Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Triplet-triplet Annihilation Upconversion Kinetics of C_{60}-Bodipy Dyads as Organic Triplet Photosensitizers

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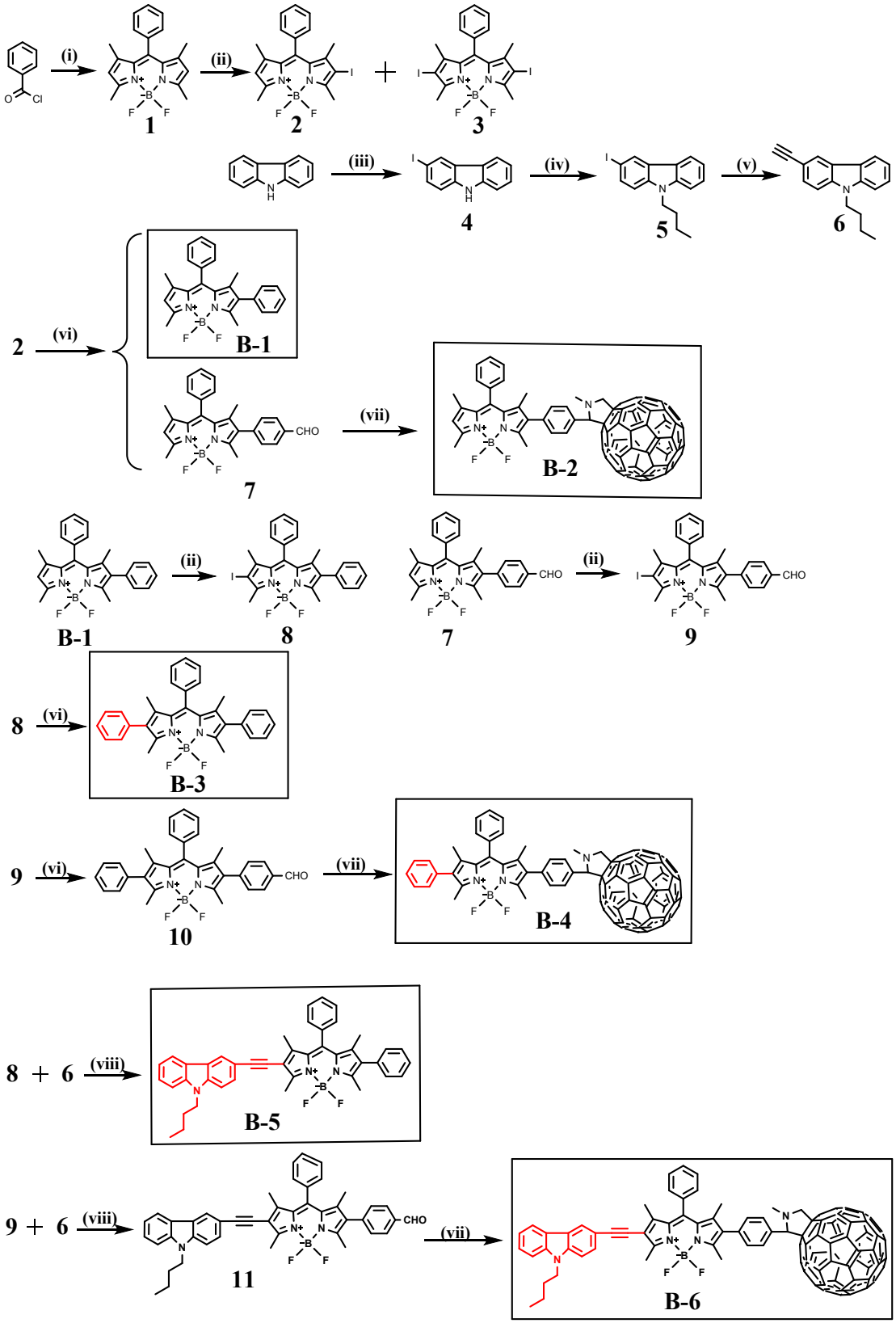
1. Synthetic processes of major compounds



Compounds 1-6 were prepared by following the synthetic methods in Ref. 48 for 1-3 and Ref. 47 for 4-6. The Suzuki and Sonogashira coupling reaction catalyzed by Pd(0) was used to connect bodipy and Phenylboronicacid (or 4-Formylphenylboronic acid) in B-1, B-3, B-5, compound 7, 10 and 11, respectively. The Prato reaction of compound 7, 10, 11 and sarcosine with C_{60} produced the C_{60}-Bodipy dyads of B-2, B-4, B-6. All the compounds were synthesized with a good yield. Their molecular structures of compounds were verified by ^{1}H NMR spectroscopy and high-resolution mass spectra.

Compound B-1. Compound 2 (180.0 mg, 0.4 mmol), Phenylboronic acid (194.0 mg, 1.6 mmol) and Potassium carbonate (167.2 mg, 1.2 mmol) were added in a dry three-necked flask. Toluene/ethanol/water (2/2/1, v/v/v, 100 ml) add the flask with stirring and argon was bubbled through the solution for 25 min. $Pd(PPh_3)_4$ (54.6 mg, 0.09 mmol) was added under argon condition. The reaction solution was heated at reflux (about 90ºC) under argon for 10 h. After removal of the solvent under reduced pressure, the residual solid was purified by Column chromatography (silica gel. CH_2Cl_2/ Petroleum ether (30-60 ºC) = 3/2, v/v) to give an Orange-red solid (140.1 mg, 81.7%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 7.2 Hz, 3H), 7.37 (t, J = 7.3 Hz, 2H), 7.34 – 7.27 (m, 3H), 7.14 (d, J = 6.9 Hz, 2H), 6.00 (s, 1H), 2.55 (d, J = 25.6 Hz, 6H), 1.39 (s, 3H), 1.29 (s, 3H).

Compound 7. Synthesis procedure is similar to that of B-1. Compound 2 (225.0 mg, 0.5 mmol), Na_2CO_3 (210 mg, 1.5 mmol) and 4-Formylphenylboronic acid (225.0 mg, 1.5 mmol) were added in a three-necked flask. Toluene/ethanol/water (2/2/1, v/v/v, 100 ml) add the flask with stirring and argon was bubbled through the solution for 25min. $Pd(PPh_3)_4$ (100.0 mg, 0.18 mmol) was added under argon condition. The reaction solution was heated at reflux (about 90 ºC) under argon for 10 h. After removal of the solvent under reduced pressure, the residual solid was purified by Column chromatography (silica gel. CH_2Cl_2/ Petroleum ether (30-60ºC) = 2/1, v/v) to give a Orange solid (177.6 mg, 83.0%).^{1}H NMR (400 MHz, $CDCl_2$): δ 10.02 (s, 1H), 7.89 (d, J = 8.5 Hz, 2H), 7.50 (d, J = 7.2 Hz, 3H), 7.33 (d, J = 8.1 Hz, 4H), 6.05 (s, 1H), 2.60 (s, 3H), 2.54 (s, 3H), 1.40 (s, 3H), 1.31 (s, 4H).

