Electronic Supplementary Information

Fluorescence Upconversion by Triplet-Triplet Annihilation in all-organic Poly(methacrylate)-Terpolymers

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Synthesis and characterization

Materials and instrumentation

All chemicals and solvents were purchased from Alfa Aesar, Sigma-Aldrich, TCI, VWR, Grüssing or Fluka and, if not mentioned otherwise, used without further purification. All syntheses were carried out in inert atmosphere under usage of standard Schlenk technique and anhydrous as well as oxygen-free solvents. For the use in synthesis, solvents were dried by refluxing over sodium (ethanol), sodium/benzophenone (THF), with activated mol sieves (DMF, toluene) or with CaCl₂ (triethylamine, o-dichlorobenzene, CH₂Cl₂ and CHCl₃) including subsequent distillation. Methyl methacrylate was passed over a short aluminum oxide plug for removing the stabilizer. Separation by column chromatography was performed with silica gel 60 from Macherey-Nagel. Reaction processes were monitored by TLC (aluminum sheets precoated with silica gel 60 F₂₅₄ (Merck)). NMR spectra (¹H, ¹³C, H,H-COSY, HSQC, HMBC) were recorded on Bruker AC 250 (250 MHz), Bruker AC 300 (300 MHz) or Bruker AC 400 (400 MHz) spectrometers at 298 K. Chemical shifts are reported in parts per million (ppm, δ scale) relative to the reference signal of the deuterated solvent. Coupling constants are given in Hz. Software-aided evaluation of the NMR spectra was executed via MestReNova v6.0.2 or Bruker TopSpin 3.2. HR-ESI-Q-TOF MS measurements were performed using a micrOTOF (Bruker Daltonics) mass spectrometer equipped with an automatic syringe pump (KD Scientific) for sample injection. The mass spectrometer was operating in the positive ion mode and ESI (standard ion source) was used for ion generation. MS spectra were evaluated using the software OriginPro 9.0. Elemental analyses were carried out on a Vario El III (Elementar) elemental analyzer. SEC measurements were performed with following set-up: Shimadzu: SCL-10A VP (controller), DGU-14A (degasser), LC-10AD VP (pump), CTO-10A VP (oven), RID-10A (RI detector), SPD-10MA VP (UV detector), Phenomenex Phenogel guard/10⁵ Å/10³ Å (10 μm particle size) (column), DMAc + 0.08 wt.% NH₄PF₆ (eluent), 1 mL × min⁻¹ at 40 °C (flow rate and column temperature), PMMA calibration.
Crystal Structure Determination

The intensity data were collected on a Nonius KappaCCD diffractometer, using graphite-monochromated Mo-Kα radiation. Data were corrected for Lorentz and polarization effects; absorption was taken into account on a semi-empirical basis using multiple-scans\(^1\). The structure was solved by direct methods (SHELXS\(^2\)) and refined by full-matrix least squares techniques against Fo\(^2\) (SHELXL-97\(^2\)). The hydrogen atoms bonded to the hydroxyl-groups of compound 1 and 2 were located by difference Fourier synthesis and refined isotropically. All other hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically\(^2\). MERCURY\(^3\) was used for structure representations.

Synthesis and characterization of the sensitizer monomer M-S

![Synthesis scheme of the sensitizer monomer M-S including a polymerizable methacrylate moiety. Reagents and conditions: a) 1. TFA, 2. DDQ, 3. Et\(_3\)N, 4. BF\(_3\)× Et\(_2\)O, THF, RT, 19 h, 29%, b) 1. I\(_2\), EtOH, 2. HIO\(_3\), H\(_2\)O, –20 °C, 20 min, 89%, c) 1. Et\(_3\)N, 2. methacryloyl chloride, CH\(_2\)Cl\(_2\), 0 °C, 2 h → RT, 21 h, 99%\(^4,5,6\)](image)

5,5-Difluoro-10-(4-hydroxyphenyl)-1,3,7,9-tetramethyl-boradiazaindacene (1)

![Image of compound 1](image)

The synthesis of 1 was performed in analogy to Sauer et al.\(^5\)

4-Hydroxybenzaldehyde (3.06 g, 25.1 mmol) was dissolved in THF (500 mL). 2,4-Dimethyl-1H-pyrrole (5.00 g, 52.6 mmol) and trifluoroacetic acid (0.82 mL, 10.6 mmol) were added and the mixture was stirred for 23 h. Subsequently, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (5.68 g, 25.0 mmol) dissolved in THF (110 mL) was added and the mixture was stirred for another 3 h. Triethylamine (150 mL, 1082.1 mmol) was added and the mixture was stirred for 45 min. Then, BF\(_3\)× Et\(_2\)O (160 mL, 1262.6 mmol) was added at –20 °C and the mixture was stirred for 19 h. Afterwards, saturated NaHCO\(_3\) (aq.) (600 mL) was added carefully. The THF was removed under reduced pressure and CHCl\(_3\) (600 mL) was added. After filtration through a glass frit (G4) filled with celite, the organic layer was washed with deionized water (3 × 200 mL) and dried over Na\(_2\)SO\(_4\). The solvent was removed in vacuo and purification was executed via column chromatography (Silica gel 60, eluent: CHCl\(_3\), RF = 0.1).

