05 eV). All calculations were performed by considering the solvent effect with self-consistent reaction field (SCRF) method with the polarizable continuum model (PCM) for tetrahydrofuran (THF) on the program package Gaussian 16 [3].

3. Estimation of upconversion quantum efficiency at strong excitation limit (\(\eta_{UC}^\infty\))

Upconversion quantum efficiency of TTA-UC is a function of excitation intensity \(I_{ex}\) as [4]

\[
\eta_{UC}(I_{ex}) = \eta_{UC}^\infty \Theta(\Lambda),
\]

where

\[
\Theta(\Lambda) = 1 + \frac{1 - \sqrt{1 + 2\Lambda(I_{ex})}}{\Lambda(I_{ex})}
\]

is normalized upconversion quantum yield and

\[
\Lambda(I_{ex}) = \frac{2I_{ex}}{I_{th}}
\]

is dimensionless excitation intensity. \(I_{th}\) is threshold excitation intensity. \(\Theta(\Lambda)\) approaches to unity when \(I_{ex}\) and \(\Lambda(I_{ex})\) go infinity and \(\eta_{UC}^\infty\) is the quantum efficiency at the strong excitation limit, where 100% of emitter triplets deactivate through the second-order reaction path of the concentration. Thus, this value represents the performance of system free from the influence of the emitter triplet concentration. Saturated quantum efficiency accessed by the experiments is just an approximate value of \(\eta_{UC}^\infty\).
If $I_{th}$ is known, the value of $\eta^\infty_{UC}$ can be deduced from $I_{ex}$ and $\eta_{UC}(I_{ex})$, by putting $I_{ex}$ and $I_{th}$ into eq. S3, by putting the obtained $\Lambda(I_{ex})$ into eq. S2, and by putting the obtained $\Theta(\Lambda)$ and $\eta_{UC}(I_{ex})$ into eq. S1. The deduced $\Lambda(I_{ex})$, $\Theta(\Lambda)$, and $\eta^\infty_{UC}$ from the $I_{th}$ obtained by the excitation dependence of the UC emission intensity (Fig. S4) are shown in Table S1. The Linear curves with slopes1 and 2 that cross the calculated $I_{th}$ are also shown in Figs. S4(f) and (g).

Table S1. $I_{th}$, $\Lambda$, $\Theta$ and $\eta^\infty_{UC}$ values of the DPH derivatives obtained at excitation intensity of $I_{ex} = 1.9 \text{ W cm}^{-2}$.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$I_{th} / \text{ W cm}^{-2}$</th>
<th>$\Lambda(I_{ex})$</th>
<th>$\Theta(\Lambda)$</th>
<th>$\eta^\infty_{UC}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>unsub.</td>
<td>3.1 ± 0.5</td>
<td>1.2 ± 0.2</td>
<td>0.30 ± 0.03</td>
<td>0.00086 ± 0.0001</td>
</tr>
<tr>
<td>NMe$_2$</td>
<td>3.0 ± 0.2</td>
<td>1.3 ± 0.09</td>
<td>0.31 ± 0.01</td>
<td>0.021 ± 0.003</td>
</tr>
<tr>
<td>CN</td>
<td>4.9 ± 0.4</td>
<td>0.78 ± 0.06</td>
<td>0.23 ± 0.01</td>
<td>0.003 ± 0.0003</td>
</tr>
<tr>
<td>pico</td>
<td>1.6 ± 0.3</td>
<td>2.4 ± 0.5</td>
<td>0.42 ± 0.04</td>
<td>0.036 ± 0.0035</td>
</tr>
<tr>
<td>jul</td>
<td>1.0 ± 0.1</td>
<td>3.8 ± 0.5</td>
<td>0.49 ± 0.02</td>
<td>0.024 ± 0.002</td>
</tr>
</tbody>
</table>
Figure S1. (a) $^1$H and (b) $^{13}$C NMR spectra of pico DPH in CDCl$_3$. 
Figure S2. (a) $^1$H and (b) $^{13}$C NMR spectra of jul DPH in CDCl$_3$. 
Figure S3. Stern-Volmer plots of (a) unsub. DPH, (b) NO2 DPH, (c) NMe2 DPH, (d) CN DPH, (e) CF3 DPH, (f) pico DPH and (g) jul DPH dissolved with PdTPBP (20 μM) in THF. The concentrations of DPH derivatives were 0, 65, 125, 250, 500, 1000 and 2000 μM.
Figure S4. UC emission intensities of (a) unsub. DPH, (b) NO₂ DPH, (c) NMe₂ DPH, (d) CN DPH, (e) CF₃ DPH, (f) pico DPH and (g) jul DPH dissolved with PdTPBP (20 μM) in THF for different excitation intensities with the curve fit according to Eq. (36), Ref. 4. Reliable values for NO₂ and CF₃ could not be obtained because \( I_{th} \) is too high compared to the range of the excitation intensity employed.
Figure S5. Time profiles of UC emission (black dots) of (a) unsub. DPH, (b) NO2 DPH, (c) NMe2 DPH, (d) CN DPH, (e) CF3 DPH, (f) jul DPH mixed with PdTPBP in solution (PdTPBP 20 μM–DPHs 125 μM in THF) in N2 atmosphere, together with their fit (red line), instrument response function (IRF, blue dots) and residuals (green dots).
References