Compound 8. Compound B-1 (120.0 mg, 0.28 mmol) was dissolved in CH_2Cl_2 (30 ml) and add NIS (63.0 mg, 0.28 mmol). The mixture was stirred at room temperature for 4 h. After removal of the solvent under reduced pressure, the residual solid was purified by Column chromatography (silica gel. CH_2Cl_2/ Petroleum ether (30-60 ºC) = 3/1, v/v) to give a red solid (142.9 mg, 92.1%).

Compound 9. Synthesis procedure is similar to that of compound 8. Compound 7 (107.0 mg, 0.25 mmol) was dissolved in CH_2Cl_2 (30 ml) and add NIS (60.0 mg, 0.26 mmol). The mixture was stirred at room temperature for 4 h. After removal of the

solvent under reduced pressure, the residual solid was purified by Column chromatography (silica gel. CH_2Cl_2/ Petroleum ether (30-60ºC) = 3/1, v/v) to give a red solid (131.8 mg, 94.8%).^{1}H NMR (400 MHz, $CDCl_3$): δ 10.03 (s, 1H), 7.90 (dd, J = 8.4, 4.4 Hz, 2H), 7.51 (dd, J = 8.4, 6.2 Hz, 3H), 7.32 (t, J = 6.9 Hz, 4H), 2.68 (s, 2H), 2.60 (s, 1H), 2.54 (s, 3H), 1.41 (s, 3H), 1.31 (s, 3H).

Compound B-2. Under argon atmosphere, compound 7 (21.4 mg, 0.05 mmol), Sarcosine (14.0 mg, 0.16 mmol) and C_{60} (50.0 mg, 0.07 mmol) were suspended in dry toluene (70 mL). The solution was heated to 115℃, and refluxed for 18h with stirring. After cooled to room temperature, the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, CH_2Cl_2/ Petroleum ether (30-60 ºC) = 2/1, v/v) to give the product as a purple red solid (19.0 mg, 32.3%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, J = 5.9 Hz, 3H), 7.32 (d, J = 5.7 Hz, 4H), 7.22 (d, J = 8.7 Hz, 2H), 6.03 (s, 1H), 5.06 – 4.95 (m, 2H), 4.31 (d, J = 9.5 Hz, 1H), 2.89 (s, 3H), 2.60 (s, 3H), 2.50 (s, 3H), 1.46 (s, 3H), 1.40 (s, 3H). HRMS (MALDI): $[C_{88}H_{28}BF_2N_3]^-$, calculated *m/z* = 1175.24, found *m/z* = 1175.2477.

Compound B-3. Compound 3 (57.6 mg, 0.1 mmol), Phenylboronic acid (74.6 mg, 0.6 mmol) and Potassium carbonate (84.0 mg, 0.6 mmol) were added in a dry three-necked flask. Toluene/ethanol/water (2/2/1, v/v/v, 50 ml) add the flask with stirring and argon was bubbled through the solution for 25min. $Pd(PPh_3)_4$ (18.2 mg, 0.03 mmol) was added under argon condition. The reaction solution was heated at reflux (about 90 ºC) under argon for 10 h. After removal of the solvent under reduced pressure, the residual solid was purified by Column chromatography (silica gel. CH_2Cl_2/ Petroleum ether (30-60 ºC) = 2/1, v/v) to give an Orange-red solid (35.7 mg, 75.5%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 7.3 Hz, 3H), 7.38 (t, J = 7.3 Hz, 6H), 7.31 (d, J = 8.8 Hz, 2H), 7.16 (d, J = 6.9 Hz, 4H), 2.54 (s, 6H), 1.31 (s, 6H).

Compound 10. Synthesis procedure is similar to that of B-1. Compound 9 (26.3 mg, 0.05 mmol), Phenylboronic acid (24.3 mg, 0.2 mmol) and Potassium carbonate (26.2 mg, 0.2 mmol) were added in a dry three-necked flask. Toluene/ethanol/water (2/2/1, v/v/v, 50 ml) add the flask with stirring and argon was bubbled through the

solution for 25min. $Pd(PPh_3)_4$ (9.1 mg, 0.015 mmol) was added under argon condition. The reaction solution was heated at reflux (about 90ºC) under argon for 10 h. After removal of the solvent under reduced pressure, the residual solid was purified by Column chromatography (silica gel. CH_2Cl_2/ Petroleum ether (30-60ºC) = 3/2, v/v) to give a Orange-red solid (22.2 mg, 88.0%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.03 (s, 1H), 7.90 (s, 2H), 7.51 (d, J = 7.6 Hz, 3H), 7.37 (dd, J = 14.0, 8.3 Hz, 7H), 7.16 (d, J = 6.9 Hz, 2H), 2.56 (s, 6H), 1.33 (s, 6H).

Compound B-4. Under argon atmosphere, compound 10 (20 mg, 0.04 mmol), Sarcosine (15.1 mg, 0.17 mmol) and C_{60} (50.0 mg, 0.07 mmol) were suspended in dry toluene (50 mL). The solution was heated to 115ºC, and refluxed for 18 h with stirring. After cooled to room temperature, the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, ethyl acetate/ cyclohexane = 2/1, v/v) to give the product as a deep-red solid (19.0 mg, 37.9%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 2H), 7.47 (d, J = 6.9 Hz, 3H), 7.41 – 7.29 (m, 5H), 7.21 (d, J = 8.1 Hz, 2H), 7.15 (d, J = 7.1 Hz, 2H), 4.97 (s, 2H), 4.29 (d, J = 9.4 Hz, 1H), 2.86 (s, 3H), 2.51 (d, J = 11.4 Hz, 6H), 2.09 – 1.99 (m, 2H), 1.29 (s, 6H).

