

Supporting Information

[C₇₀] Fullerene-Sensitized Triplet-Triplet Annihilation Upconversion

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Materials. Hexadecane (HD, 99%), perylene (>99.5%), 9,10-bis(phenylethynyl)anthracene (BPEA, 97%), tetrahydrofuran (THF, >99%), methanol (99.8%), ethanol (>99.5%), and toluene (99.5%) were obtained from Aldrich and were used as received. Polyisobutylene (PIB, MW ≈ 1320 Da) was purchased from Polysciences Inc. C₇₀ (98%), C₆₀ (99.9%), and platinum(II)-octylethylporphyrin (PtOEP) were purchased from SES Research, MER Corp., and Frontier Scientific, respectively.

Preparation of Solutions. Sensitizer and acceptor stock solutions were prepared in toluene or THF and were stored in the dark throughout the experiments. Upconversion (UC) solutions were prepared by adding aliquots of sensitizer and acceptor stock solutions to PIB/HD to achieve desired concentrations of sensitizer and acceptor. The PIB/HD solutions were subsequently

placed in an oven at 70 °C for at least 12 hours to remove the residual toluene or THF. UC solutions were stored in the dark before use.

Spectroscopic Measurements. Absorption and photoluminescence spectra of the various sensitizers and acceptors were measured via a UV/visible spectrometer (Agilent 8453) and a spectrofluorophotometer (Shimadzu, RF-5301), respectively. Anti-Stokes emission spectra were measured under excitation of UC samples with either a red diode laser (635 nm) for red-to-green UC or a green diode pumped solid state laser (532 nm) for green-to-blue UC. The incident laser was focused onto the sample, which consisted of UC solutions in cuvettes and was intermittently stirred by a small magnetic stir bar to ensure proper mixing. Incident laser power was adjusted through the use of a series of neutral density filters and was measured using a Nova II power meter/photodiode detector head (Ophir). UC emission was collected normal to excitation and passed through a series of focusing lenses and an optical chopper (120 Hz) before reaching a monochromator (Oriel Cornerstone, Newport Corp.). The signal was detected by an Oriel photomultiplier tube and processed by an Oriel Merlin radiometry detection system (Newport Corp.). For stability experiments, the UC solutions were irradiated with continuous laser excitation while stirring the solutions with a magnetic stirrer. Before taking an UC emission spectrum, stirring was briefly interrupted and the system was allowed to equilibrate for 45 seconds before the measurement was made. For N₂ purged conditions, ultra-high purity N₂ gas continuously purged a closed cuvette containing UC solution.

Quantum Yield Calculation. The UC quantum yield for various sensitizer and acceptor concentrations was calculated using the following formula,¹

$$\Phi_{UC} = 2\Phi_{ref} \left(\frac{A_{ref}}{A_{UC}} \right) \left(\frac{I_{UC}}{I_{ref}} \right) \left(\frac{\eta_{UC}}{\eta_{ref}} \right)^2 \quad (\text{Eq. 1})$$

where Φ_{uc} , A_{uc} , I_{uc} , and η_{uc} represent the quantum yield, absorbance at the excitation wavelength, the integrated total photoluminescence, and the refractive index of the medium (1.360 for ethanol, 1.328 for methanol, and 1.434 for HD/PIB) for UC solutions. Likewise, the subscript “ref” refers to the reference quantum counter used for comparison, which included rhodamine 6G in ethanol and methylene blue in methanol for green-to-blue and red-to-green UC, respectively. The concentrations of reference solutions were chosen to create similar absorbances at the excitation wavelength to that of UC solutions. Values of 0.95 and 0.03 were used for the fluorescence quantum yields of rhodamine 6G and methylene blue, respectively, as reported in the literature for air equilibrated solutions.² The fluorescence for the reference and UC solutions were measured over various laser powers, integrating over 500-700 and 600-800 nm for rhodamine 6G and methylene blue reference solutions, respectively. For green-to-blue and red-to-green schemes, UC emission was integrated over 400-520 and 400-600 nm, respectively, to calculate the quantum yields.