**Yield**: 2.47 g (29%), red-green solid
\[^1\text{H}\] NMR (300 MHz, CDCl\textsubscript{3}): \(\delta = 7.12 (d, J = 8.7 \text{ Hz}, 2 \text{ H}, H_l), 6.94 (d, J = 8.7 \text{ Hz}, 2 \text{ H}, H_l), 5.98 (s, 2 \text{ H}, H_c), 5.23 (s, 1 \text{ H}, H_l), 2.55 (s, 6 \text{ H}, H_a), 1.44 (s, 6 \text{ H}, H_d) \text{ ppm.}\)

\[^{13}\text{C}\{^1\text{H}\} \text{ NMR} (75 \text{ MHz, CDCl}\textsubscript{3}): \delta = 156.4 (C_k), 155.5 (C_b), 143.3 (C_g), 141.9 (C_f), 132.0 (C_e), 129.5 (C_i), 127.3 (C_h), 121.3 (C_c), 116.3 (C_j), 14.7 (C_{a, d}) \text{ ppm.}\)

\[^{19}\text{F}\{^1\text{H}\} \text{ NMR} (377 \text{ MHz, CDCl}\textsubscript{3}): \delta = –145.84 (d, J = 33.2 \text{ Hz}, BF\textsubscript{2}), –146.02 (d, J = 33.2 \text{ Hz}, BF\textsubscript{2}) \text{ ppm.}\)

\(\text{EA:} \quad \text{C}_{19}\text{H}_{19}\text{BF}_{2}\text{N}_{2}\text{O} \) calc.: \(C \ 67.08 \quad H \ 5.63 \quad N \ 8.24\)

\(\) found: \(C \ 66.82 \quad H \ 5.63 \quad N \ 8.23\)

\(\text{MS (ESI-TOF MS, HR MS):} \quad \text{C}_{19}\text{H}_{19}\text{BF}_{2}\text{N}_{2}\text{O} \) calc.: \([M+Na]^+ \ 363.1454 \quad [M+K]^+ \ 379.1190\)

\(\) found: \([M+Na]^+ \ 363.1451 \quad [M+K]^+ \ 379.1201\)

\(\text{Error [ppm]:} \quad 0.7 \quad -1.9\)

5,5-Difluoro-2,8-diiodo-10-(4-hydroxyphenyl)-1,3,7,9-tetramethyl-boradiazaindacene (2)

5,5-Difluoro-2,8-diiodo-10-(4-hydroxyphenyl)-1,3,7,9-tetramethyl-boradiazaindacene (2)

The synthesis of 2 was performed in analogy to Zhu et al.\(^6\)

\(\text{HIO}_3 (6.10 \text{ g}, 34.7 \text{ mmol}) \) was dissolved in deionized water (13.6 mL) and the resulting solution was purged with nitrogen for 10 min. Meanwhile, 1 (5.76 g, 16.9 mmol) and iodine (10.75 g, 42.3 mmol) were dissolved in ethanol (115 mL) at –20 °C. Afterwards, the aqueous iodic acid solution was added to the reaction solution. After 20 min of stirring at –20 °C, the reaction solution was added immediately to CHCl\textsubscript{3} (300 mL). The resulting solution was washed with deionized water (3 \(\times\) 100 mL) and saturated Na\textsubscript{2}SO\textsubscript{3} (aq.) (3 \(\times\) 100 mL). The combined aqueous phases were extracted with CHCl\textsubscript{3} (100 mL) and all combined organic phases were washed with deionized water (3 \(\times\) 100 mL). After drying of the organic phase with Na\textsubscript{2}SO\textsubscript{4}, the solvent was removed in vacuo and purification was executed via column chromatography (Silica gel 60, eluent: CH\textsubscript{2}Cl\textsubscript{2}, \(R_f = 0.4\)).

Yield: 8.94 g (89%), red-green solid

\[^1\text{H}\] NMR (300 MHz, THF-\(d_8\)): \(\delta = 8.88 (s, 1 \text{ H}, H_l), 7.11 (d, J = 8.4 \text{ Hz}, 2 \text{ H}, H_l), 6.96 (d, J = 8.4 \text{ Hz}, 2 \text{ H}, H_l), 2.58 (s, 6 \text{ H}, H_a), 1.50 (s, 6 \text{ H}, H_d) \text{ ppm.}\)

\(^{13}\text{C}\{^1\text{H}\} \text{ NMR} (75 \text{ MHz, THF-\(d_8\)):} \delta = 160.3 (C_k), 157.1 (C_b), 146.1 (C_g), 143.8 (C_f), 132.9 (C_e), 130.3 (C_i), 126.3 (C_h), 117.3 (C_c), 85.9 (C_{a, d}), 85.8 (C_{a, d}), 17.6 (C_{a, d}), 16.2 (C_{a, d}) \text{ ppm.}\)