Compound B-5. Compound 8 (38.8 mg, 0.07 mmol) and Compound 6 (51.9 mg, 0.21 mmol) was added in a dry three-necked flask. Et_3N (30 ml) add the flask with stirring and argon was bubbled through the solution for 30 min. $PdCl_2(PPh_3)_2$ (14 mg, 0.07 mmol) , PPh3 (10.5 mg, 0.04 mmol) and CuI (7.6 mg, 0.04 mmol) was added under argon condition. The reaction solution was heated at reflux (about 80ºC) under argon for 5 h. After removal of the solvent under reduced pressure, the residual solid was purified by Column chromatography (silica gel. CH_2Cl_2/ Petroleum ether (30-60 ºC) = 2/1, v/v) to give a black crystalline solid (22.0 mg, 46.7%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 8.08 (d, J = 8.3 Hz, 1H), 7.59 – 7.45 (m, 5H), 7.38 (dd, J = 17.5, 6.1 Hz, 7H), 7.23 (d, J = 7.7 Hz, 1H), 7.15 (d, J = 8.3 Hz, 2H), 4.30 (t, J = 7.1 Hz, 2H), 2.78 (s, 3H), 2.55 (s, 3H), 1.90 – 1.80 (m, 2H), 1.57 (s, 3H), 1.41 (dd, J = 11.9, 6.3 Hz, 3H), 1.32 (s, 3H), 0.94 (t, J = 7.4 Hz, 3H).

Compound 11. Synthesis procedure similar to B-5. Compound 9 (26.3 mg, 0.05 mmol) and Compound 6 (49.8 mg, 0.20 mmol) was added in a dry three-necked flask.

Et_3N (30 ml) add the flask with stirring and argon was bubbled through the solution for 30 min. $PdCl_2(PPh_3)_2$ (10 mg, 0.05 mmol) , PPh3 (10.5 mg, 0.04 mmol) and CuI (7.6 mg, 0.04 mmol) was added under argon condition. The reaction solution was heated at reflux (about 80 ºC) under argon for 6 h. After removal of the solvent under reduced pressure, the residual solid was purified by Column chromatography (silica gel. CH_2Cl_2/ Petroleum ether (30-60 ºC) = 3/1, v/v) to give a black crystalline solid (29.3 mg, 87.1%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.03 (s, 1H), 8.21 (s, 1H), 8.07 (d, J = 7.4 Hz, 1H), 7.90 (d, J = 8.4 Hz, 2H), 7.58 – 7.50 (m, 4H), 7.46 (d, J = 8.2 Hz, 1H), 7.40 (d, J = 8.2 Hz, 1H), 7.37 – 7.31 (m, 5H), 7.23 (d, J = 6.9 Hz, 1H), 4.29 (t, J = 7.2 Hz, 2H), 2.80 (s, 3H), 2.56 (s, 3H), 1.85 (dt, J = 15.0, 7.4 Hz, 2H), 1.57 (d, J = 4.9 Hz, 6H), 1.39 (dd, J = 15.3, 7.5 Hz, 2H), 0.94 (t, J = 7.4 Hz, 3H).

Compound B-6. Under argon atmosphere, compound 11 (16.5 mg, 0.02 mmol), Methylaminoacetic Acid (9.0 mg, 0.10 mmol) and C_{60} (29.0 mg, 0.04 mmol) were suspended in dry toluene (50 mL). The solution was heated to 115ºC, and refluxed for 18 h with stirring. After cooled to room temperature, the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, CH_2Cl_2/ Petroleum ether (30-60ºC) = 3/1, v/v) to give the product as a Purple-black solid (12.0 mg, 34.6%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (s, 1H), 8.06 (d, J = 7.8 Hz, 1H), 7.84 (s, 2H), 7.51 (dd, J = 32.4, 10.9 Hz, 5H), 7.40 (d, J = 8.1 Hz, 1H), 7.33 (d, J = 8.6 Hz, 3H), 7.25 – 7.14 (m, 3H), 4.98 (d, J = 14.3 Hz, 2H), 4.29 (t, J = 7.3 Hz, 3H), 2.81 (d, J = 35.5 Hz, 6H), 2.50 (s, 3H), 1.90 – 1.79 (m, 2H), 1.55 (s, 3H), 1.42 (d, J = 5.0 Hz, 5H), 0.94 (t, J = 7.4 Hz, 3H). HRMS (MALDI): $[C_{106}H_{42}BF_2N_4]^-$, calculated *m/z* = 1420.36, found *m/z* = 1420.2697.

2. NMR and HR-MS spectra

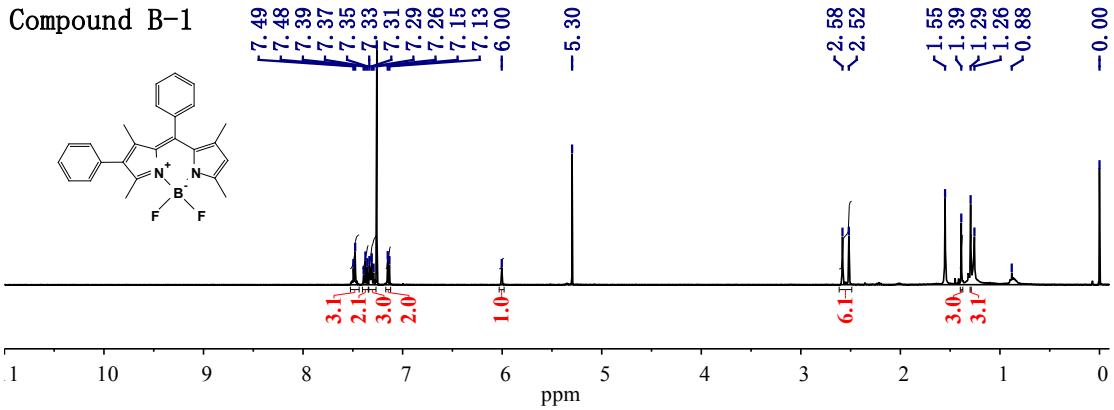


Figure S2.1 ^{1}H NMR of B-1 in $CDCl_3$ (400 MHz).

