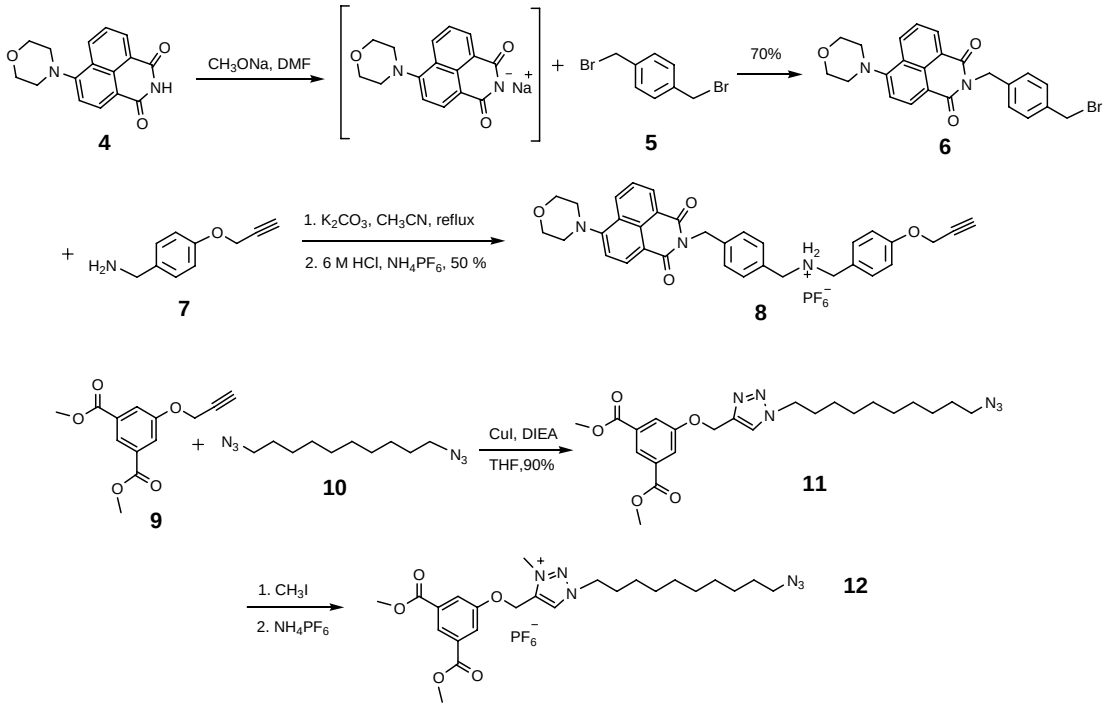
Supporting Information

Experimental section

General: ^{1}H NMR and ^{13}C NMR spectra were measured on a Brüker AV-400 spectrometer. The electronic spray ionization (ESI) mass spectra were tested on a LCT Premier XE mass spectrometer. The UV-Vis absorption spectra and fluorescence spectra were obtained on a Varian Cary 100 spectrometer and a Varian Cary Eclipse (1-cm quartz cell used), respectively. The fluorescence lifetime measurements were performed by using the Time Correlated Single Photon Counting (TCSPC) technique following excitation by nanosecond flash lamp (Edinburgh instruments FL920). HPLC analyses were determined by Agilen 1100 eluted by CH_3CN at a flow rate of 1.0 mL/min. The photoirradiation was carried on a CHF-XM 500-W high-pressure mercury lamp in a sealed Ar-saturated 1 cm quartz cell. The distance between the lamp and the sample cell was 20 cm. Photostationary states were ensured by monitoring composition changes in time by taking UV spectra at distinct intervals until no changes were observed. The fluorescence intensity of all compounds that contain 4-morpholin-naphthalimide was normalized.

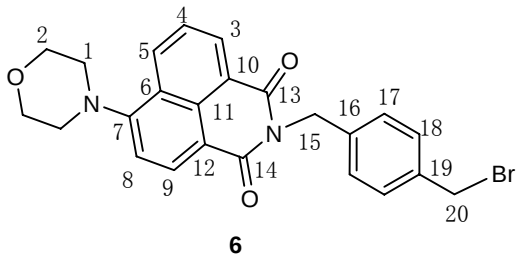
Materials: Chemicals were used as received from Acros, Aldrich, Fluka, or Merck. All solvents were reagent grade, which were dried and distilled prior to use according to standard procedures. The molecular structures were confirmed via ^{1}H NMR, ^{13}C NMR and high-resolution ESI mass spectroscopy. Compound **4**, **7**, **9**, **10**, **13** and **14** were synthesized and purified acoording to the references 1-6, respectively.

Synthesis



Scheme S1. Preparation of compound **8** and **12**

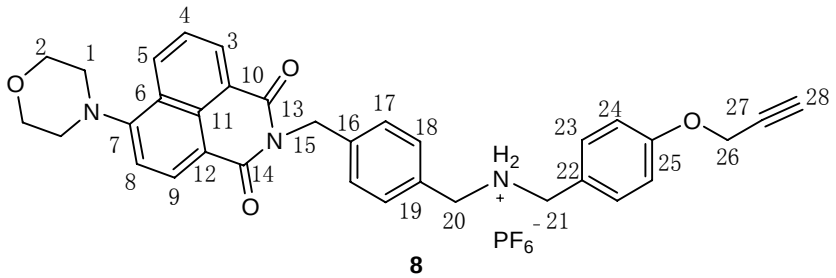
Synthesis of compound 6



6-Morpholin-4-yl-benzo[de]isoquinoline-1,3-dione **4** (1.00 g, 3.54 mmol) was dissolved in dimethylformamide (30 mL), and sodium methoxide (0.172 g, 3.186 mmol) was added. After stirring at room temperature for 1 h, the resulting transparent solution was added dropwise to a solution of 1,4-bis(bromomethyl)benzene **5** (0.934 g, 3.54 mmol) in DMF (20 ml). Then the solution was stirred for another 3 h. The yellow precipitates were filtered, washed with water and dried. The crude product was purified via column chromatography (SiO_2, CH_2Cl_2) to give compound **6** (1.15 g, 70%) as a yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 8.59 (d, J = 6.8 Hz, 1H,

H_3), 8.54 (d, J = 8.1 Hz, 1H, H_5), 8.42 (d, J = 7.6 Hz, 1H, H_9), 7.70 (dd, J = 8.2 Hz, 7.5Hz, 1H, H_4), 7.51 (d, J = 8.1 Hz, 2H, H_{17}), 7.31 (d, J = 8.0 Hz, 2H, H_{18}), 7.23 (d, J = 8.0 Hz, 1H, H_8), 5.35 (s, 2H, H_{20}), 4.44 (s, 2H, H_{15}), 4.01 (t, J = 4.4 Hz, 4H, H_2), 3.26 (t, J = 4.4 Hz, 4H, H_1). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 164.4 (C_7), 163.9 (C_{13} C_{14}), 155.8 (C_{16}), 137.8 (C_9), 136.8 (C_3), 132.8 (C_{19}), 131.4 (C_5), 130.3 (C_{18}), 129.9 (C_4), 129.4 (C_6), 129.1 (C_{17}), 126.2 (C_{10}), 125.9 (C_{11}), 123.2 (C_{12}), 117.0 (C_8), 115.0 (C_2), 66.9 (C_1), 43.1 (C_{15}), 33.3 (C_{20}). HRMS (ESI) (*m/z*): $[M + Na]^+$ calcd for $C_{24}H_{21}BrN_2NaO_3$, 487.0633; found, 487.0637.

Synthesis of compound 8

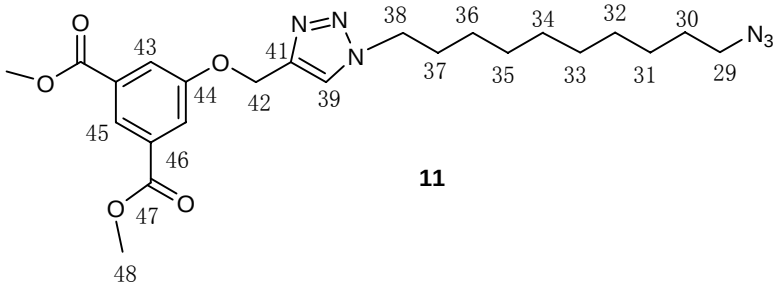


8

A mixture of compound **6** (0.2 g, 0.43 mmol), 4-(2-propynyloxy)benzylamine **7** (0.35 g, 2.15 mmol), K_2CO_3 (0.12 g, 0.86 mmol) in acetonitrile (15 ml) was stirred under reflux for 12 h. After the reaction mixture had been cooled to room temperature, solvent was removed under reduced pressure. The residue was purified via column chromatography (SiO_2, CH_2Cl_2/MeOH = 30/1) to give a yellow solid. The yellow solid (0.19 g, 0.35 mmol) was dissolved in MeOH (20 ml), and HCl (6 M, 2 ml) was added. After stirring for a few minutes, the solvent was removed under reduced pressure. The residue was dissolved in MeOH (20 ml), followed by the addition of saturated NH_4PF_6 solution. After the mixture was stirred for 2 h, the mixture was extracted with CH_2Cl_2 (3 × 20 ml). The combined organic layer was evaporated, and the residue was purified via column chromatography (SiO_2, CH_2Cl_2/MeOH = 30/1) to give **8** (0.12 g, 50%) as a yellow powder. ^{1}H NMR (CD_3COCD_3, 400 MHz, 298 K): δ 8.59 (d, J = 8.4 Hz, 1H, H_3), 8.54 (d, J = 7.2 Hz, 1H, H_5), 8.48 (d, J = 8.0 Hz, 1H, H_9), 7.81 (dd, J = 8.4 Hz, 7.3Hz, 1H, H_4), 7.49 (br d, J = 7.2 Hz, 6H, H_{17} H_{18} H_{23}), 7.39 (d, J = 8.4 Hz, 1H, H_8), 7.03 (m, 2H, H_{24}), 5.32 (s, 2H, H_{26}), 4.80 (d, J = 2.4 Hz, 2H, H_{15}),

4.46 (d, J = 4.0 Hz, 4H, H_{20} H_{21}), 3.97 (t, J = 4.4Hz, 4H, H_2), 3.29 (t, J = 4.4Hz, 4H, H_1), 3.10 (t, J = 2.4 Hz, 1H, H_{28}). ^{13}C NMR (CD_3COCD_3, 100 MHz, 298 K): δ 164.8 (C_7), 164.2 (C_{13} C_{14}), 159.3 (C_{25}), 157.1 (C_{16}), 140.3 (C_9), 133.3 (C_3), 132.4 (C_5), 131.8 & 131.7 (C_{23}), 130.9(C_{19}), 130.6 (C_{18}), 129.4 (C_4), 127.0 (C_6), 126.9 (C_{10} C_{17}), 125.6 (C_{11} C_{22}), 124.0 (C_{12}), 117.4 (C_8), 116.1 & 116.0 (C_{24}), 79.5 (C_{27}), 77.2 (C_{28}), 67.4 (C_2), 56.3 (C_{26}), 54.3 (C_{20} C_{21}), 52.2 (C_1), 43.5 (C_{15}). HRMS (ESI) (*m/z*): $[M\text{-}PF_6]^+$ calcd for $C_{34}H_{32}N_3O_4$, 546.2393; found, 546.2388.

