Electronic Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Highly Efficient Photosensitizers with Aggregation-Induced Emission Characteristics by Precise Molecular Design

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Materials and Methods

Materials and Instruments: THF was distilled from sodium benzophenone ketyl under dry nitrogen immediately prior to use. 4-Bromobenzophenone, 4,4'-dimethoxybenzophenone, 4-acetylphenylboronic acid, 4-aceyle-5-bromothiophene, malononitrile, 4-bromoiodobenzene, 2-thiophenecarbonyl chloride and other chemicals and reagents for the synthesis were purchased from Sigma-Aldrich and J&K Scientific Ltd., and used as received without any further purification. Fluorescein diacetate (FDA) were purchased from Invitrogen. NMR spectra were recorded on a Bruker ARX 400 NMR spectrometer. Chemical shifts are recorded in parts per million referenced according to residual solvent ($CDCl_3$ = 7.26 ppm and $(CD_3)_2SO$ = 2.50 ppm) in ^1H NMR and ($CDCl_3$ = 77.0 ppm and $(CD_3)_2SO$ = 40.0 ppm) in ^{13}C NMR. Mass spectra of synthetic small molecules were reported on the AmaZon X LC-MS for ESI. Mass spectra for proteomic study were recorded on a Finnigan LCQ mass spectrometer. UV-vis absorption spectra were obtained on a Shimadzu Model UV-1700 spectrometer. Photoluminescence (PL) spectra were measured on a Perkin-Elmer LS 55 spectrofluorometer. All UV and PL spectra were collected at 24 ± 1 °C.

Computational Details: The ground state of all TPE and **TP1-8** were fully optimized by the hybrid B3LYP, in combination with 6-31G (d) basis set. The excited-state characteristics were calculated by the time-dependent density functional theory (TD-DFT) using optimized ground state geometries. TD-DFT in combination with the B3LYP hybrid functional method and the 6-31G (d) basis set has been shown to provide accurate energies for excited-state of D-A molecular system with less than 0.1 eV error.[1-2]

Synthesis of cRGD-TP4 NPs and cRGD-TP8 NPs: cRGD-TP4 NPs and **cRGD-TP8 NPs** were prepared following our previous method.[3] DSPE-PEG-Mal (1.0 mg) and **TP4** (or **TP8**) (0.5 mg) in THF solution (1 mL) was poured into water (10 mL) and sonicated for 2 min with a microtip probe sonicator at 12 W output. The organic solvent was removed by stirring the mixture at room temperature to yield NPs. Then, 3.6 μL of thiol-functionalized cRGD (0.1 M in DMSO) was added into the NP solution. The mixtures were stirred overnight at room temperature. The obtained solutions were dialyzed by 12000−14000 kDa before use.

Cell culture: MDA-MB-231 breast cancer cells and NIH/3T3 mouse cells were cultured in the 8-well confocal-imaging chambers in Dulbecco's modified Eagle's medium (DMEM) containing 10% Foetal Bovine Serum (FBS) and 1% PenStrep (PS) in a humidified environment containing 5% CO_2 at 37 °C. The cells were precultured to reach confluence before experiments. When reaching 80% confluence, the culture medium was removed and the adherent cells were washed by 1 × PBS buffer twice.

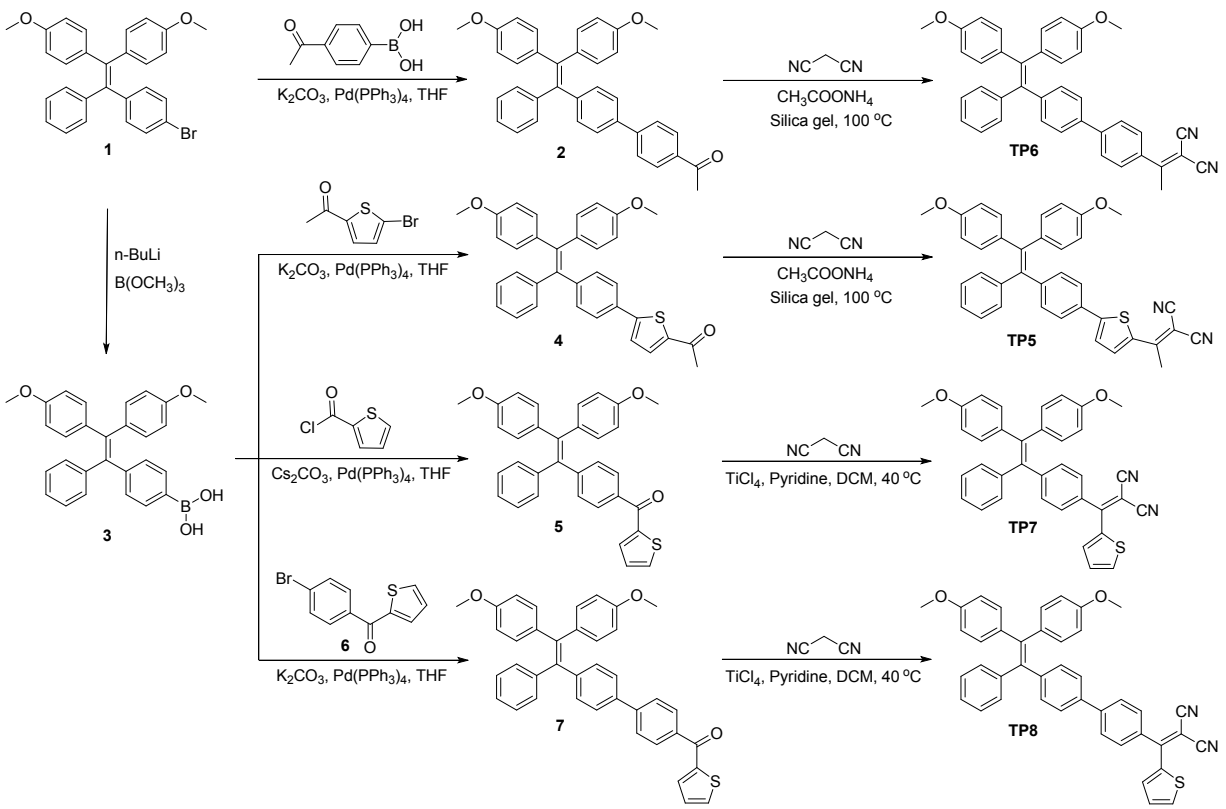
Cellular imaging: The cells were cultured in 8-well chambers at 37 °C and pre-cultured overnight. The culture medium was then removed and the cells were washed with 1 × PBS before incubation with the **c-RGD-TP8 NPs** (3 μg mL^{-1}). Confocal laser scanning microscope (CLSM, Zeiss LSM 410, Jena, Germany) was used to image the cells. The intracellular ROS generation upon light irradiation was studied using a cell permeable indicator 2',7' -dichlorodihydrofluorescein diacetate (DCF-DA, Ex: 488 nm. Em: 505–525 nm).

Live Cell Staining: The cells were cultured in 8-well chamber. After 80% confluence, the cells were treated with **c-RGD-TP8 NPs** (8 μg mL^{-1}) suspended cell culture medium for 2 h. The cells were then washed twice with 1× PBS buffer, and the selected wells were then exposed to white light irradiation (0.25 W cm^{-2}) for 10 min. After light treatment, the cells were further incubated with FDA (100 μg/mL) for 10 min to staining alive cells. After twice washing with buffer, the cells were imaged by CLSM.

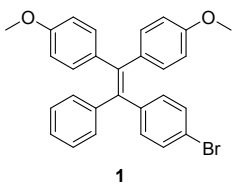
Cytotoxicity studies: To assess the metabolic activity of the cells, 3-(4,5-dimethythiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) assays was used. After incubating the cells in DMEM medium overnight, the medium was removed and the cells were incubated with **c-RGD-TP4 NPs** (or **c-RGD-TP8 NPs**) for 6 hours. The medium was then replaced with the fresh one and the cells were shined with a white light. After that, the cells were incubated for 24 hours and further washed with 1 × PBS before adding 100 μL of MTT solution (0.5 mg mL^{-1}) into each well. The cells were further incubated for 3 more hours. Then MTT solution was removed and DMSO (100 μL) was added into each well. A microplate reader (Genios Tecan) was used to study the absorbance of MTT at 570 nm. The cells without any treatment were used as the control.

Synthesis and characterization

TP1-4 were synthesized according to the previous reports.[4-5] The synthetic routes to **TP5-8** are shown in Scheme S1.

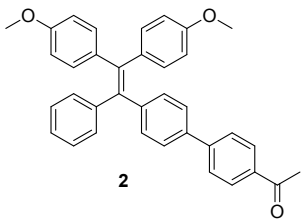


Scheme S1. Synthetic route towards **TP5-8**.



