Supplementary Information (11 Pages)

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

Manoj K. Manna\textsuperscript{a}, Siamak Shokri\textsuperscript{a}, Gary P. Wiederrecht\textsuperscript{b}, David J. Gosztola\textsuperscript{b} and A. Jean-Luc Ayitou\textsuperscript{a,*}

\textsuperscript{a} Department of Chemistry, Illinois Institute of Technology, Chicago, IL 60616, United States.
\textsuperscript{b} Center for Nanoscale Materials, Argonne National Laboratory, Argonne, IL 60439, United States.

Corresponding Author: aayitou@iit.edu

TABLE OF CONTENTS

1. GENERAL METHODS
2. SYNTHETIC PROCEDURES & CHARACTERIZATION
3. PHOSPHORESCENCE DECAY KINETICS
4. INTENSITY DEPENDENT PHOTOLUMINESCENCE
5. NMR SPECTRA
1. General Methods

All commercially obtained reagents/solvents were used as received without further purification. All organic solvents we used were of spectroscopic grade. Unless stated otherwise, reactions were conducted in oven-dried glassware under argon atmosphere. Unless otherwise stated, $^1$H-NMR and $^{13}$C-NMR spectra were recorded on Bruker® 300 MHz (75 MHz for $^{13}$C) spectrometer; data from the $^1$H-NMR spectroscopy are reported as chemical shift (δ ppm) with the corresponding integration values. Coupling constants (J) are reported in hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: s (singlet), b (broad), d (doublet), t (triplet), q (quartet), m (multiplet) and virt (virtual). Data for $^{13}$C NMR spectra are reported in terms of chemical shift (δ ppm). Time-resolved pump–probe spectroscopy was performed using an amplified Ti:sapphire laser system (Spectra Physics Spitfire) equipped with an optical parametric amplifier (OPA, Light Conversion, TOPAS). This system produces 130 fs pulses at 5 kHz centered at 800 nm. 95% of the output from the amplifier is directed to the OPA to generate tunable pump pulses in the visible and near-infrared spectral regions. For longer time scale processes, the probe light comes from a continuum light source (EOS from Ultrafast Systems®). In this case, the system operates at 1 kHz repetition rate and has a time resolution of 200 ps/point. The incident pump pulse for time-resolved nanosecond transient absorption was set at 520 nm with a power density in the sample range of 1000 nJ per pulse, focused to a 200-μm-diameter spot. The transmitted probe light was collected and fiber optically coupled to a spectrograph that used a visible (Si) array detector. Data were collected for continuum wavelengths from 400 nm to 800 nm as a function of delay track position for the continuum probe relative to the undelayed pump pulse. Fluorescence spectra were obtained with the Edinburgh Instruments® (FLS 980) Spectrofluorimeters. Fluorescence and phosphorescence spectra were measured using 470 and 520 nm excitation and detecting the emissions using a photon counting red PMT unit.
2. SYNTHETIC PROCEDURES & CHARACTERIZATION

**Synthesis of 1:** 1,4,5,8-Naphthalenetetracarboxylic dianhydride (10.0 g, 37.29 mmol) was dissolved in 200 mL DMF and degassed with N₂. The reaction mixture was heated to 140 °C and a 50 mL DMF solution of n-octylamine (5.55 mL, 33.56 mmol) was added dropwise over 2 h. The reaction was heated to reflux for 18 h, then cooled in the fridge for 2 h. The precipitate was filtered off and the filtrate was condensed in vacuo. The dark brown residue was purified by flash column chromatography (CH₂Cl₂) to afford anhydride monoimide (1) as off-white solid (5.70 g, 40%). ¹H NMR (300 MHz, CDCl₃) δ = 8.8 (s, 4H), 4.2 (t, 2H, J = 7.6, 7.7 Hz), 1.7 (m, 2H), 1.3 (m, 10H), 0.9 (t, 3H, J = 6.3, 6.8 Hz); ¹³C NMR (75 MHz, CDCl₃) δ = 162.2, 158.8, 133.2, 131.2, 127.9, 122.8, 41.2, 31.8, 29.3, 29.2, 28.0, 27.1, 22.6, 14.1; HRMS (ESI-TOF) m/z [M + H]^+ calcd for C₂₂H₂₂NO₅ 380.1498, found 380.1492.

**Synthesis of 2:** Compound 1 (1.0 g, 2.64 mmol), imidazole (0.179 g, 2.64 mmol) and 3-bromoaniline (1.36 g, 7.91 mmol) was dissolved in 80 mL DMF and degassed with nitrogen in 100 mL round bottom flask. The reaction mixture was heated to 130 °C for 18 h. The crude product
was purified by column chromatography [Hexane:DCM (70:30) to afford compound (2) as off-white solid (0.940 g, 67%).