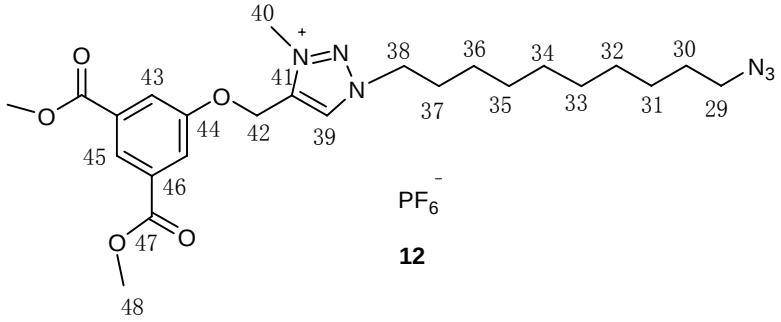
Synthesis of compound 11



11

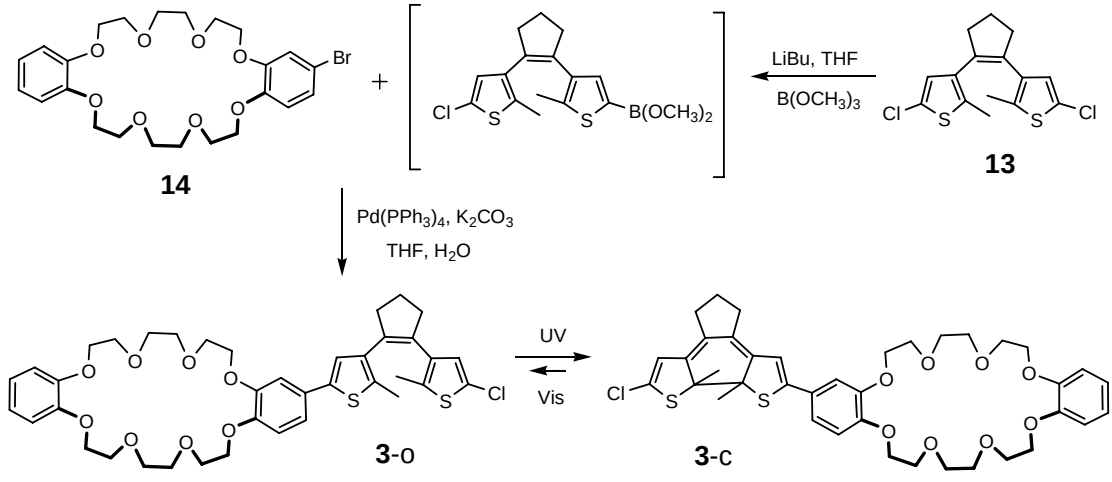
A mixture of dimethyl 5-hydroxyisophthalate propargyl ether **9** (1.00 g, 4.03 mmol), 1,10-decanediazide **10** (1.81 g, 8.06 mmol), CuI (0.153 g, 0.806 mmol), and N,N-diisopropylethylamine (1.04 g, 8.06 mmol) in anhydrous THF (20 ml) was stirred at room temperature for 12 h under nitrogen atmosphere. The resulting suspension was filtered, and the filtrate was evaporated under reduced pressure. The residue was partitioned in H_2O/CH_2Cl_2. The organic layer was dried with Na_2SO_4 and filtered, and the filtrate was evaporated to dryness. The residue was purified via column chromatography (SiO_2, CH_2Cl_2/petroleum ether = 1/1) to give **11** (2.66 g, 90%) as a white solid. ^{1}H NMR ($CDCl_3$, 400MHz, 298 K): δ 8.28 (s, 1H, H_{45}), 7.82 (s, 2H, H_{43}), 7.61 (s, 1H, H_{39}), 5.26 (s, 2H, H_{42}), 4.34 (t, J = 7.2 Hz, 2H, H_{38}), 3.91 (s, 6H, H_{48}), 3.23 (t, J = 6.9 Hz, 2H, H_{29}), 1.89 (m, 2H, H_{37}), 1.57 (m, 2H, H_{30}), 1.28 (br, 12H, $H_{31\text{-}36}$). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 165.9 (C_{47}), 158.3 (C_{44}), 143.2 (C_{41}), 131.9 (C_{46}), 123.5 (C_{42}), 122.6 (C_{39}), 120.1 (C_{43}), 62.5 (C_{42}), 52.4 (C_{38}),51.4 & 50.5 (C_{48}), 30.2 (C_{29}), 29.3 & 29.2 & 29.0 & 28.9 & 28.8 & 26.6 & 26.4 ($C_{30\text{-}37}$). HRMS (ESI) (*m/z*): $[M + Na]^+$ calcd for $C_{23}H_{32}N_6NaO_5$, 495.2332; found, 495.2326.

Synthesis of compound 12



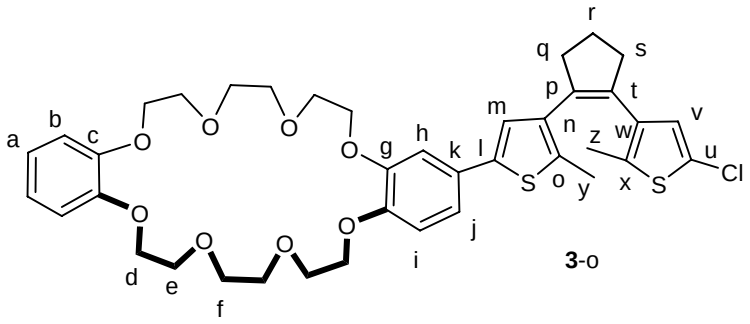
12

A solution of **11** (1 g, 2.12 mmol) in CH_3I (15 ml) was stirred at 40 ℃ for 12 h. The reaction mixture was cooled to room temperature, and CH_3I was evaporated off in vacuo. The residue was dissolved MeOH (15 ml), followed by the addition of saturated NH_4PF_6 solution. After the mixture was stirred for 2 h, the mixture was extracted with CH_2Cl_2 (3 × 20 ml). The combined organic layer was evaporated, and the residue was purified via column chromatography (SiO_2, CH_2Cl_2/MeOH = 100/1) to give **12** (1.07 g, 80%) as a white powder. ^{1}H NMR ($CDCl_3$, 400MHz, 298 K): δ 8.52 (s, 1H, H_{39}), 8.28 (s, 1H, H_{45}), 7.77 (s, 2H, H_{43}), 5.39 (s, 2H, H_{42}), 4.54 (t, J = 7.4 Hz, 2H, H_{38}), 4.34 (s, 3H, H_{40}), 3.91 (s, 6H, H_{48}), 3.25 (t, J = 6.8 Hz, 2H, H_{29}), 2.01 (m, 2H, H_{37}), 1.58 (m, 2H, H_{30}), 1.28 (br, 12H, $H_{31\text{-}36}$). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ 165.5 (C_{47}), 156.8 (C_{44}), 139.1 (C_{41}), 132.3 (C_{39}), 129.9 (C_{46}), 124.7 (C_{45}), 119.7 (C_{43}), 58.1 (C_{42}), 54.4 & 52.6 (C_{38}), 51.4 (C_{48}), 38.6 (C_{40}), 29.2 & 29.1 & 29.1 & 29.0 & 28.8 & 28.7 & 26.6 & 26.0($C_{30\text{-}37}$). HRMS (ESI) (m/z): $[M\text{-}PF_6]^+$ calcd for $C_{24}H_{35}N_6O_5$, 487.2669; found, 487.2671.



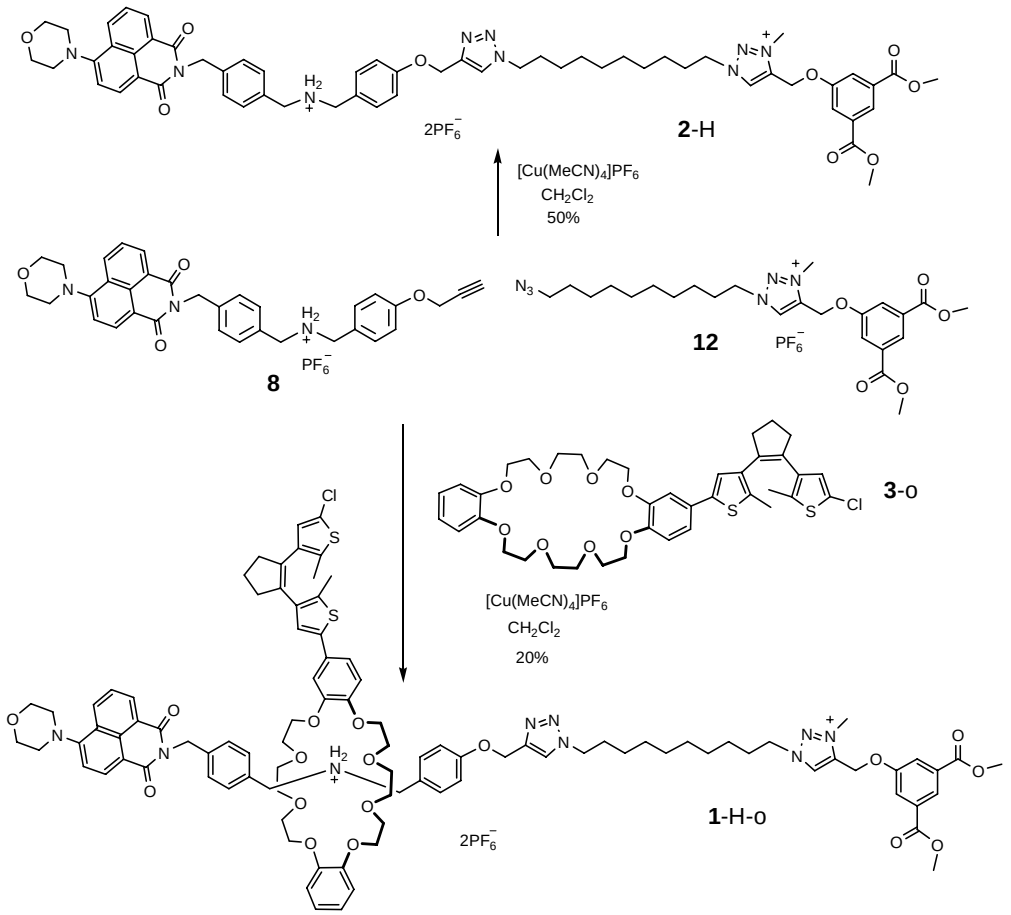
Scheme S2. Preparation of compound **3**-o and its photoinduced reversible interconversions between two states.

Synthesis of compound 3-o



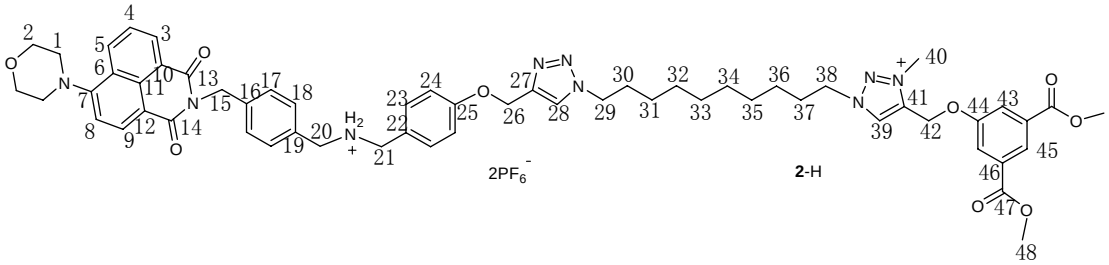
To the solution of 1,2-bis(5-chloro-2-methylthien-3-yl) cyclopentene **13** (0.50 g, 1.52 mmol) in anhydrous THF (10 ml), n-BuLi (0.5 ml of 2.5M solution in hexane, 1.6 mmol) was added using a syringe in two portions under nitrogen at -78℃ and then stirred for 1 h. After Tri-n-butyl borate (98%, 0.5 ml, 1.6 mmol) was added, the reddish solution was stirred for 8 h at room temperature. A mixture of 4-bromo-dibenzo-24-crown-8 **14** (0.8 g, 1.52 mmol) and $Pd(PPh_3)_4$ (0.10 g) was stirred in THF (10 ml) for 15 min at room temperature. Then aqueous Na_2CO_3 (10 ml, 2M) was added. The reactive mixture was stirred at 50℃, and the reddish solution of BTE-containing boronic acid dibutyl ester was added dropwise via a syringe. Subsequently, the mixture was refluxed for 24 h and cooled to room temperature. The reactive mixture was poured into H_2O and extracted with CH_2Cl_2 and dried with anhydrous Na_2SO_4. The residue was purified via column chromatography (SiO_2, CH_2Cl_2/MeOH = 50/1) to give compound **3**-o (0.3 g, 28 %). ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ 7.20-7.10 (m, 2H, H_h H_j), 7.10-7.02 (m, 5H, H_a H_b H_i), 6.89 (s, 1H, H_m), 6.63 (s, 1H, H_v), 4.35-4.27 (m, 8H, H_d), 3.83-3.76 (m, 8H, H_e), 3.67-3.60 (d, J = 4.9 Hz, 8H, H_f), 2.82 (t, J = 7.2 Hz, 2H, H_q), 2.74 (t, J = 7.3 Hz, 2H, H_s), 2.10-2.03 (m, 2H, H_r), 2.02 (s, 3H, H_y), 1.77 (s, 3H, H_z). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): 148.28 (C_c), 148.05 & 138.40 (C_g), 136.45 & 135.36 & 135.25 & 134.56 & 133.97 & 133.33 (C_o C_p C_t C_l C_n C_x C_w), 126.92 (C_k), 124.83 (C_u), 124.12 (C_m), 123.63 (C_a),

120.62 (C_j), 117.16 (C_h), 116.78 & 116.70 (C_b), 113.82 (C_i), 77.34 (C_f), 77.02 (C_e), 76.71 (C_d), 38.24 (C_q C_s), 22.93 (C_y C_z C_r). HRMS (ESI) (m/z): $[M + Na]^+$ calcd for $C_{39}H_{45}ClNaO_8S_2$, 763.2142; found, 763.2140.



