Supporting Information for

Photoexcited Perylene Diimide Radical Anions for the Reduction of Aryl Halides: A Bay-Substituent Effect

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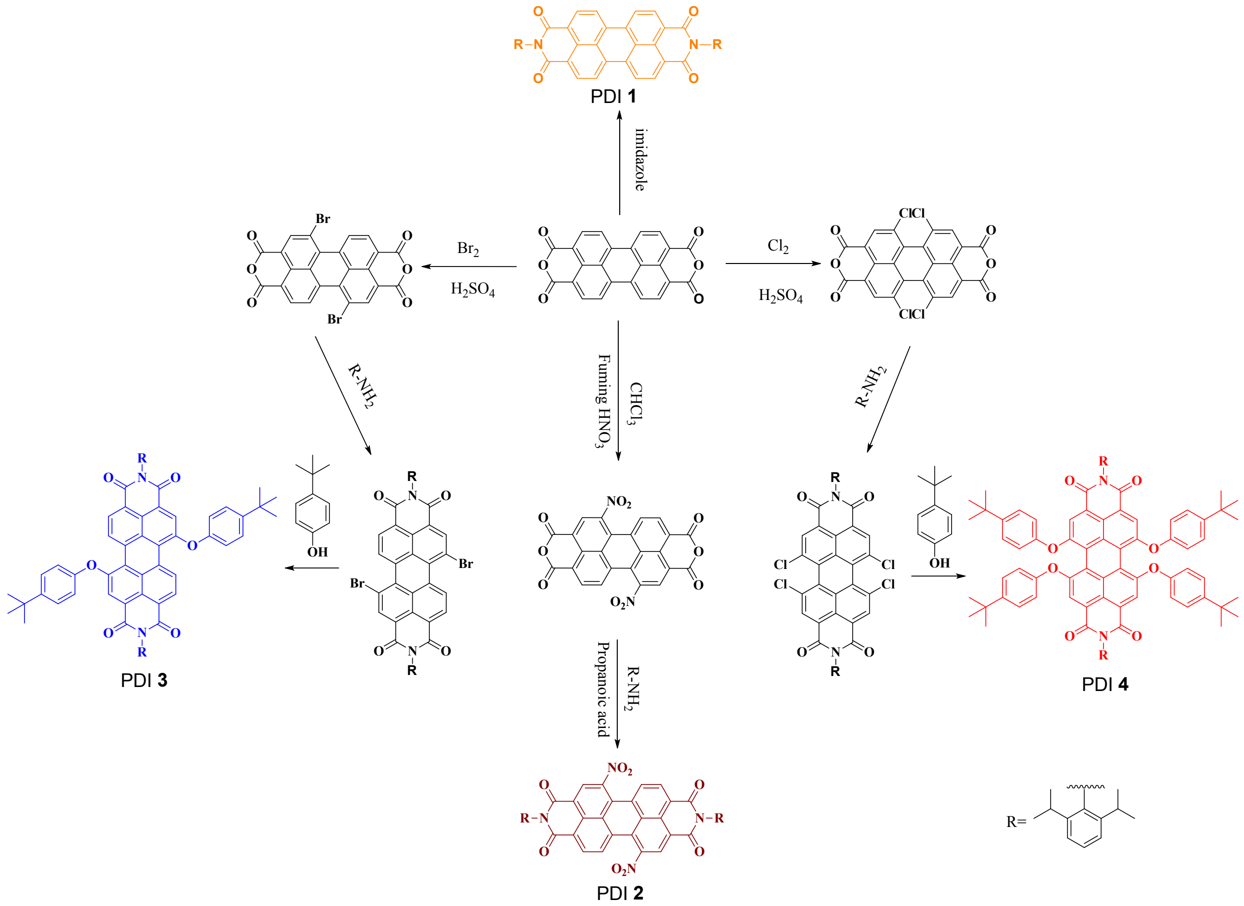
1. Syntheses of PDIs 1-4

1.1 Materials and measurements

3,4,9,10-perylene tetracarboxylic dianhydride (98%)，1,6,7,12-tetrachloroperylene-3,4,9,10-tetracarboxylic dianhydride [S1] (98%), ethyl alcohol (analytical reagent grade), methyl alcohol (analytical reagent grade), dichloromethane (analytical reagent grade), 1.2-dichloroethane (analytical reagent grade), dimethylformamide (DMF, analytical reagent grade), acetic acid (analytical reagent grade), propionic acid(analytical reagent grade), *N*-Methyl pyrrolidone (NMP, analytical reagent grade), fuming nitric acid (analytical reagent grade), hydrochloric acid (HCl) and sulfuric acid were obtained from commercial suppliers. Ethyl acetat (analytical reagent grade), iodine (analytical reagent grade), bromine (analytical reagent grade), sodium chloride (analytical reagent grade), 4-*tert*-butylphenol(analytical reagent grade), 2,6-diisopropylaniline (analytical reagent grade), Cs$_2$CO$_3$ (analytical reagent grade), anisole (analytical reagent grade), imidazole (analytical reagent grade), zinc acetate (analytical reagent grade). All chemicals and reagents were used as received unless otherwise stated. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 400 and 500 spectrometers, with working frequencies of 400 and 500 MHz, respectively. Chemical shifts are given in parts per million (ppm) and referred to TMS as internal standard. ^{1}H coupling constants *J* are given in Hertz (Hz). High-resolution mass spectra (HRMS) were acquired on the Thermo Scientific Executive plus Mass spectrometer equipped with electrospray ionization (ESI) source.



