Electronic Supplementary Material (ESI) for ChemComm.
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Supplementary Information

Efficient Energy-Level Modification of Novel Pyran-annulated Perylene Diimides for Photocatalytic Water Splitting

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Contents

1. **General**
2. **Synthesis Protocols**
3. **Samples Characteriaztions Profiles**
4. **Electrochemical Data and Theoretical Calculation Results**
5. **The Proposed Reaction Mechanism**
6. **References**

1. General

Materials. 3,4,9,10-Perylenetetracarboxylic dianhydride was purchased from TCI. 2-nitro-propane and diethyl malonate were purchased by Aladdin (Shanghai, China). N,N-dicyclohexyl-1-nitro-perylene-3,4,9,10-tetracarboxylic acid bisimide (**PDI-NO_2**) was synthesized according to literature.[1] All chemicals and solvents were directly used without further purification.

Instrumentation and Characterization. Solution NMR spectra were taken on a Bruker Advance 300 spectrometer in $CDCl_3$ at room temperature. Mass spectra were measured on a Bruker Maxis UHR-TOF MS spectrometer. Electrochemistry was carried out with a CHI 660A potentiostat, employing glassy carbon (diameter: 1.6 mm; area 0.02 cm^2), a platinum wire and Ag/AgCl (Ag/Ag^+) as working electrode, counter electrode, and reference electrode, respectively. Tetrabutyl-ammonium Hexafluorophosphate (0.1M) in dichloromethane was used as an electrolyte at room temperature under Argon. The potential was externally calibrated against the ferrocene/ferrocenium couple. UV−Vis absorption spectra were performed with a Beijing Purkinje General Instrument Co. Ltd. TU-1901 spectrophotometer. Fluorescence spectra measurements were performed using FLS-920 Edinburgh fluorescence spectrometer.Thermogravimetric analysis (TGA) was carried out on a TA Instrument TA Q50 Thermogravimetric Analyzer at a heating rate of 10 ^oC/min up to 650 ^oC.

Theoretical Calculation. The molecular geometry of four as-synthesized compounds in the ground state was fully optimized using density functional theory (DFT) at the B3LYP/6-31G*level, in the GAUSSIAN 03 program.

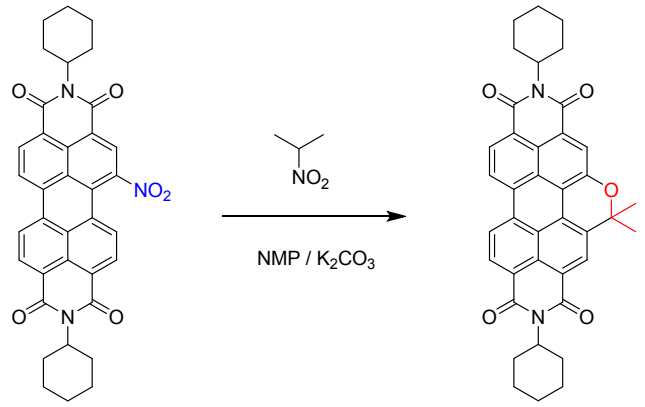
Photocatalytic Water Splitting. 20mg of the as-prepared photocatalysts were suspended in 10 mL aqueous solution containing 20 vol% methanol as sacrificial electron donor in a 20 mL Pyrex bottle with a rubber septum. Prior to photocatalysis experiment, the sample solutions were purged with N_2 for 10 minutes to remove the O_2. Each sample was irradiated by a 500 W Hg lamp at room temperature under constant

stirring of 6 hours. The amount of evolved H_2 was analyzed by gas chromatography (FULI 9750, TCD, N_2 as the carrier gas, and 5 Å molecular sieve column).

Table S1. Total amount of H_2 evolution were listed in the following:

Samples	H_2（1）/ (mmol/g)	H_2（2）/ (mmol/g)	H_2（3）/ (mmol/g)
1	0.102	0.09	0.096
2	0.486	0.516	0.492
3	0.072	0.066	0.054
4	5.10	5.52	5.58

2. Synthesis protocols

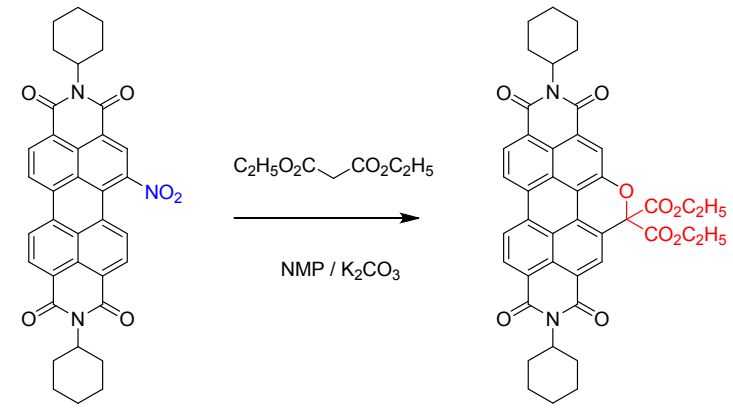


2,9-dicyclohexyl-5,5-dimethyl-5,6-dihydropyreno[2,1,10-def:7,8,9-d'e'f']diisoquinoline-6-oxa-1,3,8,10(2H,9H)-tetraone (1).

N,N-dicyclohexyl-1-nitro-perylene-3,4,9,10-tetracarboxylic acid bisimide (1) (1.5 g, 2.5 mmol), N-Methyl pyrrolidone (NMP, 50 mL), 2-nitro-propane (1.0 mL, 11.1 mmol) and grinding anhydrous potassium carbonate (1.0 g, 7.2 mmol) were added into a 100 mL flask under air and stirred at room temperature for 12 hours. Then the resulting solution was poured into 10% HCl aqueous solution (500 mL). The precipitate was collected by filtration, washed with water and methanol respectively. The crude product was purified by silica gel column chromatography using CH_2Cl_2 as eluent, yielded compound **1** as a dark-red solid (1.3 g, 85%). M.p.: 290-293 ^{o}C. ^{1}H NMR (300MHz,

$CDCl_3$, δ ppm): 8.57 (d, 1H), 8.44 (m, 3H), 8.33 (s, 1H), 8.10 (s, 1H), 5.03 (m, 2H), 2.58-2.54 (m, 4H), 1.94-1.89 (m 10H), 1.76-1.75 (m, 6H), 1.50-1.25 (m, 6H). ^{13}C-NMR (75 MHz, $CDCl_3$, δ ppm): 163.84, 163.60, 163.28, 152.18, 134.89, 134.10, 132.45, 131.24, 128.70, 128.26, 126.78, 125.91, 125.78, 124.29, 123.69, 123.52, 123.37, 122.70, 122.66, 122.36, 115.81, 80.90, 54.14, 54.10, 29.12, 28.89, 26.57, 25.50, 25.43. FT-IR (cm^{-1}): 2920, 2850, 1689, 1651. HRMS: $C_{40}H_{35}N_2O_5$ (M^+ + H), calcd 611.2415, found 611.2421.

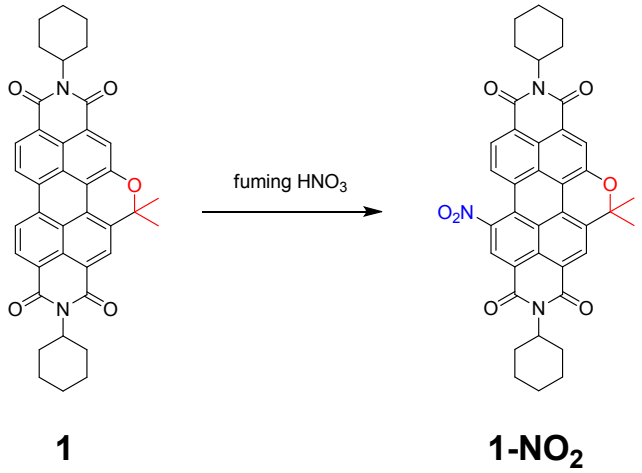
Diethyl-2,9-dicyclohexyl-1,3,8,10-tetraoxo-1,2,3,5,6,8,9,10-octahydropyreno[2,1,10-def:7,8,9-d'e'f']diisoquinoline-6-oxa -5,5-dicarboxylate (2)



PDI-NO_2 **2**

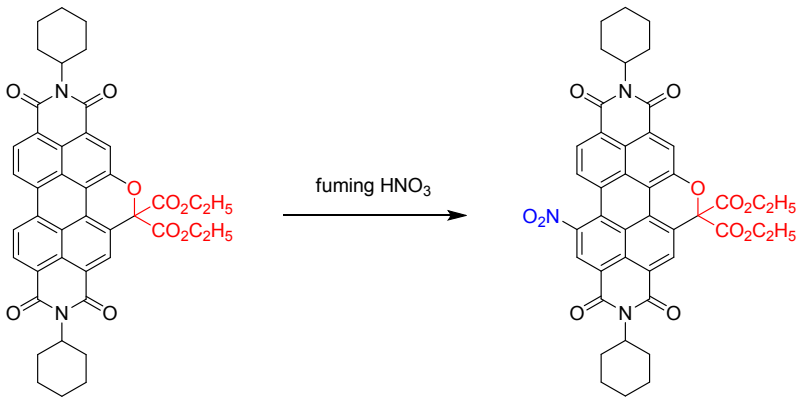
Compound **2** was synthesized following the procedure of compound **1**. **PDI-NO_2** (1.5 g, 2.5 mmol), diethyl malonate (3.3 mL, 11.1 mmol) and grinding anhydrous K_2CO_3 (1.0 g, 7.2 mmol) reacted for 12 h in NMP (50 mL) to yield compound **2** as a red solid (1.2 g 79%). M.p. : 294-297 °C. ^{1}H NMR (300MHz, $CDCl_3$, δ ppm): 8.61-8.59 (m, 2H), 8.50-8.47 (m, 3H), 8.29 (s, 1H), 5.01 (m, 2H), 4.39 (q, 4H), 4.39 (m, 4H), 2.56 (m, 4H), 1.95-1.91 (m, 4H), 1.77 (m, 6H), 1.53-1.34 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 165.89, 163.48, 163.06, 150.56, 134.81, 132.61, 132.01, 130.03, 129.58, 129.10, 126.63, 126.33, 125.27, 124.97, 123.99, 123.44, 123.09, 123.01, 122.91, 121.79, 114.96, 84.78, 63.60, 54.96, 54.22, 54.15, 29.10, 26.53, 26.41, 25.39, 25.26, 14.01. FT-IR (cm^{-1}): 2926, 2854, 1744, 1696, 1656. HRMS: $C_{44}H_{39}N_2O_9$ (M^+ + H), calcd, 727.2877, found 727.2817.