Scheme S3. Preparation of compound **2**-H and [2]rotaxane **1**-H-o

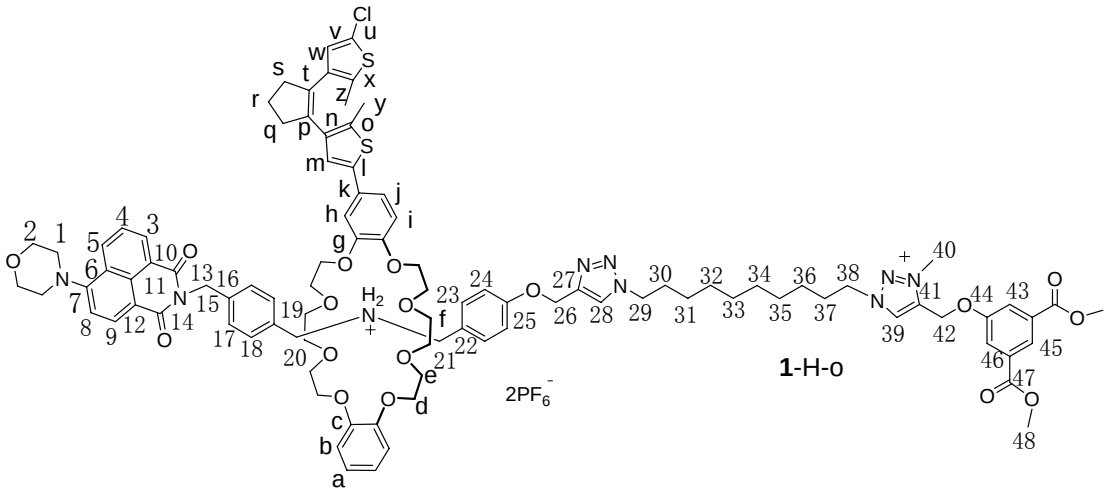
Preparation of dumbbell 2-H



A mixture of **8** (20 mg, 0.03 mmol), **12** (37.9 mg, 0.06 mmol), and $Cu(CH_3CN)_4PF_6$ (11.2 mg, 0.03 mmol) was stirred in dry CH_2Cl_2 (1 mL) at room temperature for two days. After removal of the solvent, the residue was purified via column chromatography (SiO_2, CH_2Cl_2/MeOH = 15/1) to give compound **2**-H (33.7 mg, 50 %)

as a yellow solid. ^{1}H NMR (CD_3COCD_3, 500 MHz, 298 K): δ 9.10 (s, 1H, H_{39}), 8.63 (d, J = 8.5 Hz, 1H, H_3), 8.57 (d, J = 7.5 Hz, 1H, H_5), 8.51 (d, J = 8.0 Hz, 1H, H_9), 8.27 (s, 1H, H_{45}), 8.07 (s, 1H, H_{28}), 7.90 (s, 2H, H_{43}), 7.84 (t, J = 7.5 Hz, 1H, H_4), 7.51 (d, J = 5.5 Hz, 6H, H_{17} & H_{18} & H_{23}), 7.42 (d, J = 8.0 Hz, 1H, H_8), 7.10 (d, J = 8.5 Hz, 2H, H_{24}), 5.81 (s, 2H, H_{42}), 5.34 (s, 2H, H_{26}), 5.18 (s, 2H, H_{15}), 4.84 (t, J = 7.0 Hz, 2H, H_{38}), 4.60 (s, 3H, H_{40}), 4.56 (m, 4H, H_{20} & H_{21}), 4.41 (t, J = 7.3 Hz, 2H, H_{29}), 3.98 (t, J = 4.5 Hz, 4H, H_2), 3.94 (s, 6H, H_{48}), 3.31 (t, J = 4.5 Hz, 4H, H_1), 2.11 (m, 2H, H_{37}), 1.90 (m, 2H, H_{30}), 1.37 (m, 12H, $H_{31\text{-}36}$). ^{13}C NMR (CD_3COCD_3, 100 MHz, 298 K): δ 166.0 (C_{47}), 164.8 (C_7), 164.3 (C_{44}), 160.4 (C_{13} C_{14}), 158.6 & 157.1 (C_{25}), 143.8 (C_{27}), 140.6 (C_{16}), 140.5 (C_{41} C_3 C_9), 133.3 & 133.3 & 132.7 & 132.6 & 131.8 & 131.7 & 131.1 & 131.0 & 130.9 & 130.7 & 129.8 & 129.4 & 128.7 (C_5 C_{23} C_{39} C_{46} C_4 C_6 C_{18} C_{19}), 127.0 & 126.9 (C_{17}), 124.6 & 124.5 & 124.2 & 124.0 (C_{22} C_{10} C_{11}), 122.6 (C_{45}), 120.7 (C_{12} C_{28}), 117.4 & 116.6 & 116.3 & 116.1 & 116.0 (C_8 C_{24} C_{43}), 67.4 (C_{26}), 62.4 (C_2), 59.8 (C_{42}), 54.9 & 54.3 & 52.9 & 52.2 &52.1 (C_{29} C_{38} C_{20} C_{21} C_{48}), 50.6 (C_1), 43.5 (C_{15}), 39.3 (C_{40}), 31.0 & 27.0 & 26.6 ($C_{30\text{-}37}$). HRMS (ESI) (*m/z*): $[M\text{-}2PF_6]^{2+}$ calcd for $C_{58}H_{67}N_9O_9/2$, 516.7531; found, 516.7522.

Preparation of [2]rotaxane 1-H-o



A mixture of **8** (20 mg, 0.03 mmol) and crown ether **3**-o (44.5 mg, 0.06 mmol) was stirred in dry CH_2Cl_2 (1 mL) at room temperature for 2 h. After **12** (37.9 mg, 0.06 mmol) and $Cu(CH_3CN)_4PF_6$ (11.2 mg, 0.03 mmol) were added to the solution, the mixture was stirred for two days. After removal of the solvent, the residue was

purified via column chromatography (SiO_2, CH_2Cl_2/MeOH = 15/1) to give compound **1**-H-o (12.4 mg, 20 %) as a yellow solid. ^{1}H NMR (CD_3COCD_3, 400 MHz, 298 K): δ 9.10 (s, 1H, H_{39}), 8.63 (d, J = 8.4 Hz, 1H, H_3), 8.56 (d, J =7.2 Hz, 1H, H_5), 8.51 (d, J = 8.0 Hz, 1H, H_9), 8.27 (s, 1H, H_{45}), 7.99 (s, 1H, H_{28}), 7.90 (s, 2H, H_{43}), 7.83 (t, J = 7.8 Hz, 1H, H_4), 7.41 (dd, J = 8.4Hz, 4.0 Hz, 3H, H_{17}), 7.34 (d, J = 8.0 Hz, 2H, H_{18}), 7.26 (d, J = 8.0 Hz, 2H, H_{23}), 7.05 (s, 2H, H_{24}), 6.95-6.70 (m, 9H, Ha Hb Hh Hi Hj Hm H_v), 5.81 (s, 2H, H_{42}), 5.20 (m, 2H, H_{15}), 5.04 (s, 2H, H_{26}), 4.84 (t, J = 7.2 Hz, 2H, H_{38}), 4.72 (br, 4H, H_{20} H_{21}), 4.60 (s, 3H, H_{40}), 4.41 (t, J = 7.2 Hz, 2H, H_{29}), 4.26 (m, 2H, H_d), 4.19-4.10 (m, 6H, H_d), 3.97 (t, J = 4.4Hz, 4H, H_2), 3.94 (s, 6H, H_{48}), 3.90 (m, 2H, H_e), 3.88-3.80 (m, 6H, H_e), 3.70-3.57 (m, 8H, H_f), 3.30 (t, J = 4.4Hz, 4H, H_1), 2.11 (m, 2H, H_{37}), 1.99 (s, 3H, H_y), 1.91 (s, 3H, H_z), 1.89 (m, 2H, H_{30}), 1.30 (m, 12H, $H_{31\text{-}36}$). ^{13}C NMR (CD_3COCD_3, 100 MHz, 298 K): δ 166.1 (C_{47}), 164.8 (C_7), 164.3 (C_{44}), 160.1 (C_{13} C_{14}), 158.7 & 157.1 (C_{25}), 148.9 & 148.6 & 148.6 & 148.1 (C_c C_g), 144.0 (C_{27}), 140.8 & 140.5 & 140.0 (C_{16} C_{41} C_3 C_9), 137.4 & 136.7 & 136.7 & 134.7 & 134.4 & 134.3 (C_o C_p C_t C_l C_n C_x C_w), 133.4 & 131.9 & 131.9 & 131.8 & 130.9 & 130.8 & 130.4 & 129.3 & 128.8 & 128.3 (C_5 C_{23} C_{39} C_{46} C_4 C_6 C_{18} C_{19}), 127.1 & 127.0 (C_{17} C_k), 125.5 & 125.2 & 124.7 & 124.6 & 124.6 & 124.2 (C_{22} C_{10} C_{11} C_u C_m C_a), 122.2 (C_{45}), 122.1 & 120.8 (C_{12} C_{28} C_j), 119.0, 117.6 & 116.1 & 115.7 (C_8 C_{24} C_{43} C_h C_b), 113.8 (C_i), 113.5, 110.6, 71.7 & 71.7 & 71.3 & 71.2 & 69.2 & 68.9 (C_d C_e C_f), 67.5 (C_{26}), 62.5 (C_2), 59.9 (C_{42}), 55.1 & 54.4 & 53.1 & 53.0 (C_{29} C_{38} C_{20} C_{21} C_{48}), 50.7 (C_1), 43.6 (C_{15}), 39.4 (C_{40}), 39.0 & 38.8 (C_q C_s), 31.2 & 27.2 & 26.7 ($C_{31\text{-}37}$), 23.7 & 14.5 & 14.4 (C_y C_z C_r). HRMS (ESI) (*m/z*): $[M\text{-}2PF_6]^{2+}$ calcd for $C_{97}H_{112}ClN_9O_{17}S_2/2$, 887.3670; found, 887.3704.

Molecular modelling of four states of rotaxane **1**-H-o

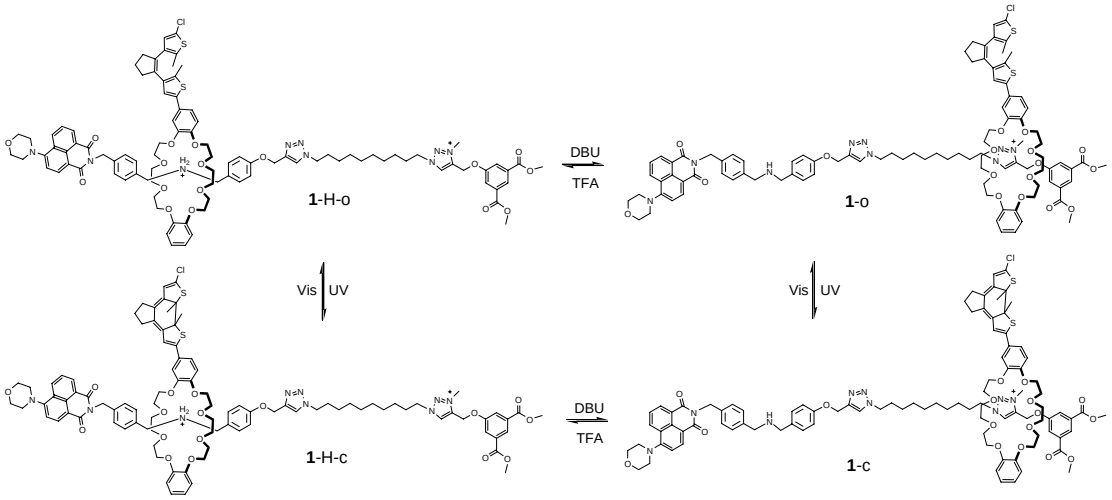
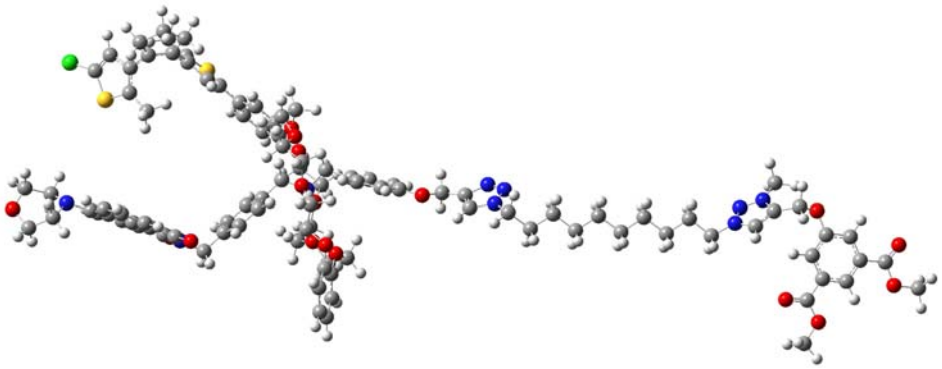
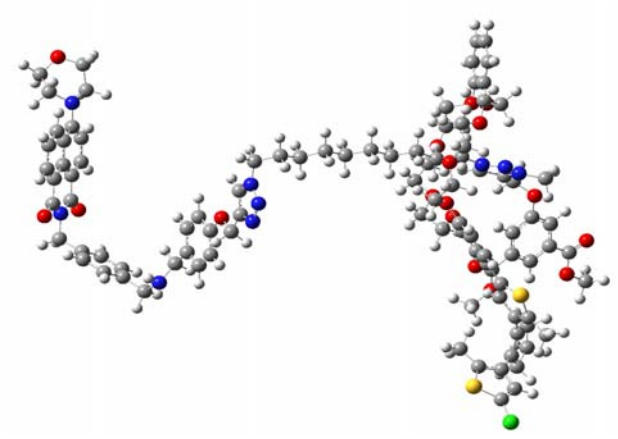


Figure S1. Interconversions of rotaxane **1**-H-o under different combination of chemical and photochemical stimuli.