Scheme S1: Synthesis of PDIs **1**-**4**

1.2 Syntheses and characterizations

Synthesis of N,N-bis(2,6-diisopropylphenyl)perylene-3,4,9,10-bis(dicarboximide) (PDI 1): A mixture of 3,4,9,10-perylene tetracarboxylic dianhydride (1.0 g, 2.55 mmol), 2,6-diisopropylaniline (4.0 ml, 30.6 mmol) and imidazole (7.0 g, 102.7 mmol) were degassed with three vacuum-argon cycles and heated at 150 °C for 10 h under argon atmosphere. The solution was cooled down and quenched with 250 mL of 2 M hydrochloric acid. Red precipitate was obtained, which was filtered and washed with deionized water until the filtrate was pH neutral. After column chromatography (SiO_2, DCM/PE = 3/2) 856 mg (49%, 1.20 mmol) of a red product were obtained. ^1H NMR (400 MHz, $CDCl_3$) δ 8.84 (s, 4H), 8.80 – 8.75 (m, 4H), 7.54 (t, J = 7.7 Hz, 2H), 7.39 (d, J = 7.7 Hz, 4H), 2.79 (dt, J = 13.7, 6.8 Hz, 4H), 1.22 (d, J = 6.7 Hz, 24H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.51, 145.64, 135.13, 132.11, 130.52, 130.22, 129.68, 124.14, 123.44, 123.35, 29.24, 24.01 ppm. MS (ESI): calculated for PDI **1**, 710.3139; found, 710.3161.

Synthesis of 1,7-dinitro-perylene-3,4,9,10-tetracarboxylic dianhydride: To a 50 ml two-necked flask was charged 5 g (12.75 mol) of 3,4,9,10-perylene tetracarboxylic dianhydridean and 150 ml of $CHCl_3$, and then the flask was stirred at room temperature, then fuming nitric acid (50 ml) was dropwise added to a solution were added to the flask. The reaction mixture was stirred at room temperature for 3 h. The reaction mixture was poured into a mixture solvent of 100 ml of water, stirred for one hour at room temperature. Then, the resultant precipitate was filtered and washed with a large amount of water until the filtrate became neutral. The solid residue was dried under vacuum at 80 °C for 12 h to give a red solid and used in the later reaction without further purification.

Synthesis of *N*,*N*-di(2,6-diisopropylphenyl)-1,7-dinitroperylene-3,4,9,10-tetracarboxylic diimide (PDI 2): 2,6-diiso- propylaniline (7.05 g 39.76 mmol) was added to a mixture of 1,7-dinitro-perylene-3,4,9,10-tetracarboxylic dianhydride (5.8 g) and propionic acid (100 mL) under argon atmosphere, the reaction mixture was stirred and heated at 140 °C for 12 h. After being cooled to room temperature, then, the resultant precipitate was filtered and washed with a large amount of water until the filtrate became neutral. The crude product was purified by silica gel column chromatography with petroleum ether (PE)/dichloromethane (DCM) as eluent to yield product as a red solid PDI **2** 6.55g (68 %, 8.18 mmol). ^1H NMR (400 MHz, $CDCl_3$) δ 8.98 (s, 2H), 8.82 (dd, J = 18.4, 8.0 Hz, 2H), 8.43 (dd, J = 8.0, 5.1 Hz, 2H), 7.60 – 7.52 (m, 2H), 7.40 (dt, J = 7.6, 3.6 Hz, 4H), 2.78 – 2.65 (m, 4H), 1.21 (d, J = 6.8 Hz, 24H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.53, 162.13, 161.62, 161.25, 148.56, 145.59, 145.51, 133.43, 133.23, 131.70, 130.78, 130.36, 130.18, 130.01, 129.81, 129.53, 129.41, 129.23, 129.13, 128.28, 128.01, 127.86, 126.88, 125.97, 125.80, 125.54, 124.63, 124.45, 124.43, 124.25, 123.65, 29.44, 29.37, 29.29, 24.03 ppm. MS (ESI): calculated for PDI **2**, 800.2841; found, 800.2855.

Synthesis of 1,7-dibromo-perylene-3,4,9,10-tetracarboxylic dianhydride: To a 50 ml two-necked flask was charged 0.5 g (1.275 mol) of 3,4,9,10-perylene tetracarboxylic dianhydridean and 4 ml of concentrated sulfuric acid, and then the flask was heated to 85 °C. Subsequently, the iodine (11.8mg, 46.5μmol) and bromine (144μL 2.88mmol) was added to a solution were added to the flask. The reaction mixture was heated at 85 °C for 24 h. After being cooled down to room temperature, the reaction mixture was poured into a mixture solvent of 100 ml of water, stirred for one hour at room temperature. Then, the resultant precipitate was filtered and washed with a large amount of water until the filtrate became neutral. The solid residue was dried under vacuum at 80 °C for 12 h to give a red solid and used in the later reaction without further purification.