$^1$H NMR (300 MHz, CDCl$_3$) $\delta = 8.8$ (s, 4H), 7.6 (d, 1H, $J = 8.5$ Hz), 7.5 (s, 1H), 7.4 (t, 1H, $J = 8.2$, 8.2 Hz), 7.3 (d, 1H), 4.2 (t, 2H), 1.7 (m, 2H), 1.2 (m, 10H), 0.8 (m, 3H).

$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta = 162.7$, 162.6, 135.7, 132.3, 131.8, 131.4, 131.0, 130.6, 127.3, 127.1, 126.9, 126.4, 122.8, 41.0, 31.7, 29.2, 29.1, 28.0, 27.0, 22.6, 14.0.

HRMS (ESI-TOF) m/z [$M + H]^+$ calcd for C$_{28}$H$_{26}$BrN$_2$O$_4$ 533.1076, found 533.1070.

**Synthesis of 3:** Compound 2 (0.940 g, 1.76 mmol) and Lawesson’s reagent (4.9 g, 12.34 mmol) were added to anhydrous toluene (50 mL) in a 2-neck round-bottom flask with an attached condenser under an argon atmosphere. The mixture was stirred at reflux (130 °C) for 48 h. The resulting solution was cooled to room temperature and concentrated under reduced pressure to give a dark red-brown sticky solid. The crude product was purified by column chromatography [Toluene: Dichloromethane (70:30)] to yield (3) (120 mg, 12%) a red powdered solid.

$^1$H NMR (300 MHz, CD$_2$Cl$_2$) $\delta = 9.0$ (AB quartet, 2H, $^3J_{AB} = 9.2$ Hz), 7.9 (s, 1H), 7.8 (s, 1H), 7.7 (d, 1H, $J = 7.7$ Hz), 7.6 (s, 1H), 7.4 (m, 2H), 7.0 (m, 2H), 4.8 (t, 2H, $J = 7.4$, 7.7 Hz), 2.0 (m, 2H), 1.3 (m, 10 H), 0.9 (t, 3H).

$^{13}$C NMR (75 MHz, CD$_2$Cl$_2$) $\delta = 181.4$, 179.0, 146.8, 134.1, 134.0, 132.5, 132.2, 132.0, 131.4, 131.0, 130.5, 130.2, 126.0, 125.8, 125.3, 123.4, 122.7, 118.7, 118.7, 58.5, 31.8, 29.2, 29.2, 28.1, 26.7, 22.6, 13.9.

HRMS (ESI-TOF) m/z [$M + H]^+$ calcd for C$_{28}$H$_{28}$BrN$_2$S$_2$ 535.0877, found 535.0872.

**Synthesis of 4:** In a 250 mL round bottom flask, N-Bromosuccinimide (0.705 g, 3.96 mmol) in dry DMF (15 mL) was added to a solution of perylene (1g, 3.96 mmol) in dry DMF (15 mL) with stirring at room temperature for 24 h. The mixture was poured into water (100 mL), extracted with dichloromethane (100 mL) and the extract dried with Na$_2$SO$_4$. 3-bromoperylene was precipitated from solution by storing the extract at 0°C. Solid 3-bromoperylene (4) was collected by filtration (0.980 g, 74%) leaving primarily unreacted perylene in the mother liquor.
$^1$H NMR (300 MHz, CDCl$_3$) $\delta = 8.3$-$8.2$ (m, 3H), 8.1 (d, 1H, $J = 8.8$ Hz), 8.0 (d, 1H, $J = 8.1$ Hz), 7.7 (d, 1H, $J = 8.3$ Hz), 7.7-$7.6$ (m, 2H), 7.5 (t, 1H, $J = 7.7$, 8.2 Hz), 7.5-$7.4$ (m, 2H).

$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta = 134.5$, 133.1, 131.6, 131.3, 131.2, 130.7, 130.6, 130.5, 129.9, 128.3, 128.2, 127.6, 126.9, 126.7, 126.6, 122.4, 120.9, 120.7, 120.5, 120.4.

HRMS (ESI-TOF) m/z [M]$^+$ calcd for C$_{20}$H$_{11}$Br 330.0044, found 330.0039.