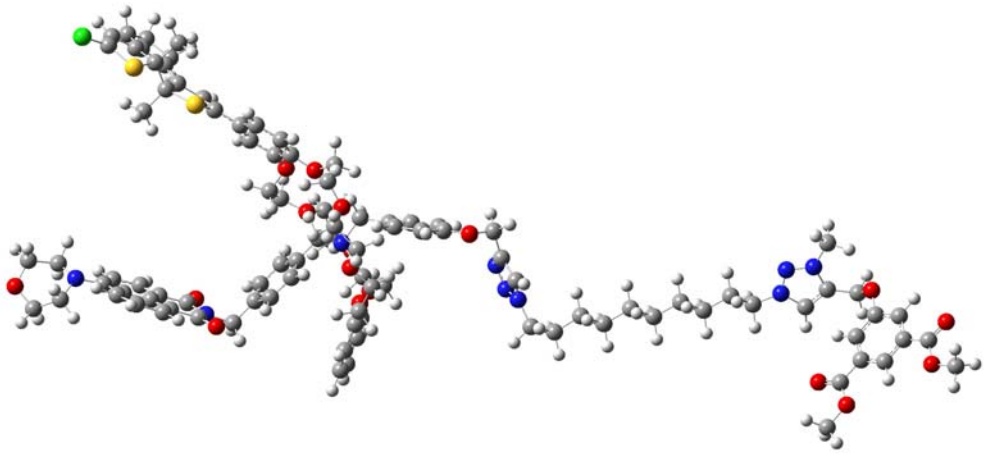
a)



b)



c)



d)

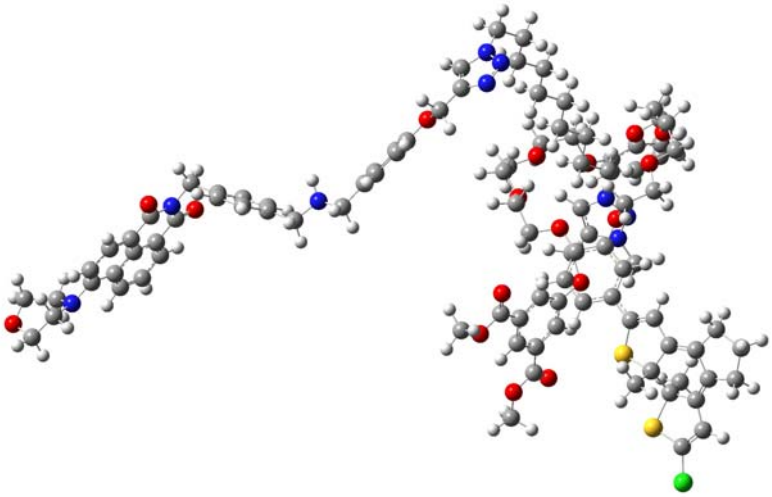


Figure S2. Four perspectives of the global energy minimum conformer of a) rotaxane**1**-H-o, b) rotaxane **1**-o, c) rotaxane **1**-H-c, d) rotaxane **1**-c.

The photophysical properties of **1**-H-o, **2**-H and **3**-o

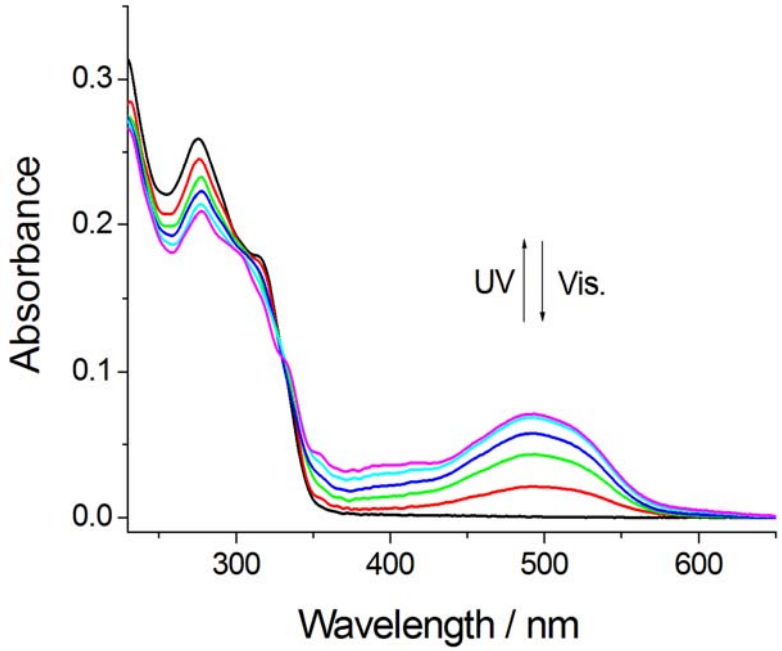


Figure S3. Changes in the UV/Vis absorption spectra of a dichloromethane solution of **3**-o when irradiated with 254 nm light to reach the photostationary state. The concentration of **3**-o in dichloromethane was 1.0×10^{-5} M.

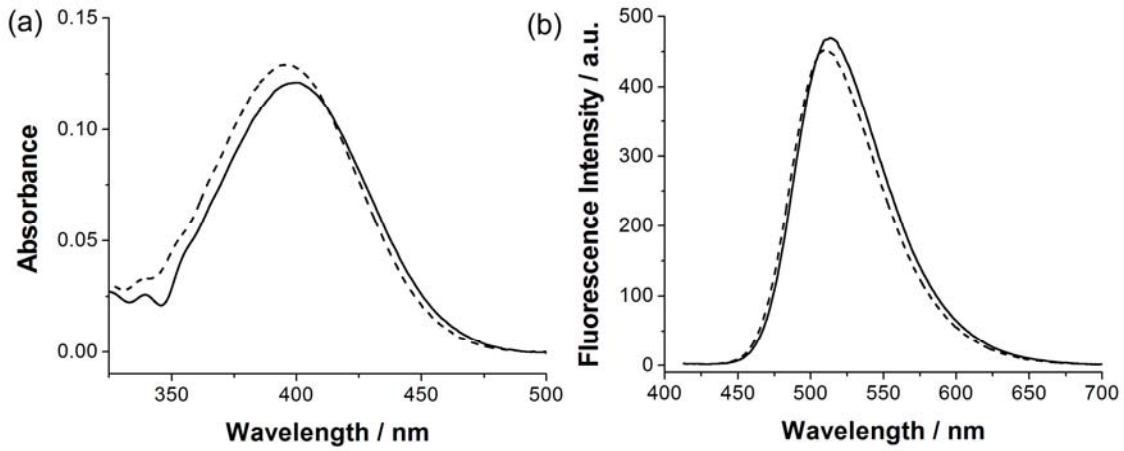


Figure S4. (a) Absorption and (b) fluorescence spectral changes of **2**-H in dichloromethane upon addition of 5 eq of DBU. The concentration of **2**-H in dichloromethane was 1.0×10^{-5} M.

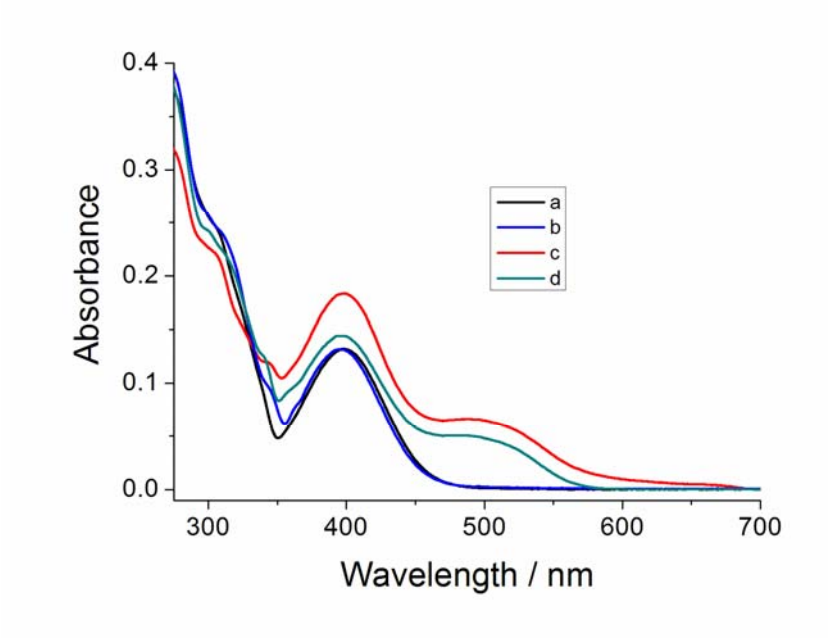


Figure S5. UV/Vis spectra of [2]rotaxane **1**-H-o in CH_2Cl_2 (1×10^{-5} M) at room temperature in the presence of different combinations of chemical and photochemical stimuli. a) original spectrum, b) upon addition of 5 eq DBU to solution a, c) irradiation of solution b at 254 nm for 210 s to reach the PSS, d) after addition of 5 eq TFA to solution c.

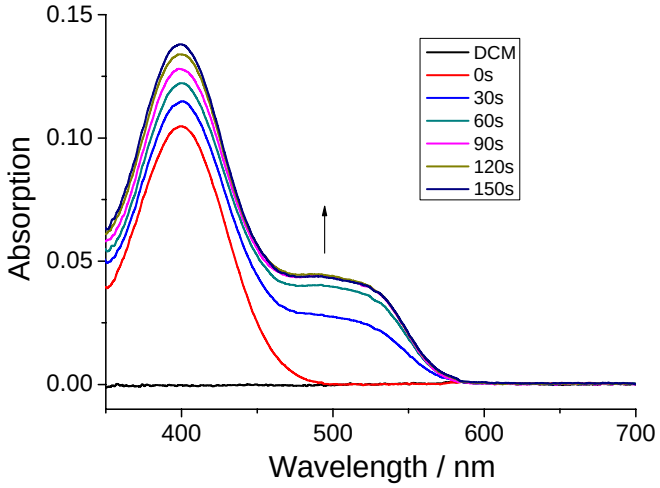


Figure S6. UV/Vis spectral change of a mixture of compound **3**-o and dumbbell **2**-H at the same concentration in CH_2Cl_2 (1×10^{-5} M) at room temperature upon irradiation at 254 nm to reach the photostationary state.