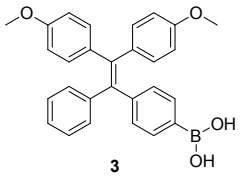
Synthesis of 1. To the solution of 4-bromobenzophenone (5.3 g, 20.3 mmol) and 4,4'-dimethoxybenzophenone (3.8 g, 15.7 mmol) in dry THF (80 mL) was added zinc powder (5.9 g, 90.8 mmol). Then the suspension was cooled down to −78 °C. Titanium tetrachloride (5.0 ml) was added to the above mixture dropwise. After addition, the mixture was slowly warmed up to room temperature, followed by refluxing for 8 hours. Then the mixture was cooled down in ice-water bath and saturated sodium bicarbonate aqueous solution (50 mL) was added slowly. The mixture was extracted with ethyl acetate (100 mL × 3). The combined organic phase was washed with brine (100 mL × 2), and dried over $MgSO_4$. Then the mixture was filtered and the filtrate was concentrated under reduced pressure. The desired residue was purified with chromatography (hexane/ethyl acetate = 100/1 to 30/1, v/v) to give the desired product as a yellow solid (3.1 g, 41.8% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, J = 8.0 Hz, 2H), 7.10 (m, 3H), 7.00 (m, 2H), 6.87-6.94

(m, 6H), 6.67 (d, J = 8.8 Hz, 2H), 6.63 (d, J = 8.8 Hz, 2H), 3.76 (s, 3H), 3.73 (3, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 158.0, 143.8, 143.1, 140.9, 137.8, 136.1, 135.9, 133.0, 132.5, 131.3, 130.8, 127.7, 126.2, 113.2, 113.0, 55.0. MS (EI) calcd for $[M]^+$:470.09, found: 470.30.



2

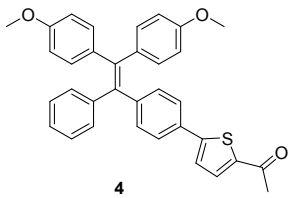
Synthesis of 2. 4-acetylphenylboronic acid (1.04g, 6.36 mmol) and **1** (2.00g, 4.24 mmol) were dissolved in THF (20.0 mL), and then 2 M aqueous K_2CO_3 solution (4.0 mL) and Aliquat 336 were added. The mixture was stirred for 40 min under an argon atmosphere at room temperature. Then the $Pd(PPh_3)_4$ catalyst was added and the reaction mixture was stirred at 75 °C for 16 h. After cooling to room temperature, the mixture was extracted with ethyl acetate (50 mL × 3). The combined organic phase was concentrated and purified by silica gel column chromatography (hexane/ethyl acetate = 40/1-5/1, v/v). The product was dried under vacuum to afford compound **2** as a yellow solid (1.80 g, 83.0% yield).^{1}H NMR (400 MHz, CDCl3) δ 7.92 (d, J = 8.3 Hz, 2H), 7.58 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.3 Hz, 2H), 7.09 – 6.96 (m, 6H), 6.89 (dd, J = 15.0, 8.7 Hz, 4H), 6.58 (t, J = 8.6 Hz, 4H), 3.67 (s, 6H), 2.55 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 158.2, 158.1, 145.2, 144.5, 144.1, 140.7, 138.4, 137.0, 136.1, 135.6, 132.5, 131.9, 131.4, 128.9, 128.8, 127.7, 127.4, 126.8, 126.3, 126.2, 113.1, 113.0, 77.3, 77.0, 76.7, 55.0, 55.0, 26.6, 26.5. EI-MS, m/z: $[M+1]^+$ calcd 510.2, found 510.5. MS (EI) calcd for $[M]^+$:510.22, found: 510.30.



3

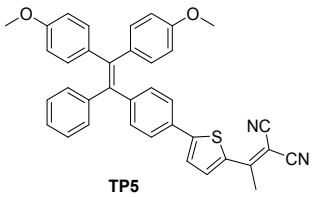
Synthesis of 3: To the solution of compound **1** (7.7 g, 16.3 mmol) in THF (150 mL) was added n-butyllithium (1.6 M in hexane, 16.0 mL) at −78 °C. The mixture was stirred at the same temperature for 2 h, before trimethyl borate (3.8 mL, 33.4 mmol) was added. The reaction mixture was then allowed to warm up and stirred at room temperature for 3 h. The reaction was quenched by addition of HCl solution (3 M, 45 mL) and the resulting solution was stirred at room temperature for 5 h. Then the mixture was diluted with ethyl

acetate (100 mL) and brine (200 mL). The organic phase was separated, washed with brine (100 mL × 2), and dried over $MgSO_4$. The mixture was filtered and the filtrate was concentrated under reduced pressure. The desired residue was subjected to flash chromatography (hexane/ethyl acetate = 10/1 to 2/1, v/v) to yield compound **3** as a white solid (2.9 g, 40.8% yield), which was used directly in the next step without further purification.



4

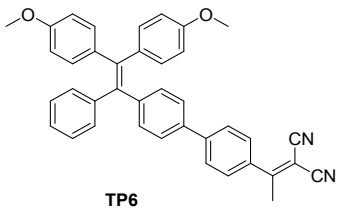
Synthesis of 4: 4-aceyle-5-bromothiophene (246.0 mg, 1.20 mmol) and **3** (500.0 mg, 0.96 mmol) were dissolved in THF (8.0 mL), and then 2 M aqueous K_2CO_3 solution (1.0 mL) and Aliquat 336 were added. The mixture was stirred for 40 min under an argon atmosphere at room temperature. Then the $Pd(PPh_3)_4$ catalyst was added and the reaction mixture was stirred at 75 ^oC for 16 h. After cooling to room temperature, the mixture was extracted with ethyl acetate (50 mL × 3). ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 3.8 Hz, 1H), 7.34 (m, 2H), 7.29-7.26 (m, 1H), 7.01 (dd, J = 26.6, 7.6 Hz, 7H), 6.91 – 6.84 (m, 4H), 6.60 – 6.54 (m, 4H), 3.68 – 3.65 (m, 6H), 2.59 (s, 3H). MS (EI) calcd for $[M]^+$: 516.18, found 516.30.



TP5

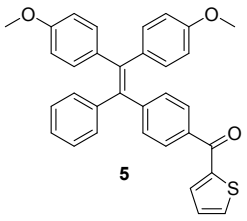
Synthesis of TP5: 4 (92.3 mg, 0.18 mmol), malononitrile (100 mg, 1.50 mmol) and ammonium acetate (139 mg, 1.80 mmol) were dissolved in a mixture of dichloromethane (20 mL) and methanol (4 mL). Then silica gel (2.0 g) was added to the above mixture, and the solvent was removed under reduced pressure. The resulting mixture was heated at 100 ^oC for 4 h. The mixture was cooled down and subsequently separated with chromatography (hexane/ethyl acetate = 8/1, v/v) to give the desired product as a orange powder (74 mg, 73.6% yield).^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 4.2 Hz, 1H), 7.36 – 7.31 (m, 2H), 7.28 (d, J = 4.3 Hz, 1H), 7.07 – 6.94 (m, 7H), 6.91 – 6.84 (m, 4H), 6.61 – 6.55 (m, 4H), 3.69 – 3.66 (m, 6H), 2.60 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.153, 29.701, 55.108, 55.137, 113.063, 113.276, 113.990, 114.486, 124.582, 125.708, 126.428, 127.902, 129.745, 131.409, 132.294, 132.600, 132.637, 135.196, 135.952,

136.393, 138.069, 141.514, 143.767, 146.460, 154.082, 158.326, 158.465, 161.548. EI-MS, m/z: $[M]^+$ calcd 564.19, found 565.20.



TP6

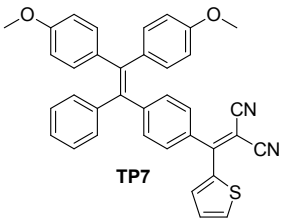
Synthesis of TP6: 2 (100 mg, 0.18 mmol), malononitrile (100 mg, 1.50 mmol) and ammonium acetate (139 mg, 1.80 mmol) were dissolved in a mixture of dichloromethane (20 mL) and methanol (4 mL). Then silica gel (2.4 g) was added to the above mixture, and the solvent was removed under reduced pressure. The resulting mixture was heated at 100 ^oC for 4 h. The mixture was cooled down and subsequently separated with chromatography (hexane/ethyl acetate = 20/1, v/v) to give the desired product as a yellow powder (74 mg, 73.6% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.50 (m, 4H), 7.31 (d, J = 8.4 Hz, 2H), 7.11–6.95 (m, 7H), 6.92–6.80 (m, 4H), 6.65–6.49 (m, 4H), 3.67 (d, J = 0.7 Hz, 6H), 2.59 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 158.30, 158.2, 144.8, 144.8, 144.0, 140.9, 138.4, 136.4, 136.1, 134.2, 132.6, 132.5, 132.0,131.4,128.0, 127.8, 127.2,126.3, 113.1, 113.0, 112.9, 83.8, 77.3, 77.0, 76.7, 60.3, 55.0, 55.0, 23.9, 21.0, 14.1; EI-MS, m/z: $[M]^+$ calcd.558.23, found 558.50.