2,9-dicyclohexyl-5,5-dimethyl-12-nitro-5,6-dihydropyreno[2,1,10-def:7,8,9-d'e'f']diisoquinoline-6-oxa-1,3,8,10(2H,9H)-tetraone (1-NO_2).



compound **1-NO_2** (611.0 mg, 1.0 mmol) and dichloromethane (50 mL) was mixed in 100mL round-bottom flask at room temperature. Then, fuming nitric acid(65-68%, 1 mL, 1.4 mmol) was added dropwise to the above mixture and stirred for 30 mins. The resulting solution was poured into a 10% Na_2CO_3 aqueous solution (300mL), extracted using dichloromethane and dried over $MgSO_4$. the solvent was evaporated. The crude product was purified by chromatography (SiO_2,dichloromethane) to give compound **1-NO_2** as a purple solid (600.1mg, 92%). ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 8.57 (s, 1H), 8.47 (s, 1H), 8.41 (d, 1H), 8.18 (m, 2H), 5.02 (m, 2H), 2.56 (m, 4H), 1.93 (m, 10H), 1.77-1.74 (m, 6H), 1.50-1.31 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 163.24, 163.12, 163.02, 162.10, 153.18, 147.09, 135.03, 128.77, 128.47, 128.01, 127.56, 127.25, 126.69, 126.24, 125.31, 124.16, 123.34, 123.00, 114.83, 81.08, 54.46, 54.28, 29.06, 29.01, 26.48, 25.34. HRMS: $C_{39}H_{33}N_3O_7$ (M^+), calcd, 656.2230, found 656.2254.

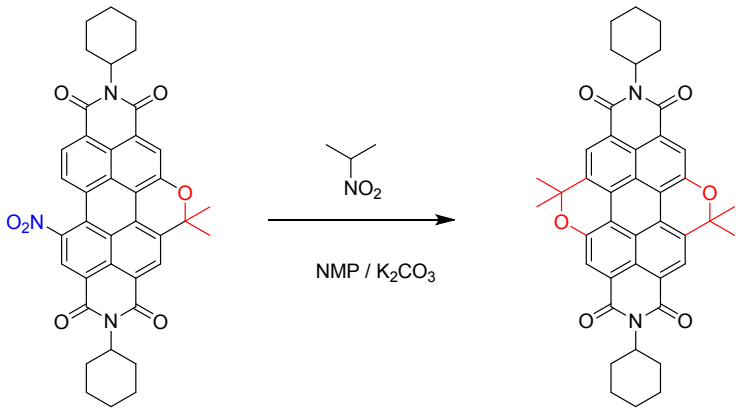
Diethyl-2,9-dicyclohexyl-12-nitro-1,3,8,10-tetraoxo-1,2,3,5,6,8,9,10-octahydropyreno[2,1,10-def:7,8,9-d'e'f']diisoquinoline-6-oxa -5,5-dicarboxylate (2-NO_2)



2 **2-NO_2**

Compound **2-NO_2** was synthesized following the procedure of compound **1-NO_2**. Compound **2** (727.0 mg, 1.0 mmol) and fuming nitric acid (1 mL, 1.4 mmol) reacted for 30 mins in dichloromethane (50 mL) to yield compound **2-NO_2** as a purple solid (690.2 mg 79%).^{1}H NMR (300 MHz $CDCl_3$, δ ppm): 8.71 (s, 1H), 8.60 (s, 1H), 8.44 (d, 1H), 8.38 (s, 1H), 8.19 (d, 1H), 5.01 (m, 2H), 4.39 (q, 4H), 2.52 (m, 4H), 1.93 (m, 4H), 1.77-1.74 (m, 6H), 1.48-1.31 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 165.54, 162.82, 162.71, 162.64, 161.85, 151.33, 147.13, 131.57, 129.43, 129.18, 128.27, 127.62, 127.47, 127.26, 126.70, 126.21, 125.50, 125.41, 125.13, 124.65, 124.15, 123.83, 123.10, 121.98, 113.87, 84.65, 63.84, 54.57, 54.39, 29.05, 28.99, 26.46, 25.33, 13.99. HRMS: $C_{43}H_{37}N_3O_{11}$ (M^+), calcd, 771.2428, found 771.2414.

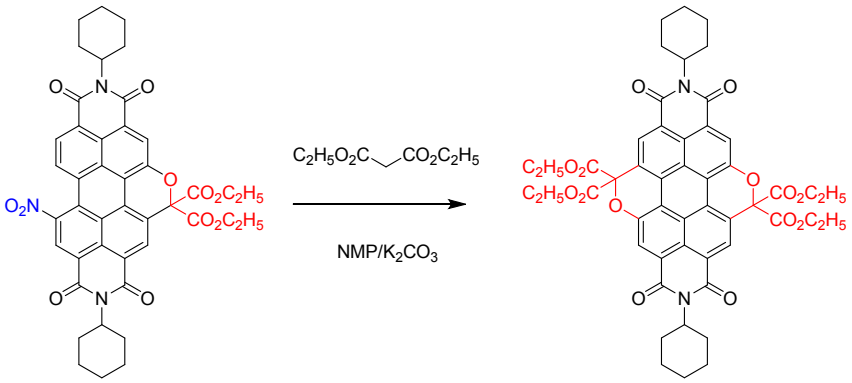
2,9-dicyclohexyl-5,5,12,12-tetramethyl-5,6-dihydropyreno[2,1,10-def:7,8,9-d'e'f']diisoquinoline-6,13-dioxa-1,3,8,10(2H,9H)-tetraone (3).



1-NO_2 **3**

Compound **3** was synthesized following the procedure of compound **1**. Compound **1-NO_2** (600 mg, 1.0 mmol), 2-nitro-propane (0.5 mL, 5.6 mmol) and K_2CO_3 (500 mg, 3.6 mmol) reacted for 12h in NMP (20 mL) to yield compound **3** as a dark-purple solid (534.1 mg 79%).M.p.: 297-300 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 8.16 (s, 2H), 8.07 (s, 2H), 5.03 (m, 2H), 2.56 (m, 4H), 1.90 (m, 16H), 1.77-1.74 (m, 6H), 1.49-1.31 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 163.97, 163.42, 152.09, 135.08, 124.87, 124.48, 123.75, 123.30, 122.26, 116.56, 81.85, 54.11, 29.31, 29.12, 26.56, 25.44. FT-IR (cm^{-1}): 2925, 2851, 1687, 1651. HRMS: $C_{42}H_{38}N_2O_6$ (M^++H), calcd, 667.2630; found 667.2675.

Tetraethyl-2,9-dicyclohexyl--1,3,8,10-tetraoxo-1,2,3,5,6,8,9,10-octahydropyreno[2,1,10-def:7,8,9-d'e'f']diisoquinoline-6,13-dioxa -5,5,12,12-tetracarboxylate (4)



2-NO_2 **4**

Compound **4** was synthesized following the procedure of compound **2**. Compound **2-NO_2** (730mg, 1.0 mmol), diethyl malonate (1.5 mL, 5.5 mmol)and K_2CO_3 (500.0 mg, 3.6 mmol) reacted for 12h in NMP (20 mL) to yield compound **4** as a dark-red solid (534.1 mg 79%).M.p.: 301-304 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 8.49 (s, 2H), 8.31 (s, 2H), 5.02 (m, 2H), 4.38 (q, 8H), 2.56 (m, 4H), 1.90 (m, 6H), 1.75-1.71 (m, 6H), 1.47-1.33 (m, 18H). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 165.59, 163.26, 162.92, 150.61, 128.33, 125.71, 124.98, 124.57, 124.14, 123.75, 122.76, 122.10, 115.30, 85.07, 63.60, 54.30, 29.09, 26.52, 25.39, 13.99. FT-IR (cm^{-1}): 2926, 2852, 1744, 1693, 1656. HRMS: $C_{42}H_{38}N_2O_6$ (M^++H), calcd, 899.2949; found 899.2924.