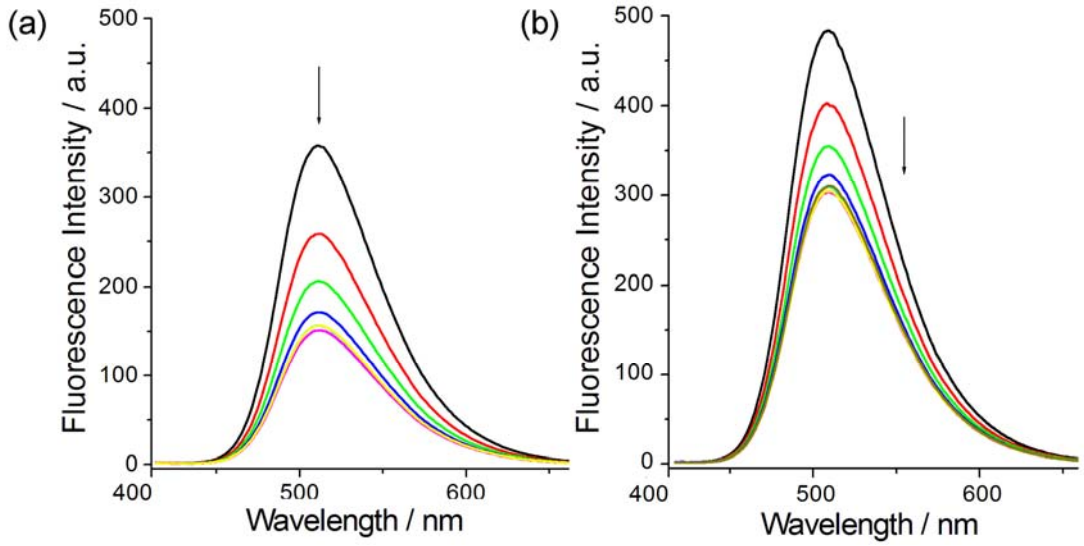


Figure S7. Fluorescence spectral changes of a) **1**-H-o, and b) **1**-H-o in the presence of of 5 eq DBU. The concentration of **1**-H-o in dichloromethane was 1.0×10^{-5} M.

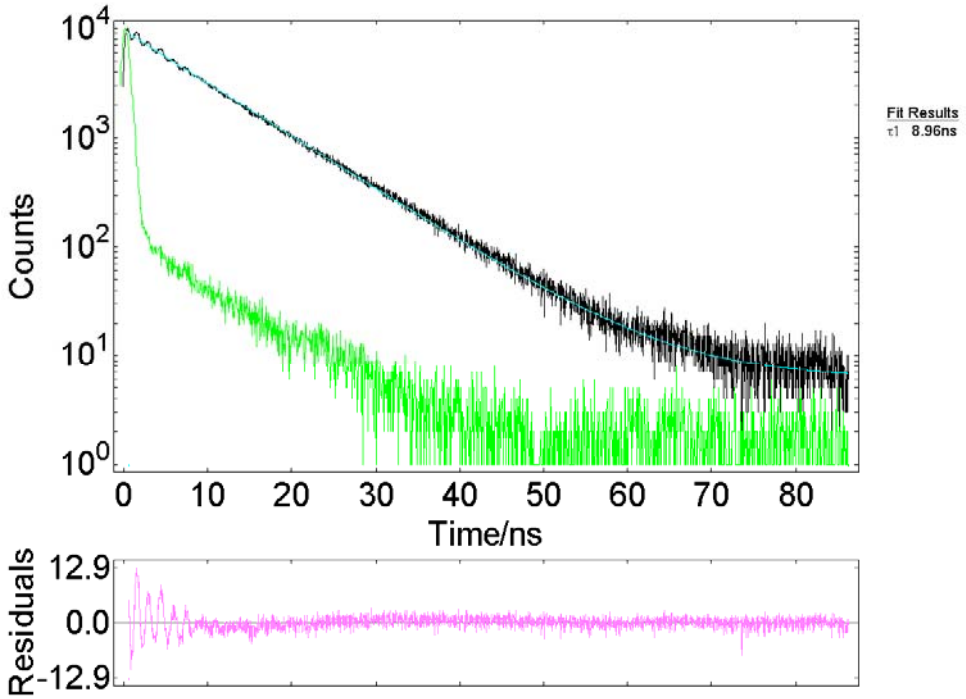


Figure S8. Fluorescence decay curve for **2**-H in CH_2Cl_2 solution (1×10^{-5}M).

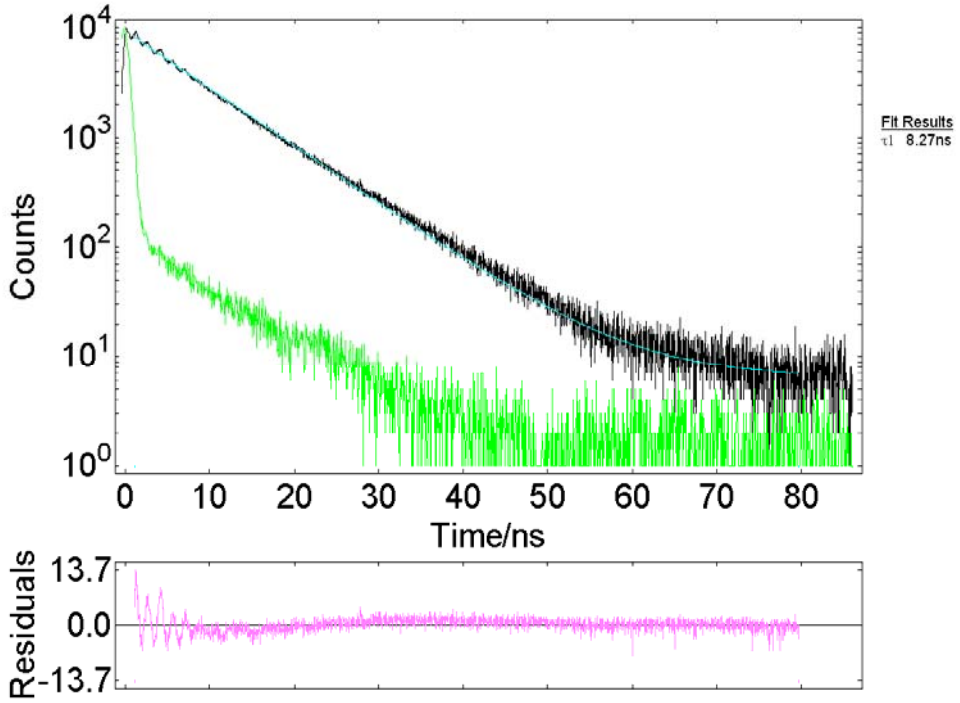


Figure S9. Fluorescence decay curve for **2**-H in CH_2Cl_2 solution (1×10^{-5}M) in the presence of 5 eq DBU.

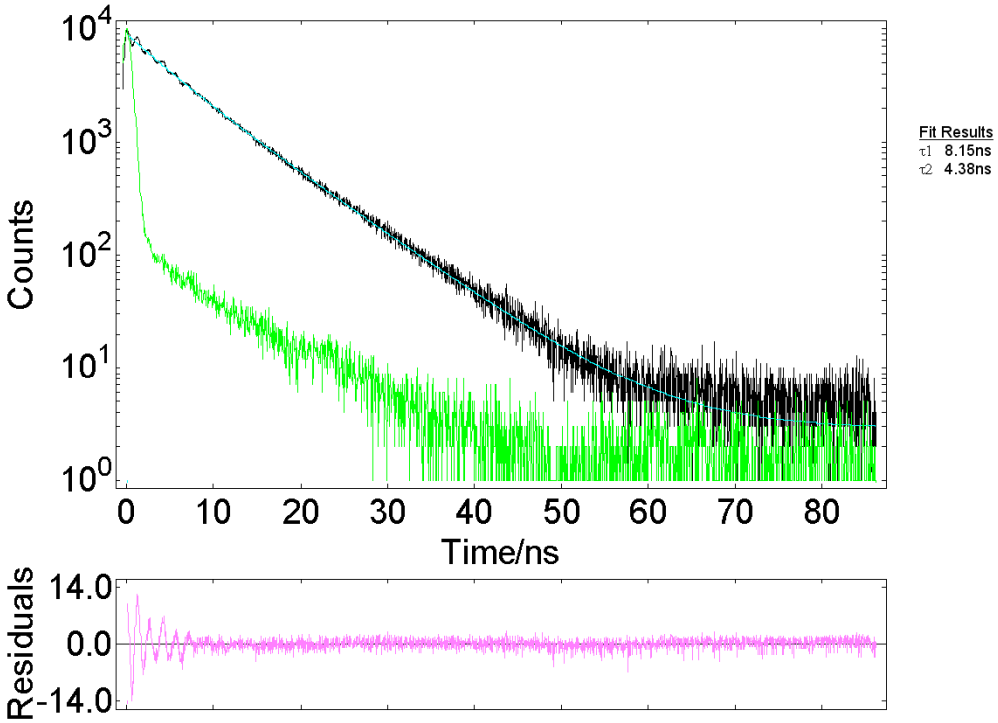


Figure S10. Fluorescence decay curve for **1**-H-o in CH_2Cl_2 solution (1×10^{-5}M).

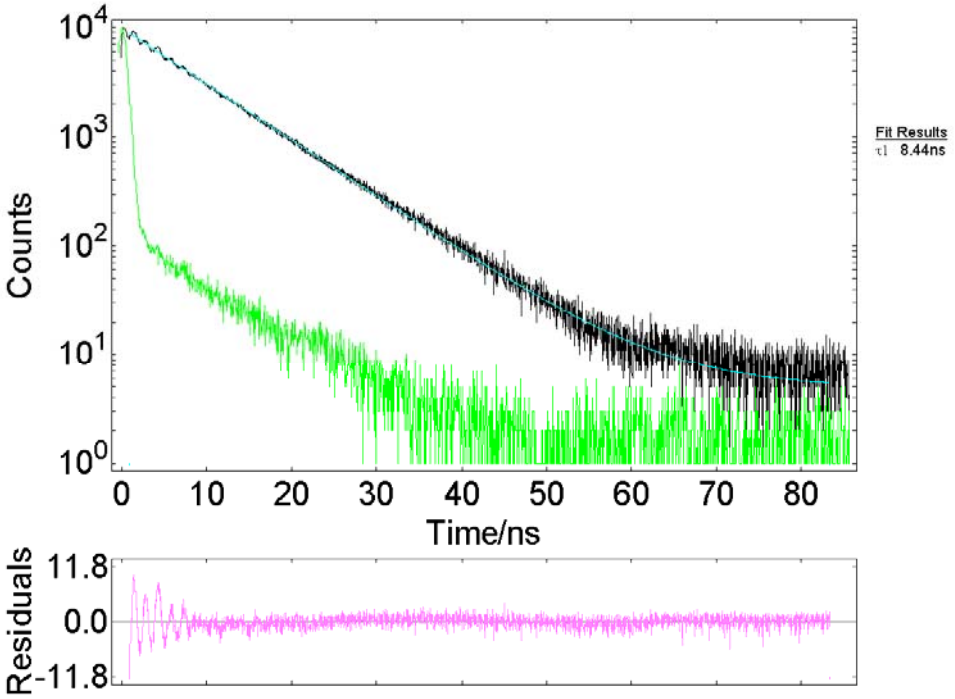


Figure S11. Fluorescence decay curve for **1**-H-o in CH_2Cl_2 solution (1×10^{-5}M) in the presence of 5 eq DBU..

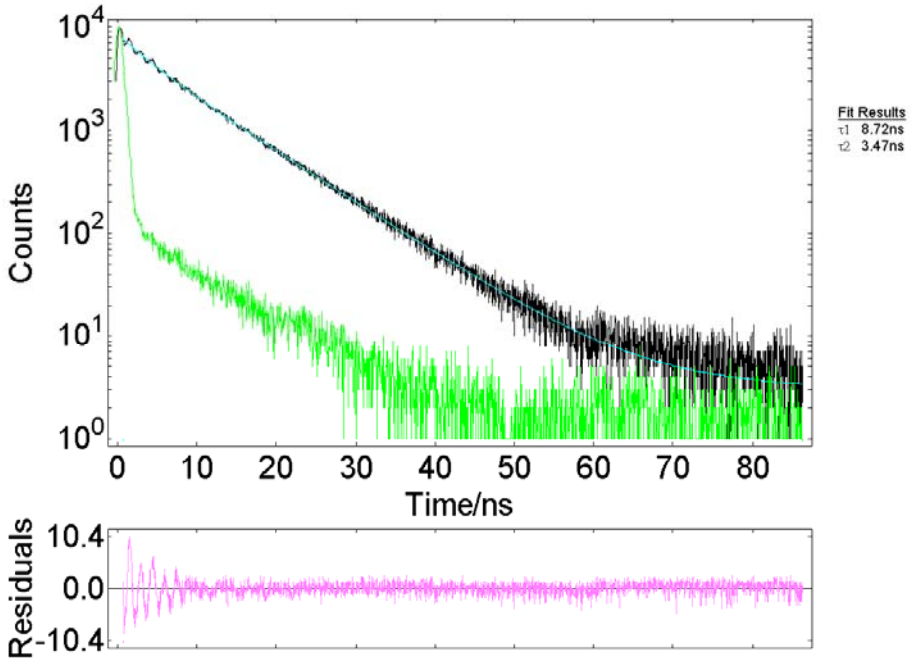


Figure S12. Fluorescence decay curve for **1**-H-o in CH_2Cl_2 solution (1×10^{-5} M) upon irradiation at 254 nm to reach the PSS.

