Supporting Information

for

Mechanochemical Activation of Red Light-Excited Triplet-Triplet Annihilation Photon Upconversion

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1. Materials and methods

1.1. Materials

The used chemicals 1-hexanethiol (>95%), meta-chloroperoxybenzoic acid (mCPBA, >77%), α-bromisobutyrylbromide (98%), triethylamine (>99.5%), and methacryloyl chloride (97%) were acquired from Sigma-Aldrich Corporation. Platinum(II)chloride (98%) from Alpha Aesar was inserted. 4-Nitrophthalonitrile (>98%) was obtained from TCI Deutschland GmbH. For the polymerization reactions, methyl acrylate (97%), tris-[2-(dimethylamino)-ethyl]-amine (97%), and copper(II)bromide (99%) were acquired from Acros Organics.

1.2. Methods

1.2.1. Quantum chemical calculations

Quantum chemical simulations were performed using Gaussian 16 and GaussView 6.1.1.1,2 The ground state geometry optimization was performed using density-functional theory (DFT) and excited state geometry optimization on time-dependent DFT (TDDFT) using three different functionals B3LYP, PBE0, and M06-2X in combination with 6-311++G** basis set. Two empirical dispersion models GD3 for M06-2X and GD3BJ for B3LYP and PBE0 were used. Additionally, the solvent model SMD was used with CHCl₃ as a solvent.

1.2.2. NMR spectroscopy

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance II 400 (¹H: 400 MHz, ¹³C: 100 MHz) or Bruker Avance III HD 400 (¹H: 400 MHz, ¹³C: 100 MHz) nuclear resonance spectrometer. The signals and chemical shift in δ-units were calibrated to the residual proton signals of the deuterated solvent (¹H: DMSO-d₆ (δH = 2.50 ppm), CDCl₃ (δH = 7.26 ppm); ¹³C: DMSO-d₆ (δC = 39.52 ppm), CDCl₃ (δC = 77.16 ppm)). The following abbreviations were used: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, etc. m = multiplet. Coupling constants (J) are reported in Hz and are referred to H,H-couplings.

1.2.3. ESI mass spectrometry

ESI mass spectra were obtained using a ThermoFisher Scientific LTQ-Orbitrap XL spectrometer. The source voltage was 4.49 kV and the capillary temperature was 299.54 K. The tube lens voltage was between 100 and 130 V. MeCN or MeOH were used as solvent.

1.2.4. UV-Vis spectroscopy

UV-Vis absorption spectroscopy was performed on a Thermo Evolution 300 spectrometer. All spectroscopic measurements were carried out with quartz cuvettes purchased from Hellma Analytics at room temperature.

1.2.5. Luminescence spectroscopy

Luminescence spectroscopy was performed on a Horiba Fluoromax-4P spectrometer at room temperature. The data interval was set to 1 nm and the integration time was 0.1 s. The upconversion data were recorded through a longpass filter (500 nm) purchased from Thorlabs placed on the detection window to reduce the detection of higher modes from the excitation beam. The spectral bandwidths were set to 10 nm, respectively for excitation and emission. The samples were prepared by flushing with Ar for 30 s. The quartz cuvettes containing solutions were placed in a square sample holder and the upconversion signal was recorded by the detector at right angle to the incident beam.

All quantum yield measurements were carried out on the Horiba Fluoromax-4P with a Horiba QuantaPhi-2 integrating sphere. Excitation spectra according to the spectral data of the measured substance were recorded using a 1% transmission filter for both the blank cuvette containing only solvent (Lₒ) and the sample cuvette (Lₛ). Peak integration in a range of λₑₓc ± 10 nm was performed.

Fluorescence spectral region intensities were measured without filter for blank and sample.
Integration of the emission-signal region for blank \((E_a)\) and sample \((E_c)\) was performed in accordance with the substance spectral data. Quantum yields were calculated according to:

\[
\phi_{\text{TTA UC}} = \text{CF} \cdot \frac{(E_c - E_a)}{L_a - L_c}
\]

Where \(\phi_{\text{TTA UC}}\) represents the upconversion quantum yield and CF the correction factor for the transmission filter.