5

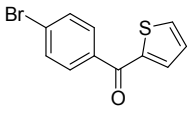
Synthesis of 5: To the suspension of compound **3** (2.9 g, 6.5 mmol) in toluene (80 mL) was added anhydrous cesium carbonate (5.3 g, 16.2 mmol) and $Pd(PPh_3)_4$ (228 mg, 0.32 mmol). Thiophene-2-carbonyl chloride (2.0 g, 13.6 mmol) was added to the above mixture. Then the mixture was stirred at 100 ^oC for 12 h. After it was cooled down to room temperature, the mixture was washed with water (50 mL) and brine (50 mL). The organic layer was dried over $MgSO_4$, filtered and the filtrate was concentrated and purified by chromatography (hexane/ethyl acetate = 50/1 to 10/1) to give the desired product as an orange solid (2.8 g, 85.8% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, J_1 = 1.2 Hz, J_2 = 4.8 Hz, 1H), 7.64 (m, 2H), 7.60 (dd, J_1 = 1.2 Hz, J_2 = 4.0 Hz, 1H), 7.11-7.15 (m, 6H), 7.05 (m, 2H), 6.94-6.97 (m, 4H), 6.63-6.67 (m, 4H), 3.75 (s, 3H), 3.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.0, 158.4, 158.3, 143.7, 143.6, 141.8, 138.1, 135.8,

135.7, 135.4, 134.3, 133.7, 132.6, 132.5, 131.4, 131.3, 128.8, 127.8, 127.7, 126.4, 113.2, 113.0, 55.1, 55.0; HRMS (EI) calcd for $[M]^+$: 502.1603, found: 502.1605.



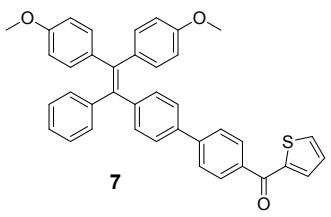
TP7

Synthesis of TP7: To the solution of compound **5** (0.26 g, 0.52 mmol) and malononitrile (45 mg, 0.68 mmol) in dichloromethane (10 mL) was added titanium tetrachloride (0.20 mL, 1.8 mmol) slowly at 0°C. After the reaction mixture was stirred for 30 min, pyridine (0.15 mL, 1.8 mmol) was injected and stirred for another 30 min. Then the mixture was heated at 40 °C for 4h. After the mixture was cooled down to room temperature, the reaction was quenched by water (10 mL) and the mixture was extracted with dichloromethane. The collected organic layer was washed by brine (20 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The desired residue was purified by column chromatography (hexane/ethyl acetate = 50/1 to 10/1, v/v) to give the desired product as a red solid (230 mg, 81.0% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, J_1 = 1.2 Hz, J_2 = 5.2 Hz, 1H), 7.73 (dd, J_1 = 1.2 Hz, J_2 = 5.2 Hz, 1H), 7.13-7.22 (m, 8H), 7.06 (m, 2H), 8.91-8.98 (m, 4H), 8.64-8.68 (m, 4H), 3.75 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 158.6, 158.4, 148.7, 143.2, 142.4, 138.7, 137.7, 136.1, 135.7, 135.5, 133.5, 132.6, 132.5, 131.5, 131.3, 129.1, 128.8, 127.9, 126.5, 114.5, 113.8, 113.2, 113.0, 55.1, 55.0. MS (EI) calcd for $[M]^+$: 550.1709, found: 550.1708.



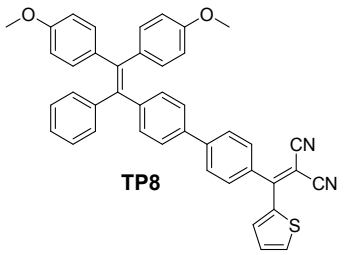
6

Synthesis of 6: A solution of *i*-PrMgCl (30.0 mmol) in THF (15 mL) was added dropwise to 4-bromoiodobenzene (10.0 mmol, 2.83 g) in THF (160 mL) under N_2 at −78 °C. The mixture was stirred at -78 °C for 3 h. A solution of CuCN·2LiCl (11 mmol) in THF (20 mL) and 2-thiophenecarbonyl chloride (4.7 g, 22.0 mmol) were added successively at −78 °C. The mixture was warmed to room temperature overnight. After hydrolysis with saturated NH_4Cl, the mixture was extracted with CH_2Cl_2 (3 × 150 mL). The combined organic layers were dried over Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by chromatography using n-hexane/dichloromethane (3/1, v/v) as eluent to yield **6** as yellow powder.



7

Synthesis of 7: To the previous yellow powder, **3** (87.3 mg, 0.20 mmol), potassium carbonate (276 mg, 2.0 mmol), THF (6 mL), water (2 mL) and $Pd(PPh_3)_4$ (3 mol%) were added under N_2 protection. Then the reaction mixture was stirred at 60 °C for 18 h. After cooling to ambient temperature, the reaction was stopped by addition of water, extracted with dichloromethane and washed with brine. The organic layer was dried over anhydrous Na_2SO_4 and purified by chromatography using n-hexane/dichloromethane (2/1, v/v) as eluent to afford **7** as a yellow solid (107.2 mg, 92.7% yield).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (dd, *J* = 7.7, 4.1 Hz, 2H), 7.68 (d, *J* = 8.8 Hz, 2H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 4.8 Hz, 1H), 7.08 (dd, *J* = 26.5, 7.9 Hz, 7H), 6.95 (dd, *J* = 12.3, 8.8 Hz, 4H), 6.64 (t, *J* = 8.5 Hz, 4H), 3.73 (d, *J* = 2.3 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.76, 158.29, 158.21, 144.79, 144.06, 138.71, 138.66, 136.34, 136.17, 135.91, 132.58, 132.07, 131.41, 130.27, 128.90, 127.78, 126.92, 126.36, 126.25, 113.17, 113.04, 109.98, 55.12. ESI-MS, m/z: $[M+1]^+$ calcd 579.2, found 579.2.



TP8

Synthesis of compound TP8. To the solution of compound **7** (57.9 mg, 0.10 mmol) and malononitrile (19.8 mg, 0.30 mmol) in dichloromethane (10 mL) was added titanium tetrachloride (0.04 mL, 0.35 mmol) slowly at 0 °C. After the reaction mixture was stirred for 30 min, pyridine (0.03 mL, 0.35 mmol) was injected and stirred for another 30 min. Then the mixture was heated at 40 °C for 4 h. After the mixture was cooled down to room temperature, the reaction was quenched by water (10 mL) and the mixture was extracted with dichloromethane. The collected organic layer was washed with brine (20 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The desired residue was purified by column chromatography using n-hexane/dichloromethane (2/1 to 1/1, v/v) as eluent to give the desired product **TP8** as a red solid (48.2 mg, 80.0% yield).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (dd, *J* = 6.8, 4.5 Hz, 2H), 7.68 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 8.3 Hz, 2H), 7.23 – 7.20 (m, 1H), 7.11 (d, *J* = 7.9 Hz, 5H), 7.05 (d, *J* =

7.6 Hz, 2H), 6.95 (dd, *J* = 12.3, 8.7 Hz, 4H), 6.64 (t, *J* = 8.5 Hz, 4H), 3.73 (d, *J* = 2.4 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.77, 158.30, 158.21, 144.79, 144.49, 144.06, 140.87, 138.71, 138.47, 136.61, 136.35, 136.18, 135.93, 134.56, 132.61, 132.08, 131.42, 130.27, 128.91, 127.79, 126.92, 126.37, 126.25, 114.48, 114.00, 113.18, 113.05, 55.12, 55.10. ESI-MS, m/z: $[M+1]^+$ calcd 627.2, found 627.2.

Supplemental Tables and Figures

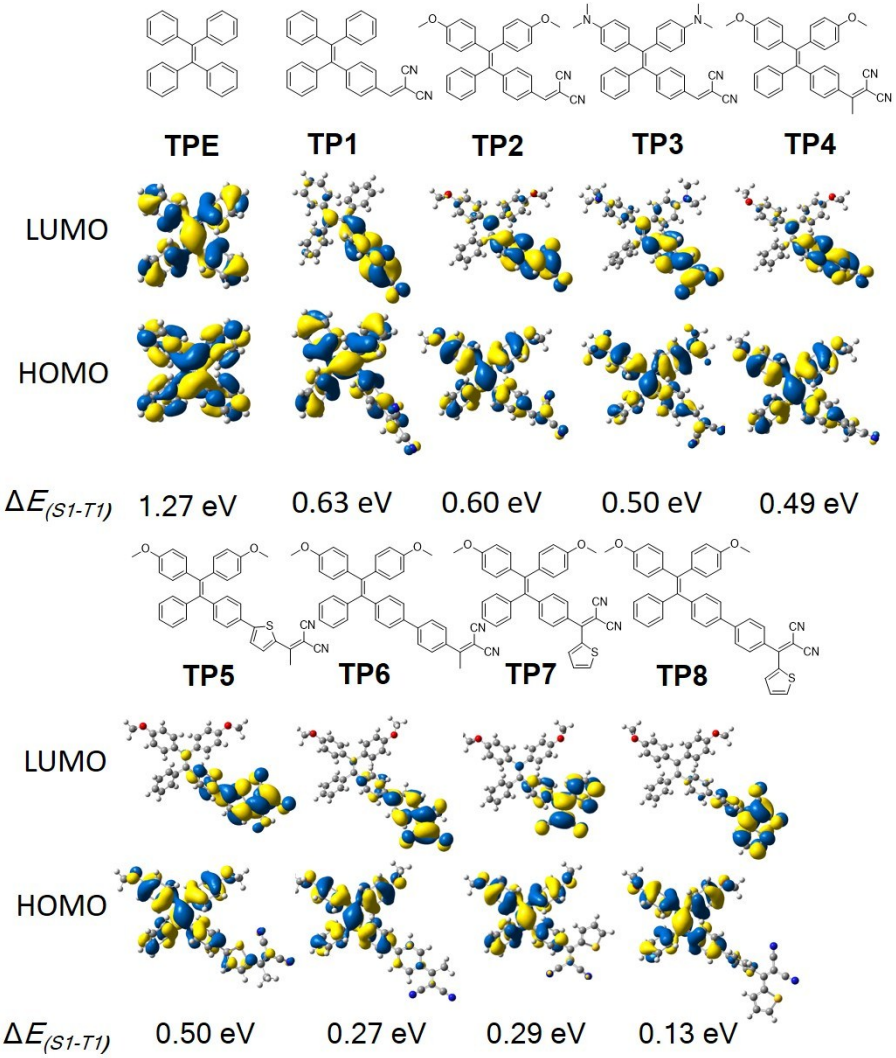


Figure S1. Molecular structures and HOMO-LUMO distributions of TPE and **TP1**-**TP8**. Optimized structures of the HOMO and LUMO at S_1 were calculated by TD-DFT (Gaussian 09/B3LYP/6-31G(g)d).