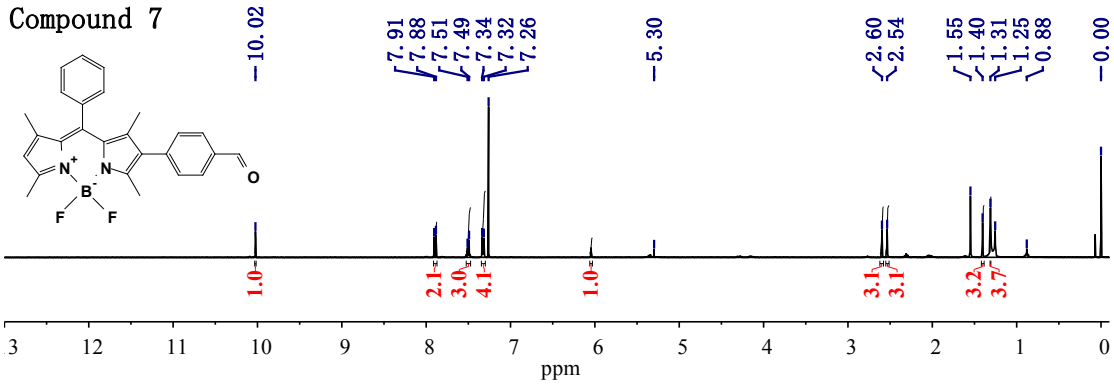


Figure S2.2 ^{1}H NMR of 7 in $CDCl_3$ (400 MHz).

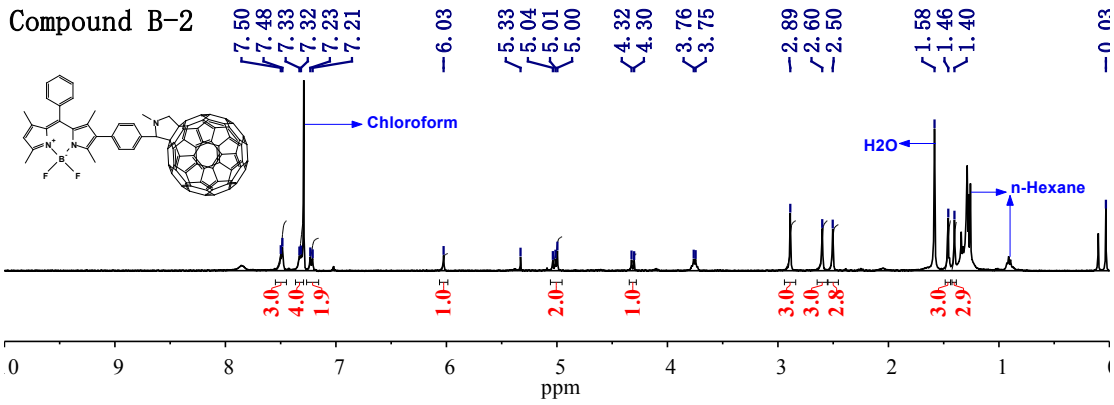


Figure S2.3 ^{1}H NMR of B-2 in $CDCl_3$ (400 MHz).

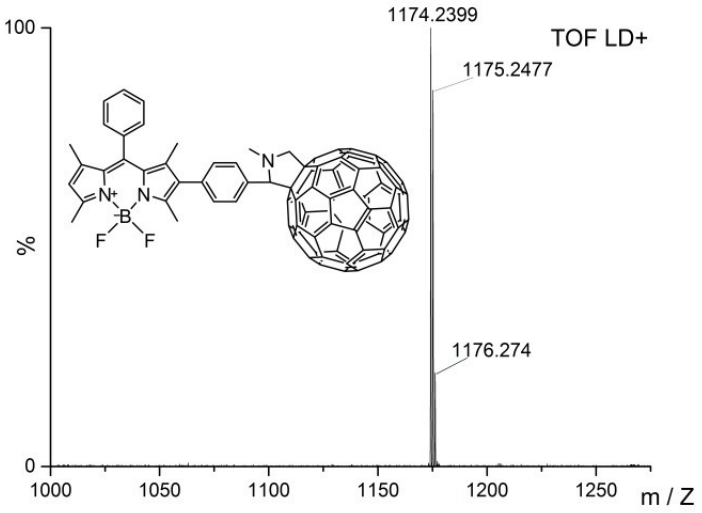


Figure S2.4 TOF MS LD+ of Compound **B-2**.

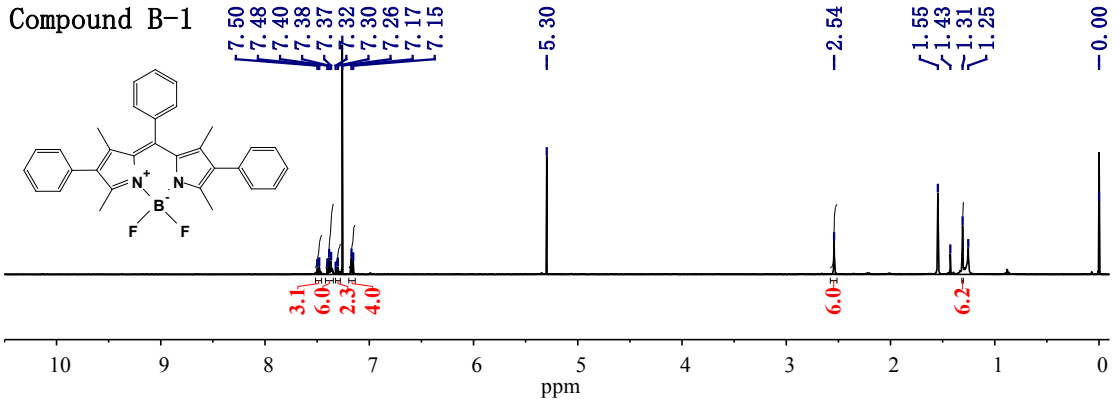


Figure S2.5 ^{1}H NMR of B-3 in $CDCl_3$ (400 MHz).

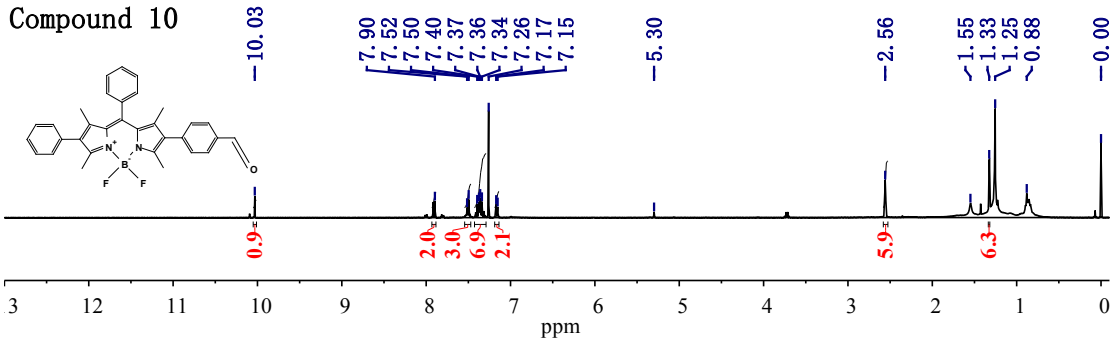


Figure S2.6 ^{1}H NMR of 10 in $CDCl_3$ (400 MHz).