\(^{19}\text{F}\{^1\text{H}\} \text{ NMR} (377 \text{ MHz, THF-\(d_8\)):} \delta = –146.15 (d, J = 31.7 \text{ Hz}, BF\textsubscript{2}), –146.32 (d, J = 32.4 \text{ Hz}, BF\textsubscript{2}) \text{ ppm.}\)
5,5-Difluoro-2,8-diiodo-10-(4-methacryloylphenyl)-1,3,7,9-tetramethyl-boradiazaindacene (M-S)

The synthesis procedure was adapted from literature and applied for the synthesis of M-S.

Compound 2 (7.88 g, 13.3 mmol) was dissolved in CH$_2$Cl$_2$ (230 mL) and cooled to 0 °C. Triethylamine (6.00 mL, 43.3 mmol) was added and the solution was stirred for 30 min. Then, methacryloyl chloride (2.00 mL, 20.8 mmol) was added and the solution was stirred for 2 h at 0 °C followed by 21 h at RT. The solvent and triethylamine were removed under reduced pressure and the residue was dissolved in CH$_2$Cl$_2$ (200 mL). After washing with deionized water (3 × 100 mL), the organic phase was dried with Na$_2$SO$_4$. The solvent was removed in vacuo and purification was executed via column chromatography (Silica gel 60, eluent: CH$_2$Cl$_2$, R$_f$ = 0.8).

**Yield:** 8.69 g (99%), red solid

$^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta = 7.35 - 7.31$ (m, 4 H, H$_{i,j}$), 6.38 (t, $J = 1.2$ Hz, 1 H, H$_m$), 5.82 (t, $J = 1.2$ Hz, 1 H, H$_m$), 2.62 (s, 6 H, H$_a$), 2.08 (t, $J = 1.2$ Hz, 3 H, H$_o$), 1.47 (s, 6 H, H$_d$) ppm.

$^{13}$C{$^1$H} NMR (100 MHz, CD$_2$Cl$_2$): $\delta = 165.9$ (C), 157.4 (C), 152.6 (C), 146.0 (C), 141.3 (C), 136.3 (C), 132.5 (C), 131.9 (C), 129.7 (C), 128.0 (C$^\text{m}$), 123.6 (C), 86.1 (C$^\text{c}$), 18.7 (C), 17.5 (C$^\text{a}$), 16.4 (C$^\text{b}$) ppm.

$^{19}$F{$^1$H} NMR (377 MHz, CD$_2$Cl$_2$): $\delta = -145.60$ (d, $J = 32.1$ Hz, BF$_2$), $-145.77$ (d, $J = 32.4$ Hz, BF$_2$) ppm.

EA:

C$_{23}$H$_{21}$BF$_2$I$_2$N$_2$O$_2$  

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(660.05 g/mol)  

MS (ESI-TOF MS, HR MS):

C$_{23}$H$_{21}$BF$_2$I$_2$N$_2$O$_2$  

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(659.9754 g/mol)  

Error [ppm]:  

3.1
Fig. S 2 $^1$H NMR spectrum (CD$_2$Cl$_2$, 400 MHz) of 5,5-difluoro-2,8-diiodo-10-(4-methacryloylphenyl)-1,3,7,9-tetramethylboradiazaindacene (M-S).
Crystallographic data

Crystal Data for 1: C_{19}H_{19}BF_{2}N_{2}O, Mr = 340.17 g/mol, colourless prism, size 0.122 x 0.110 x 0.088 mm³, monoclinic, space group P 2₁/n, a = 14.4922(3), b = 14.2458(2), c = 15.9319(3) Å, β = 91.960(1)°, V = 3287.26(10) Å³, T = -140 °C, Z = 8, ρ_calcd. = 1.375 g/cm³, µ (Mo-Kα) = 1 cm⁻¹, multi-scan, transmin: 0.7031, transmax: 0.7456, F(000) = 1424, 19788 reflections in h(-18/18), k(-18/18), l(-15/20), measured in the range 2.01° ≤ θ ≤ 27.48°, completeness Θ_max = 99.8%, 7523 independent reflections, R_int = 0.0540, 5331 reflections with F_o > 4σ(F_o), 467 parameters, 0 restraints, R1_obs = 0.0600, wR²_obs = 0.1089, R1_all = 0.0944, wR²_all = 0.1222, GOOF = 1.094, largest difference peak and hole: 0.258 / -0.245 e Å⁻³.