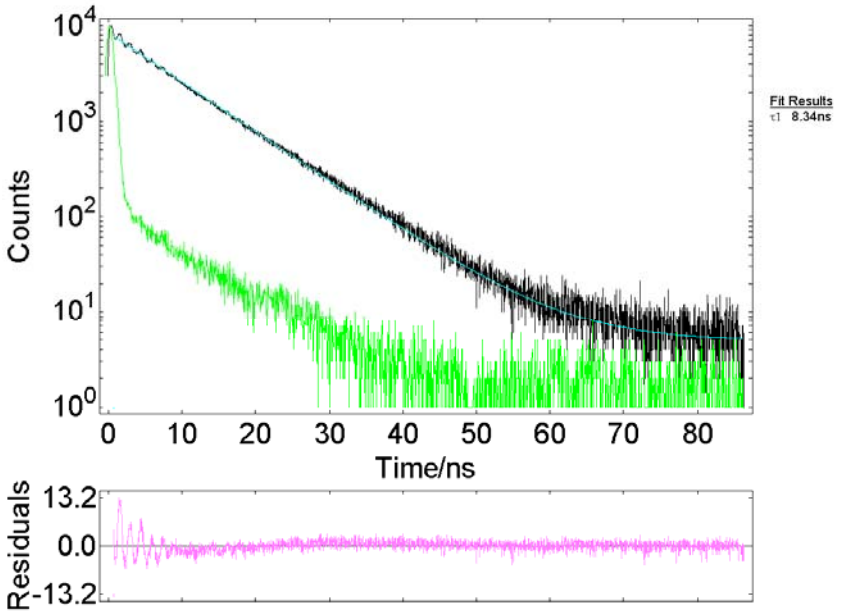
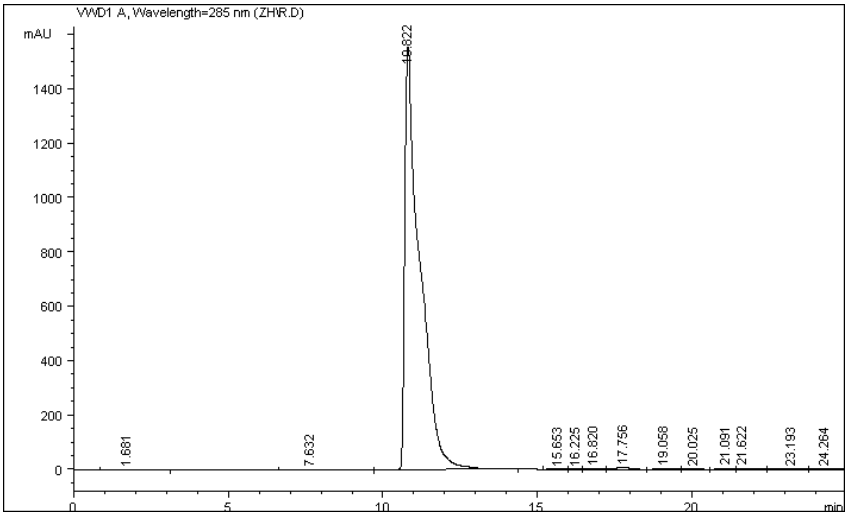


Figure S13. Fluorescence decay curve for **1**-H-o in the photostationary state (upon irradiation at 254 nm) in CH_2Cl_2 solution (1×10^{-5}M) in the presence of 5 eq DBU.



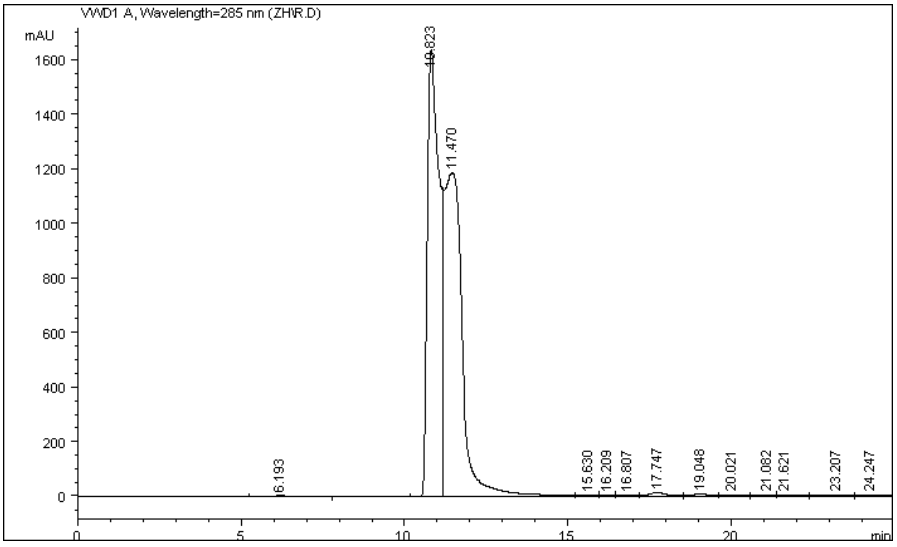


Figure S14. HPLC traces of **1**-H-o (in CH_3CN, 2.0×10^{-5} mol L^{-1}) at 25 °C eluted by CH_3CN at a flow rate of 1.0 mL/min detected at the isobestic wavelength of 335 nm: (upper) before UV light irradiation, and (below) under UV light irradiation at 365 nm until reaching photostationary state. The ratio of open/close form at the PSS state was determined as 1:1.

References:

[1] Ren, J.; Zhao, X.-L.; Wang, Q.-C.; Ku, C.-F.; Qu, D.-H.; Chang, C.-P.; Tian, H. *Dyes and Pigments* **2005**, *64*, 179-186.

[2] Wang, J.-Y.; Han, J.-M.; Yan, J.; Ma, Y.-G.; Pei, J. *Chem.-Eur. J.* **2009**, *15*, 3585-3594.

[3] Ji, F.-Y.; Zhu, L.-L.; Ma, X.; Wang, Q.-C.; Tian, H. *Tetrahedron Lett.* **2009**, *50*, 597-600.

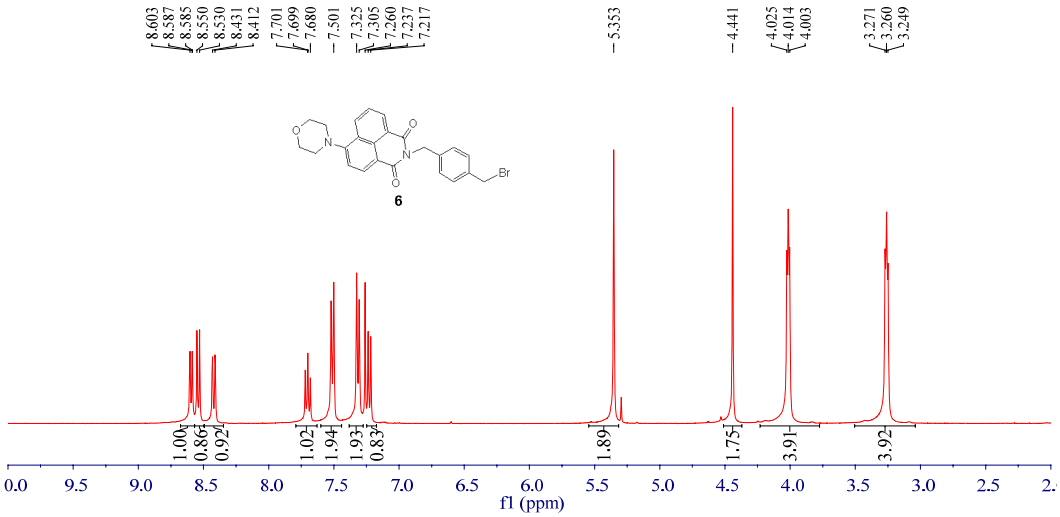
[4] Thomas, J. R.; Liu, X.-J.; Hergenrother, P. J. *J. Am. Chem. Soc.* **2005**, *127*, 12434-12435.

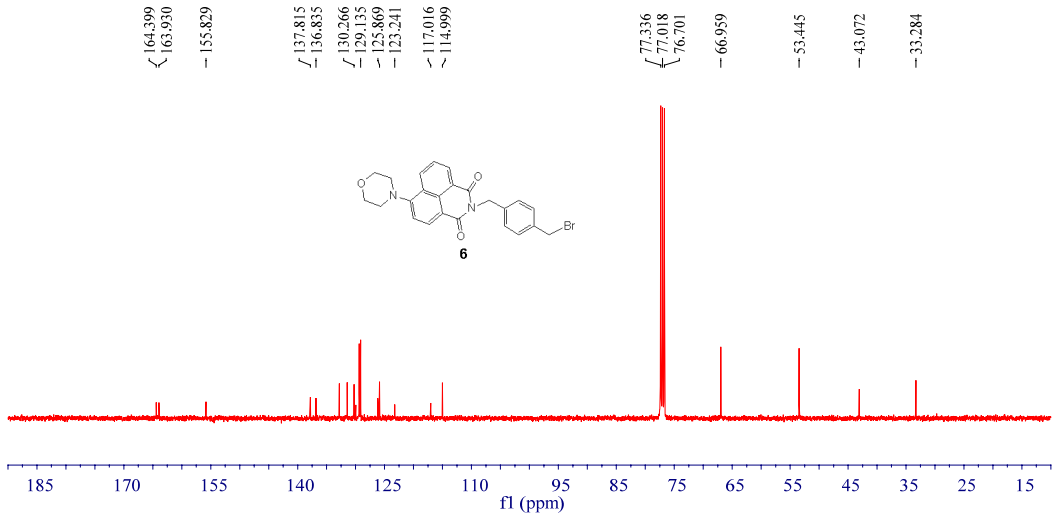
[5] (a) Lucas, L. N.; De Jong, J. J. D.; Van Esch, J. H.; Kellogg, R. M.; Feringa, B. L. *Eur. J. Org.Chem.* **2003**, *1*, 155-156; (b) Qin, B.; Yao, R.-X.; Zhao, X.-L.; Tian, H. *Org. Biomol. Chem.* **2003**, *1*, 2187-2191.

[6] Dixon, S.; Brown, R. C. D.; Gale, P. A. *Chem. Commun.* **2007**, 3565-3567.

^{1}H NMR, ^{13}C NMR and mass spectra

Compound **6**



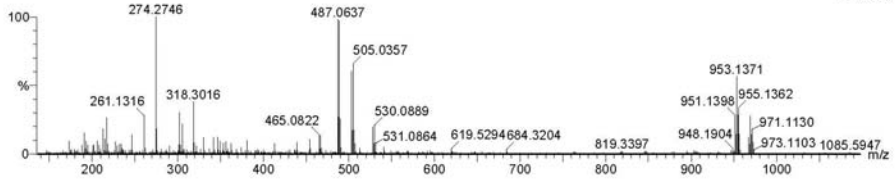


Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 4

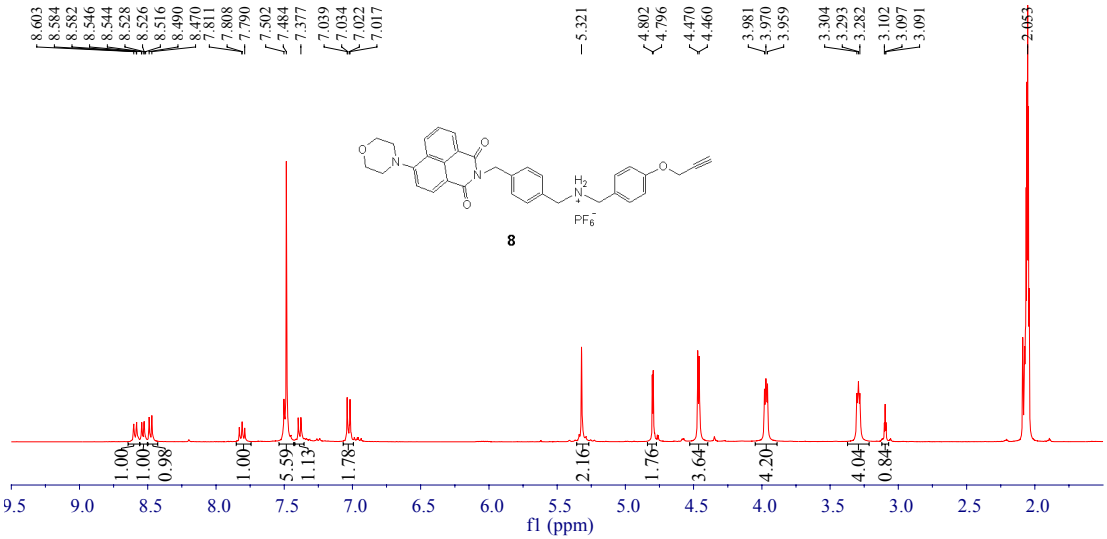
Monoisotopic Mass, Even Electron Ions
2037 formula(e) evaluated with 21 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C: 12-30 H: 0-50 N: 0-6 O: 0-11 Na: 0-1 Br: 0-8