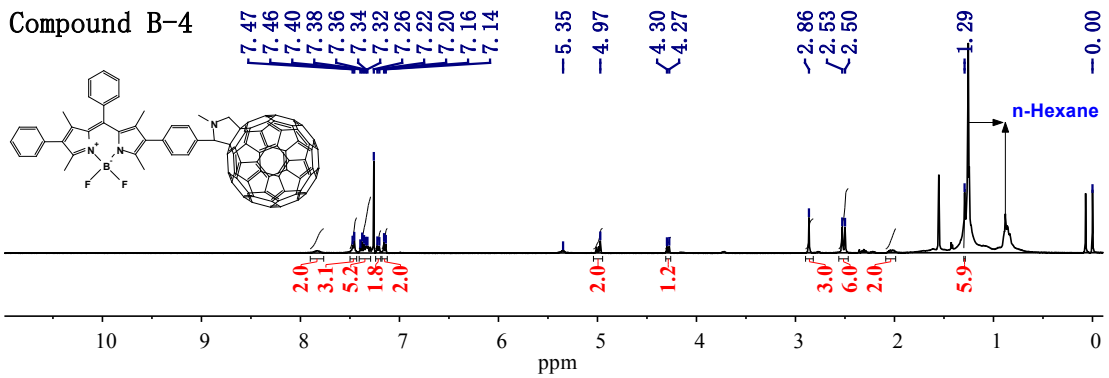


Figure S2.7 ^{1}H NMR of B-4 in $CDCl_3$ (400 MHz).

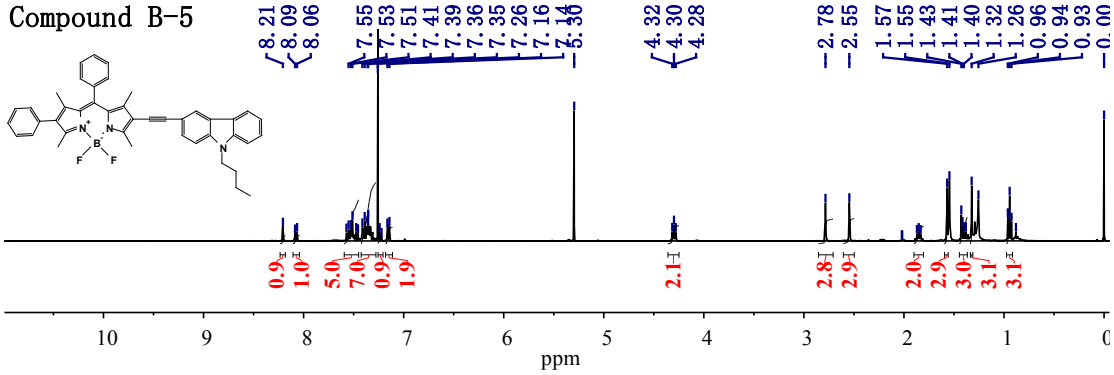


Figure S2.8 ^{1}H NMR of B-5 in $CDCl_3$ (400 MHz).

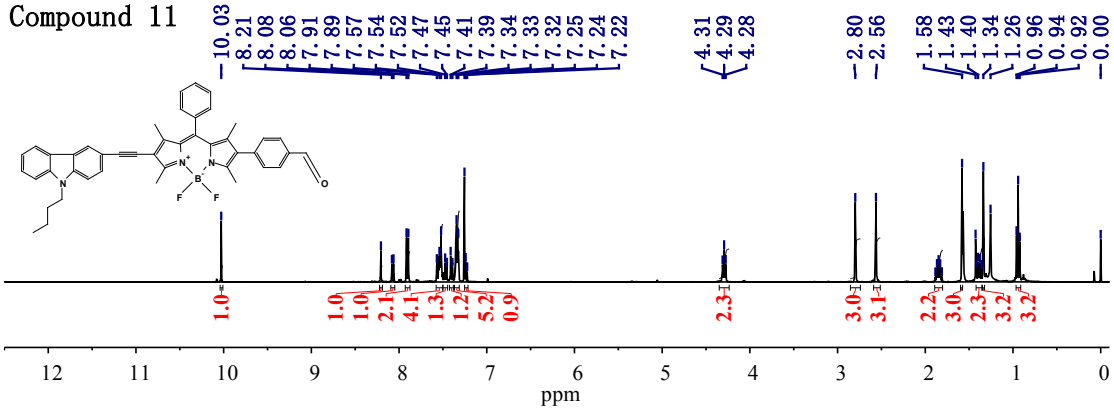


Figure S2.9 ^{1}H NMR of 11 in $CDCl_3$ (400 MHz).

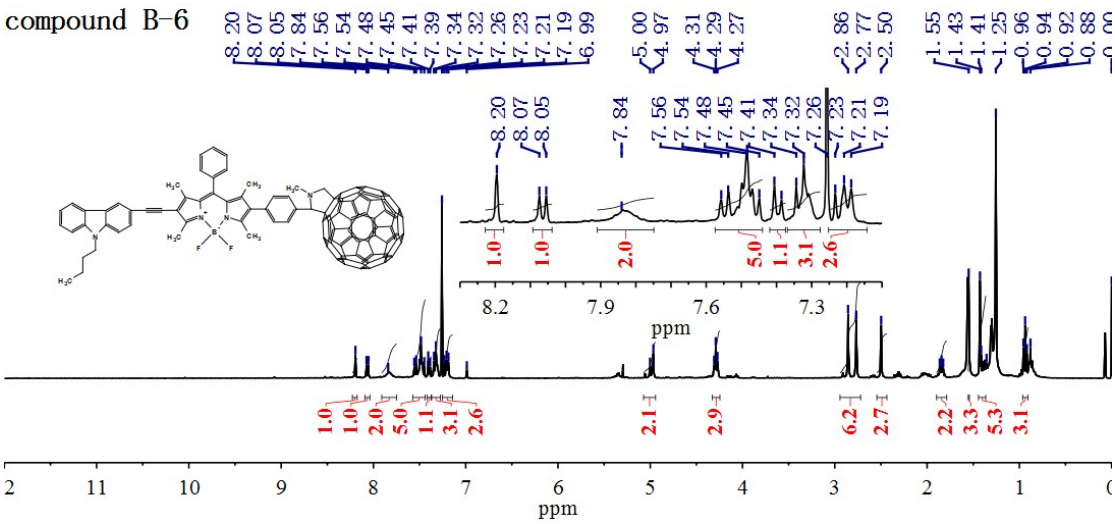


Figure S2.10 ^{1}H NMR of B-6 in $CDCl_3$ (400 MHz).