Crystal Data for 2: C_{19}H_{17}BF_{2}I_{2}N_{2}O, Mr = 591.96 g/mol, bordeaux-red prism, size 0.088 x 0.082 x 0.078 mm³, monoclinic, space group P 2₁/c, a = 21.8579(4), b = 10.5698(2), c = 18.2672(4) Å, β = 112.645(1)°, V = 3894.98(13) Å³, T = -140 °C, Z = 8, ρ_calcd. = 2.019 g/cm³, µ (Mo-Kα) = 32.6 cm⁻¹, multi-scan, transmin: 0.6276, transmax: 0.7456, F(000) = 2256, 32978 reflections in h(-28/27), k(-13/13), l(-19/23), measured in the range 2.18° ≤ θ ≤ 27.48°, completeness Θ_max = 99.3%, 8873 independent reflections, R_int = 0.0520, 6854 reflections with F_o > 4σ(F_o), 503 parameters, 0 restraints, R1_obs = 0.0554, wR²_obs = 0.0961, R1_all = 0.0805, wR²_all = 0.1062, GOOF = 1.132, largest difference peak and hole: 1.160 / -1.095 e Å⁻³.

Supporting Information Available: Crystallographic data deposited at the Cambridge Crystallographic Data Centre under CCDC-1885573 for 1, and CCDC-1885574 for 2 contain the supplementary crystallographic data excluding structure factors; this data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Fig. S 3 Molecular structures and labeling scheme of 5,5-difluoro-10-(4-hydroxyphenyl)-1,3,7,9-tetramethyl-boradiazaindacene (1, left panel) and 5,5-difluoro-2,8-diido-10-(4-hydroxyphenyl)-1,3,7,9-tetramethyl-boradiazaindacene (2, right panel). Thermal ellipsoids are shown at a probability level of 50%. With exception of the bonded hydrogens to the hydroxy-groups H atoms are neglected for clarity reasons.
Synthesis and characterization of the annihilator monomer M-A

![Synthesis diagram]

Fig. S 4 Schematic representation of the synthesis of perylen-3-ylmethyl methacrylate (M-A) as annihilator monomer with polymerizable methacrylate moiety. Reagents and conditions: d) POCl₃, DMF, o-dichlorobenzene, reflux, 2 h, 50%, e) NaBH₄, EtOH, THF, RT, 6 h, 92%, f) 1. Et₃N, 0 °C, 30 min, 2. methacryloyl chloride, THF, 0 °C, 2 h → RT, 21 h, 70%.

Perylene-3-carbaldehyde (3)

The synthesis of 3 was performed in analogy to Qiu et al.⁷

Perylene (10.01 g, 39.7 mmol) was dissolved in a mixture of DMF (67 mL) and o-dichlorobenzene (34 mL). The reaction mixture was heated to reflux and POCl₃ (20.34 mL, 222.9 mmol) was added and heated for further 2 h under reflux. After cooling, the reaction mixture was neutralized with 0.2 M NaOAc (aq). After storage for 33 h at 4 °C, precipitates were filtered out and were washed with deionized water until the filtrate became colorless. The orange solid was dried under reduced pressure. Purification was executed via column chromatography (Silica gel 60, eluent: CHCl₃, Rf = 0.4).

Yield: 5.56 g (50%), orange solid

¹H NMR (300 MHz, THF-d₈): δ = 10.30 (s, 1 H, Hₐ), 9.22 (d, J = 8.4 Hz, 1 H), 8.43 – 8.31 (m, 4 H), 8.24 (d, J = 7.8 Hz, 1 H), 7.82 (d, J = 8.1 Hz, 1 H), 7.75 (d, J = 8.1 Hz, 1 H), 7.65 (t, J = 7.8 Hz, 1 H), 7.52 (tt, J = 7.8, 3.6 Hz, 2 H) ppm.

¹³C{¹H} NMR (75 MHz, THF-d₈): δ = 192.9 (C), 138.1, 137.9, 135.6, 133.2, 132.2, 131.7, 131.5, 131.3, 130.8, 129.9, 129.8, 129.3, 129.1, 127.8, 127.6, 125.5, 123.8, 122.5, 122.0, 120.3 ppm.
Perylen-3-ylmethanol (4)

The synthesis of 4 was performed in analogy to Qiu et al.\textsuperscript{7}

Compound 3 (5.56 g, 19.8 mmol) was dissolved in THF (580 mL). Then, sodium borohydride (840 mg, 22.2 mmol) dissolved in ethanol (60 mL) was added and subsequent stirring for 6 h was executed. The solvent was removed under reduced pressure and the residue was dissolved in CHCl\(_3\) (700 mL). The solution was washed with deionized water (3 \times 200 mL). Afterwards, deionized water (100 mL) was added to the organic phase and a subsequent concentration resulted in the crystallization of a yellow solid, which was filtered off and dried \textit{in vacuo}.

\textbf{Yield}: 5.15 g (92%), yellow solid

\textbf{\textsuperscript{1}H NMR} (300 MHz, THF-\textsubscript{d}8): \(\delta = 8.36 – 8.17 \text{ (m, 4 H)}, 7.94 \text{ (d, } J = 8.4 \text{ Hz, 1 H)}, 7.73 – 7.34 \text{ (m, 6 H)}, 4.99 \text{ (d, } J = 5.4 \text{ Hz, 2 H, } H^a\)), 4.56 \text{ (t, } J = 5.4 \text{ Hz, 1 H, } H^b\) ppm.