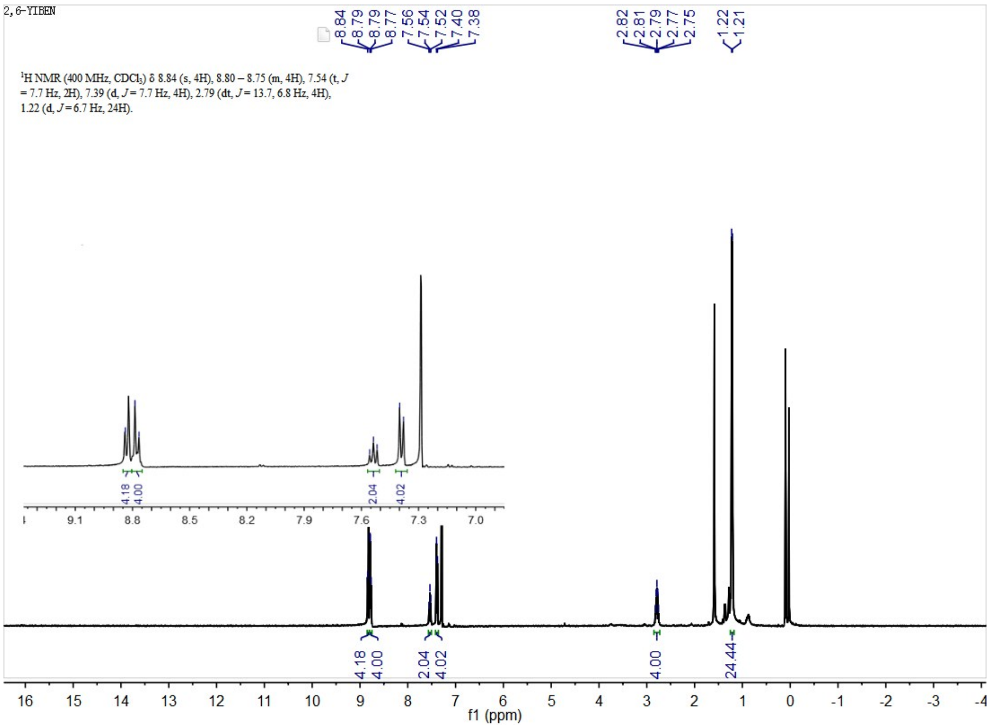
Synthesis of *N,N*-bis(2,6-diisopropylphenyl)-1,7-dibromoperylene-3,4,9,10-tetracarboxylic diimide: 2,6-diisopropylaniline (0.8 mL 1.1mmol) was added to a mixture of 1,7-dibromo-perylene-3,4,9,10-tetracarboxylic dianhydride (0.5g 0.17mmol) and propionic acid (30 mL) under argon atmosphere, the reaction mixture was stirred and heated at 130 °C for 20 h. After being cooled to room temperature, then, the resultant precipitate was filtered and washed with a large amount of water until the filtrate became neutral. The crude product was purified by silica gel column chromatography with petroleum ether (PE)/dichloromethane (DCM) as eluent to yield product as a yellow solid Br_2-PDI (577 mg), (73%, 0.66 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.60 (d, J = 8.8 Hz, 2H), 9.05 (s, 2H), 8.84 (d, J = 8.2 Hz, 2H), 7.55 (t, J = 7.6 Hz, 2H), 7.40 (d, J = 7.7 Hz, 4H), 2.77 (dt, J = 13.2, 6.6 Hz, 4H), 1.22 (d, J = 6.5 Hz, 24H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.50, 145.60, 138.47, 133.45, 130.64, 130.12, 129.90, 129.64, 128.72, 124.21, 123.45, 123.20, 122.87, 121.06, 29.29, 24.00 ppm. MS (ESI): calculated for Br_2-PDI, 868.1346; found, 868.1358.

Synthesis of *N,N*-bis(2,6-diisopropylphenyl)-1,7-(4-(tert-butyl)phenoxy)perylene-3,4,9,10-tetracarboxylic diimide (PDI 3): A portion of N,N-bis(2,6-diisopropylphenyl)-1,7-dibromoperylene-3,4,9,10-tetracarboxylic diimide (804 mg 0.926 mmol), 4-t-butylphenol (461mg 3.07mmol) and Cs_2CO_3 (560mg 1.72mmol) were suspended in 32 ml DMF and stirred under argon at 160 °C for 75 min. After being cooled to room temperature and then glacial acetic acid (5 ml) was added to a solution, stirred for 1.5 h at room temperature. Subsequently, the reaction mixture was dropped into 100 mL 1 N HCl under stirring. The solid was separated by filtration, and then washed successively with water (3 × 30 mL) and methanol (3 × 30 mL). The crude product was purified by column chromatography on silica gel using petroleum ether/dichloromethane as an eluent. After removing the solvent with rotary evaporator, PDI **3** was collected as a dark red solid of 700.7 mg (75 %, 0.696 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.66 (dd, J = 22.1, 8.2 Hz, 2H), 8.75 (dd, J = 24.3, 8.2 Hz, 2H), 8.44 (d, J = 30.9 Hz, 2H), 7.49 (d, J = 7.6 Hz, 6H), 7.34 (d, J = 7.3 Hz, 4H), 7.14 (d, J = 8.3 Hz, 4H), 2.84 – 2.65 (m, 4H), 1.38 (s, 18H), 1.18 (d, J = 6.3 Hz, 24H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.50, 162.99, 155.31, 152.60, 148.05, 145.62, 133.85, 130.80, 130.44, 129.73, 129.62, 129.01, 127.44, 124.74, 124.54, 124.05, 123.98, 122.29, 118.70, 34.53, 31.45, 29.18, 24.02, 23.98 ppm. MS (ESI): calculated for PDI **3**, 1006.4915; found, 1006.4947.