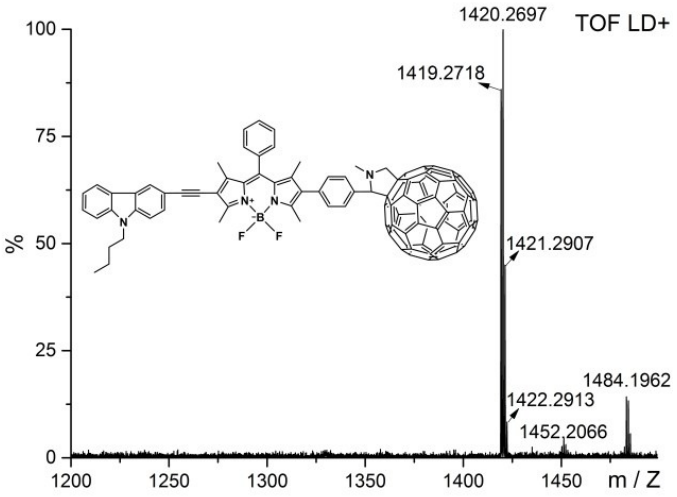


Figure S2.11 TOF MS LD+ of Compound **B-6**.

3. Femtosecond transient difference absorption spectra

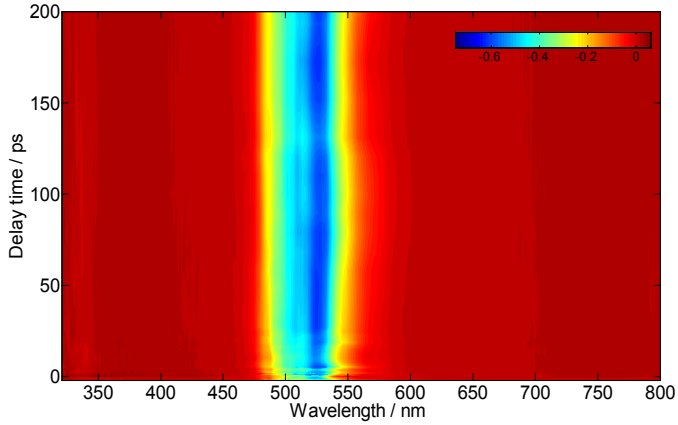


Figure S3.1 Femtosecond transient difference absorption spectra of B-2, in toluene, excited at 532 nm, 25ºC.

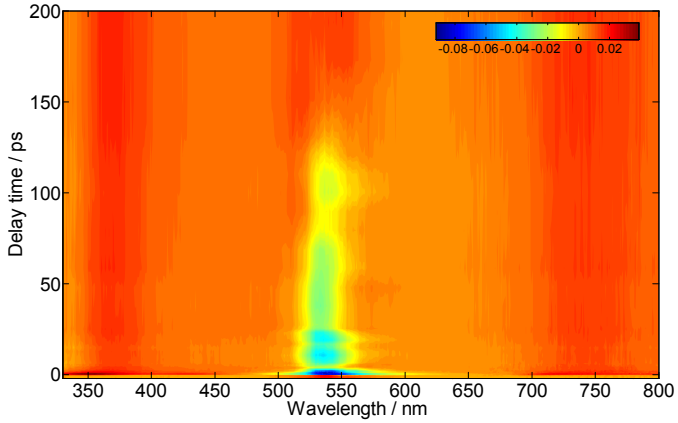


Figure S3.2 Femtosecond transient difference absorption spectra of B-4, in toluene, excited at 532 nm, 25ºC.

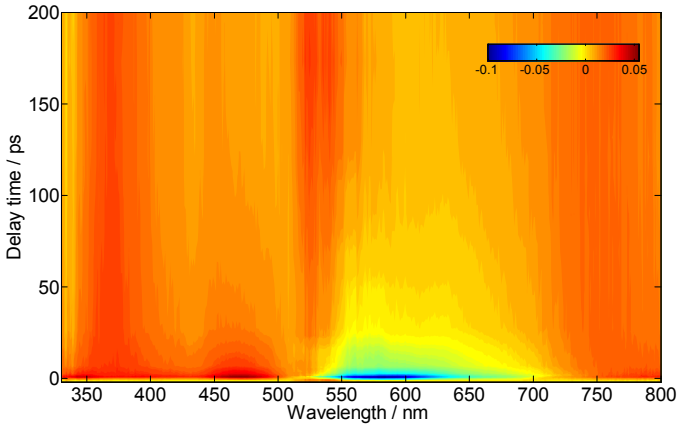


Figure S3.3 Femtosecond transient difference absorption spectra of B-6, in toluene, excited at 532 nm, 25ºC.

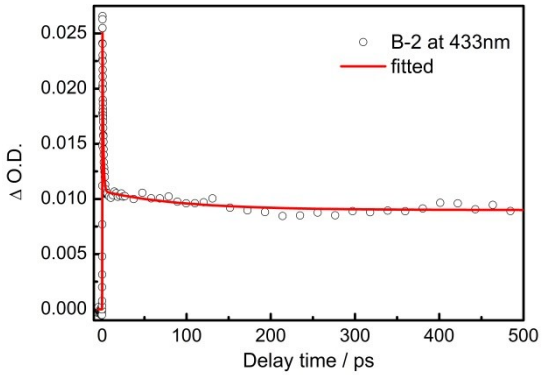


Figure S3.4 The experimental (dotted lines) and fitted (solid lines) decay curves of the absorption band for B-2 at 433 nm, in toluene, excited at 532 nm, 25ºC.

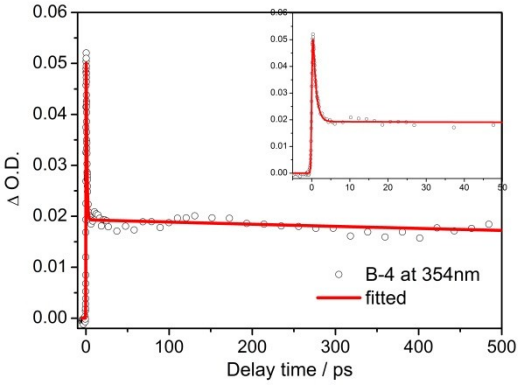


Figure S3.5 The experimental (dotted lines) and fitted (solid lines) decay curves of the absorption band for B-4 at 354 nm, in toluene, excited at 532 nm, 25 ºC.