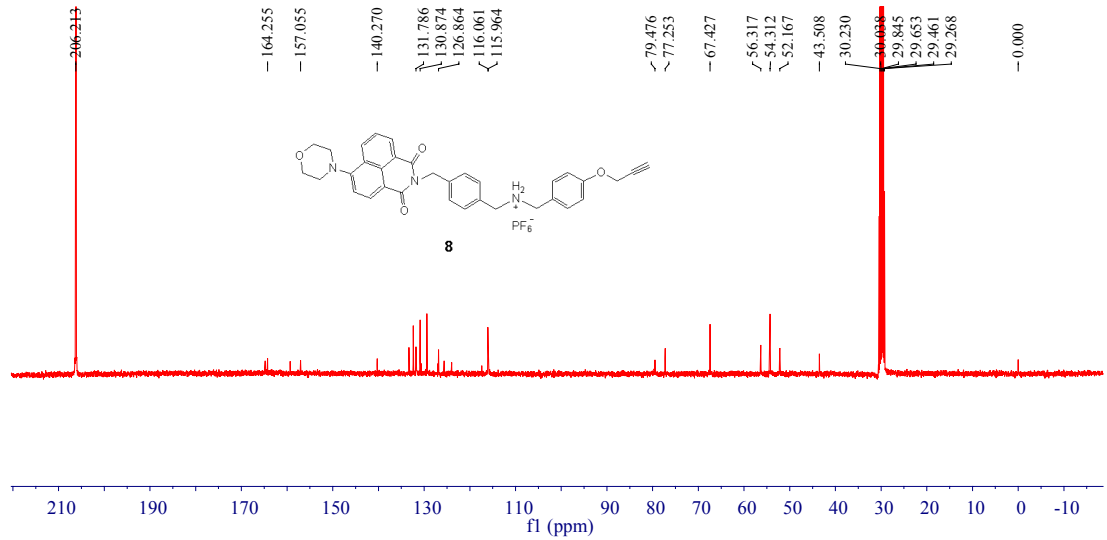
TIAN-H LCT Premier
TH-ZH-103-1 38 (1.439) Cm (29:45) Key Lab for Advanced Materials --- ECUST
1: TOF MS ES+
1.43e+004



Minimum:				-1.5			
Maximum:		5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
487.0637	487.0633	0.4	0.8	14.5	405.0	0.0	C24 H21 N2 O3 Na Br

Compound **8**



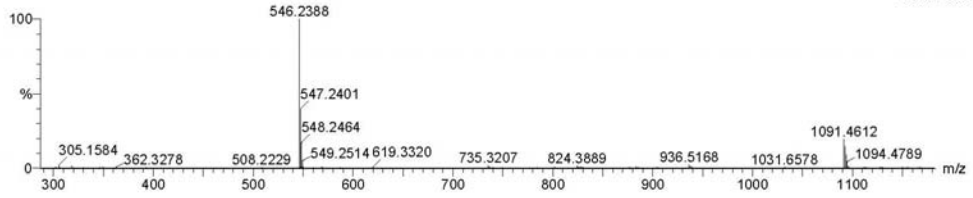


Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 4

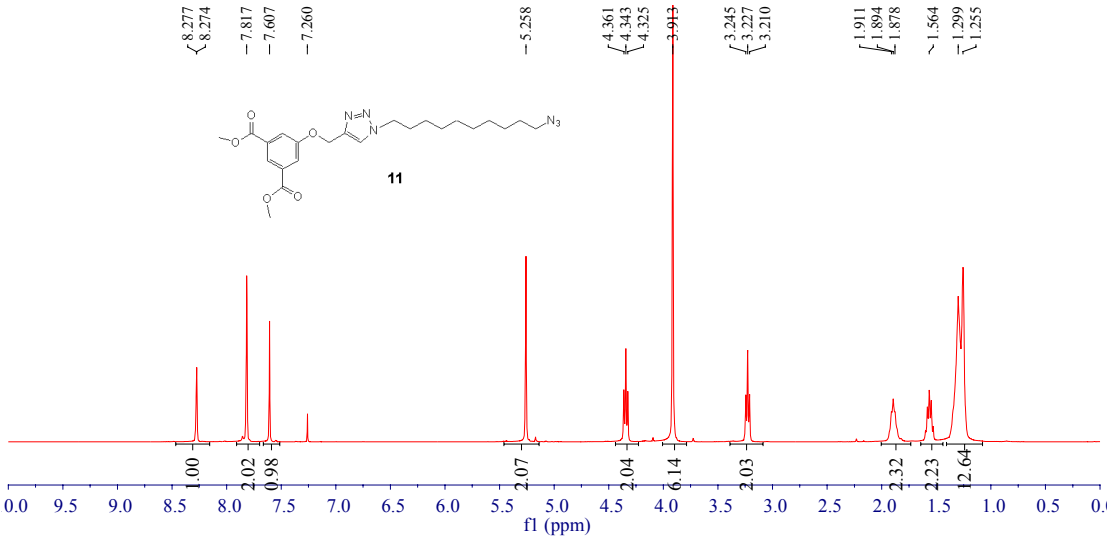
Monoisotopic Mass, Even Electron Ions
33 formula(e) evaluated with 1 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C: 5-35 H: 0-35 N: 0-5 O: 0-5

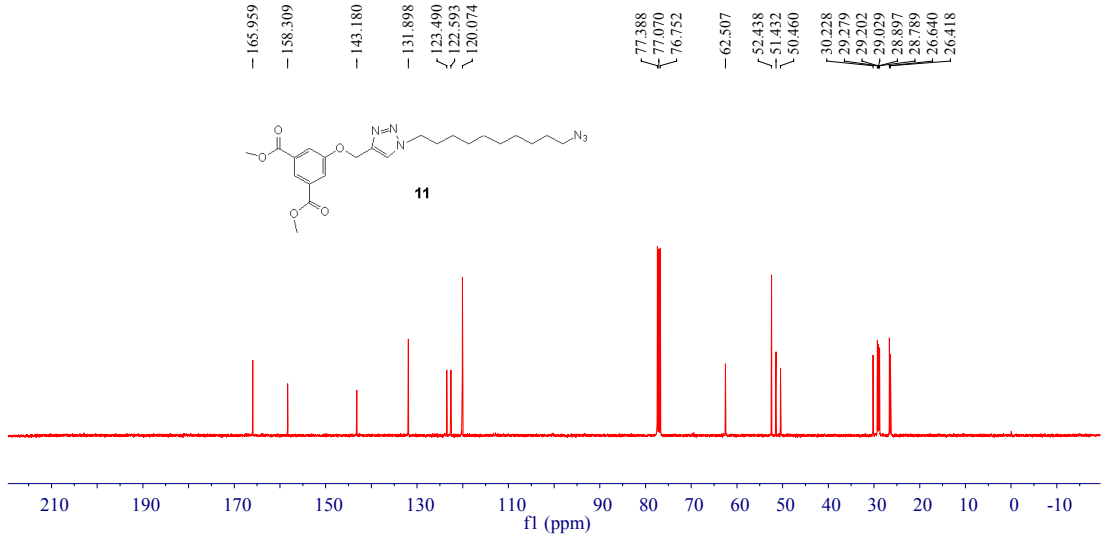
TIAN-H LCT Premier
Key Lab for Advanced Materials --- ECUST
TH-ZH-103-A3 31 (0.956) Cm (26:43) 1: TOF MS ES+
8.91e+005



Minimum:				-1.5			
Maximum:		5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
546.2388	546.2393	-0.5	-0.9	20.5	826.3	0.0	C34 H32 N3 O4

Compound **11**



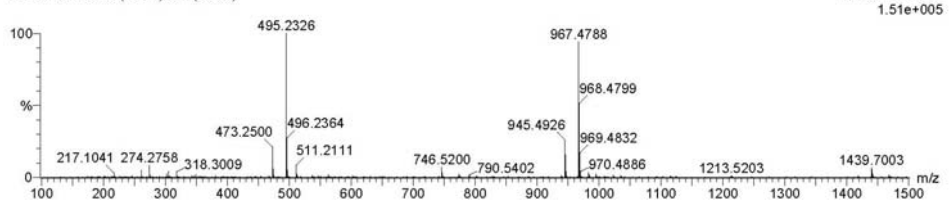


Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 4

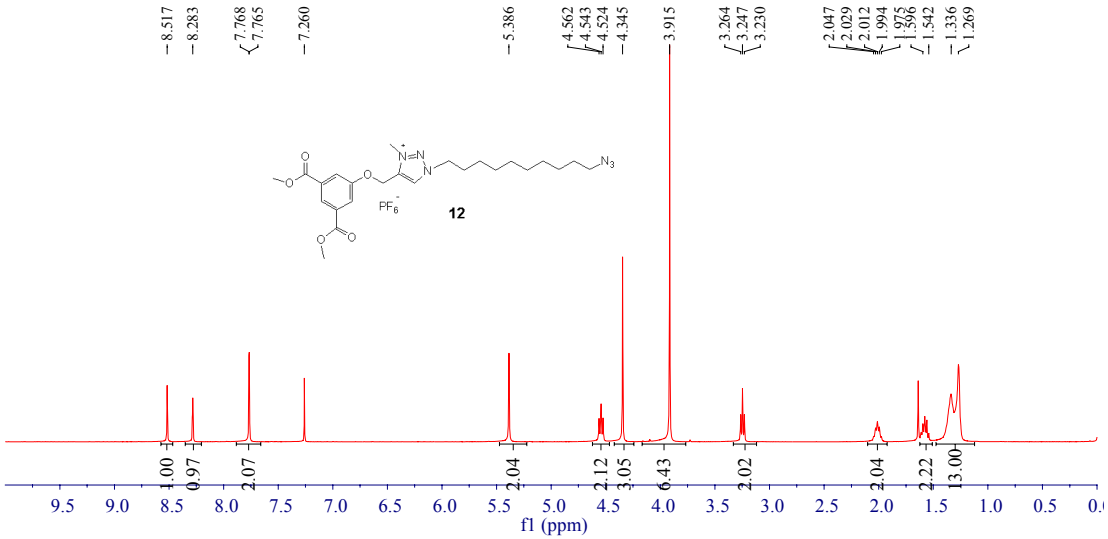
Monoisotopic Mass, Even Electron Ions
77 formula(e) evaluated with 1 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C: 0-24 H: 0-35 N: 0-6 O: 0-5 Na: 0-1

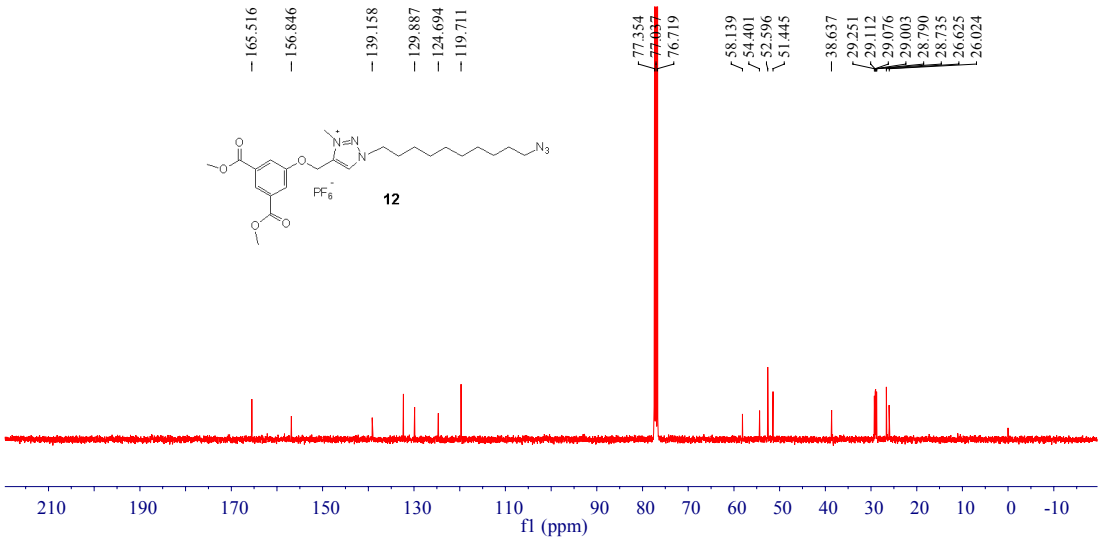
TIAN-H LCT Premier
Key Lab for Advanced Materials --- ECUST
TH-ZH-103-B2 55 (1.611) Cm (55:66) 1: TOF MS ES+ 1.51e+005