3. Samples Characteriaztions Profiles

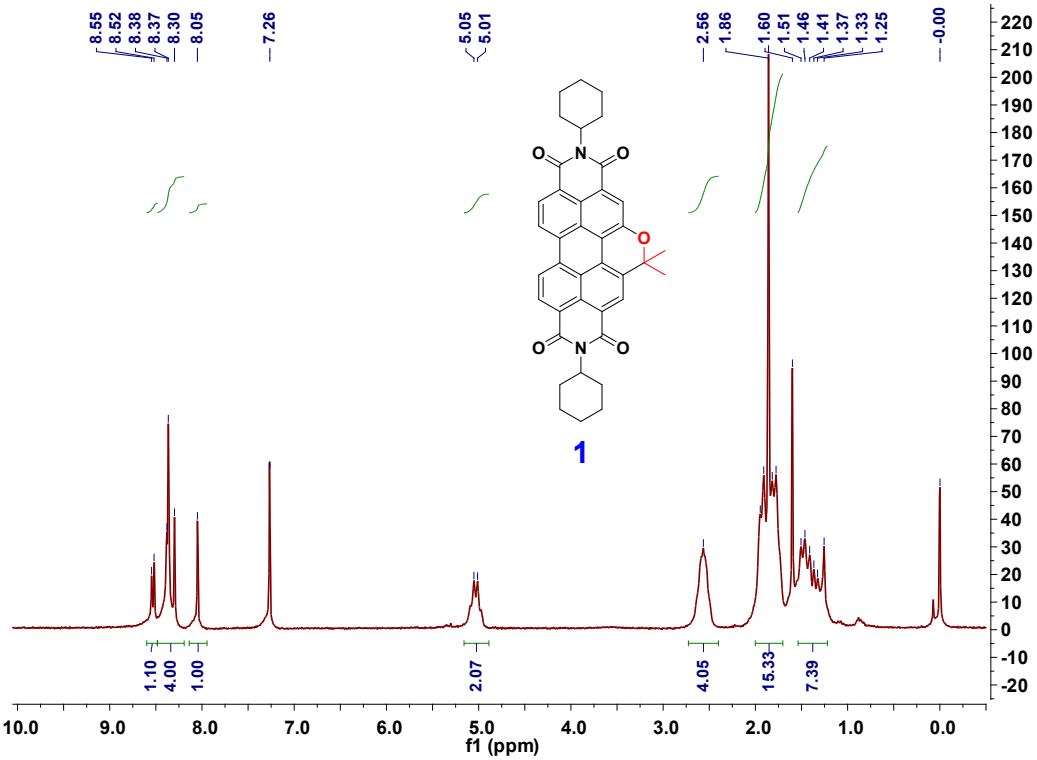


Figure S1. ^{1}H NMR spectrum of compound **1.**

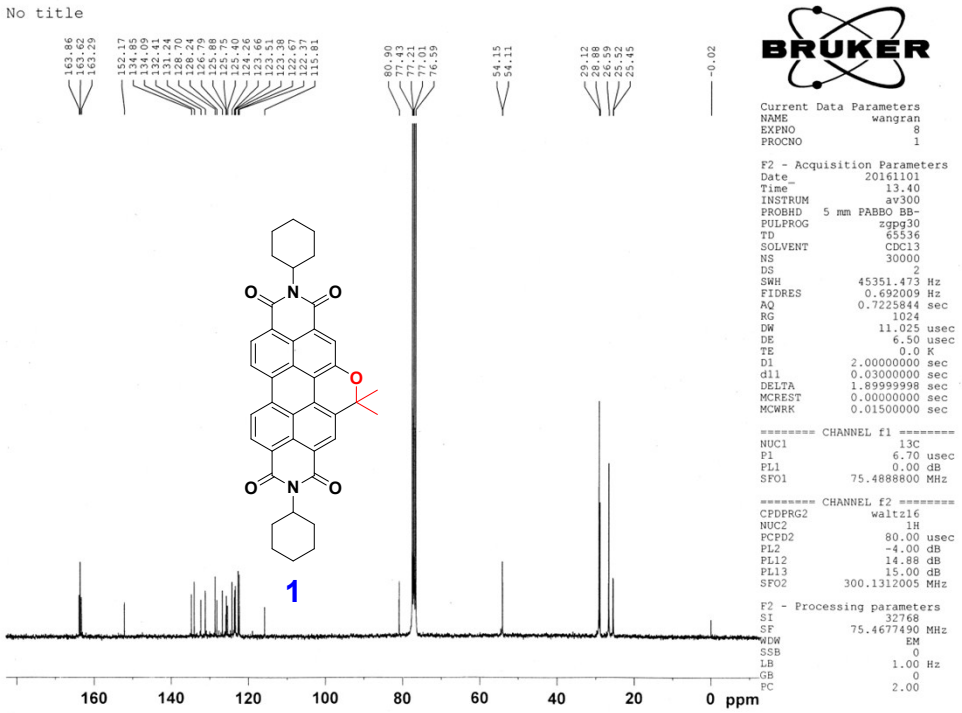


Figure S2. ^{13}C NMR spectrum of compound **1.**

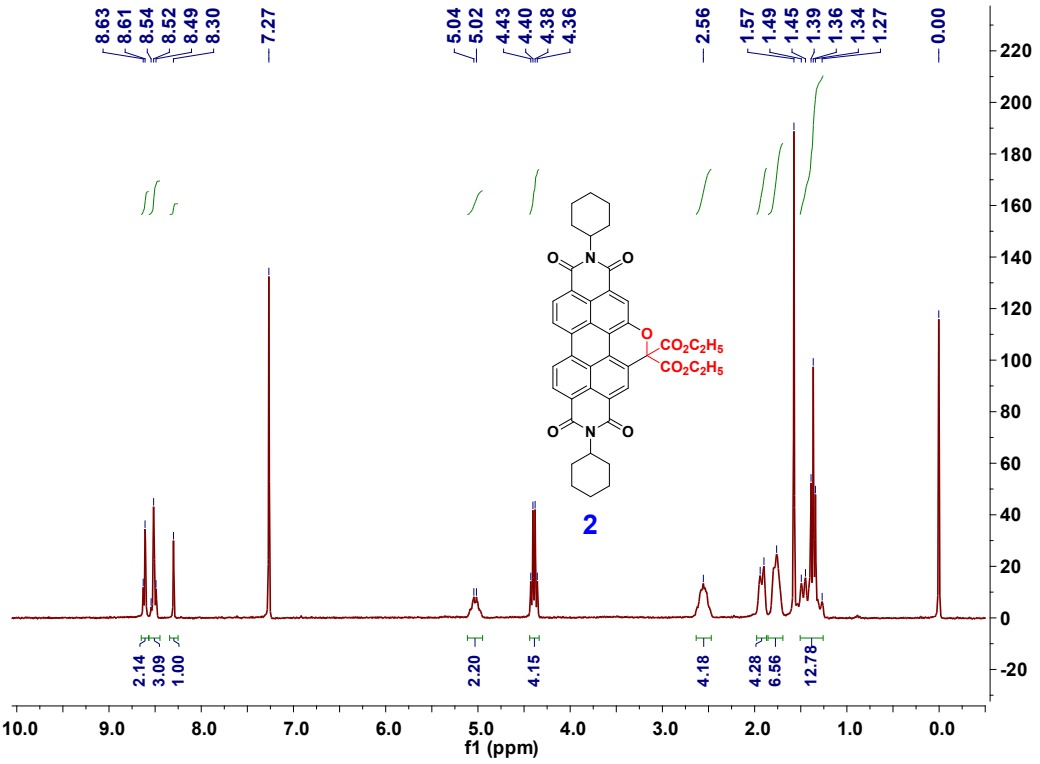


Figure S3. ^{1}H NMR spectrum of compound **2.**

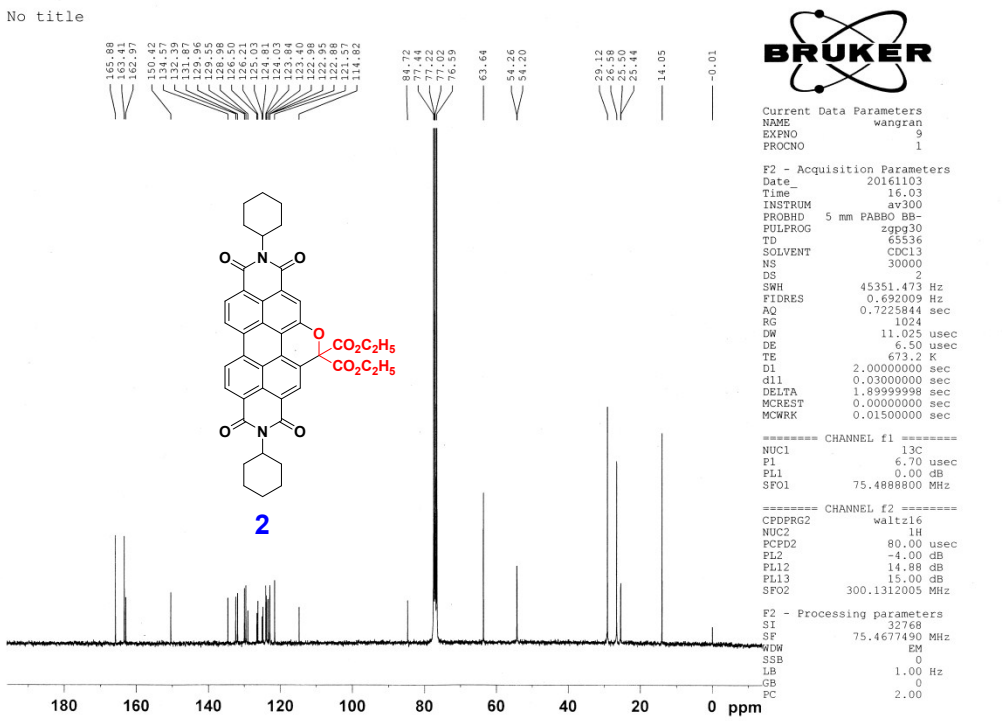


Figure S4. ^{13}C NMR spectrum of compound **2.**