Synthesis of N,N'-bis(2,6-diisopropylphenyl)-1,6,7,12-tetrachloroperylene-3,4,9,10-tetracarboxy bisimide: 2,6-diiso- propylaniline (1.68 g 9.44 mmol) was added to a mixture of 1,6,7,12-tetrachloroperylene-3,4,9,10-tetracarboxylic dianhydride (1.0 g 1.88 mmol) and propionic acid (20 mL) under argon atmosphere, the reaction mixture was stirred and heated at 140 °C for 24 h. After being cooled to room temperature, then, the resultant precipitate was filtered and washed with a large amount of water until the filtrate became neutral. The crude product was purified by silica gel column chromatography with petroleum ether (PE)/dichloromethane (DCM) as eluent to yield product as a red solid Cl_4-PDI 1.36 g (85 %, 1.61 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (s, 4H), 7.57 (t, J = 7.8 Hz, 2H), 7.41 (d, J = 7.8 Hz, 4H), 2.78 (dt, J = 13.5, 6.8 Hz, 4H), 1.23 (dd, J = 6.6, 4.5 Hz, 24H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.34, 145.61, 135.65, 133.46, 131.77, 130.05, 129.96, 128.94, 124.29, 123.96, 123.25, 29.31, 24.05 ppm. MS (ESI): calculated for Cl4-PDI, 848.1560; found, 848.1579.

Synthesis of N,N-bis(2,6-diisopropylphenyl)-1,7-(4-(tert-butyl)phenoxy)perylene-3,4,9,10-tetracarboxylic diimide (PDI 4): A portion of N,N'-bis(2,6-diisopropylphenyl)-1,6,7,12-tetrachloroperylene-3,4,9,10-tetracarboxy bisimide (100 mg 0.12 mmol), 4-t-butylphenol (124 mg 0.83 mmol)) and Cs_2CO_3 (308 mg 0.95 mmol) were suspended in 6 ml DMF and stirred under argon at 100 °C for 3 h. After being cooled to room temperature, and stirred for 1.5 h at room temperature. Whereafter, the reaction mixture was dropped into 200 mL 1 N HCl under stirring. The solid was separated by filtration, and then washed successively with water (3 × 30 mL) and methanol (3 × 30 mL). The crude product was purified by column chromatography on silica gel using petroleum ether/dichloromethane as an eluent. After removing the solvent with rotary evaporator, N,N-bis(2,6-diisopropylphenyl)-1,7-(4-(tert-butyl)phenoxy)perylene-3,4,9,10-tetracarboxylic diimide was collected as a dark red solid BY4-PDI 120 mg. (78 %, 0.09 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 4H), 7.45 (s, 2H), 7.32 (s, 2H), 7.29 (s, 8H), 6.90 (s, 8H), 2.75 (s, 4H), 1.31 (s, 36H), 1.16 (d, J = 6.7 Hz, 24H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.35, 155.92, 152.79, 147.35, 145.62, 133.24, 130.69, 129.39, 126.67, 123.87, 122.69, 120.73, 120.21, 119.20, 34.37, 31.45, 29.08 , 24.02 ppm. MS (ESI): calculated for PDI **4**, 1302.6692; found, 1302.6764.

2. NMR Spectra of PDIs 1-4



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (s, 4H), 8.80 – 8.75 (m, 4H), 7.54 (t, *J* = 7.7 Hz, 2H), 7.39 (d, *J* = 7.7 Hz, 4H), 2.79 (dt, *J* = 13.7, 6.8 Hz, 4H), 1.22 (d, *J* = 6.7 Hz, 24H).

Figure S1. ^{1}H NMR spectrum of PDI **1** (400 MHz, $CDCl_3$, 298K)