### 1.2.6. Ultrasonication

Polymer (100 mg) was dissolved in degassed toluene (10 mL) under \(N_2\) and placed in an ice bath. The solution was sonicated with a 13 mm immersion probe. The frequency of ultrasonication was 20 kHz, at 30% of the maximum amplitude of 125 \(\mu\)m. The pulse frequency was set to 1 s on/1 s off for 6 h. The solvent was removed in vacuo and the sample was again dissolved in THF for GPC or \(\text{CHCl}_3\) for spectroscopy.

### 1.2.7. Gel permeation chromatography

Analysis of molar masses and molar mass distributions was performed by GPC. The GPC analyses were run using THF (99.8%, non-stabilized, HiPerSolVChromarom® HPLC grade, VWR) as the eluent. The machine was equipped with a HPLC pump (1260 Infinity II, Agilent), a refractive index (RI) detector (1260 Infinity II, Agilent), a UV detector (UV-2075plus, Jasco), and a multi-angle light scattering (MALS) system (SLD 7100, Polymer Standards Service). One precolumn (8×50 mm) and four SDplus gel columns (8×300 mm, MZ Analytical Technique) were run at a flow rate of 1.0 mL min\(^{-1}\) at 20 °C. Diameter of the gel particles was 5 \(\mu\)m, and the nominal pore widths were 50, 102, 103 and 104 Å. Calibration was performed using narrowly distributed poly(methyl methacrylate) (PMMA) standards (Polymer Standards Service). The results were analyzed with the PSS WinGPC Uni Chrom software (version 8.3.2).

## 2. Syntheses

The synthesis of BTD OFP, its control molecules, and polymers was carried out as described by us before.\(^{4,5}\) \(\text{PtPc}\) was synthesized according to an adapted protocol of \(\text{Işci}\) and coworkers, visualized in Scheme S1.\(^6\)

![Scheme S1. Synthesis pathway toward \(\text{PtPc}\).](image)
2.1. 4-(Hexylthio)phthalonitrile 1

4-Nitrophthalonitrile (500 mg, 2.89 mmol, 1.0 equiv.) and 1-hexanethiol (341 mg, 2.89 mmol, 1.0 equiv.) were dissolved in absolute DMF (50 mL) and DMSO (2 mL) under Ar atmosphere and stirred for 10 min. K$_2$CO$_3$ (799 mg, 5.78 mmol, 2.0 equiv.) was added portion wise under vigorous stirring. The solution was stirred for 48 h. After removing the solvents in vacuo, an aq. solution of Na$_2$CO$_3$ (50 mL) was added and extracted with CH$_2$Cl$_2$ (3×25 mL). The organic layer was dried over Na$_2$SO$_4$, filtered through celite, and purified by column chromatography (75:25 pentane:EtOAc). The solvents were removed in vacuo and the product 4-(hexylthio)phthalonitrile 1 was obtained as a red solid (310 mg, 1.27 mmol, 44%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.63 (d, $J$ = 8.4 Hz, 1H, i), 7.54 (d, $J$ = 1.8 Hz, 1H, h), 7.48 (dd, $J = 8.4$, 1.8 Hz, 1H, g), 3.00 (t, $J = 7.4$ Hz, 2H, f), 1.71 (p, $J = 7.4$ Hz, 2H, e), 1.50 – 1.42 (m, 2H, d), 1.32 (dt, $J = 6.8$, 3.9 Hz, 4H, c-b), 0.93 – 0.86 (m, 3H, a) ppm (cf. Figure S9). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ = 147.7, 133.3, 130.1, 130.0, 116.4, 115.7, 115.3, 110.8, 32.0, 31.4, 28.6, 28.3, 22.6, 14.1 ppm (cf. Figure S10). ESI$^+$ MS: $m/z$ (%) = calcd.: 267.09264 [C$_{14}$H$_{16}$N$_2$S]Na$^+$, found: 267.09324 [C$_{14}$H$_{16}$N$_2$S]Na$^+$, calcd.: 127.02907 [C$_8$H$_3$N$_2$]$^+$, found: 127.02911 [C$_8$H$_3$N$_2$]$^+$, calcd.: 119.08913 [C$_9$H$_{15}$S]$^+$, found: 119.08913 [C$_9$H$_{15}$S]$^+$.