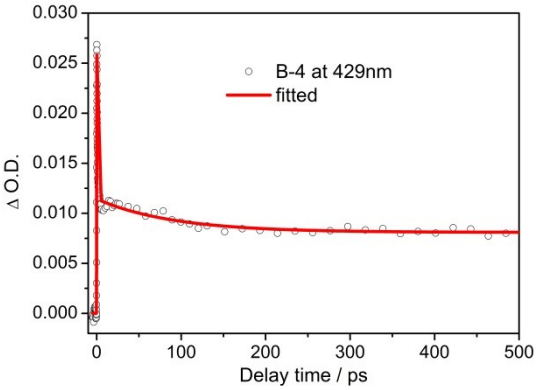


Figure S3.6 The experimental (dotted lines) and fitted (solid lines) decay curves of the absorption band for B-4 at 429 nm, in toluene, excited at 532 nm, 25ºC.

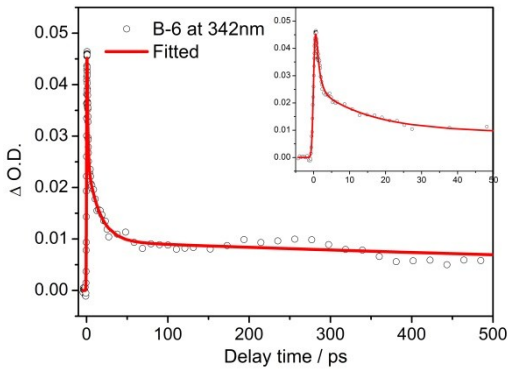


Figure S3.7 The experimental (dotted lines) and fitted (solid lines) decay curves of the absorption band for B-6 at 342 nm, in toluene, excited at 532 nm, 25ºC.

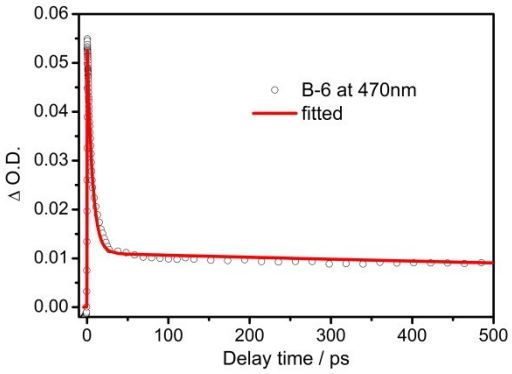


Figure S3.8 The experimental (dotted lines) and fitted (solid lines) decay curves of the absorption band for B-6 at 470 nm, in toluene, excited at 532 nm, 25 ºC.

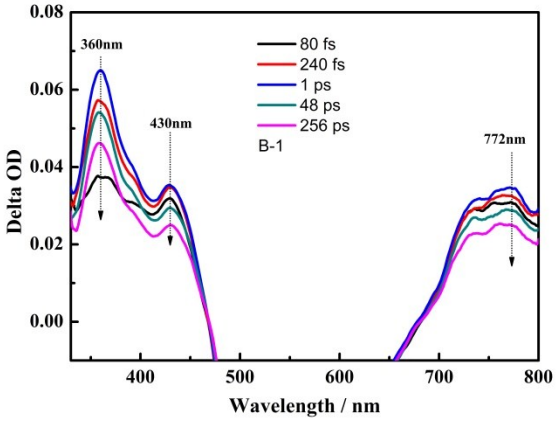


Figure S3.9 Femtosecond transient difference absorption spectra of B-1, in toluene, excited at 532 nm, 25ºC.

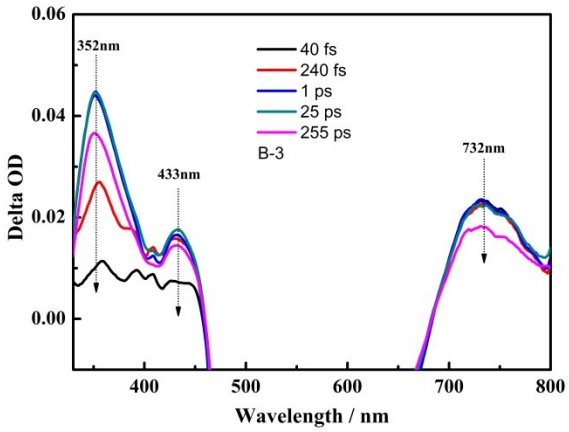


Figure S3.10 Femtosecond transient difference absorption spectra of B-3, in toluene, excited at 532 nm, 25ºC.

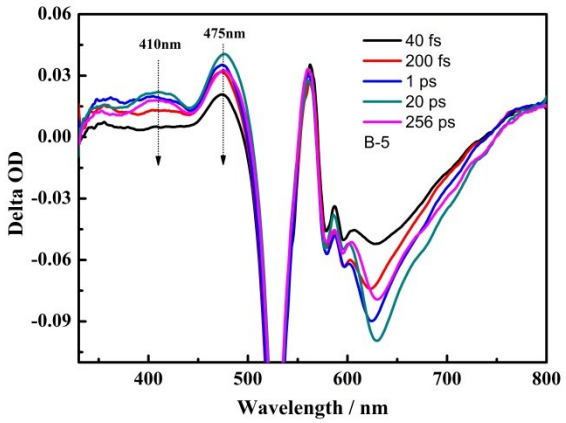


Figure S3.11 Femtosecond transient difference absorption spectra of B-5, in toluene, excited at 532 nm, 25ºC.

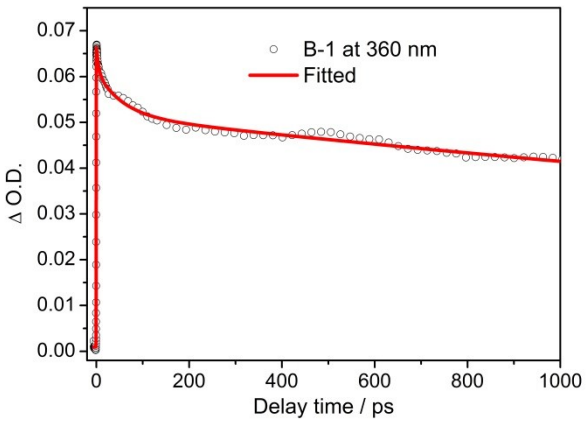


Figure S3.12 The experimental (dotted lines) and fitted (solid lines) decay curves of the absorption band for B-1 at 360 nm, in toluene, excited at 532 nm, 25 ºC.