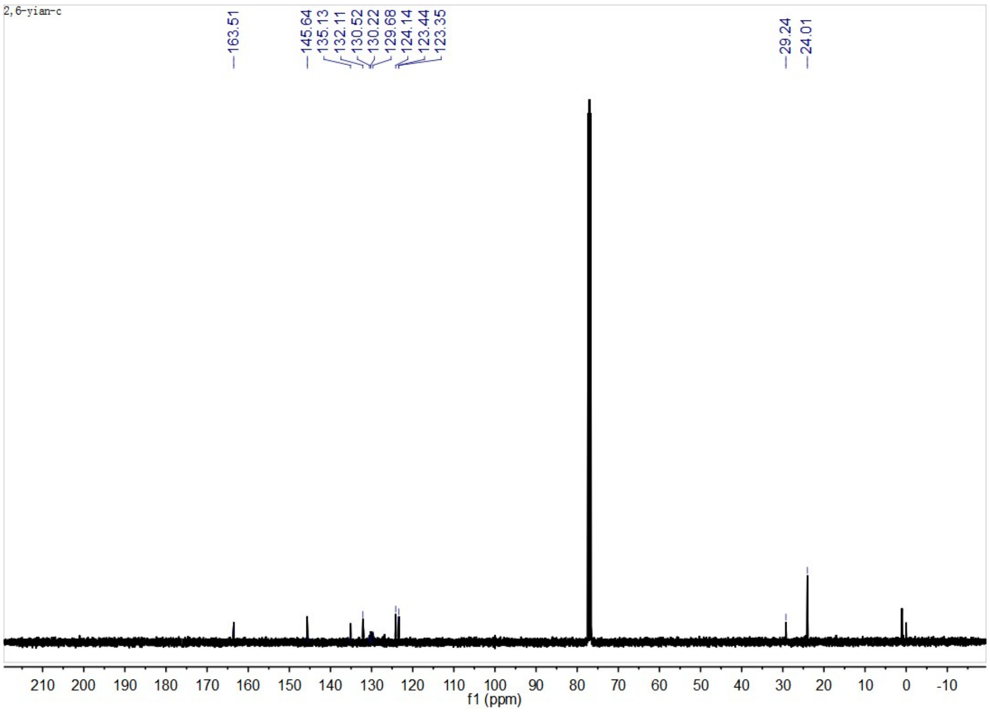


Figure S2. ^{13}C NMR spectrum of PDI **1** (100 MHz, $CDCl_3$, 298K)

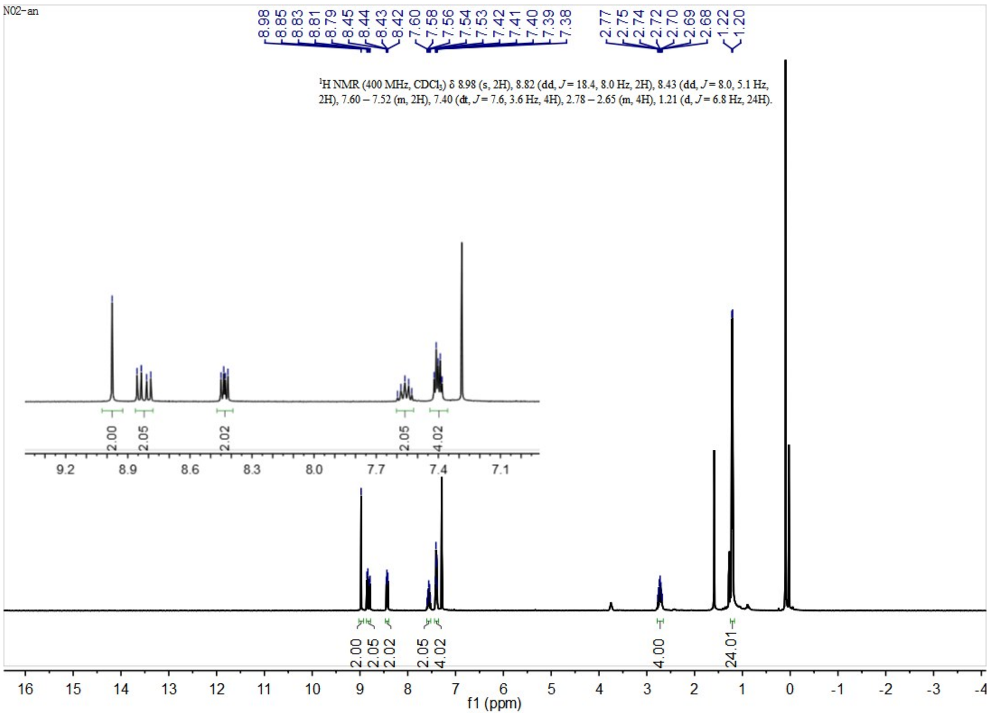

^1H NMR (400 MHz, $CDCl_3$) δ 8.98 (s, 2H), 8.82 (dd, J = 18.4, 8.0 Hz, 2H), 8.43 (dd, J = 8.0, 5.1 Hz, 2H), 7.60 – 7.52 (m, 2H), 7.40 (dt, J = 7.6, 3.6 Hz, 4H), 2.78 – 2.65 (m, 4H), 1.21 (d, J = 6.8 Hz, 24H).

Figure S3. ^1H NMR spectrum of PDI **2** (400 MHz, $CDCl_3$, 298K)