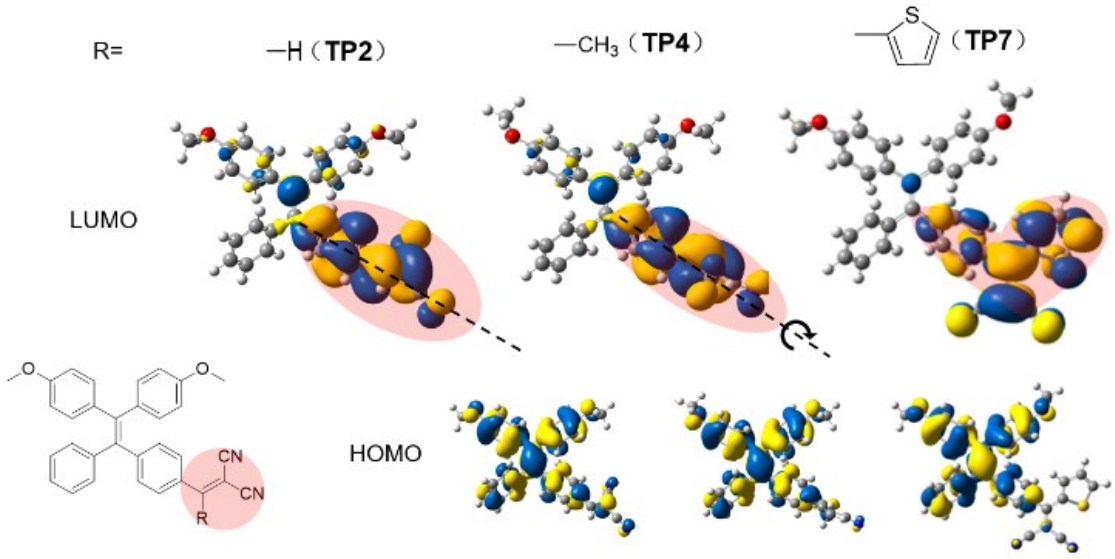


Figure S2. Examples of LUMO engineering for **TP2**, **TP4** and **TP7**, with optimized structures of the HOMO and LUMO at S_1 calculated by TD-DFT (Gaussian 09/B3LYP/6-31G(d)).

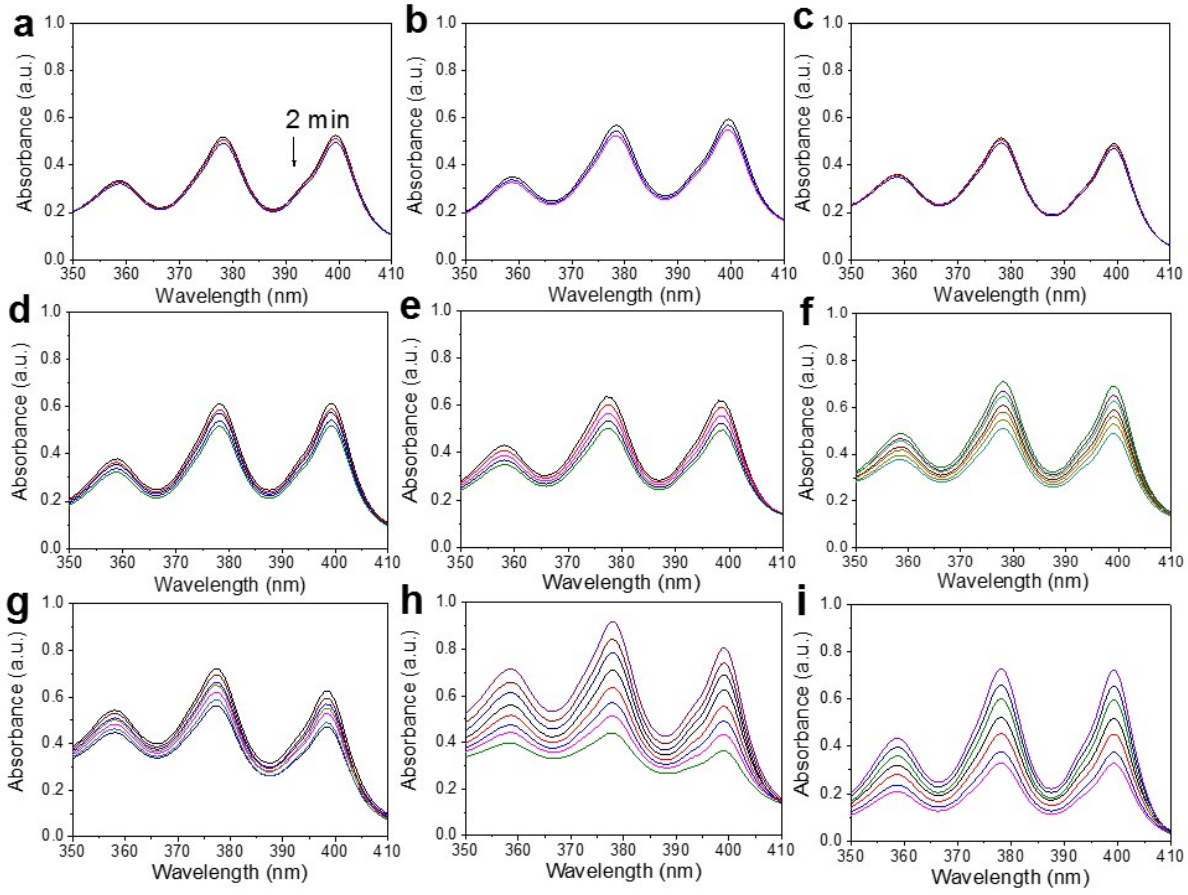


Figure S3. Photo-degradation of ABDA with **TP1**-**TP8** (a-h) and RB (i) in DMSO/water (v/v = 1/99) in two minutes, concentration of PSs: 1×10^{-5} M.