\textbf{\textsuperscript{13}C\{\textsuperscript{1}H\} NMR} (75 MHz, THF-\textsubscript{d}8): \(\delta = 139.1, 135.9, 133.5, 132.5, 132.4, 131.3, 129.8, 129.5, 128.6, 128.4, 127.5, 127.4, 127.3, 125.8, 124.6, 121.2, 121.1, 121.0, 120.9, 63.2 \text{ (C\textsuperscript{a}) ppm.}

Perylen-3-ylmethyl methacrylate (M-A)

The synthesis procedure was adapted from literature\textsuperscript{4} and applied for the synthesis of M-A.

Compound 4 (4.02 g, 14.2 mmol) was dissolved in THF (183 mL). The solution was purged with nitrogen for 10 min and cooled to 0 °C. Triethylamine (6.60 mL, 47.6 mmol) was added and stirring for 30 min followed. Then, methacryloyl chloride (2.20 mL, 22.5 mmol) was added and the solution was stirred for 2 h at 0 °C and, furthermore, for 21 h at RT. Precipitates were filtered off and were extracted with THF. The filtrate and the extract were combined and the solvent was removed under reduced pressure. The residue was dissolved in CH\(_2\)Cl\(_2\) (200 mL) and the resulting solution was washed with deionized water (3 \times 100 mL). The organic phase was dried with Na\(_2\)SO\(_4\) and the solvent was removed \textit{in vacuo}. Purification was executed via column chromatography (Silica gel 60, eluent: CHCl\(_3\), \(R_f = 0.6\)). Finally, recrystallization in CHCl\(_3\) provided a precipitation, which was washed with a small amount of water and CHCl\(_3\).

\textbf{Yield}: 3.47 g (70%), yellow solid

\textbf{\textsuperscript{1}H NMR} (300 MHz, CDCl\(_3\)): \(\delta = 8.23 – 8.04 \text{ (m, 4 H)}, 7.81 \text{ (d, } J = 8.4 \text{ Hz, 1 H), 7.66 \text{ (t, } J = 8.1 \text{ Hz, 2 H), 7.56 – 7.37 \text{ (m, 4 H)}, 6.17 \text{ (s, 1 H, } H^b\)), 5.59 \text{ (t, } J = 1.5 \text{ Hz, 1 H, } H^a\)), 5.55 \text{ (s, 2 H, } H^a\)), 1.99 \text{ (s, 3 H, } H^b\) ppm.

\textbf{\textsuperscript{13}C\{\textsuperscript{1}H\} NMR} (75 MHz, CDCl\(_3\)): \(\delta = 167.5 \text{ (C\textsuperscript{b})}, 136.3 \text{ (C\textsuperscript{c})}, 134.7, 133.0, 132.2, 131.9, 131.2, 131.1, 131.0, 129.1, 128.5, 128.2, 128.1, 128.1, 127.9, 127.1, 126.7, 126.2, 123.4 \text{ (C\textsuperscript{a})}, 120.6, 120.4, 120.3, 119.7, 65.0 \text{ (C\textsuperscript{a})}, 18.5 \text{ (C\textsuperscript{d}) ppm.}
EA:

\[ \text{C}_{25}\text{H}_{18}\text{O}_2 \]

- calc.: C 85.69 H 5.18
- (350.42 g/mol) found: C 85.67 H 5.10

MS (ESI-TOF MS, HR MS):

\[ \text{C}_{25}\text{H}_{18}\text{O}_2 \]

- calc.: ([M+Na]^+) 373.1199
- (350.1307 g/mol) found: ([M+Na]^+) 373.1202

Error [ppm]: -0.7

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**Fig. S 5** \(^1\)H NMR spectrum (CDCl\(_3\), 300 MHz) of perylen-3-ylmethyl methacrylate (M-A).
Synthesis and characterization of the co- & terpolymers

\[ \text{M-S} \quad \text{M-A} \]

Fig. S6 Schematic representation of the copolymerization of the monomers MMA, M-S and/or M-A. Reagents and conditions: AIBN, DMF, 70 °C, 17.5 h.
Tab. S 1 Overview of the amounts of monomers, solvent and initiator of the polymerizations.