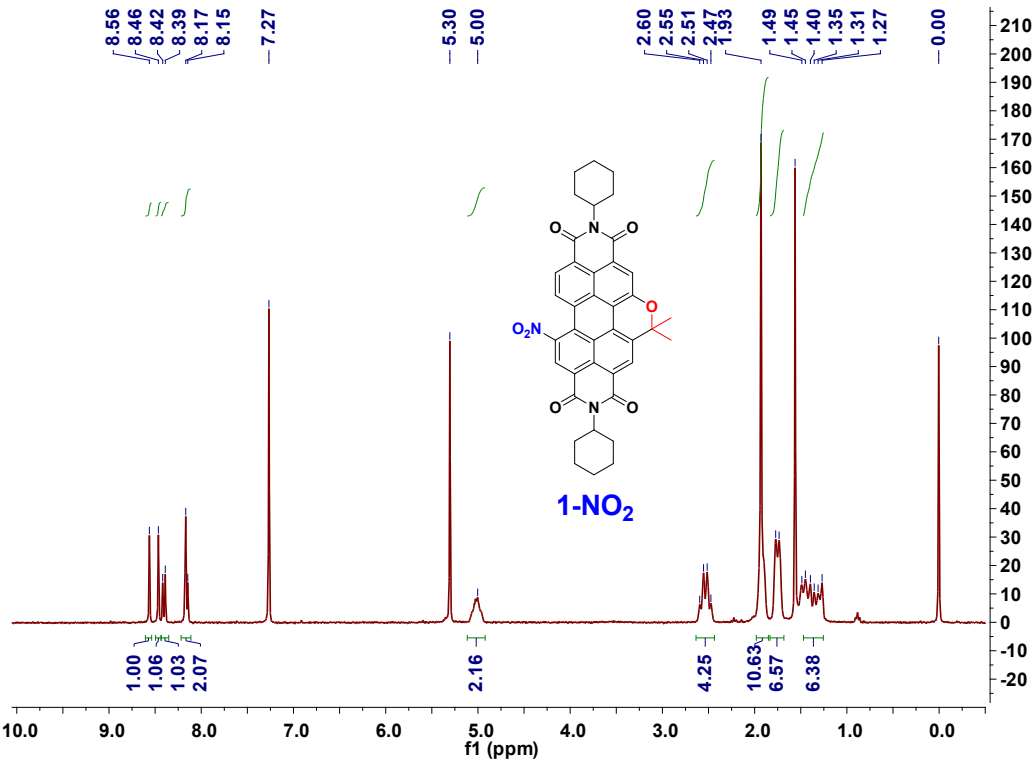


Figure S5. ^{1}H NMR spectrum of compound **1-NO$_2$.**

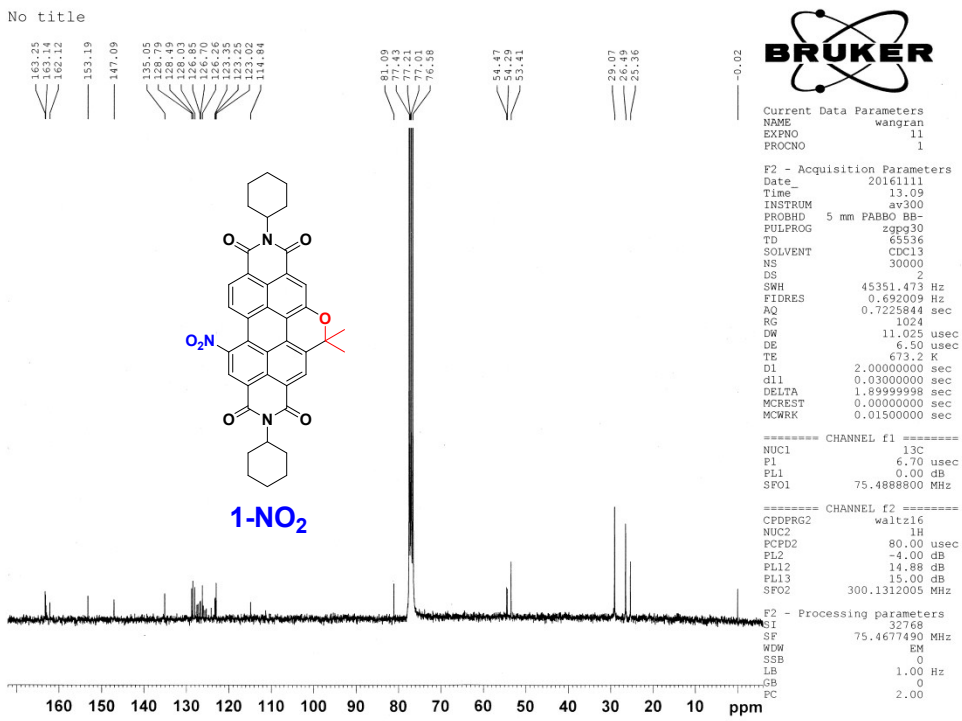


Figure S6. ^{13}C NMR spectrum of compound **1-NO$_2$.**

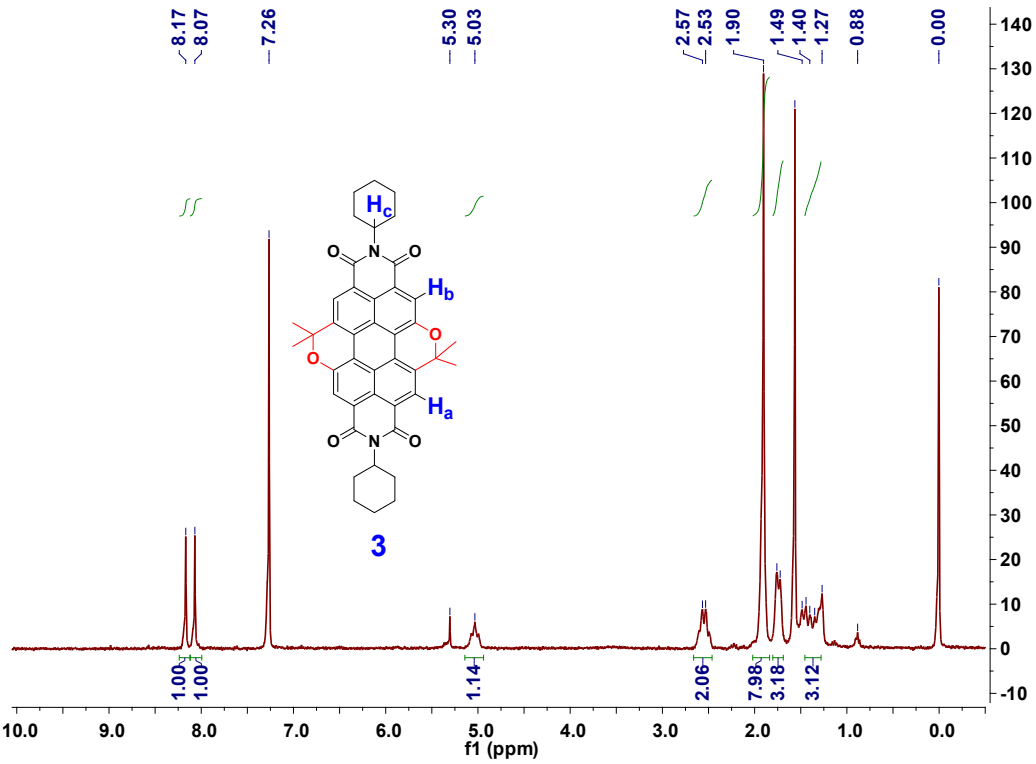


Figure S7. ^{1}H NMR spectrum of compound **3.**

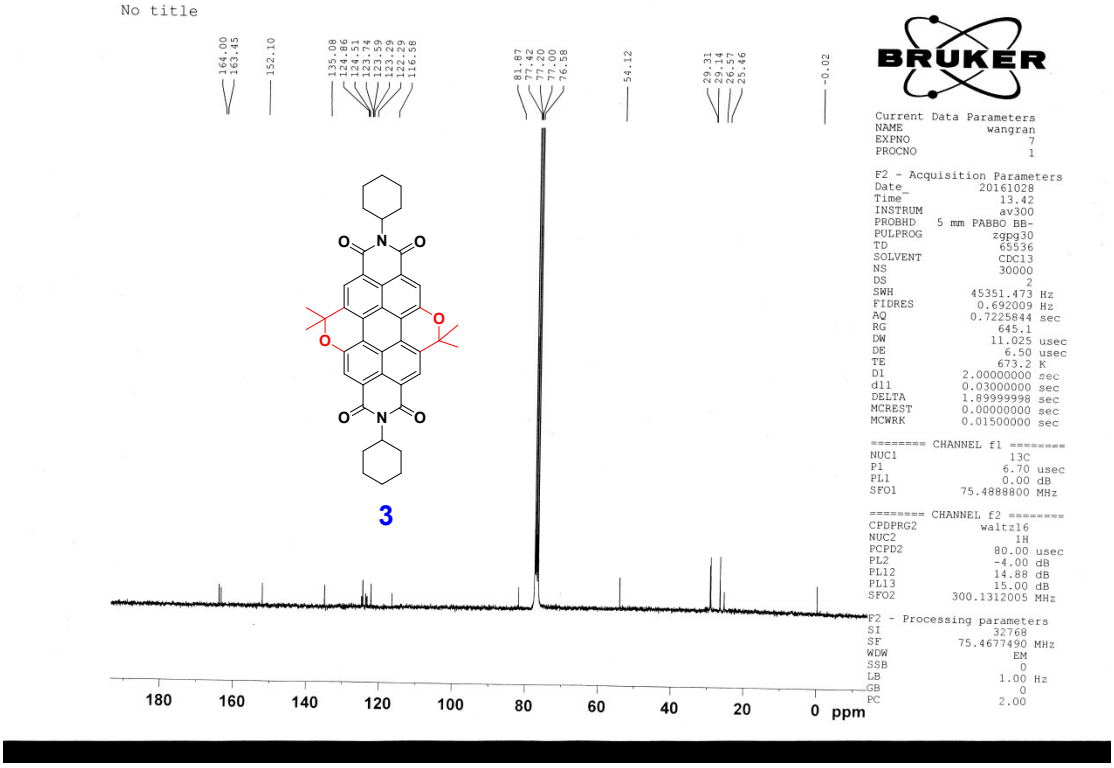


Figure S8. ^{13}C NMR spectrum of compound **3.**

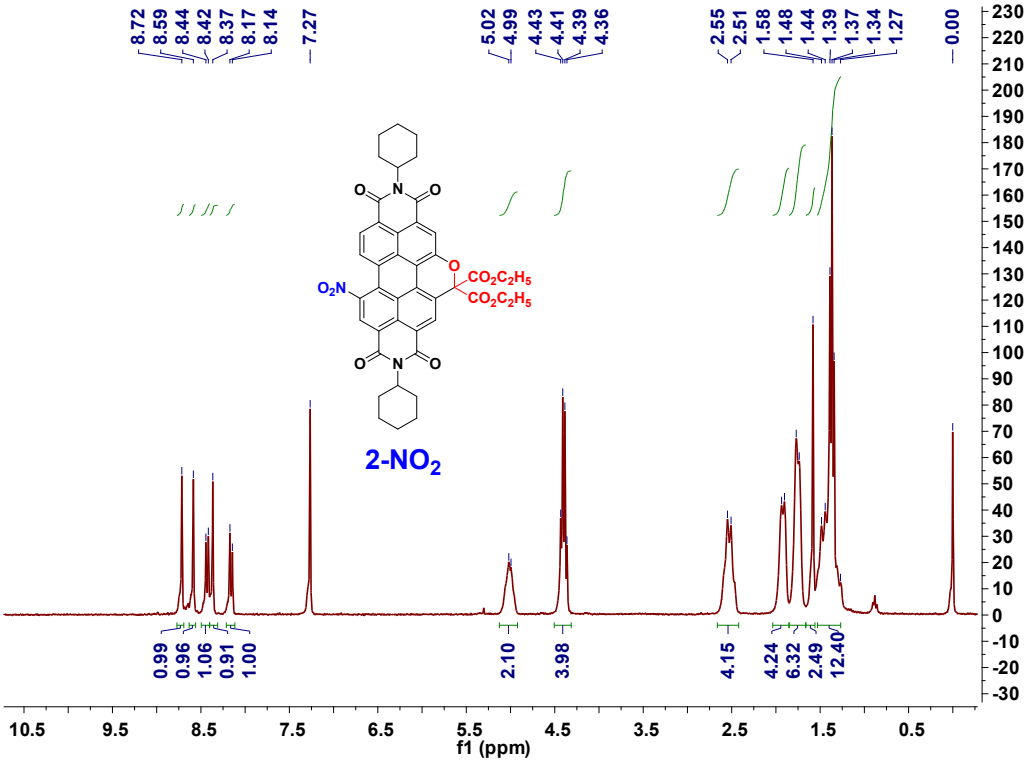