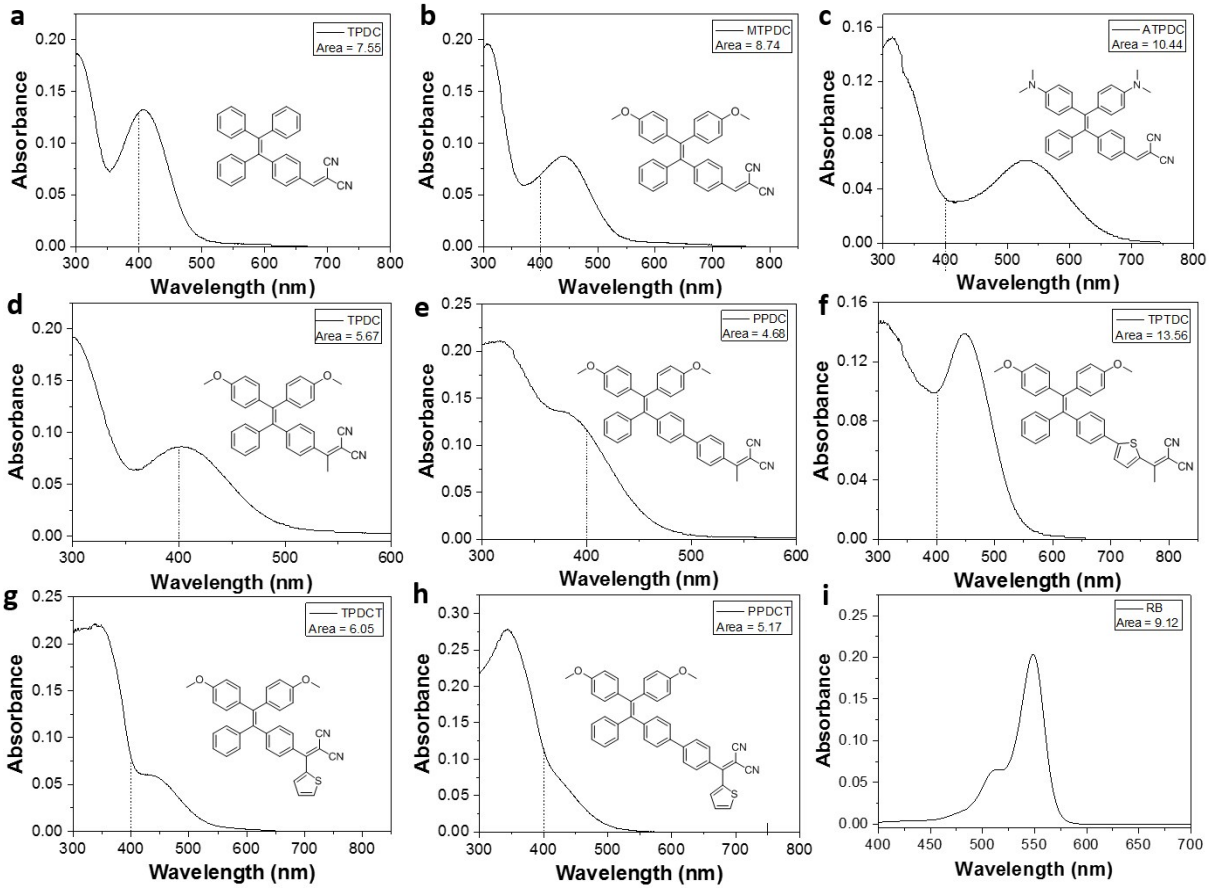


Figure S4 The absorption peak areas of **TP1**- **TP8** (a-h) and RB (i) in DMSO/water (v/v = 1/99), concentration of PSs: 1×10^{-5} M.

Table S1 Photophysical and photochemical properties.

	λ_{abs}/nm	λ_{em} /nm	r/μmol min^{-1}	Area	$\Delta E_{(S1\text{-}T1)}$ /eV	r'/μmol min^{-1}
TPE	308	474	0	0	1.27	0
TP1	406	574	0.75	7.55	0.63	0.1
TP2	441	641	1.1	8.74	0.60	0.1
TP3	529	-	-	10.44	0.50	-
TP4	395	602	3.8	5.67	0.49	0.7
TP5	450	651	12.0	13.56	0.50	0.8
TP6	390	595	7.8	4.68	0.27	1.6
TP7	431	636	9.1	6.05	0.29	1.5
TP8	439	665	20.3	5.17	0.13	3.9
RB	-	-	15.0	9.12	-	1.6

All measurements were in DMSO/water (v/v, 1:99) mixtures at a concentration of 10 μM based on the molecules. Area value is the integrated area of absorption in the range of 400-700 nm.

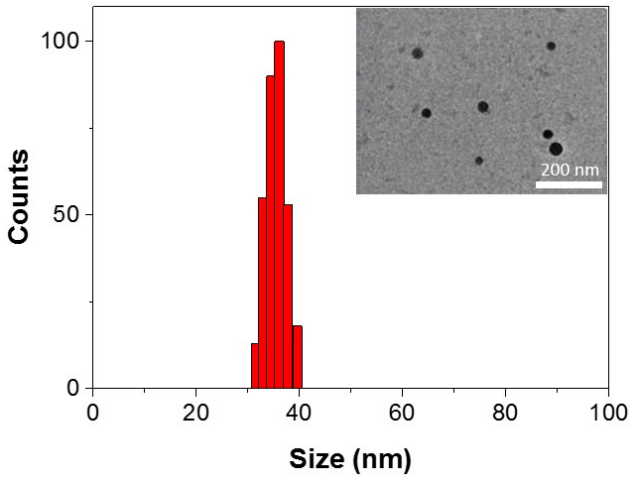


Figure S5. Size distribution and TEM images (inset) of **cRGD-TP8 NPs**.

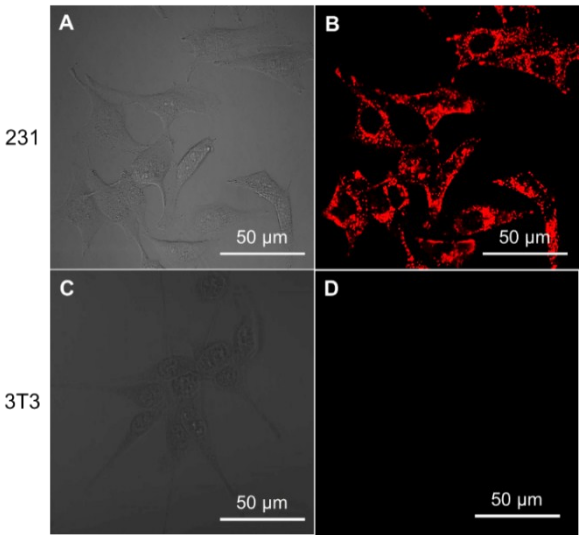


Figure S6. White field images (A&C) and fluorescence images (B&D) of MDA-MB-231 and NIH/3T3 cancer cells after incubation with **cRGD-TP8 NPs** (3 μg mL^{-1}, 2 h).

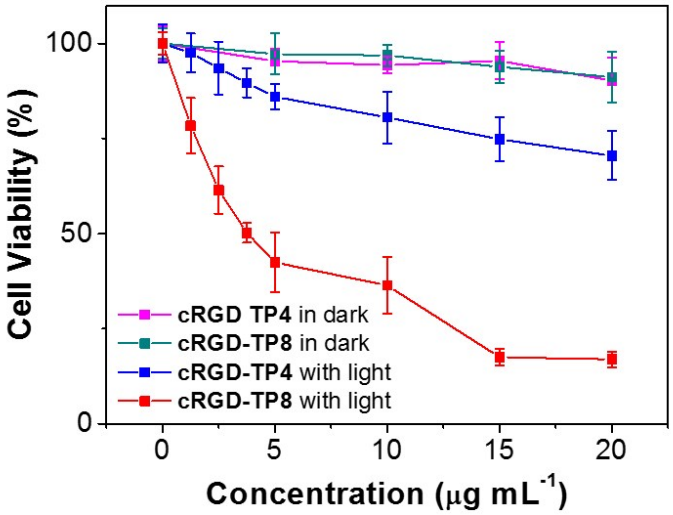


Figure S7. Cell viabilities of MDA-MB-231 cancer cells at various **cRGD-TP8 NPs** and **cRGD-TP4 NPs** concentrations with and without light exposure (0.25 W cm^{-2}, 5 min).

Computational details and geometry data

The ground-state geometry structures of all molecules were optimized by the hybrid B3LYP along with 6-31G (d) basis set. The excited-state characteristics were calculated by the time-dependent density functional theory (TD-DFT) using optimized ground state geometries.

Geometry Data for **TPE** (S_0 optimization: unit Å)

C	-3.57082400	-3.06991100	0.40528900
C	-3.32920800	-2.01530200	1.28740300
C	-2.18296400	-1.23403800	1.15159800
C	-1.25157300	-1.49067700	0.13133500
C	-1.49745700	-2.57019100	-0.73526700
C	-2.64951600	-3.34387800	-0.60742300
C	-0.00000500	-0.68306800	-0.00000200
C	-0.00000300	0.68306600	0.00000000
C	1.25156600	-1.49067500	-0.13133700
C	1.25156900	1.49067000	0.13133600
C	-1.25157000	1.49067900	-0.13133600
C	2.18295100	-1.23404200	-1.15160700

C	3.32919700	-2.01530300	-1.28741100
C	3.57082200	-3.06990300	-0.40528900
C	2.64952000	-3.34386400	0.60743100
C	1.49745800	-2.57018000	0.73527400
C	-2.18296800	1.23403700	-1.15159100
C	-3.32920900	2.01530600	-1.28739500
C	-3.57081500	3.06992300	-0.40528800
C	-2.64949900	3.34389300	0.60741600
C	-1.49744300	2.57020200	0.73525900
C	1.49747000	2.57016700	-0.73528200
C	2.64953300	3.34384800	-0.60743900
C	3.57082700	3.06989300	0.40529000
C	3.32919300	2.01530200	1.28742000
C	2.18294500	1.23404300	1.15161500
H	-4.46508200	-3.67730300	0.51046900
H	-4.03294400	-1.80153600	2.08685500
H	-2.00104700	-0.41597800	1.84060900
H	-0.77849500	-2.79718800	-1.51665500
H	-2.82541200	-4.16506900	-1.29654900
H	2.00102700	-0.41598900	-1.84062500
H	4.03292800	-1.80154200	-2.08686900
H	4.46508100	-3.67729300	-0.51046800
H	2.82542300	-4.16504800	1.29656400
H	0.77850100	-2.79717200	1.51666800
H	-2.00106000	0.41597100	-1.84059800
H	-4.03295000	1.80153800	-2.08684200
H	-4.46507000	3.67731900	-0.51046700
H	-2.82538700	4.16509000	1.29653800
H	-0.77847400	2.79720100	1.51664100

H	0.77851800	2.79715400	-1.51668300
H	2.82544300	4.16502500	-1.29657800
H	4.46508700	3.67728200	0.51046900
H	4.03291700	1.80154700	2.08688500
H	2.00101400	0.41599600	1.84063800

Geometry Data for **TP1** (S_0 optimization: unit Å)