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<th>DMF V / mL</th>
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<td>2.00</td>
<td>8.30</td>
<td>2.52</td>
</tr>
<tr>
<td></td>
<td>MMA</td>
<td>500</td>
<td>4.99</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Tab. S 2 Ratios (theoretical and found on basis of \(^1\)H NMR measurement in CDCl\(_3\) or EA) between used co-monomers in solution for each polymer.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Monomer</th>
<th>Ratio (theoretical) [A]:[B]:[C]</th>
<th>Ratio ((^1)H NMR) [A]:[B]:[C]</th>
<th>Ratio (EA) [A]:[B]:[C] or [A]:[B+C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-1</td>
<td>M-S</td>
<td>1 : 20.0 : 79.0</td>
<td>1 : 11.4 : 39.9</td>
<td>1 : 4.6</td>
</tr>
<tr>
<td>P-5</td>
<td>M-S</td>
<td>1 : 4.0 : 15.0</td>
<td>1 : 3.6 : 16.1</td>
<td>1 : 5.0</td>
</tr>
<tr>
<td>P-10</td>
<td>M-S</td>
<td>1 : 2.0 : 7.0</td>
<td>1 : 1.9 : 7.2</td>
<td>1 : 3.2</td>
</tr>
<tr>
<td>P-S</td>
<td>M-S</td>
<td>1 : 0 : 100</td>
<td>1 : 0 : 103.0</td>
<td>1 : 0 : 11.3</td>
</tr>
</tbody>
</table>
Fig. S 7 $^1$H NMR spectrum (CDCl$_3$, 300 MHz) of P-1.

Fig. S 8 $^1$H NMR spectrum (CDCl$_3$, 300 MHz) of P-5.
Fig. S 9 $^1H$ NMR spectrum (CDCl$_3$, 300 MHz) of P-10.

Fig. S 10 $^1H$ NMR spectrum (CDCl$_3$, 400 MHz) of P-S.
Fig. S 11 SEC graphs of the polymers P-1 (green), P-5 (blue), P-10 (black), P-S (red) (eluent: DMAc + 0.08 wt.% NH$_4$PF$_6$, PMMA calibration, RI detection).

Fig. S 12 3D SEC plot of M-A with absorption detection in the range of $\lambda = 270$ to 600 nm (eluent: DMAc/NH$_4$PF$_6$, PMMA calibration).
Fig. S 13 3D SEC plot of M-S with absorption detection in the range of $\lambda = 270$ to 600 nm (eluent: DMAc/NH$_4$PF$_6$, PMMA calibration).

Fig. S 14 3D SEC plot of P-1 with absorption detection in the range of $\lambda = 270$ to 600 nm (eluent: DMAc/NH$_4$PF$_6$, PMMA calibration).
**Fig. S 15** 3D SEC plot of P-5 with absorption detection in the range of $\lambda = 270$ to 600 nm (eluent: DMAc/NH$_4$PF$_6$, PMMA calibration).

**Fig. S 16** 3D SEC plot of P-10 with absorption detection in the range of $\lambda = 270$ to 600 nm (eluent: DMAc/NH$_4$PF$_6$, PMMA calibration).
Fig. S 17 3D SEC plot of P-S with absorption detection in the range of λ = 270 to 600 nm (eluent: DMAc/NH₄PF₆, PMMA calibration).

Fig. S 18 DOSY NMR (CDCl₃, 400 MHz) spectrum of P-1.

Fig. S 19 DOSY NMR (CDCl₃, 400 MHz) spectrum of P-5.
Spectroscopic characterization of monomers and UC polymers

Sample preparation for UC measurements in solution

The THF used for UC studies was stirred for at least 1 h over basic aluminium oxide to remove containing peroxides. The absence of peroxides was confirmed with peroxide test stripes. Subsequently, the solvent was filtered and degassed with 5 freeze-pump-thaw cycles. UC samples were prepared in Schlenk-cuvettes with an optical pathway of 1 cm. Prior to the sample preparation the cuvettes were rinsed with neat deaerated solvent. A suitable amount of monomer/polymer was weighed under atmospheric conditions and moved into the glovebox, where a stock solution of the compound in THF was prepared. These stock solutions were further diluted to receive samples of defined concentrations.
Fig. S 22 (A, C) Steady state emission spectra of P-1, P-5 and P-10 after photoexcitation at $\lambda = 400$ nm. (B) Steady state UC emission spectra of P-1, P-5 and P-10 after photoexcitation at $\lambda = 532$ nm. (D) Steady state UC emission spectra of P-5 with photoexcitation at $\lambda = 532$ nm of an oxygen-free and an aerated solution.

Fig. S 23 Normalized steady state emission spectra of M-S (black), P-S (red) and P-1, P-5 and P-10 (blue solid, dashed and dotted) after photoexcitation at $\lambda = 510$ nm in deaerated THF.
Determination of sensitizer and TTA-UC emission quantum yield