Figure S9. ^{1}H NMR spectrum of compound **2-NO$_2$.**

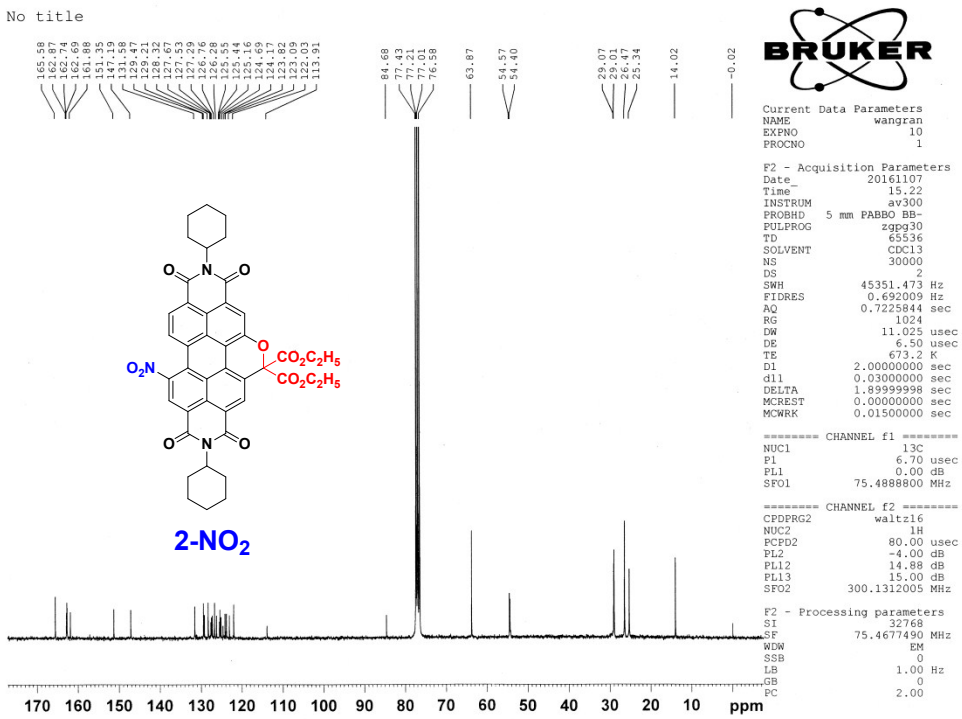


Figure S10. ^{13}C NMR spectrum of compound **2-NO$_2$.**

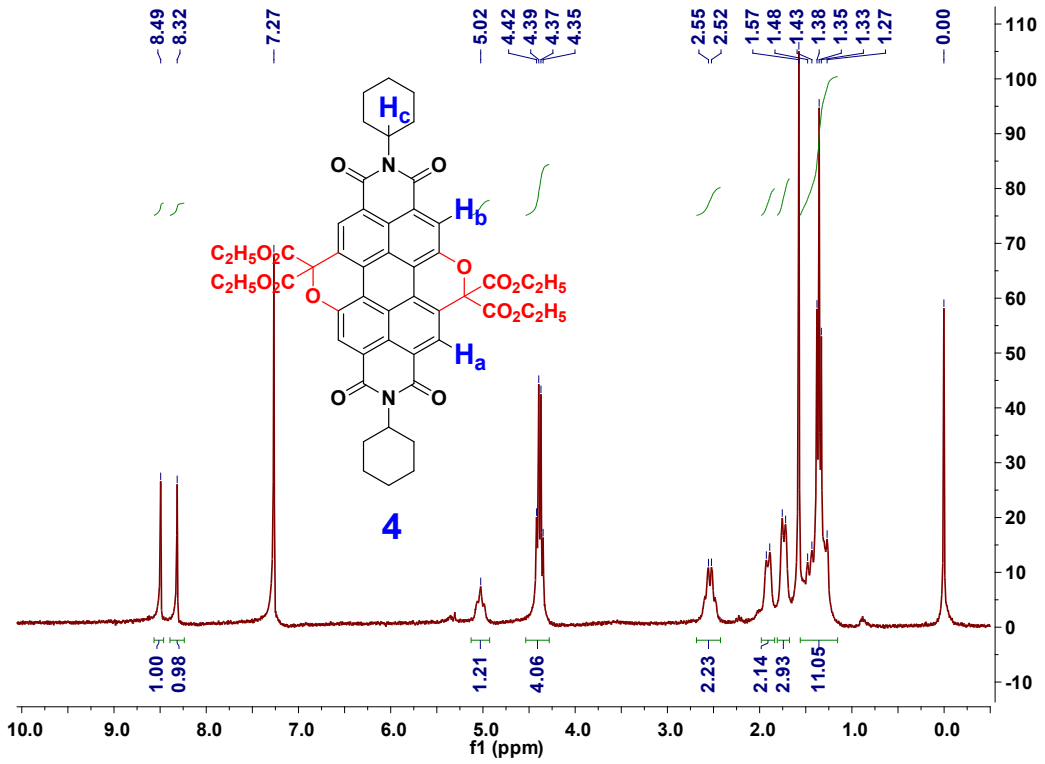


Figure S11. ^{1}H NMR spectrum of compound **4.**

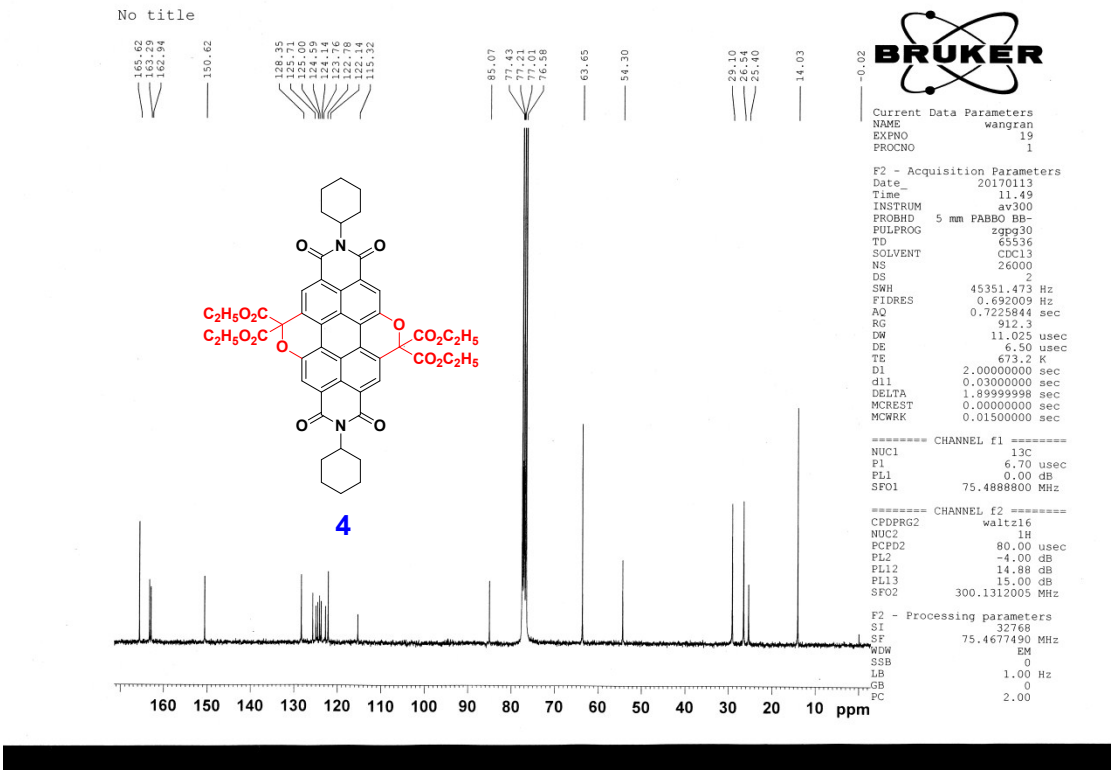


Figure S12. ^{13}C NMR spectrum of compound **4.**

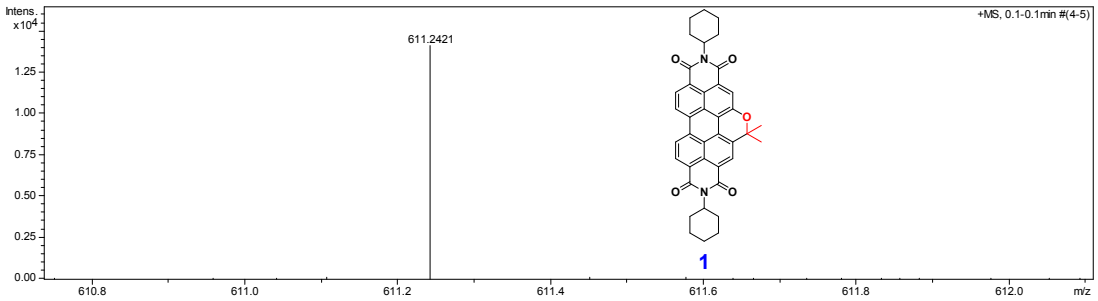


Figure S13. HRMS profile of compound **1**.