C	5.89821500	0.82655900	0.90010200
C	5.03515000	0.05948400	1.68486000
C	3.68156000	-0.02299200	1.36484400
C	3.16077100	0.66461800	0.25533500
C	4.03740000	1.45199700	-0.51191000
C	5.39389600	1.52189000	-0.20054500
C	1.70439400	0.61795800	-0.07102100
C	1.07739100	1.94670900	-0.33785200
C	1.00051100	-0.55394500	-0.13316900
C	-0.48735000	-0.59573900	-0.19805500
C	1.66319000	-1.89486800	-0.14901300
C	0.29855500	2.16701000	-1.48654200
C	-0.26273400	3.41736900	-1.74025600
C	-0.05849500	4.47275500	-0.84995500
C	0.72345600	4.27225200	0.28966500
C	1.29640700	3.02650500	0.53628400
C	2.69379000	-2.18516700	-1.05843300
C	3.28474900	-3.44710500	-1.08909800
C	2.85811700	-4.44525200	-0.21130500
C	1.82868500	-4.17436200	0.69202500
C	1.23086800	-2.91550200	0.71576600
C	-1.14132000	-1.47433600	-1.08289800
C	-2.52490300	-1.54029900	-1.12682600

C	-3.32741700	-0.75394000	-0.26995700
C	-2.67058400	0.10815300	0.63729400
C	-1.28726700	0.18164800	0.66455900
C	-4.76155000	-0.90649800	-0.39204300
C	-5.79986200	-0.31625200	0.27804000
C	-7.14573000	-0.66977400	-0.06844800
N	-8.23548300	-0.96117200	-0.35496000
C	-5.66805400	0.64987800	1.32548800
N	-5.58376700	1.43625800	2.17981000
H	6.95362000	0.88793300	1.14862700
H	5.41540800	-0.47374700	2.55130200
H	3.01631800	-0.61989400	1.97962500
H	3.64888100	2.00643500	-1.36071700
H	6.05640500	2.12501900	-0.81459400
H	0.14127400	1.35151100	-2.18498900
H	-0.85683000	3.56818900	-2.63686300
H	-0.49904400	5.44575700	-1.04579300
H	0.89074200	5.08882300	0.98591200
H	1.91297500	2.88008700	1.41785400
H	3.02981000	-1.41315000	-1.74279700
H	4.07758100	-3.65160200	-1.80273500
H	3.32023000	-5.42772600	-0.23460500
H	1.48835600	-4.94483800	1.37780700
H	0.42560600	-2.71439100	1.41625700
H	-0.55164800	-2.10161400	-1.74309100
H	-3.00523200	-2.21354300	-1.83191900
H	-3.24008500	0.71794300	1.32686400
H	-0.80711400	0.84807800	1.37193000
H	-5.07355200	-1.61738400	-1.15364100

Geometry Data for **TP2** (S_0 optimization: unit Å)

C	5.46794300	0.47896800	0.57114300
C	4.66576300	-0.37554800	1.33763600
C	3.30064100	-0.46670400	1.06824700
C	2.69670800	0.28249300	0.04804600
C	3.52085100	1.15381000	-0.69349100
C	4.88241700	1.24414700	-0.44928900
C	1.23188500	0.21302300	-0.21145300
C	0.55850300	1.52809800	-0.40129200
C	0.55326000	-0.97733500	-0.28795800
C	-0.93149400	-1.05982300	-0.25176600
C	1.25058100	-2.29364600	-0.42644800
C	-0.32362800	1.75695400	-1.47627300
C	-0.93296300	2.98797600	-1.66168600
C	-0.68289800	4.04159700	-0.76861500
C	0.20118900	3.84301900	0.29972500
C	0.81776500	2.60290400	0.46290500
C	0.91618200	-3.37500800	0.40744800
C	1.54325700	-4.61177500	0.26391600
C	2.50629500	-4.79953300	-0.72921300
C	2.83629900	-3.73986200	-1.57631200
C	2.21514800	-2.50120800	-1.42705700
C	-1.62506200	-1.93817900	-1.10813200
C	-3.00563500	-2.04254000	-1.05682800
C	-3.76809100	-1.29639700	-0.12985200
C	-3.07092000	-0.43499500	0.74875200
C	-1.69244300	-0.32373500	0.68188200
C	-5.20123100	-1.48478000	-0.15584900
C	-6.20662200	-0.93409900	0.59539500

O	6.81000400	0.64415300	0.73992700
O	-1.33368000	5.20803200	-1.03146200
C	-1.12979100	6.30769500	-0.15529500
C	7.45793700	-0.10269500	1.75923500
C	-7.56325100	-1.31783200	0.33508300
N	-8.66237400	-1.63395300	0.11851500
C	-6.02800700	0.01687300	1.64934400
N	-5.90545800	0.79040600	2.51093800
H	5.08736200	-0.96536100	2.14268300
H	2.69066900	-1.13130000	1.67062500
H	3.08095700	1.76065400	-1.47861700
H	5.51704400	1.90426600	-1.03121500
H	-0.52243700	0.95485500	-2.17939900
H	-1.60437200	3.16421100	-2.49545000
H	0.41755500	4.63966400	1.00121500
H	1.50788500	2.46462700	1.28956200
H	0.16270900	-3.23933700	1.17792100
H	1.27718600	-5.43002500	0.92699400
H	2.99072800	-5.76450400	-0.84589100
H	3.57575200	-3.87868600	-2.35981700
H	2.47517700	-1.68187700	-2.08934400
H	-1.06815800	-2.53399700	-1.82349100
H	-3.51583400	-2.71408900	-1.74241900
H	-3.60654800	0.14357700	1.49045000
H	-1.18237000	0.34050600	1.36999600
H	-5.54726300	-2.19004500	-0.90800200
H	-1.74685100	7.11874700	-0.54367100
H	-0.07980500	6.62608600	-0.14403400
H	-1.44567800	6.07186900	0.86846800

H	8.51126600	0.17667100	1.71295700
H	7.06295600	0.14253500	2.75317500
H	7.36276000	-1.18286400	1.59170800

Geometry Data for **TP3** (S_0 optimization: unit Å)

C	5.39905800	-0.35257000	-0.30117200
C	4.80640100	0.58077100	0.58164100
C	3.42665300	0.70096900	0.67425100
C	2.55350200	-0.10084800	-0.08311300
C	3.14820100	-1.01180300	-0.97474400
C	4.52457500	-1.13425100	-1.09358000
C	1.08041800	0.05451700	0.01868200
C	0.58718200	1.45355900	0.10930200
C	0.22488400	-1.02414400	0.04961400
C	-1.23651600	-0.89246000	-0.17534300
C	0.69624100	-2.41621000	0.32596700
C	1.10051700	2.46746800	-0.71984100
C	0.64890300	3.77799600	-0.64713000
C	-0.34328700	4.15714600	0.28856500
C	-0.82841100	3.14941900	1.15578100
C	-0.37709200	1.84114400	1.05618300
C	0.28780000	-3.48980900	-0.48532000
C	0.70066100	-4.79340000	-0.21375500
C	1.51963700	-5.05588700	0.88570900
C	1.92076900	-4.00272700	1.71020600
C	1.51362800	-2.69910800	1.43404700
C	-1.75931000	-0.09133200	-1.21241800
C	-3.12203400	-0.01644600	-1.43732300
C	-4.04617900	-0.73130600	-0.63858900
C	-3.52424900	-1.54458500	0.39411300

C	-2.15777900	-1.62816200	0.60352000
C	-5.44587700	-0.57223000	-0.95250000
C	-6.57738200	-1.09252400	-0.37625400
N	6.77404600	-0.49481600	-0.38636000
N	-0.81651200	5.45677400	0.35433500
C	-1.70768800	5.84471100	1.43485300
C	7.34898100	-1.34018300	-1.41872000
C	7.63843100	0.44524300	0.30637900
C	-0.16614500	6.49967100	-0.42055600
C	-7.85828300	-0.74427200	-0.91658800
N	-8.89502500	-0.45581500	-1.36095800
C	-6.60290300	-1.97352900	0.74999200
N	-6.64640100	-2.69053800	1.66663600
H	5.42506200	1.22003000	1.19900400
H	3.01124400	1.43227800	1.36068000
H	2.51372400	-1.63000300	-1.60100600
H	4.92078600	-1.83889200	-1.81382600
H	1.86684800	2.21794200	-1.44754200
H	1.07499500	4.51108000	-1.32073200
H	-1.55591800	3.38904000	1.92106700
H	-0.77111700	1.09935100	1.74351300
H	-0.35511700	-3.29631300	-1.33911500
H	0.37946700	-5.60502400	-0.86046600
H	1.83666000	-6.07189600	1.10191300
H	2.54811800	-4.19716400	2.57551900
H	1.82860500	-1.88545400	2.07914700
H	-1.07885900	0.46844400	-1.84363300
H	-3.49481700	0.60051100	-2.25091900
H	-4.18777700	-2.11357800	1.03298200