The emission quantum yield of the sensitizer $S$, (e.g. fluorescence quantum yield $\phi_{S,fl}$ and phosphorescence quantum yield $\phi_{S,ph}$) as well as the TTA-UC emission quantum yield $\phi_{UC}$ in deaerated THF were determined relative to the fluorescence quantum yield of M-S in aerated THF ($\phi_{S,fl,abr} = 1.72\%$) according to the following equations (1) and (2):

$$\phi_{S,fl(ph)} = \phi_{std} \frac{1 - 10^{-A_{std} I_{std}}} {1 - 10^{-A_x I_x}} \left( \frac{\eta_x}{\eta_{std}} \right)^2$$  \hfill (1)

$$\phi_{UC} = 2\phi_{std} \frac{1 - 10^{-A_{std} I_{std}}} {1 - 10^{-A_x I_x}} \left( \frac{\eta_x}{\eta_{std}} \right)^2$$  \hfill (2)

where $A$, $I$ and $\eta$ represent the absorbance at the excitation wavelength, the integrated emission intensity and the refractive index of the medium. The corresponding indices $std$ and $x$ are referring to the reference standard and the sample. Equation (2) is multiplied with the factor 2 to set the maximum quantum yield to unity. The overall TTA-UC quantum yield $\phi_{UC}$ depends on the efficacy of all individual processes contributing to upconversion according to the following equation (3):

$$\phi_{UC} = f_\text{ISC} \phi_{TTET} \phi_{TTA} \phi_{A,fl}$$  \hfill (3)

where the parameter $f$ is the statistical factor for population of a singlet excited state $\phi_{ISC}$ is the intersystem crossing quantum yield of $S$, $\phi_{TTET}$ is the quantum efficacy of the triplet-triplet energy transfer, $\phi_{TTA}$ is the quantum yield of triplet-triplet annihilation and $\phi_{A,fl}$ is the fluorescence quantum yield of $A$.

Excitation power density dependent measurement of the TTA-UC

A variable neutral density filter was used to modulate the excitation power arriving the sample position. The integrated TTA-UC emission intensities were plotted as a function of the measured excitation power density in double logarithmic fashion. Within these measurement, the slopes 1 and 2 are corresponding to the weak and strong annihilation regimes, respectively. The dependencies of the integrated upconversion emission intensity versus excitation power density can be rationalized by the equations (4) and (5), which have been previously described by Castellano et al.[8]

$$I_{UC} = \frac{\phi_{A,fl} k_{TTA}[^3A^*]^2}{2k_T} \quad \text{weak annihilation regime}$$  \hfill (4)

$$I_{UC} = \phi_{A,fl}[^3A^*] \quad \text{strong annihilation regime}$$  \hfill (5)

where $I_{UC}$ is the integrated UC emission intensity, $k_T$ describes the sum of all unimolecular and pseudo-first-order decay pathways of the annihilator triplet state $[^3A^*]$, $k_{TTA}$ is the rate constant of bimolecular triplet-triplet annihilation and $\phi_{A,fl}$ is the fluorescence quantum yield of the annihilator. Thereby, in the strong annihilation limit, the integrated UC emission intensity is linearly proportional to the
excitation power density and consequently to $[3A^*]$, while within the weak annihilation regime the integrated UC emission intensity becomes proportional to $[3A^*]^2$.

Fig. S 24 Excitation power density dependence of the integrated UC emission intensity of (A) M-S/M-A (B) P-1 (C) P-5 (D) P-10 in deaerated THF, plotted in double-logarythmic fashion.
Fig. S 25 (A) ns-time resolved UC emission spectra at selected delay times after photoexcitation at $\lambda_{\text{exc}} = 550$ nm of a mixture of M-S ($c = 3 \, \mu\text{M}$) and M-A ($c = 1 \, \text{mM}$) dissolved in deaerated THF. (B) ns-time resolved transient absorption spectra at selected delay times after excitation at $\lambda_{\text{exc}} = 550$ nm. (C) Selected kinetic traces at early delay times showing the rise of the upconverted emission ($\tau_{\text{UC rise}} = 0.2 \, \mu\text{s}$).
Determination of $k_{\text{TTET}}$ by Stern-Volmer analysis

Fig. S 26 (A) ns-time resolved transient absorption decay at $\lambda_{\text{obs}} = 540$ nm after photoexcitation at $\lambda_{\text{exc}} = 550$ nm of M-S ($c = 3$ µM) and varying concentrations of M-A dissolved in deaerated THF. (B) Stern-Volmer plot obtained for the monomers in THF.

Quenching experiments were performed addressing the dark state $^3S^*$ of M-S in the presence of varying concentrations of M-A.

The Stern-Volmer constant $k_{SV}$ and the bimolecular triplet-triplet energy transfer rate constant $k_{\text{TTET}}$ was obtained using the dynamic quenching of the triplet GSB of the M-S in presence of M-A. The rate constants were estimated by the Stern-Volmer equation (6):

$$\frac{\tau_0}{\tau} - 1 = k_{SV} [\text{M-A}] = k_{\text{TTET}} \tau_0 [\text{M-A}]$$

Where $\tau_0$ and $\tau$ is the sensitizer triplet state lifetime in the absence and presence of the quencher M-A, respectively. The bimolecular rate constant of the TTET $k_{\text{TTET}}$ is estimated to $3.2 \times 10^9$ M$^{-1}$s$^{-1}$ in THF, which is in line with a diffusion controlled process.\(^{[9]}\)
Determination of $k_{\text{TTA}}$

\[\frac{d[A^*]}{dt} = -k_T[A^*] - 2k_{\text{TTA}}[A^*]^2\]  \hfill (7)

where $k_T$ describes all unimolecular and pseudo-first order decay of the triplet state and $k_{\text{TTA}}$ corresponds to the bimolecular TTA rate constant. One analytical solution of equation (7) is displayed in the equations (8) and (9):[10]

\[\begin{align*}
[A^*] &= [A^*]_0 \frac{1 - \beta}{e^{k_T t} - \beta} \\
\beta &= k_T + 2k_{\text{TTA}} [A^*]_0
\end{align*}\]  \hfill (8, 9)