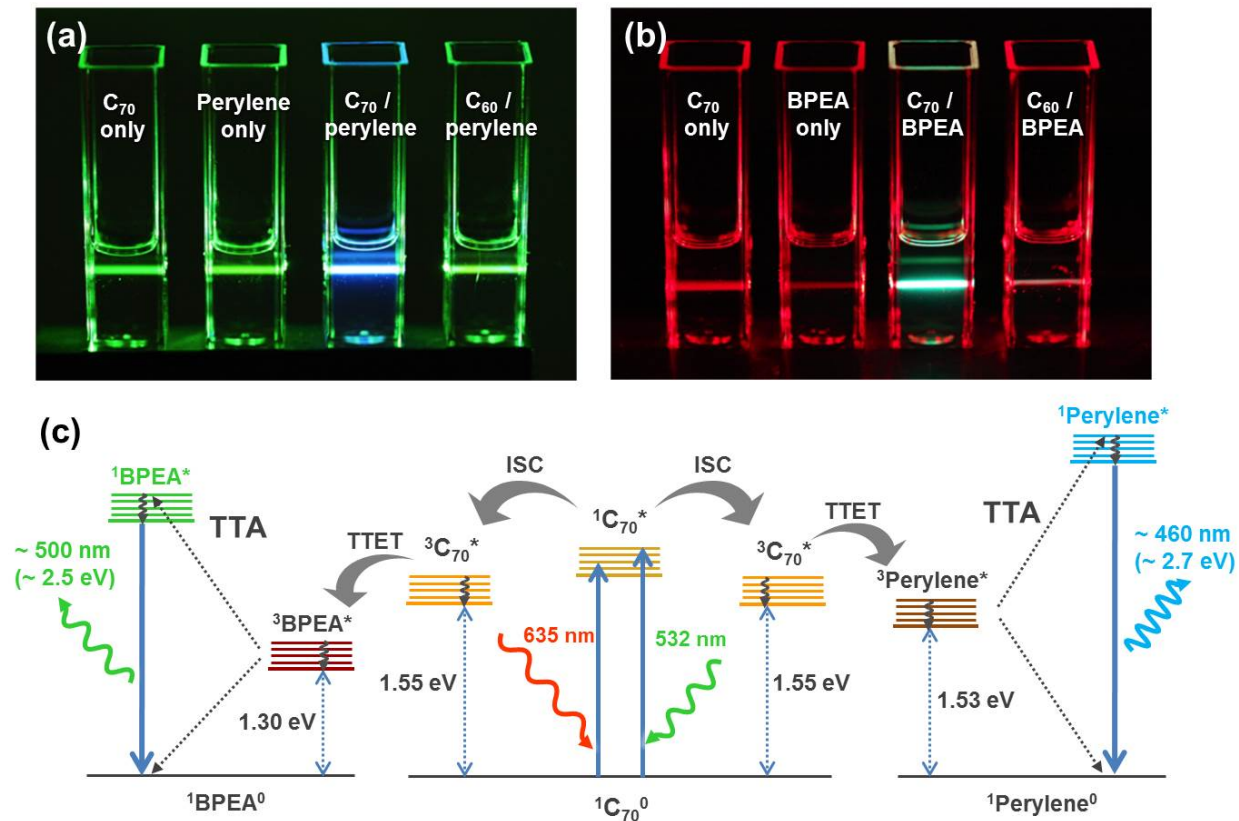


Figure S1. (a) Photograph of various compositions of chromophores in PIB/HD irradiated by a green laser ($\lambda_{\text{ex}} = 532 \text{ nm}$) and (b) a red laser ($\lambda_{\text{ex}} = 635 \text{ nm}$). Solutions were not degassed and were composed of (a) $[C_{70}] = [C_{60}] = 5 \mu\text{M}$; [perylene]: 1 mM and (b) $[C_{70}] = [C_{60}] = 25 \mu\text{M}$; [BPEA]: 1 mM. (c) Energy level diagram of the C_{70} /perylene or C_{70} /BPEA upconversion process. ISC: intersystem crossing, TTET: triplet-triplet energy transfer, TTA: triplet-triplet annihilation.