2.2. 4-(Hexylsulfonyl)phthalonitrile 2

4-(Hexylthio)phthalonitrile 1 (305 mg, 1.25 mmol, 1.0 equiv.) was dissolved in dry DMF (1 mL) and cooled down to 0 °C. A solution of mCPBA (526 mg, 3.05 mmol, 2.4 equiv.) in absolute DMF (20 mL) was slowly added over a period of 30 min. The mixture was warmed to r.t. and vigorously stirred for 18 h. An aqueous solution of Na$_2$SO$_4$ (50 mL) was added and extracted with CH$_2$Cl$_2$ (3×25 mL). The organic layer was dried over Na$_2$SO$_4$, filtered through celite, and purified by column chromatography (40:60 pentane:EtOAc). The solvents were removed in vacuo and the product 4-(hexylsulfonyl)phthalonitrile 2 was obtained as an orange solid (195 mg, 0.71 mmol, 57%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.34 (d, $J = 1.4$ Hz, 1H, h), 8.26 (dd, $J = 8.1$, 1.6 Hz, 1H, g), 8.05 (d, $J = 8.1$ Hz, 1H, i), 3.18 – 3.09 (m, 2H, f), 1.78 – 1.66 (m, 2H, e), 1.44 – 1.34 (m, 2H, d), 1.26 (dt, $J = 8.6$, 5.5 Hz, 4H, c-b), 0.87 (t, $J = 6.8$ Hz, 3H, a) ppm (cf. Figure S11). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ = 144.6, 134.7, 133.1, 132.6, 120.6, 117.6, 114.2, 114.0, 56.4, 31.2, 28.0, 22.6, 22.4, 14.0 ppm (cf. Figure S12). ESI$^+$ MS: $m/z$ (%) = calcd.: 299.08247 [C$_{14}$H$_{16}$O$_2$S]Na$^+$, found: 299.08309 [C$_{14}$H$_{16}$O$_2$S]Na$^+$, calcd.: 150.07090 [C$_8$H$_{15}$O$_2$S]$^+$, found: 150.07122 [C$_8$H$_{15}$O$_2$S]$^+$, calcd.: 127.02907 [C$_8$H$_3$N$_2$]$^+$, found: 127.02911 [C$_8$H$_3$N$_2$]$^+$.
2.3. Platinum(II)hexylsulfonyl-phthalocyanine PtPc

4-(Hexylsulfonyl)phthalonitrile 2 (193 mg, 0.70 mmol, 1.0 equiv.) and PtCl₂ (93 mg, 0.35 mmol, 0.5 equiv.) were dissolved in a mixture of DMF/o-DCB (0.5 mL/1.5 mL) under Ar atmosphere. The solution was stirred for 16 h at 130 °C. After removing the solvents in vacuo, the remaining solid was purified by column chromatography (100:1 CH₂Cl₂:MeOH). The solvents were removed in vacuo and the product PtPc was obtained as a blue solid (96 mg, 0.07 mmol, 11%).

1H NMR (400 MHz, CDCl₃): δ = 8.41 – 7.77 (m, 12 H), 3.14 (m, 8 H), 1.66 (m, 8 H), 1.31 (m, 8 H), 1.25 – 1.09 (m, 16 H), 0.87 – 0.71 (m, 12 H) ppm (cf. Figure S13).