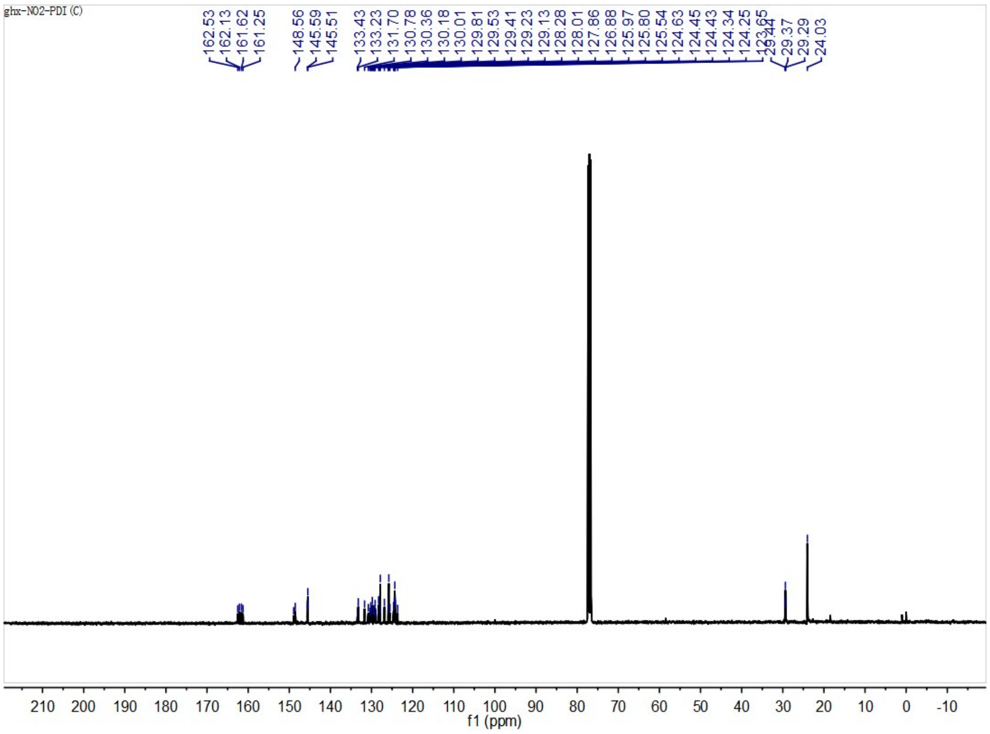
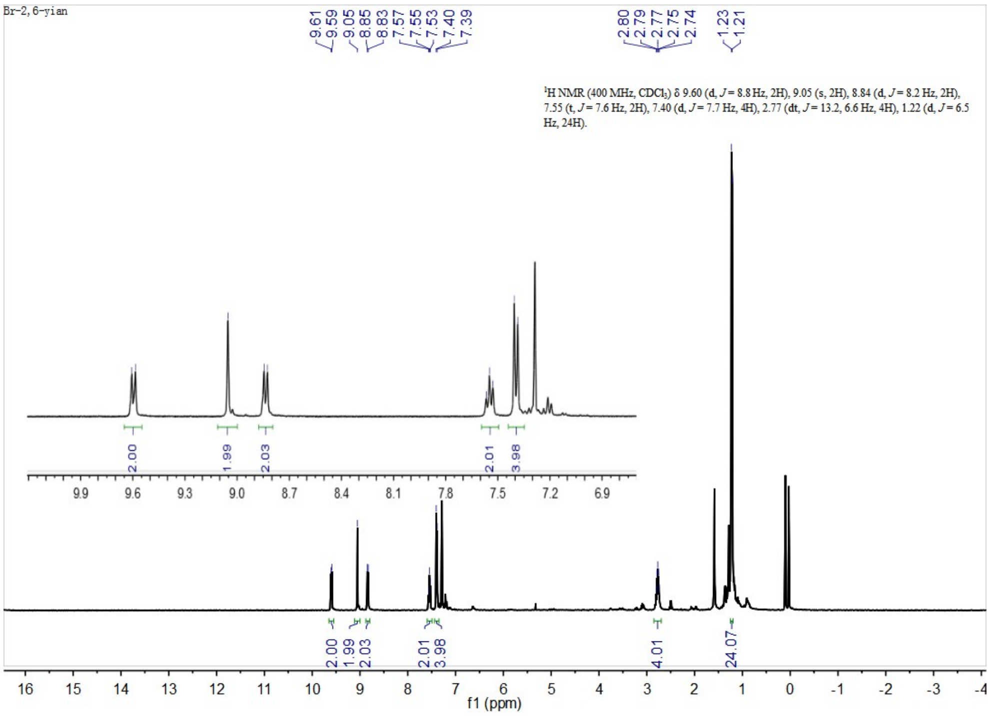


Figure S4. ^{13}C NMR spectrum of PDI **2** (100 MHz, $CDCl_3$, 298K)



^{1}H NMR (400 MHz, $CDCl_3$) δ 9.60 (d, *J* = 8.8 Hz, 2H), 9.05 (s, 2H), 8.84 (d, *J* = 8.2 Hz, 2H), 7.55 (t, *J* = 7.6 Hz, 2H), 7.40 (d, *J* = 7.7 Hz, 4H), 2.77 (dt, *J* = 13.2, 6.6 Hz, 4H), 1.22 (d, *J* = 6.5 Hz, 24H).