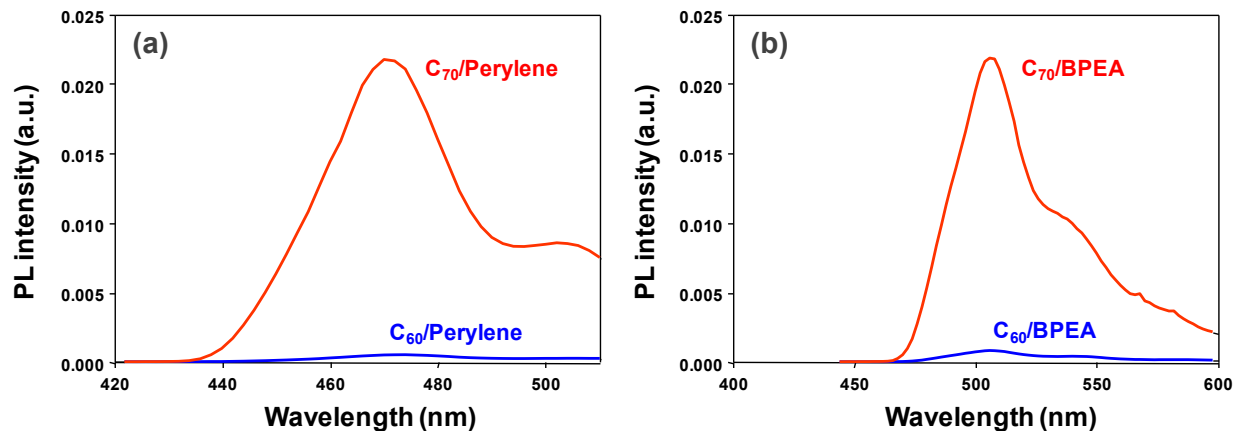


Figure S2. Emission profiles of (a) C₇₀ or C₆₀ with perylene as the acceptor molecule and (b) C₇₀ or C₆₀ with BPEA as the acceptor in air-equilibrated PIB/HD solution (7.5 wt%) with incident laser power intensities of (a) 9375 mW/cm² (532 nm) and (b) 19167 mW/cm² (635 nm). UC solutions consisted of (a) 5 μM fullerene and 1 mM perylene and (b) 25 μM fullerene and 1 mM BPEA.

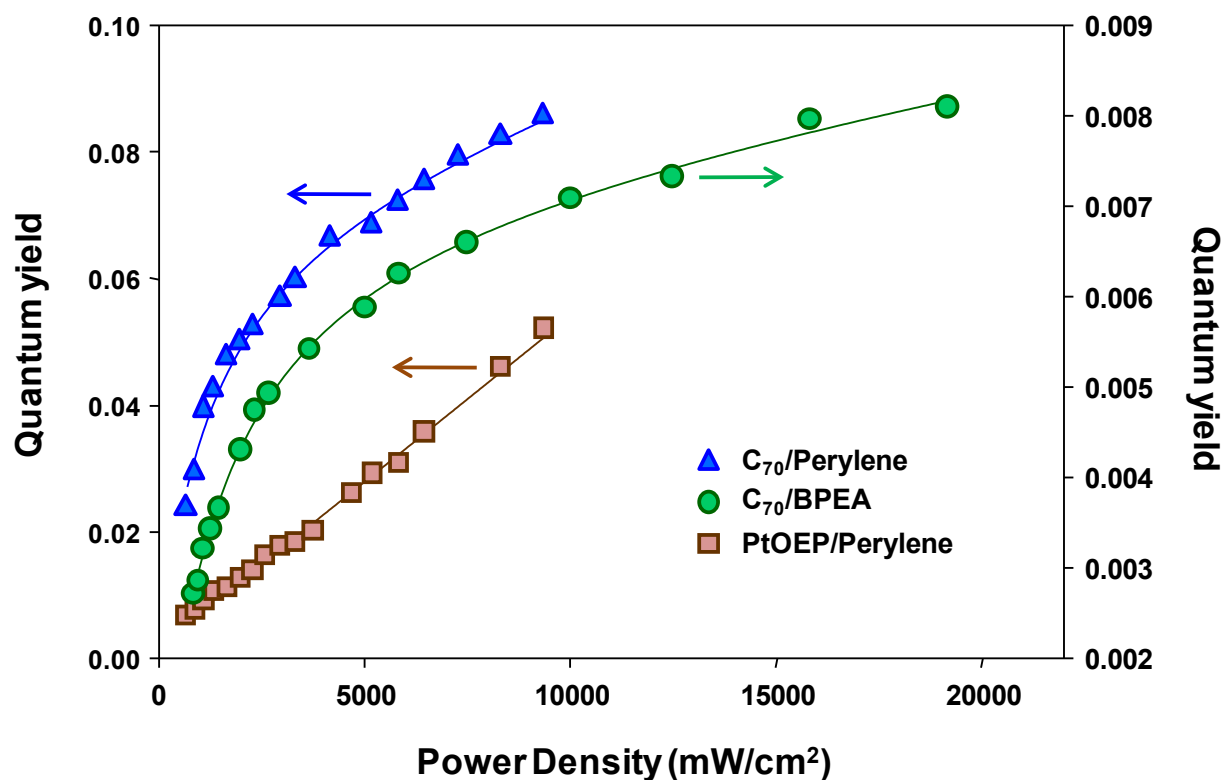


Figure S3. Quantum yield of C₇₀/perylene, C₇₀/BPEA, and PtOEP/perylene pair in PIB/HD (7.5 wt %) as a function of laser power density at 532 nm for C₇₀/perylene and PtOEP/perylene and at 635 nm for C₇₀/BPEA, respectively. [C₇₀]: 5 μM (green-to-blue), 25 uM (red-to-green); [PtOEP]: 5 μM; [Perylene]: 1 mM; [BPEA]: 1 mM.