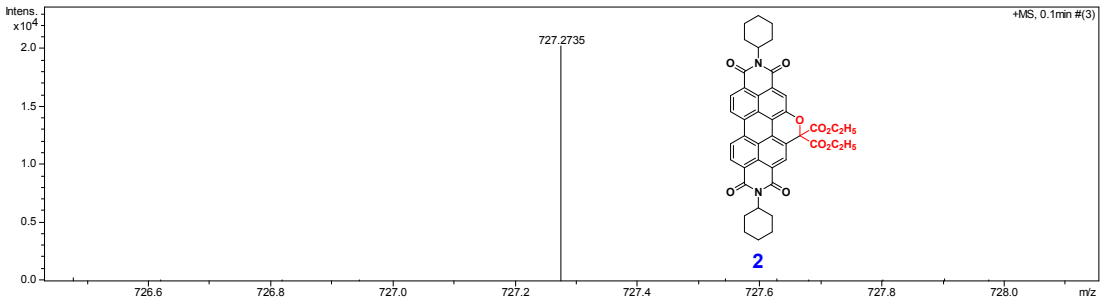


Figure S14. HRMS profile of compound **2**.

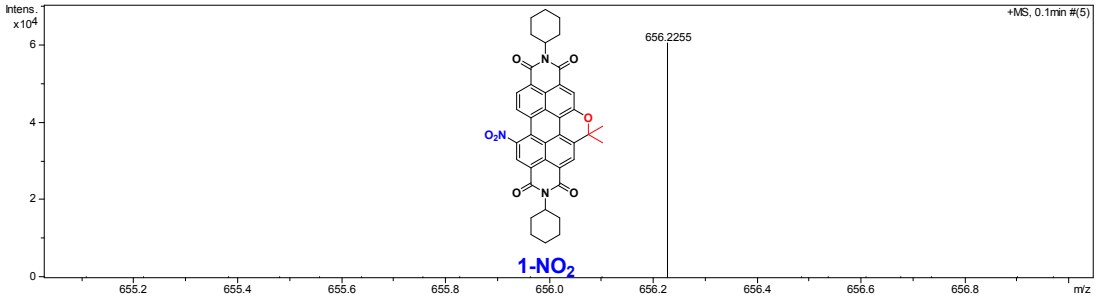


Figure S15. HRMS profile of compound **1-NO$_2$**.

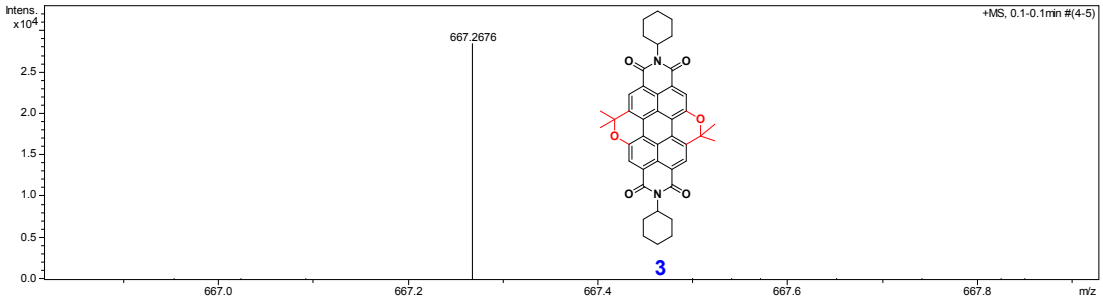


Figure S16. HRMS profile of compound **3**.

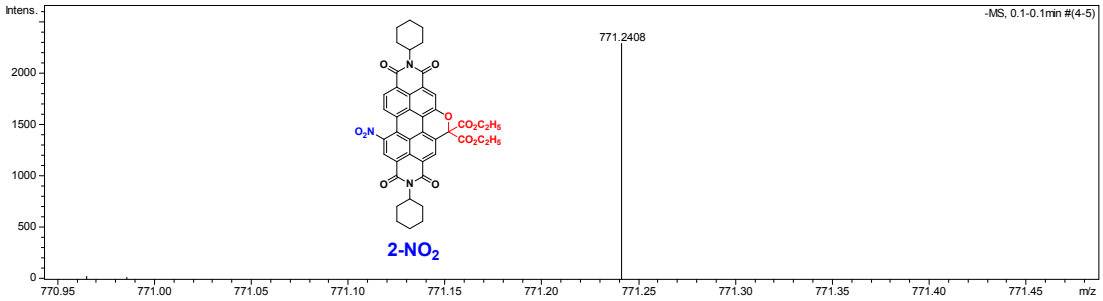


Figure S17. HRMS profile of compound **2-NO$_2$**.

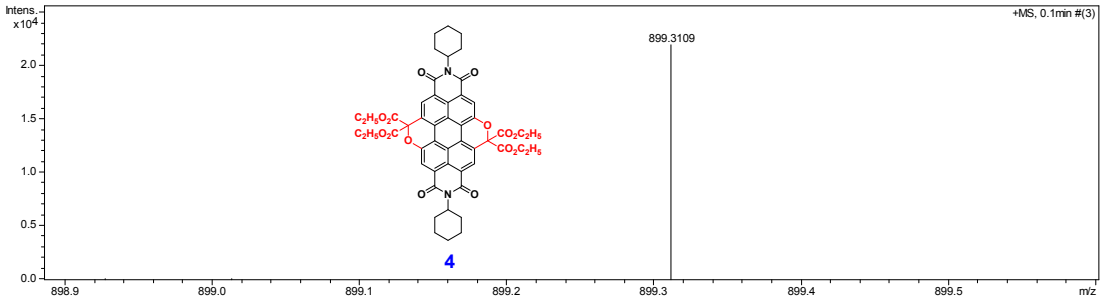


Figure S18. HRMS profile of compound **4**.