H	-1.78333900	-2.26807700	1.39553100
H	-5.64366500	0.08266600	-1.79814600
H	-1.24089000	5.75169000	2.42730400
H	-2.00657800	6.88443400	1.29591400
H	-2.61911100	5.23634400	1.43220300
H	6.98565300	-2.37050700	-1.33283500
H	8.43293900	-1.36346200	-1.29908200
H	7.12396700	-0.98508800	-2.43609200
H	7.50611500	1.48128100	-0.04093100
H	8.67899800	0.16229900	0.14257200
H	7.45759900	0.42657100	1.38740500
H	-0.69035200	7.44284300	-0.26167100
H	0.88912000	6.64266100	-0.14221200
H	-0.20495200	6.27779400	-1.49330400

Geometry Data for **TP4** (S_0 optimization: unit Å)

C	5.64169400	-0.15306100	0.85960800
C	4.70824900	-0.98307600	1.50178000
C	3.35856300	-0.88500500	1.19666700
C	2.88599500	0.04306300	0.24714400
C	3.83258400	0.87830700	-0.36611900
C	5.19552200	0.78348600	-0.08189900
C	1.43278600	0.18136700	-0.05448800
C	0.92496000	1.58282100	-0.09836700
C	0.62341300	-0.89818200	-0.28944400
C	-0.86365100	-0.80006200	-0.30660700
C	1.16071600	-2.26763900	-0.56001900
C	0.15624800	2.05004700	-1.17443500
C	-0.29923200	3.36794200	-1.23759800
C	0.01206300	4.25737800	-0.20129900

C	0.79136400	3.81264900	0.87974100
C	1.24769100	2.50329900	0.91935000
C	0.67005300	-3.38364600	0.14098400
C	1.14958700	-4.66572100	-0.12679700
C	2.11633800	-4.86186200	-1.11610300
C	2.59847500	-3.76500400	-1.83457100
C	2.12581300	-2.48200300	-1.55935800
C	-1.61492300	-1.42109800	-1.32275200
C	-3.00133900	-1.35297300	-1.33929600
C	-3.70738200	-0.70744100	-0.30330600
C	-2.95772300	-0.09769200	0.72329300
C	-1.57022900	-0.13973600	0.71598400
O	6.94292600	-0.32727100	1.22480600
C	7.93265200	0.50073800	0.61610400
O	-0.37995700	5.56149100	-0.15323000
C	-1.16943100	6.07088700	-1.22692200
C	-5.17570300	-0.64388800	-0.33825100
C	-5.95100300	-0.71414200	0.79790600
C	-5.83557500	-0.50938500	-1.68314600
C	-5.44839200	-0.99881400	2.10899200
N	-5.10600600	-1.25137500	3.19283900
C	-7.37634800	-0.57387500	0.74935300
N	-8.53544700	-0.46196300	0.74063600
H	5.06354100	-1.69142800	2.24340800
H	2.65207600	-1.52897600	1.70936800
H	3.50124200	1.61493000	-1.09154900
H	5.89082000	1.43988900	-0.59086400
H	-0.08469700	1.37352900	-1.98796400
H	-0.88132600	3.68799700	-2.09314300

H	1.02939800	4.51308300	1.67386900
H	1.85583200	2.17879200	1.75804900
H	-0.08543000	-3.24134000	0.90818800
H	0.76636800	-5.51196500	0.43602800
H	2.48567800	-5.86053800	-1.32939200
H	3.34008100	-3.90857300	-2.61514600
H	2.50124300	-1.63449100	-2.12378300
H	-1.10025500	-1.95104400	-2.11740600
H	-3.53943800	-1.83243900	-2.14928000
H	-3.46049800	0.44410400	1.51566500
H	-1.02012100	0.34740700	1.51320500
H	7.75509100	1.56044200	0.83170000
H	8.88514600	0.19808200	1.05161200
H	7.96672300	0.35295900	-0.46924800
H	-0.63166200	6.01618700	-2.18025900
H	-1.36743800	7.11497100	-0.98362900
H	-2.11978900	5.53245200	-1.31592200
H	-6.90098300	-0.29441400	-1.60329800
H	-5.35145700	0.27729600	-2.26760100
H	-5.72673800	-1.44336500	-2.24630700

Geometry Data for **TP5** (S_0 optimization: unit Å)

C	1.62316300	-3.17499400	-0.65731200
C	0.05139900	0.47917800	-0.99882800
C	-1.29630900	0.76934100	-1.15510700
C	-2.27058000	0.15589200	-0.34307700
C	-1.83199500	-0.77502200	0.61724500
C	-0.48349700	-1.07429600	0.75860400
O	8.45992900	-1.05201400	-0.35791100
C	8.94865100	-1.93883900	-1.35269300

O	1.88353000	5.67307400	0.93547700
C	2.50058500	6.67139300	0.13712400
C	-3.68557100	0.48267800	-0.51040500
C	-7.63330200	0.24108400	-0.39636900
C	-8.21720600	-0.87494600	0.17560800
C	-8.53768400	1.31883600	-0.95406700
C	-4.23877300	1.62627300	-1.06550900
C	-5.64271300	1.62325100	-1.06661200
C	-6.21613300	0.48029800	-0.51361500
S	-4.93625300	-0.61685400	0.00542400
C	-9.64016100	-1.02066100	0.24191000
N	-10.79555800	-1.15509600	0.30406100
C	-7.50109800	-1.97082700	0.74847300
N	-6.96161000	-2.88600600	1.22678800
H	6.47437700	-2.04655900	-1.97035600
H	4.10100600	-1.51247400	-1.69474600
H	5.03278800	1.05266200	1.61873500
H	7.43504600	0.48779500	1.36779900
H	3.97626800	2.23503600	-1.25700100
H	3.55676600	4.63266600	-0.97404200
H	0.89899100	3.78109100	2.29708100
H	1.30251100	1.35457500	1.98345700
H	3.45615100	-2.07826400	1.98197000
H	3.84410900	-4.50744200	2.21888600
H	2.82471100	-6.10002100	0.60147200
H	1.39459000	-5.23180900	-1.24042900
H	0.98800300	-2.80498100	-1.45679200
H	0.77817300	0.96021500	-1.64407600
H	-1.60318500	1.45627000	-1.93735500

H	-2.55223500	-1.25618200	1.27259000
H	-0.17622600	-1.80171900	1.50295100
H	8.73957500	-1.56818000	-2.36432200
H	10.02839800	-1.98972800	-1.20610700
H	8.52152000	-2.94372100	-1.24412900
H	3.59345000	6.64934700	0.23416200
H	2.23313300	6.56556600	-0.92199700
H	2.12669500	7.62679000	0.50766700
H	-8.33926100	1.47121400	-2.01938300
H	-9.58962900	1.06298400	-0.83576500
H	-8.35808700	2.27024100	-0.44365700
H	-3.64296900	2.45432900	-1.42923800
H	-6.22974900	2.44737200	-1.45143700

Geometry Data for **TP6** (S_0 optimization: unit Å)

C	7.23864300	-0.43716200	-0.61107000
C	6.28188200	-1.14129500	-1.35157000
C	4.92501800	-0.94469000	-1.09168000
C	4.48196300	-0.05352800	-0.10428000
C	5.46391100	0.66175100	0.61084600
C	6.81685700	0.46876700	0.37414500
C	3.03008700	0.17774200	0.14844200
C	2.62889500	1.61144700	0.24821800
C	2.13378200	-0.84878100	0.28384000
C	0.65641500	-0.63962800	0.24908600
C	2.55624800	-2.27003600	0.48069100
C	3.09599300	2.55665200	-0.67707500
C	2.74919300	3.90600700	-0.59245700
C	1.93136900	4.34546700	0.45538400

C	1.47329000	3.42045100	1.40593300
C	1.81679100	2.08100800	1.29960700
C	3.49216100	-2.62219800	1.46829800
C	3.85292100	-3.95320500	1.67182900
C	3.28599300	-4.96375300	0.89238600
C	2.34716700	-4.63140700	-0.08629600
C	1.97961900	-3.30092100	-0.28241600
C	0.04364300	0.13644000	-0.75083500
C	-1.33679100	0.29149200	-0.79942000
C	-2.17303400	-0.32679100	0.14704800
C	-1.56348800	-1.11335800	1.14026500
C	-0.18294200	-1.27250600	1.18401200
O	8.58834300	-0.55160400	-0.77366600
C	9.07219200	-1.45918400	-1.75107700
O	1.53473300	5.63718900	0.64486400
C	1.98473600	6.62040600	-0.27371300
C	-3.64268000	-0.16303700	0.09189300
C	-4.22616600	1.04762400	-0.32490600
C	-5.60452700	1.20517200	-0.37018800
C	-6.47254500	0.14843200	-0.02722400
C	-5.88908000	-1.06002000	0.40106500
C	-4.50946700	-1.20711800	0.46092100
C	-7.93139300	0.34627600	-0.07688100
C	-8.81599700	-0.64741300	-0.42082300
C	-8.45565400	1.72226400	0.25250000
C	-10.23389200	-0.42607000	-0.40329900
N	-11.38550700	-0.25699600	-0.39110800
C	-8.43803100	-1.95389400	-0.87606100
N	-8.18575200	-3.02258700	-1.26164300