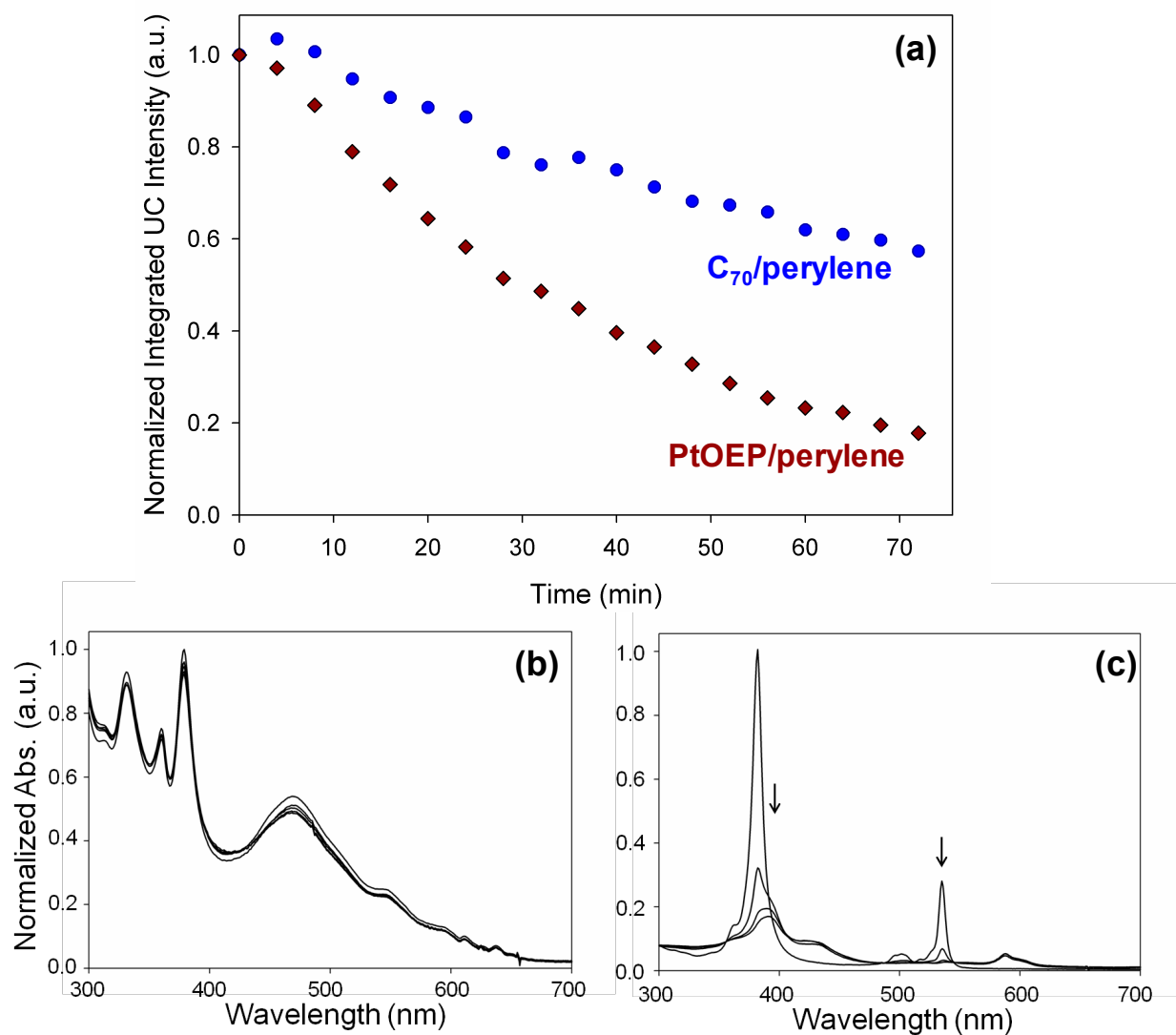


Figure S4. Normalized (a) integrated UC emission intensity of C₇₀/perylene (blue circles) and PtOEP/perylene (brown diamonds) and absorption spectra of (b) C₇₀ and (c) PtOEP solutions measured as a function of laser exposure time (532 nm) for N₂ purged conditions.

References

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2. (a)D. Magde, R. Wong and P. G. Seybold, *Photochem. Photobiol.*, 2002, **75**, 327-334;
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