Minimum:				-1.5			
Maximum:		5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
495.2326	495.2332	-0.6	-1.2	10.5	675.8	0.0	C23 H32 N6 O5 Na

Compound **12**



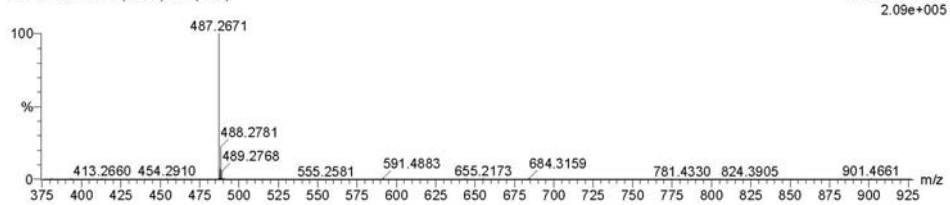


Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 4

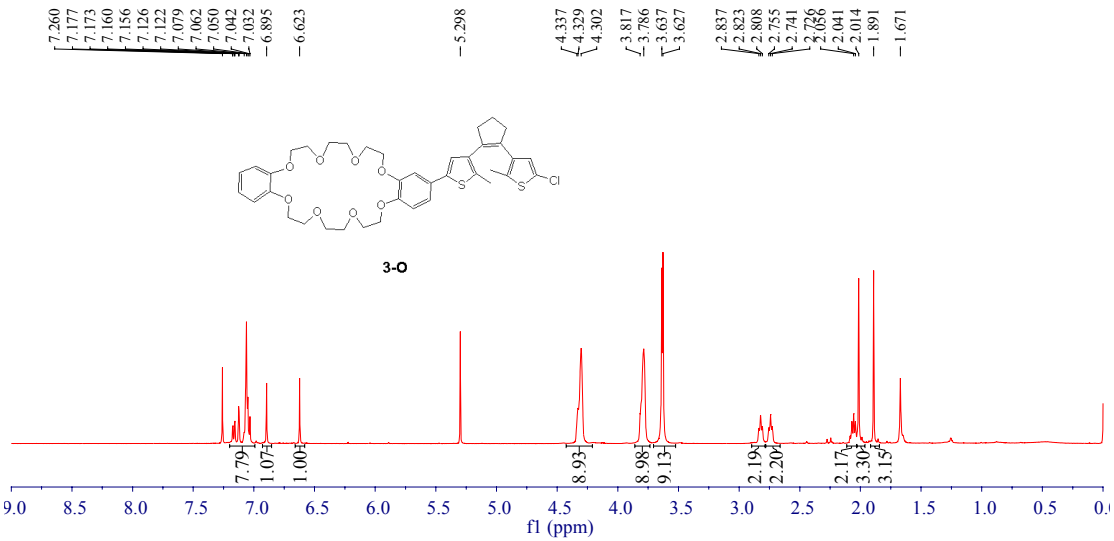
Monoisotopic Mass, Even Electron Ions
69 formula(e) evaluated with 1 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C: 24-24 H: 0-50 N: 0-6 O: 0-10

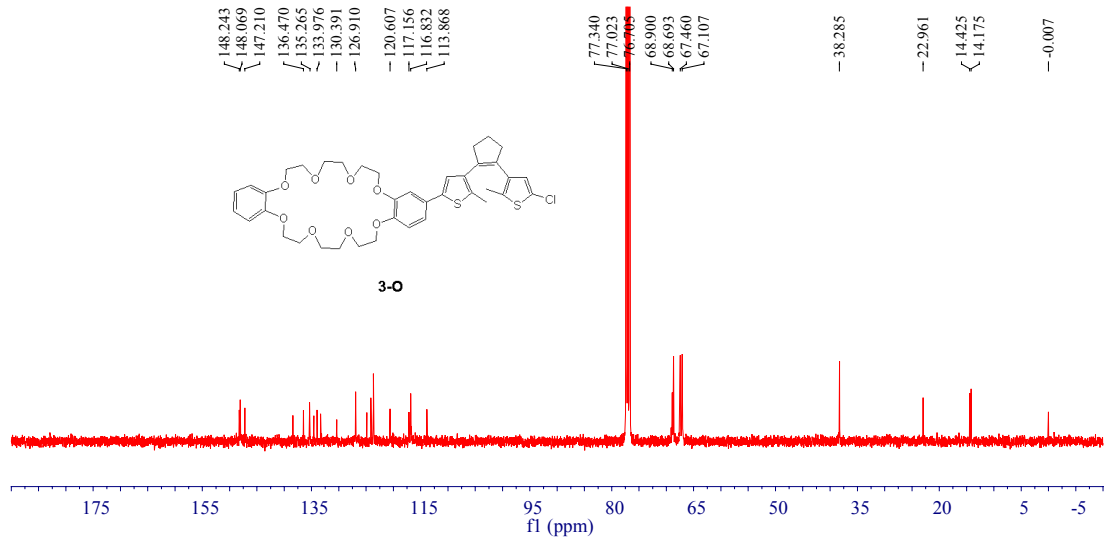
TIAN-H LCT Premier
Key Lab for Advanced Materials --- ECUST
TH-ZH-103-B3 11 (0.395) Cm (5:16) 1: TOF MS ES+
2.09e+005



Minimum:				-1.5			
Maximum:		5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
487.2671	487.2669	0.2	0.4	10.5	753.1	0.0	C24 H35 N6 O5

Compound **3**-o



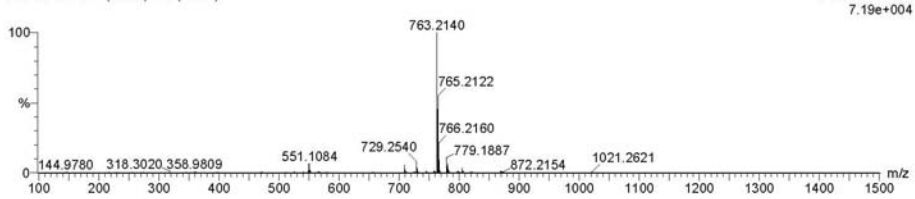


Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 4

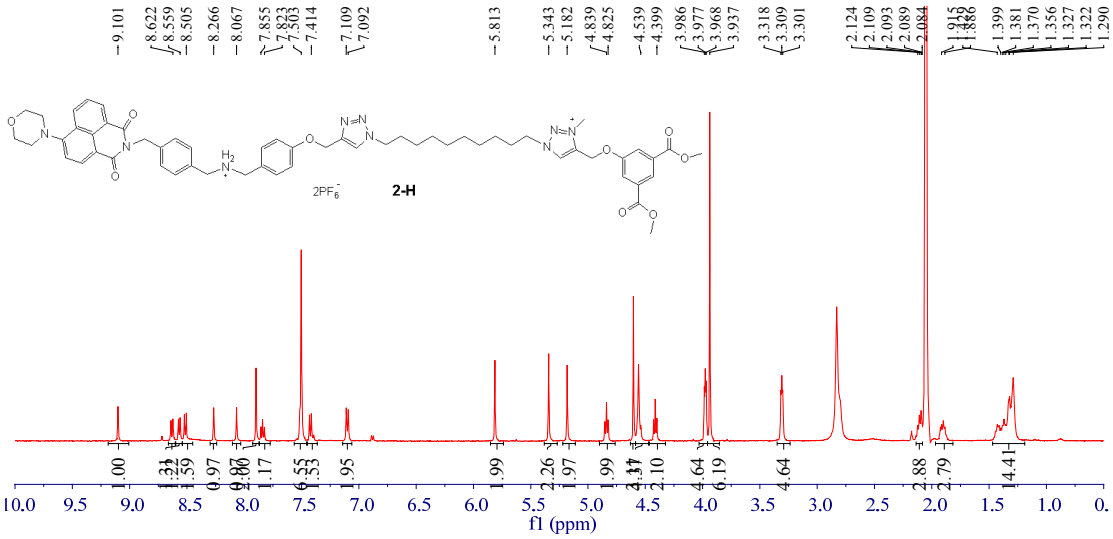
Monoisotopic Mass, Even Electron Ions
4816 formula(e) evaluated with 12 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C: 12-40 H: 0-50 O: 0-11 Na: 0-1 S: 0-6 Cl: 0-8

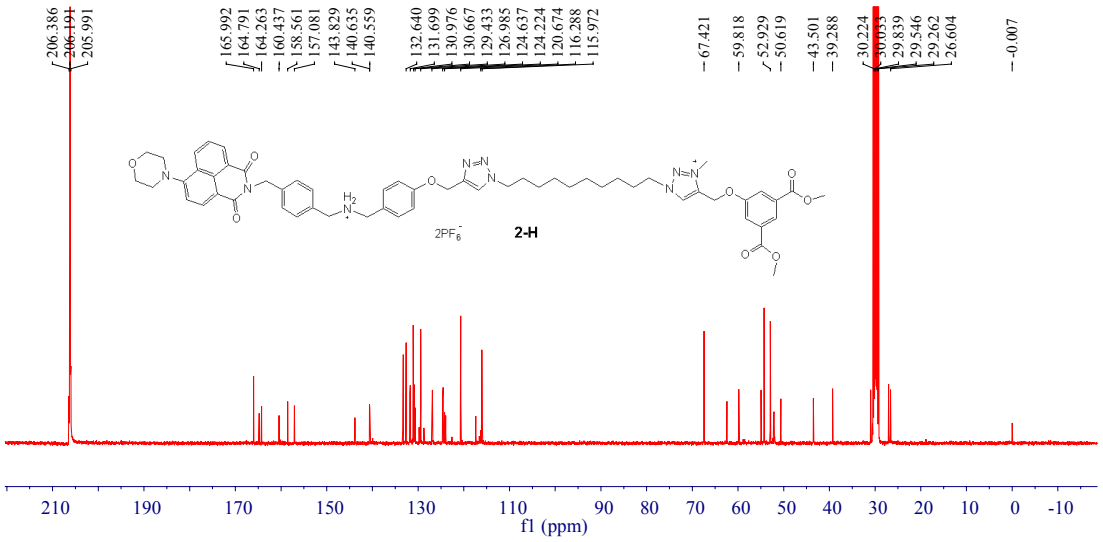
TIAN-H LCT Premier
Key Lab for Advanced Materials --- ECUST
TH-ZH-103-2 26 (1.005) Cm (25:44) 1: TOF MS ES+
7.19e+004

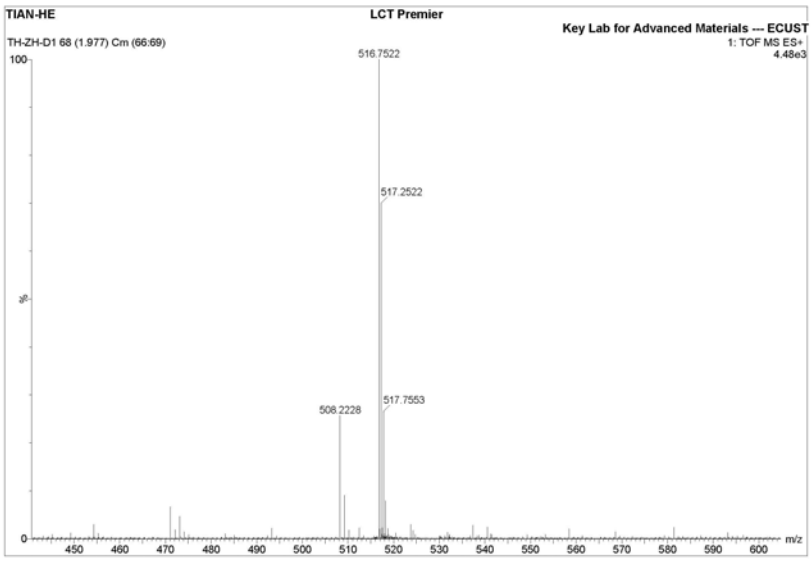


Minimum:				-1.5			
Maximum:		5.0	5.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
763.2140	763.2142	-0.2	-0.3	16.5	447.3	0.0	C39 H45 O8 Na S2 Cl

Compound **2**-H


2PF6-
2-H
f1 (ppm)


2PF6-
2-H
f1 (ppm)


TIAN-HE
LCT Premier
Key Lab for Advanced Materials --- ECUST
TH-ZH-D1 68 (1.977) Cm (66:69)
1: TOF MS ES+
4.48e3
516.7522
517.2522
517.7553
508.2228
m/z

Rotaxane **1**-H-o