Figure S5. ^{1}H NMR spectrum of Br_2-PDI (400 MHz, $CDCl_3$, 298K)

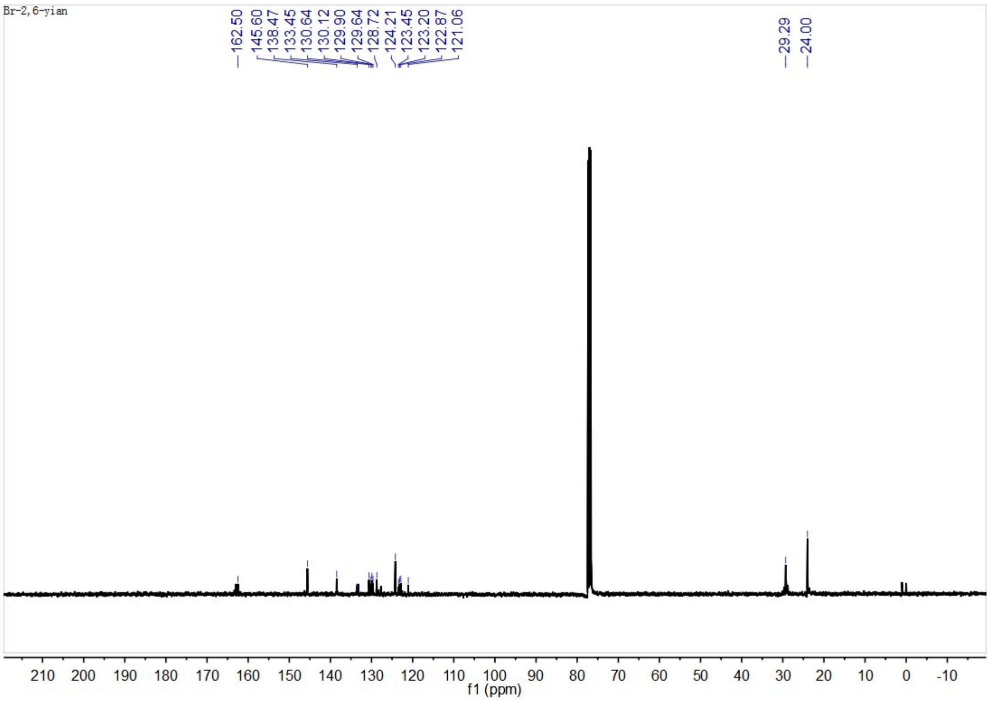
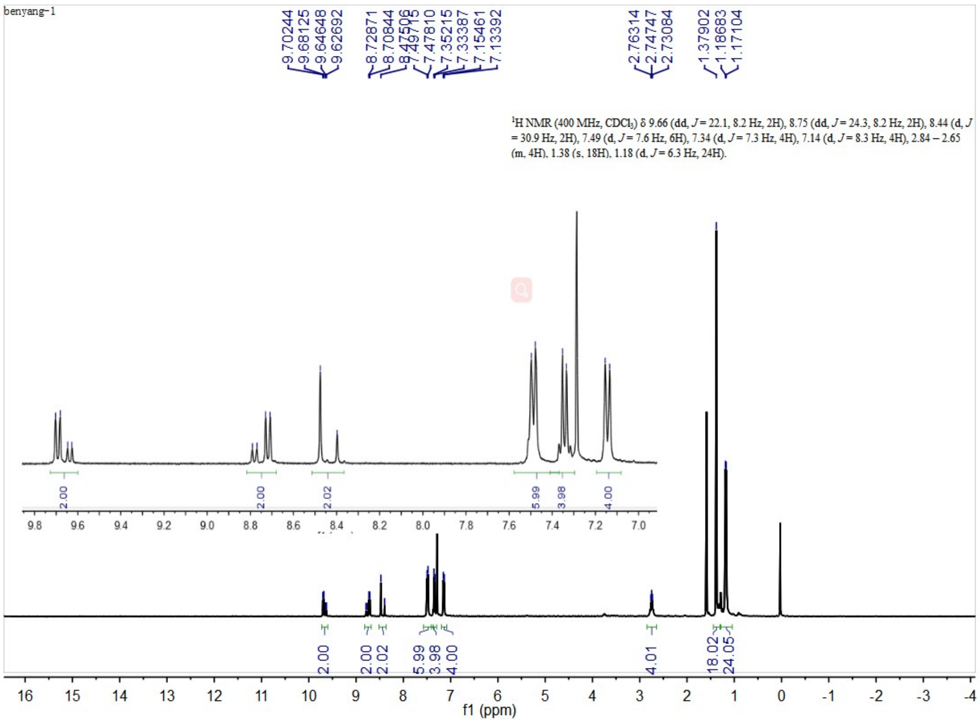


Figure S6. ^{13}C NMR spectrum of Br_2-PDI (100 MHz, $CDCl_3$, 298K)



^{1}H NMR (400 MHz, CDCl$_3$) δ 9.66 (dd, *J* = 22.1, 8.2 Hz, 2H), 8.75 (dd, *J* = 24.3, 8.2 Hz, 2H), 8.44 (d, *J* = 30.9 Hz, 2H), 7.49 (d, *J* = 7.6 Hz, 6H), 7.34 (d, *J* = 7.3 Hz, 4H), 7.14 (d, *J* = 8.3 Hz, 4H), 2.84 – 2.65 (m, 4H), 1.38 (s, 18H), 1.18 (d, *J* = 6.3 Hz, 24H).