H	6.57664700	-1.83616500	-2.12977400
H	4.19473100	-1.49733600	-1.67426100
H	5.15494800	1.37406000	1.37052000
H	7.57031500	1.01094600	0.93720200
H	3.74103900	2.23101600	-1.48814600
H	3.12386000	4.59800200	-1.33808100
H	0.85551300	3.77956600	2.22327500
H	1.45829700	1.38009700	2.04684300
H	3.93625200	-1.84199600	2.07869700
H	4.57519400	-4.20153500	2.44526300
H	3.56778300	-6.00128400	1.05115500
H	1.89612200	-5.40979600	-0.69644100
H	1.24032200	-3.05234000	-1.03892600
H	0.66154500	0.61293200	-1.50494900
H	-1.77611600	0.87021300	-1.60722200
H	-2.17558300	-1.58572300	1.90357400
H	0.25848800	-1.88833200	1.96214600
H	10.16097600	-1.39832400	-1.70320600
H	8.75621200	-2.48871100	-1.53714900
H	8.73797100	-1.18270600	-2.75989600
H	1.55854600	7.56574700	0.06710700
H	3.08003600	6.69743900	-0.27861900
H	1.63431000	6.41188700	-1.29331300
H	-3.58826500	1.88579800	-0.58854400
H	-6.01036900	2.15875300	-0.69202200
H	-6.51644900	-1.88810000	0.70894700
H	-4.09608100	-2.15900400	0.77949400
H	-8.24174100	2.41760200	-0.56959900
H	-9.53566200	1.72398800	0.40832900

H	-7.96312200	2.11728700	1.14644200

Geometry Data for **TP7** (S_0 optimization: unit Å)

C	-6.44829400	0.34843100	-0.43127400
C	-5.84342700	1.15980500	0.54057600
C	-4.46883300	1.12536800	0.71949600
C	-3.64865200	0.26857500	-0.04240500
C	-4.27237900	-0.52576000	-1.01505600
C	-5.65205700	-0.49327500	-1.21731500
C	-2.17017300	0.25767400	0.14775300
C	-1.53774300	1.60421300	0.26976500
C	-1.44094600	-0.89981900	0.21542600
C	0.04803300	-0.90897600	0.11863000
C	-2.06362100	-2.24519700	0.40591100
C	-3.00646800	-2.47160900	1.42351900
C	-3.55423900	-3.73724600	1.62246500
C	-3.17094200	-4.80600800	0.80969400
C	-2.22683200	-4.59988700	-0.19763400
C	-1.67247300	-3.33555400	-0.39097200
C	0.82275500	-1.67218100	1.01049800
C	2.21006300	-1.69451100	0.92439100
C	2.87739300	-0.95712600	-0.06697800
C	2.10841000	-0.21189000	-0.97781000
C	0.72237400	-0.19923300	-0.89162800
C	-1.86442700	2.63975400	-0.61757000
C	-1.28953000	3.90723600	-0.51510000
C	-0.37767400	4.17239400	0.51362400
C	-0.05917400	3.15866900	1.43021700
C	-0.63029700	1.90073000	1.30585700

O	-7.80352200	0.45821500	-0.53584500
C	-8.47130100	-0.34508100	-1.49719500
O	0.24119500	5.37130100	0.71532200
C	-0.06538800	6.44232600	-0.16498400
C	4.36324200	-0.95873800	-0.15084200
C	5.00740000	0.34247100	-0.12651600
C	5.02594200	-2.17092200	-0.23227400
C	4.40523900	1.52678000	0.28418800
C	5.24800600	2.65808900	0.19672400
C	6.49304400	2.34505200	-0.28913700
S	6.66586700	0.66513900	-0.62748600
C	4.32472100	-3.41095700	-0.38679500
N	3.80857800	-4.44522000	-0.52741600
C	6.44786300	-2.32138600	-0.20141000
N	7.59918900	-2.49791600	-0.17964800
H	-6.47375800	1.80953600	1.13874700
H	-4.01553400	1.76637600	1.46918400
H	-3.66745900	-1.18317000	-1.63041500
H	-6.08922800	-1.11925800	-1.98595500
H	-3.30612500	-1.64604600	2.06064500
H	-4.27700700	-3.89018400	2.41888600
H	-3.59699400	-5.79266500	0.96623500
H	-1.91484100	-5.42557700	-0.83052100
H	-0.92890300	-3.18800100	-1.16844700
H	0.32830900	-2.24525800	1.78805000
H	2.78250000	-2.27155800	1.64299500
H	2.60346900	0.34335000	-1.76794200
H	0.14774800	0.37045900	-1.61335500
H	-2.57866700	2.45008700	-1.41301100

H	-1.56139900	4.67252900	-1.23232500
H	0.62716600	3.38799700	2.23898900
H	-0.37925800	1.12995400	2.02704900
H	-9.53190800	-0.10842200	-1.40239200
H	-8.32127300	-1.41494300	-1.30508900
H	-8.14035100	-0.11452400	-2.51782500
H	0.52402800	7.29312800	0.17941400
H	-1.13057800	6.70309400	-0.12903600
H	0.21114400	6.20739400	-1.20067800
H	3.38565400	1.56583200	0.64448600
H	4.94761800	3.65932200	0.48091600
H	7.32833700	3.01086900	-0.46023300

Geometry Data for **TP8** (S_0 optimization: unit Å)

C	-4.44661200	-4.70030400	-1.61212700
C	-3.49112200	-4.57489400	-0.60199200
C	-3.06664900	-3.31237300	-0.19083000
C	-3.60175900	-2.14583800	-0.76520400
C	-4.55481400	-2.28945300	-1.78813900
C	-4.97262000	-3.55154500	-2.20624700
C	-3.11821600	-0.79605600	-0.34009100
C	-3.96872100	0.23114500	-0.02986600
C	-1.63300400	-0.65414100	-0.29035100
C	-3.50618700	1.64296100	0.10638000
C	-5.42900200	0.02332200	0.19284900
C	-0.82790900	-1.13528100	-1.33833800
C	0.55699400	-1.01760800	-1.29773600
C	1.20432200	-0.43608500	-0.19406500
C	0.40264900	0.01738800	0.86805500

C	-0.98239200	-0.08825700	0.82021300
C	-6.37864100	0.88569200	-0.39118700
C	-7.73837300	0.71555400	-0.17864800
C	-8.19825900	-0.31738000	0.65205600
C	-7.27323800	-1.17178500	1.26324500
C	-5.90941700	-0.99460300	1.02799200
C	-3.92665600	2.44005300	1.19019600
C	-3.51006500	3.75579600	1.32571400
C	-2.66973700	4.33277800	0.36113200
C	-2.26265600	3.57024500	-0.74005100
C	-2.68143600	2.24438900	-0.85445200
O	-9.55174300	-0.39800000	0.80497400
O	-2.31671600	5.63121100	0.58149400
C	2.67860500	-0.30387100	-0.15122500
C	3.38804400	-0.43475600	1.05639800
C	4.77096700	-0.31033900	1.09648200
C	5.50220900	-0.02757700	-0.07164900
C	4.79884400	0.10457700	-1.28112400
C	3.41776600	-0.03857400	-1.31808800
C	6.97674500	0.12842300	-0.01711400
C	7.57499700	1.22777100	-0.60870300
C	7.74997700	-0.90199400	0.65801100
C	-10.07391300	-1.42362000	1.63524100
C	8.98752400	-0.82724600	1.27685400
C	9.43767400	-2.06684300	1.79154400
C	8.55167100	-3.08988900	1.56000200
S	7.14216500	-2.55480300	0.72786600
C	-1.45527400	6.26188600	-0.35494000
C	6.81768900	2.32890500	-1.12506200

N	6.25208200	3.25426200	-1.54898100
C	8.99066800	1.38896500	-0.74135000
N	10.13582100	1.55844000	-0.86913500
H	-4.77273700	-5.68366000	-1.93820200
H	-3.07187600	-5.46187400	-0.13528600
H	-2.31467900	-3.22332900	0.58773700
H	-4.96691800	-1.40093800	-2.25504000
H	-5.70688700	-3.63743200	-3.00226400
H	-1.29850400	-1.60634000	-2.19569100
H	1.14646400	-1.40949200	-2.12120800
H	0.86765700	0.48543700	1.73041400
H	-1.57569300	0.28254500	1.64903400
H	-6.03833400	1.69689600	-1.02733900
H	-8.46770100	1.37289000	-0.64051700
H	-7.59767300	-1.96814500	1.92230800
H	-5.20301700	-1.66308600	1.50878600
H	-4.58390700	2.01168800	1.94074900
H	-3.82326100	4.36209200	2.16932200
H	-1.62967300	3.99414000	-1.51041700
H	-2.35948500	1.66553300	-1.71382400
H	2.85044700	-0.66091000	1.97143600
H	5.29168300	-0.41528600	2.04261500
H	5.33911400	0.31152600	-2.19852400
H	2.89950800	0.08464000	-2.26330800
H	-11.15823900	-1.30615400	1.61302900
H	-9.81118200	-2.42128000	1.26099200
H	-9.72198800	-1.32574300	2.67015200
H	9.54697400	0.09368500	1.37030300
H	10.37775100	-2.19567700	2.31435100

H	8.65004700	-4.13041800	1.83809800
H	-1.29175600	7.27290400	0.02042700
H	-0.49099100	5.74397100	-0.43013800
H	-1.91148500	6.31686100	-1.35149900

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