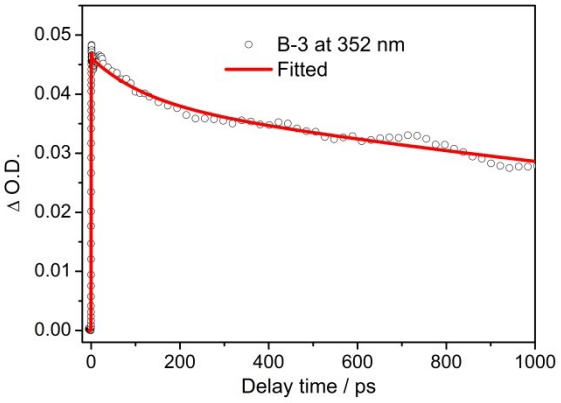


Figure S3.13 The experimental (dotted lines) and fitted (solid lines) decay curves of the absorption band for B-3 at 352 nm, in toluene, excited at 532 nm, 25 ºC.

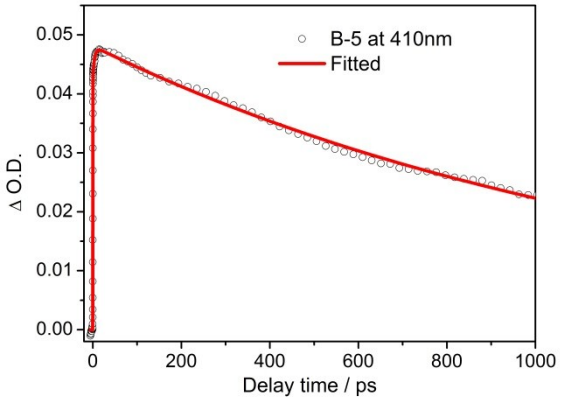


Figure S3.14 The experimental (dotted lines) and fitted (solid lines) decay curves of the absorption band for B-5 at 410 nm, in toluene, excited at 532 nm, 25 ºC.

4. TTA-UC Spectra

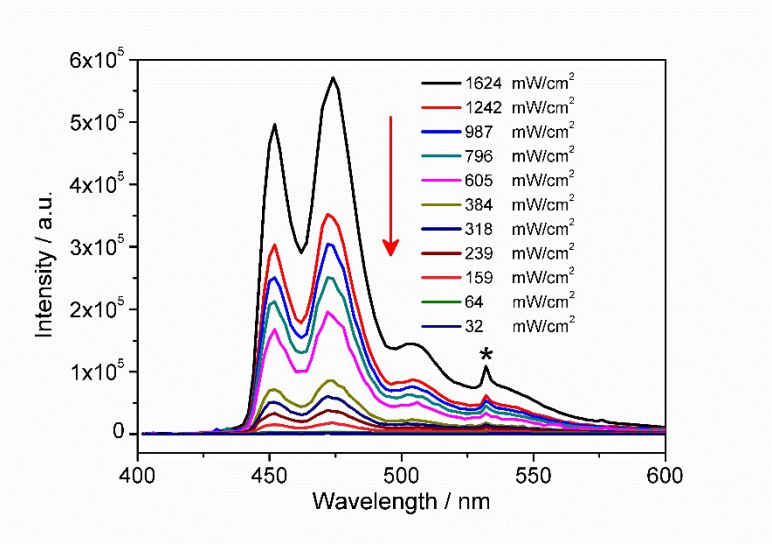


Figure S4.1 The upconverted emission intensity of B-2 and perylene dependence on the excitation power density. c[B-2]=5×10^{-6} M, c[perylene]=3×10^{-4} M, in toluene, excited at 532 nm, 25ºC.

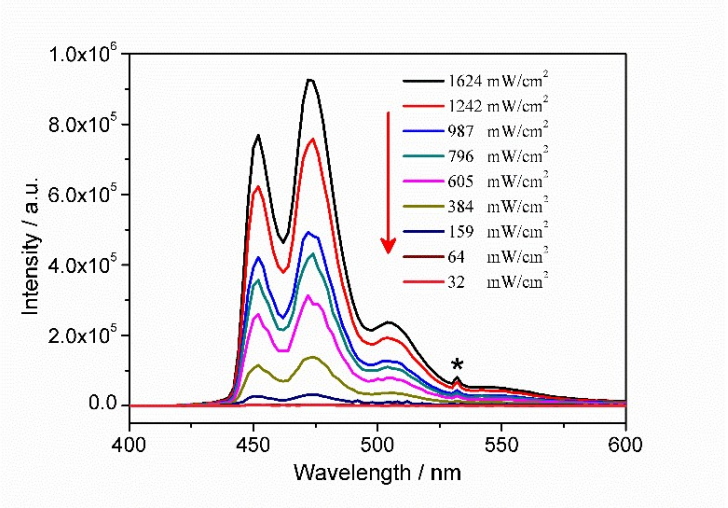


Figure S4.2 The upconverted emission intensity of B-4 and perylene dependence on the excitation power density. c[B-4]=5×10^{-6} M, c[perylene]=3×10^{-4} M, in toluene, excited at 532 nm, 25ºC.

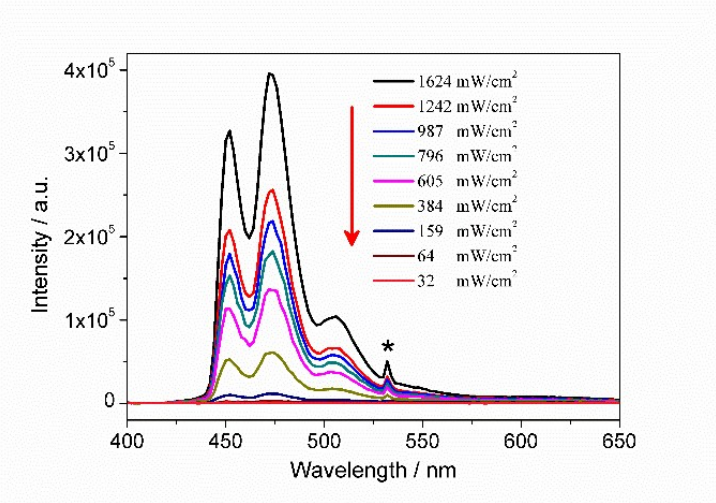


Figure S4.3 The upconverted emission intensity of B-6 and perylene dependence on the excitation power density. c[Photosensitizer]=5×10^{-6} M, c[annihilator]=3×10^{-4} M annihilator, in toluene, excited at 532 nm, 25ºC.