The measured $A^*$ decay in OD units was converted into the corresponding $[A^*]$ using the molar triplet-triplet extinction coefficient of perylene, $1.34 \times 10^4$ M\(^{-1}\)cm\(^{-1}\).[11] The bimolecular rate constant of TTA $k_{\text{TTA}}$ accessed by monitoring decay of the triplet annihilator ESA located around 480 nm was estimated to $4.8 \times 10^{10}$ M\(^{-1}\)s\(^{-1}\) accounting for a diffusion limited process.[12]
Fig. S 28 ns-time resolved transient absorption spectra at selected delay times of P-S in deaerated THF after excitation at $\lambda_{exc} = 550$ nm and inverted ground state absorption spectra (dark grey) of P-S in THF.

Fig. S 29 (A) ns-time resolved UC emission spectra at selected delay times after photoexcitation at $\lambda_{exc} = 550$ nm of P-5 dissolved in deaerated THF. Inset shows selected kinetic emission of P-5 and the corresponding exponential fit in red. (B) ns-time resolved transient absorption spectra at selected delay times after excitation at $\lambda_{exc} = 550$ nm of P-5 and inverted ground state absorption spectra (dark grey) of P-5 in THF.
Fig. S 30 (A) ns-time resolved UC emission spectra at selected delay times after photoexcitation at \( \lambda_{\text{exc}} = 550 \text{ nm} \) of P-10 dissolved in deaerated THF. Inset shows selected kinetic emission of P-10 and the corresponding exponential fit in red. (B) ns-time resolved transient absorption spectra at selected delay times after excitation at \( \lambda_{\text{exc}} = 550 \text{ nm} \) of P-10 and inverted ground state absorption spectra (dark grey) of P-10 in THF.

Tab. S 3 Estimated averaged distance of A to S \( d_{\text{A to S}} \) and of S to A \( d_{\text{S to A}} \) in lengths of MMA units in polymers with statistically distributed monomers in the chain.

<table>
<thead>
<tr>
<th>Polymer composition ratio MMA / M-A / M-S</th>
<th>( d_{\text{A to S}} )/ length of MMA units</th>
<th>( d_{\text{S to A}} )/ length of MMA units</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-1 79 / 20 / 1</td>
<td>50.2</td>
<td>2.8</td>
</tr>
<tr>
<td>P-5 75 / 20 / 5</td>
<td>10.3</td>
<td>2.8</td>
</tr>
<tr>
<td>P-10 70 / 20 / 10</td>
<td>5.3</td>
<td>2.8</td>
</tr>
</tbody>
</table>

Discussion of ns-transient absorption spectra of M-S, P-S and M-A/M-S in deaerated THF

The \( \text{ns-TA} \) spectrum of M-S (see Fig. 7A in the manuscript) reveals a broad and unstructured excited state absorption (ESA) band ranging from 400 to 480 nm. This band is accompanied by ground state bleach (GSB) around 530 nm.\(^\text{13}\) Global fitting of the kinetics required two time constants, \( i.e. \) 72 and 277 \( \mu \text{s} \). The long-lived excited state signal is assigned to a non-emitting BODIPY triplet \( ^3\text{S}^* \), which is known to be efficiently populated \( \text{via} \) ISC in halogenated BODIPY derivatives.\(^\text{14}\)

The \( \text{ns-TA} \) spectra of P-S (see ESI Fig. S 27) obtained upon excitation at \( \lambda_{\text{exc}} = 550 \text{ nm} \) resemble the same spectral features as the monomer M-S. However, the decay of the excited sensitizer unit within P-S (27 and 230 \( \mu \text{s} \)) is slightly faster than in M-S (see Tab. 2). The blended solution of M-S and M-A reveals \( \text{ns-TA} \) spectra (Fig. 7B) characterized by an intense, structured ESA with maxima at 460, 480 and 500 nm accompanied by a GSB above 460 nm. By comparing the TA spectra to those of the neat sensitizer M-S, the decay of the GSB together with the formation of a long lived ESA below 530 nm (associated with \( ^3\text{A}^* \))\(^\text{9, 11, 15}\) is indicative of \( ^3\text{S}^* \rightarrow ^3\text{A}^* \) TTET. TTET yields a residual S-lifetime of \( \tau_{\text{T, S}} = 0.3 \mu \text{s} \) and an annihilator triplet state lifetime corresponding to \( \tau_{\text{T, A}} = 56/274 \mu \text{s} \).
References