2.4. BTD activated control

The route toward BTD activated control followed a synthesis established by us previously.4 (Anthracen-9-yldithynyl)trimethylsilane (101 mg, 0.37 mmol, 1.0 equiv.) and K₂CO₃ (77 mg, 0.56 mmol, 1.5 equiv.) were dissolved in a mixture of CH₂Cl₂ and MeOH (1.2 mL and 2.5 mL) and stirred for 2 h at r.t. Subsequently, the solution was diluted with H₂O and extracted with Et₂O (3x20 mL). The combined organic layers were dried over MgSO₄. The solvents were removed under reduced pressure and the product 9-ethynylantracene 9 was used in the next synthesis step without further purification.

9-ethynylantracene (71 mg, 0.35 mmol, 1.0 equiv.), 4-(7-bromobenzo[c][1,2,5]thiadiazol-4-yl)-2-methylbut-3-yn-2-ol (104 mg, 0.35 mmol, 1.0 equiv.), Pd(PPh₃)₄Cl₂ (12 mg, 0.02 mmol, 0.05 equiv.), and CuI (3.4 mg, 0.02 mmol, 0.05 equiv.) were suspended in Et₃N (1 mL). The mixture was degassed with three freeze-pump-thaw circles, backfilled with Ar, and stirred at 60 °C for 48 h. Afterwards the reaction was diluted with THF and filtered over celite. Column chromatography (hexane:EtOAc; gradient starting from 9:1 to 1:1) yielded 4-(7-(anthracen-9-ylethynyl)benzo[c][1,2,5]thiadiazol-4-yl)-2-methylbut-3-yn-2-ol d as a red solid (78 mg, 0.19 mmol, 53%).

1H NMR (400 MHz, CDCl₃): δ = 8.87 (d, J = 8.7 Hz, 2H), 8.51 (s, 1H), 8.06 (d, J = 8.5 Hz, 2H), 7.96 (d, J = 7.3 Hz, 1H), 7.79 (d, J = 7.4 Hz, 1H), 7.70 (d, J = 7.4 Hz, 1H), 7.57 (d, J = 7.7 Hz, 1H), 7.53 (d, J = 9.0 Hz, 1H), 1.75 (s, 6H) ppm (cf. Figure S14).
Stock solutions of CuBr$_2$ ($\rho = 4.0$ mg·mL$^{-1}$) and Me$_6$TREN ($\rho = 33.2$ mg·mL$^{-1}$) in DMSO were prepared. Cu$^0$-wire (4.5 cm) was wrapped around a stir bar and attached to the top of a Schlenk flask with a magnet. Filtered (Al$_2$O$_3$) monomer methyl acrylate (1.14 mL, 12.55 mmol, 697 equiv.), BTD initiator$^4$ (20 mg, 0.02 mmol, 1.00 equiv.), an aliquot of the CuBr$_2$ stock solution (0.9 µmol, 0.05 equiv.), an aliquot of the Me$_6$TREN stock solution (2.9 µmol, 0.16 equiv.), and dry DMSO (1 mL) were degassed and backfilled with Ar. The polymerization commenced after dropping the Cu-wire into the mixture. The reaction mixture was stirred at 30 °C for 6 h. Precipitation in cold MeOH yielded the desired polymer with $M_n = 60$ kDa and $D_M = 1.46$ (cf. Figure 5a of the manuscript for GPC).
3. Supporting figures and tables

![Figure S1.](image1)

**Figure S1.** Concentration (c)-dependent plots of UV-Vis absorption of activated BTD OFP control in (a, c) CHCl₃ and (b, d) toluene. (a, b) UV-Vis spectra. (d, e) Absorption (A) at 465 nm in dependence of c including linear fit for the extraction of molar absorptivity ε.