**Synthesis of D4-A1:** An oven-dried 50 mL round bottom flask cooled under N$_2$ was charged with 80 mg (241.54 µmol) of 3-bromoperylene (4) and 20 mL of freshly distilled THF. The flask was flushed with N$_2$ gas, and the mixture was cooled to -78 °C using an acetone bath. After that, 196.25 µL (314.00 µmol) of n-BuLi (1.6 M in hexanes) was added dropwise via syringe into the stirring solution. The solution was stirred at -78 °C for 2 h and then triethylborate (41.10 µL, 241.54 µmol) was added and slowly warm to room temperature. After stirring the solution for 4 h at room temperature, the flask was transferred to a preheated silicon oil bath and compound 3 (123.36 mg, 241.54 µmmol) was added. Tetrais(triphenylphosphine)palladium(0) (140 mg), K$_2$CO$_3$ (40 mg, 289.54 µmol) was also added and refluxed for 24 h under Argon. After cooling down to r.t., water (10 mL) was added to the reaction solution. Then, the resulting mixture was extracted with CH$_2$Cl$_2$ (3×30 mL) and the combined organic layers were dried with Na$_2$SO$_4$. Removal of the solvents in vacuo gave a residue, which was subjected to column chromatography on silica gel. Elution with [DCM/Acetone (80:20)] gave red solid D4-A1, 138 mg, with a yield of 78%.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta = 9.2$ (AB quartet, 2H, $^3J_{AB} = 9.2$ Hz), 8.2 (m, 4H), 7.9 (m, 2H), 7.8 (s, 1H), 7.7 (m, 5H), 7.5 (m, 5H), 7.0 (s, 2H), 4.8 (m, 2H), 2.0 (m, 2H), 1.4-$1.3$ (m, 10H), 0.9 (m, 3H).

$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta = 181.7$, 179.2, 146.0, 142.4, 138.0, 134.7, 134.3, 132.7, 132.2, 131.9, 131.8, 131.2, 131.0, 130.6, 130.5, 129.9, 129.1, 128.9, 128.5, 128.0, 127.9, 127.1, 126.6, 125.8, 125.6, 125.4, 125.3, 123.3, 123.0, 120.5, 120.3, 119.0, 118.6, 58.6, 31.8, 29.7, 29.2, 28.1, 26.8, 22.6, 14.1.

HRMS (ESI-TOF) m/z [M + 3H]$^+$ calcd for C$_{48}$H$_{41}$N$_2$S$_2$ 709.2711, found 709.2706.
3. **Phosphorescence Decay Kinetics**

![Phosphorescence Decay Diagrams](image)

**Figure S1.** Phosphorescence decay traces and fittings for a) **D4** and b) **D4–A1** after pulsed excitation at 77 K.

4. **Intensity Dependent Data**

![Intensity Data Diagrams](image)

**Figure S2.** a) & c) Intensity-dependent upconverted photoluminescence (PL) of free **A1** in the presence of 100 and 50 mol% of **D4–A1** excited at 532 nm in deaerated THF respectively. b) & d) Best quadratic fit ($x^2$) of the PL intensity at 470 nm for the two experiments. Inset: Double logarithmic plot PL intensity vs. power density of the incident light producing a linear fit with slope = 1.5 and 2 respectively.
5. NMR SPECTRA

Figure S3. $^1$H NMR spectrum (300 MHz, CDCl$_3$, δ$_{ppm}$) of anhydride monoimide 1. *Residual solvent peak.

Figure S4. $^{13}$C NMR spectrum (75 MHz, CDCl$_3$, δ$_{ppm}$) of anhydride monoimide 1.
Figure S5. $^1$H NMR spectrum (300 MHz, CDCl$_3$, $\delta$) of compound 2. *Residual solvent peak.

Figure S6. $^{13}$C NMR spectrum (75 MHz, CDCl$_3$, $\delta_{ppm}$) of compound 2.
Figure S7. $^1$H NMR spectrum (300 MHz, CD$_2$Cl$_2$, $\delta_{ppm}$) of compound 3. *Residual solvent peak.

Figure S8. $^{13}$C NMR spectrum (75 MHz, CD$_2$Cl$_2$, $\delta_{ppm}$) of compound 3.
Figure S9. $^1$H NMR spectrum (300 MHz, CDCl$_3$, δ) of compound 4. *Residual solvent peak.

Figure S10. $^{13}$C NMR spectrum (75 MHz, CDCl$_3$, δ) of compound 4.
Figure S11. $^1$H NMR spectrum (300 MHz, CDCl$_3$, $\delta$) of D4-A1. *Residual solvent peak.

Figure S12. $^{13}$C NMR spectrum (75 MHz, CDCl$_3$, $\delta$) of D4-A1.