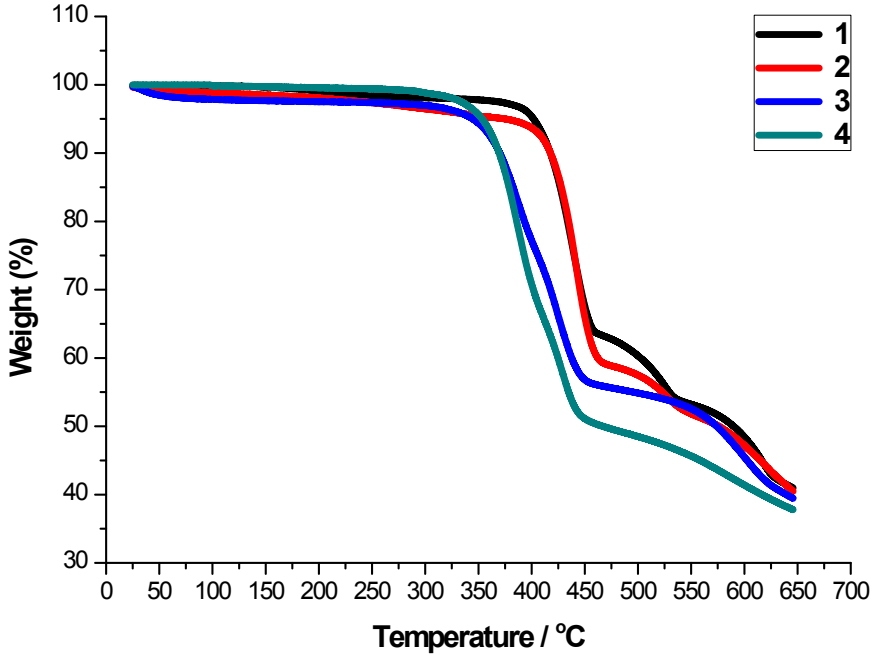


Figure S19. TGA profile of compound **1-4**.

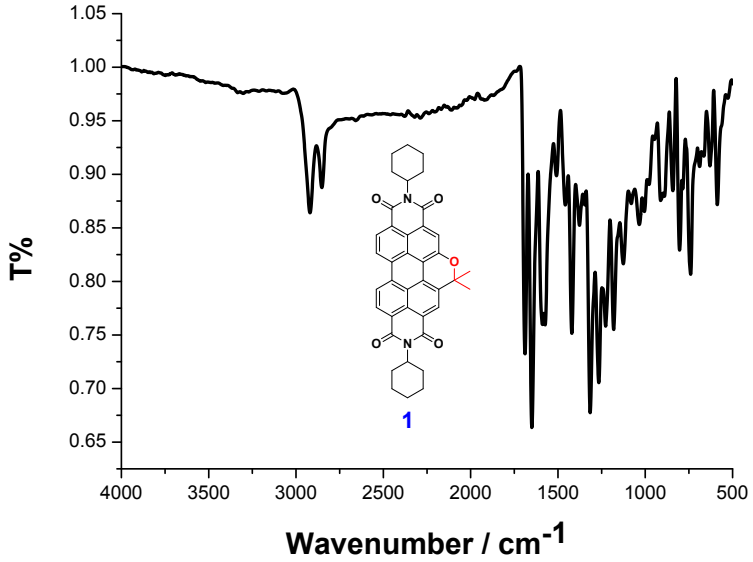


Figure S20. FT-IR profile of compound **1**.

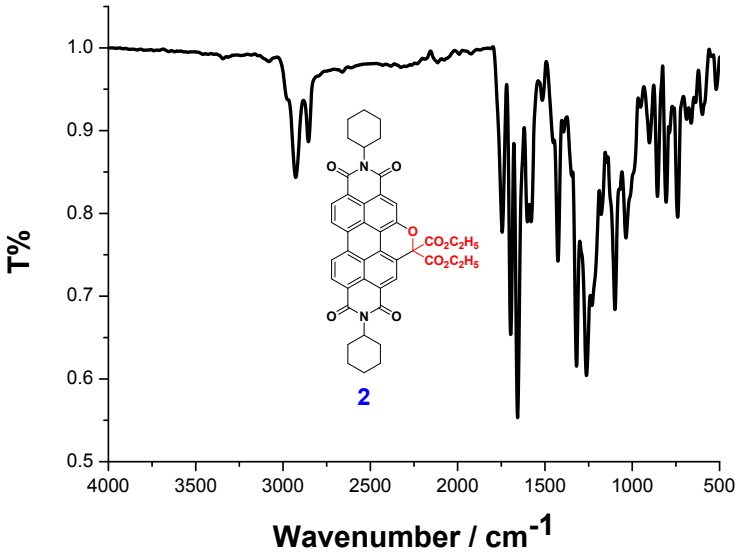


Figure S21. FT-IR profile of compound **2**.

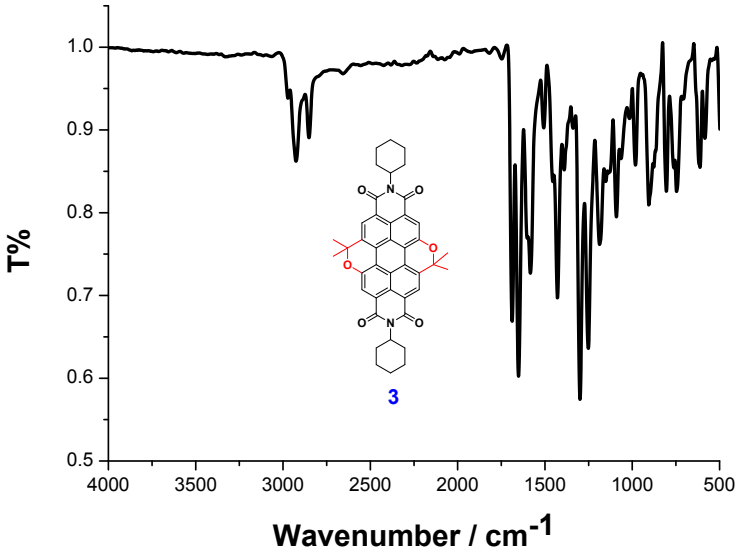


Figure S22. FT-IR profile of compound **3**.

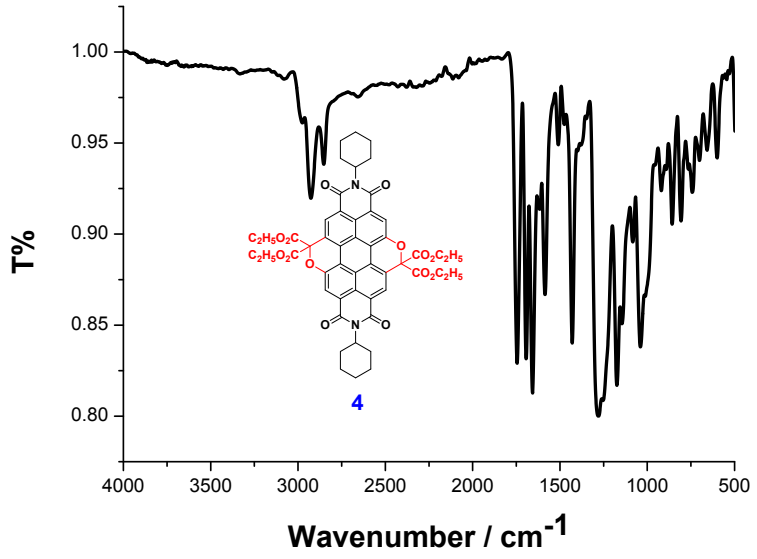


Figure S23. FT-IR profile of compound **4**.

4. Electrochemical Data and Theoretical Calculation Results.

Table S2. Electrochemical data of compounds **1**−**4**.

Compound	$E_{red}1$(V)	E_{LUMO}(eV)	$E_{ox}1$(V)	E_{HOMO}(eV)	E_{gap}(eV)	E^{opt}_{gap}(eV)[a]
1	− 0.90	− 3.50	1.05	− 5.45	1.95	2.02
2	− 0.84	− 3.56	1.20	− 5.60	2.04	2.11
3	− 1.09	− 3.31	0.92	− 5.32	2.01	1.95
4	− 0.80	− 3.60	1.16	− 5.56	1.96	2.03

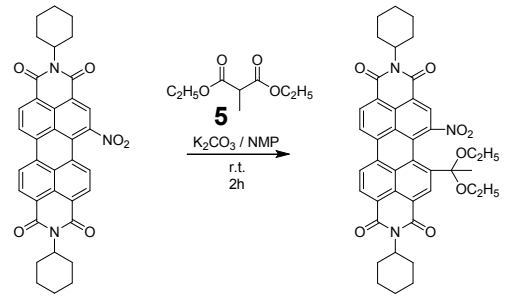
[a] Optical band gap, $E_{gap} = 1240 / \lambda_{max}$.