![Figure S2.](image2)

**Figure S2.** Comparison of the measured (green) normalized absorption (solid) and emission (dashed) spectra with those calculated by DFT using the three different functionals B3LYP (pink), M06-2X (purple), and PBE (blue). (a) BTD activated control (cf. Figure S3 and Chart 1 of the manuscript). (b) Truncated BTD activated control (cf. Figure S3) compared to measured BTD activated control from panel a. (c) Truncated BTD non-activated control (cf. Figure S3) compared to measured BTD non-activated control (cf. Chart 1 of the manuscript). (d) BTD activated control (cf. Figure S3 and Chart 1 of the manuscript). All spectra were calculated and measured in CHCl₃, except for measured BTD non-activated control in panel c, which was measured in MeCN.
Figure S3. Energy diagrams of BTD activated control, a truncated BTD activated control, and a truncated non-activated version simulated using TDDFT with the best fitting functional M06-2X. T₁ and S₁ energy levels were calculated for the optimized ground state (GS), first singlet excited state (¹ES), and first triplet excited state (³ES) geometries. The inset molecular structures with orbitals represent natural transition orbitals (NTOs) with the hole on the left and the electron on the right side. The NTOs are determined in the ground state geometry (S₀).

Table S1. Energies obtained by TDDFT calculations in Figure S3.

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Figure S4. Concentration (c)-dependent plots of UV-Vis absorption of PtPc in (a, c) CHCl₃ and (b, d) toluene. (a, b) UV-Vis spectra. (d, e) Absorption (A) at 648 nm in dependence of c including linear fit for the extraction of the molar absorptivity ε.
Figure S5. Concentration- and excitation wavelength-dependent TTA UC emission intensity in CHCl₃ of BTD activated control annihilator and PtPc triplet sensitizer under fixed BTD annihilator concentration $c_{\text{BTD}} = 1.0 \times 10^{-3}$ M and $c_{\text{PtPc}} = (a) 2.50 \times 10^{-6}$ M, (b) $1.25 \times 10^{-5}$ M, (c) $2.50 \times 10^{-5}$ M, (d) $1.25 \times 10^{-4}$ M, and (e) $2.50 \times 10^{-4}$ M.
Figure S6. Concentration- and excitation wavelength-dependent TTA UC emission intensity in CHCl₃ of BTD activated control annihilator and PtPc triplet sensitizer under fixed PtPc sensitizer concentration $c_{\text{PtPc}} = 2.5 \times 10^{-5} \text{ M}$ and $c_{\text{BTD}} = (a) 1.0 \times 10^{-5} \text{ M}, (b) 5.0 \times 10^{-5} \text{ M}, (c) 1.0 \times 10^{-4} \text{ M}, (d) 3.0 \times 10^{-4} \text{ M}$, and (e) $5.0 \times 10^{-4} \text{ M}$. 
Figure S7. Concentration- and excitation wavelength-dependent TTA UC emission intensity in CHCl₃ of BTD-PMA after ultrasonication for 6 h and PtPc triplet sensitizer under fixed PtPc concentration $c_{PtPc} = 2.5 \times 10^{-5}$ M and $c_{BTD-PMA}$ = (a) $3.73 \times 10^{-5}$ M, (b) $1.87 \times 10^{-4}$ M, and (c) $3.73 \times 10^{-4}$ M.

Figure S8. Upconverted emission of activated and non-activated BTD-PMA in CHCl₃ at $c = 1.0 \times 10^{-3}$ M sensitized by PtPc at $c_{PtPc} = 2.50 \times 10^{-5}$ M under excitation at $\lambda_{exc} = 675$ nm.
Figure S9. $^1$H NMR spectrum of 4-(hexylthio)phthalonitrile 1.

Figure S10. $^{13}$C NMR spectrum of 4-(hexylthio)phthalonitrile 1.
Figure S11. $^1$H NMR spectrum of 4-(hexylsulfonyl)phthalonitrile 2.

Figure S12. $^{13}$C NMR spectrum of 4-(hexylsulfonyl)phthalonitrile 2.
Figure S13. $^1$H NMR spectrum of platinum(II)hexylsulfonyl-phthalocyanine PtPc.

Figure S14. $^1$H NMR spectrum of BTD activated control.
4. References