Table S3. Calculated HOMO, LUMO, and bandgap of compounds **1−4**.

Compound	E_{LUMO}(eV)	E_{HOMO}(eV)	E^{cal}_{g}(eV)
1	− 3.36	− 5.72	2.36
2	− 3.35	− 5.77	2.42
3	− 3.24	− 5.53	2.29
4	− 3.29	− 5.61	2.32

5. The Proposed Reaction Mechanism .

In order to investigate the reaction mechanism, the four cyclic condensation reactions were carried out under a dry, inert argon atmosphere using standard Schlenk-techniques in glassware that was flame-dried prior to use. All of the compounds (**1-4**) were also obtained identical to that of reacting under air. Furthermore, the following reactant of diethyl methylmalonate with only an α -H was designed and reacted under the similar conditions with manuscript, we obtained compound **6**.



Compound **6** was synthesized following the procedure of compound **1**. **PDI-NO_2** (60 mg, 0.1mmol), diethyl methylmalonate (0.52 mL, 3.0 mmol) and grinding anhydrous K_2CO_3 (690 mg, 5.0 mmol) reacted for 2 h in NMP (10 mL) to yield compound **6** as a dark-red solid (42 mg, 39%). ^{1}H NMR (300MHz, $CDCl_3$, δ ppm): 9.10 (s, 1H), 8.75 (d, 1H), 8.68 (m, 2H), 8.58 (d, 1H), 8.51 (d, 1H), 5.04 (m, 2H), 4.22 (m, 2H), 3.95 (m, 1H),

3.77 (m, 1H), 2.56 (m, 4H), 1.91 (m, 4H), 1.91 (m, 4H), 1.82-1.77(m,9H), 1.50-1.36 (m, 6H), 1.25 (t, 3H), 1.07 (t, 3H).^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 185.72, 165.32, 164.86, 163.77, 163.43, 163.16, 162.56, 141.64, 133.80, 132.44, 131.92, 131.45,128.58, 128.15, 127.41, 126.61, 126.38, 125.55, 125.39, 125.30, 123.75, 122.32, 120.97, 85.71, 63.87, 54.55, 54.33, 29.16, 29.10, 28.89, 26.47, 25.34,21.61, 13.90, 13.69, 13.48. HRMS: $C_{44}H_{41}N_3NaO_{10}$ (M^+ + Na), calcd, 794.2690, found 794.2755.

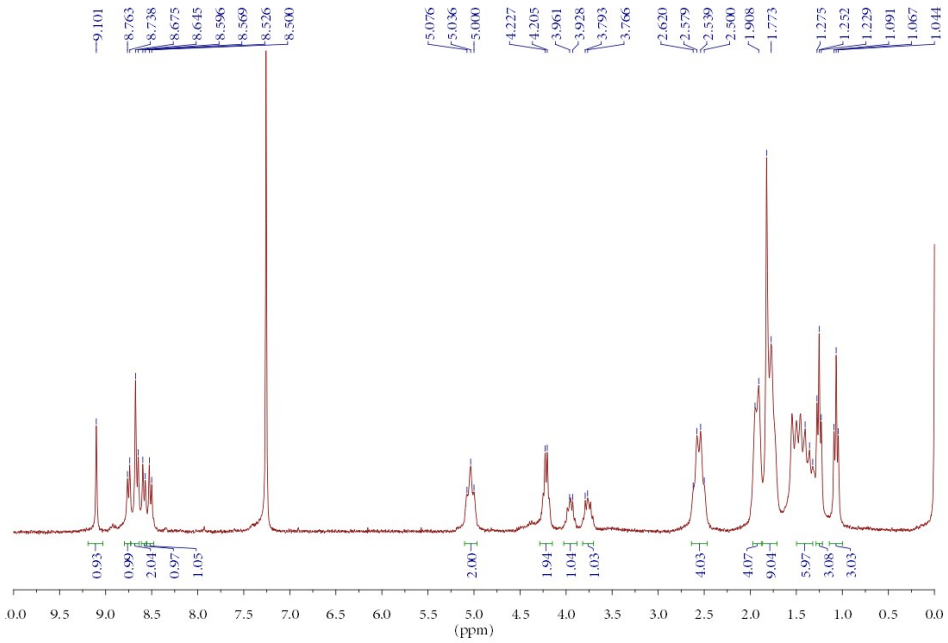


Figure S24. ^{1}H NMR spectrum of compound **6.**

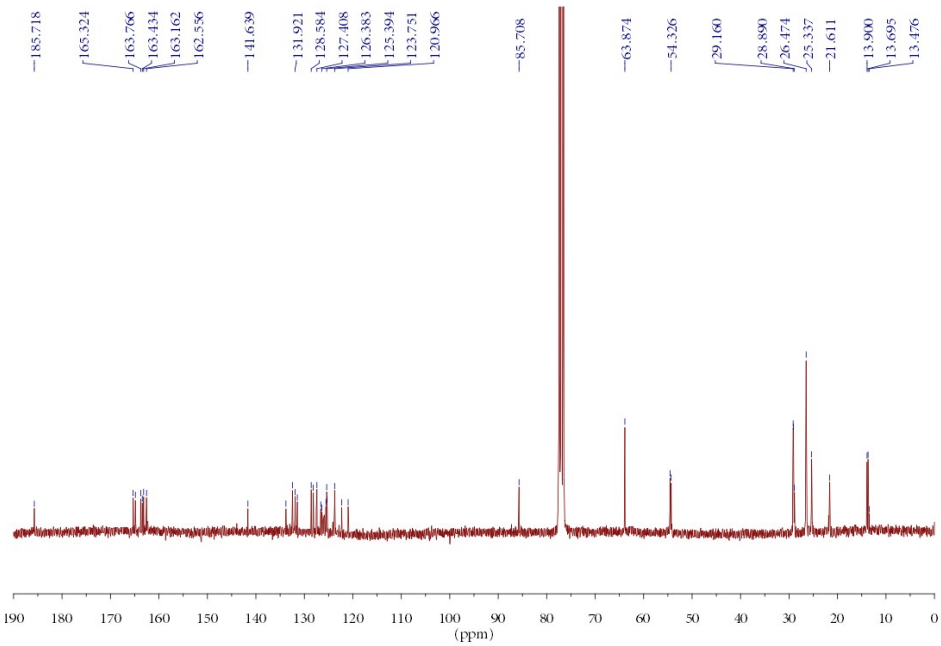


Figure S25. ^{13}C NMR spectrum of compound **6.**

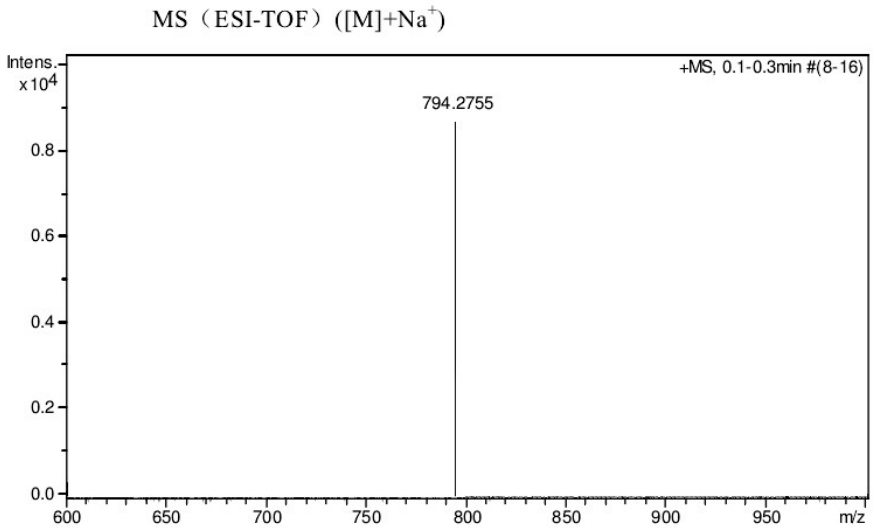
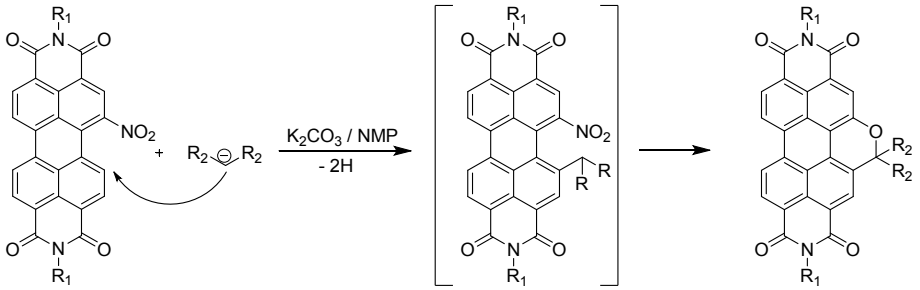


Figure S26. HRMS profile of compound **6.**

So, we can speculate the reaction mechanism illustrating in the following scheme:



6. References

1. Li, G.; Zhao, Y.; Li, J.; Cao, J.; Zhu, J.; Sun, X. W.; Zhang, Q., Synthesis, Characterization, Physical Properties, and OLED Application of Single BN-Fused Perylene Diimide. *J. Org. Chem.* **2015,** *80*, 196-203.