Figure S7. ^{1}H NMR spectrum of PDI **3** (400 MHz, CDCl$_3$, 298K)

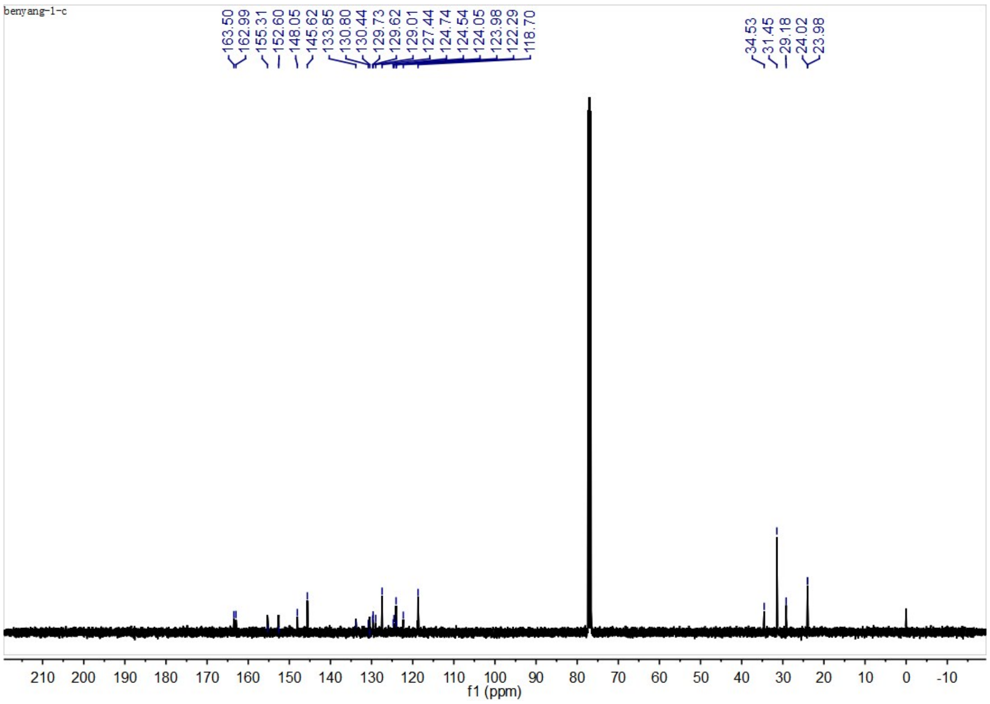
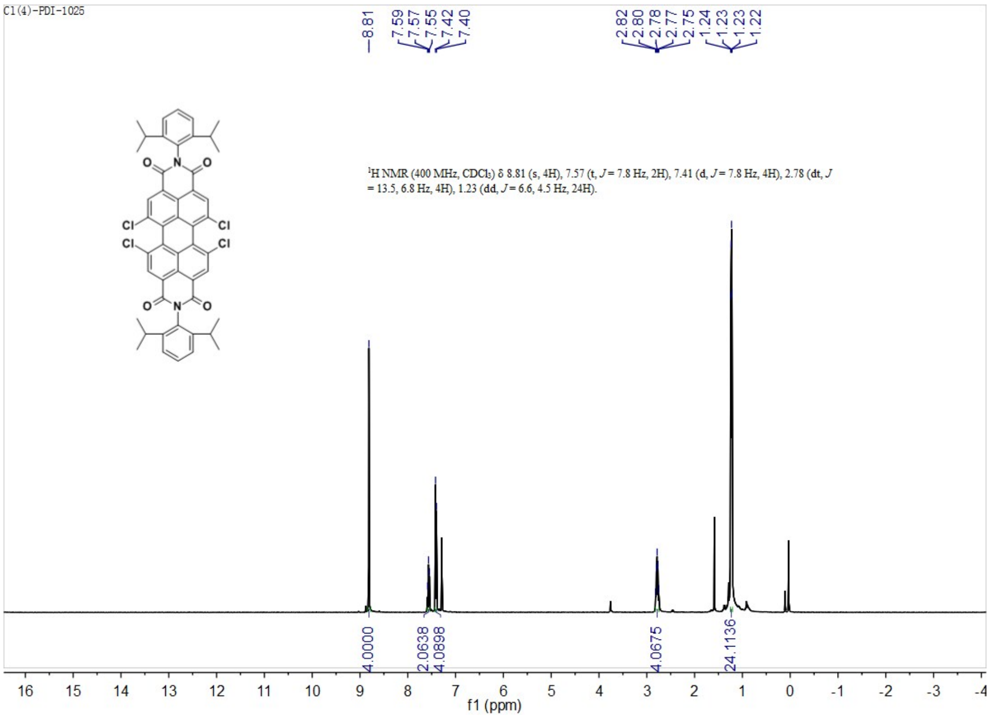


Figure S8. ^{13}C NMR spectrum of PDI **3** (100 MHz, CDCl$_3$, 298K)



^{1}H NMR (400 MHz, CDCl$_3$) δ 8.81 (s, 4H), 7.57 (t, *J* = 7.8 Hz, 2H), 7.41 (d, *J* = 7.8 Hz, 4H), 2.78 (dt, *J* = 13.5, 6.8 Hz, 4H), 1.23 (dd, *J* = 6.6, 4.5 Hz, 24H).

Figure S9. ^{1}H NMR spectrum of Cl$_4$-PDI (400 MHz, CDCl$_3$, 298K)

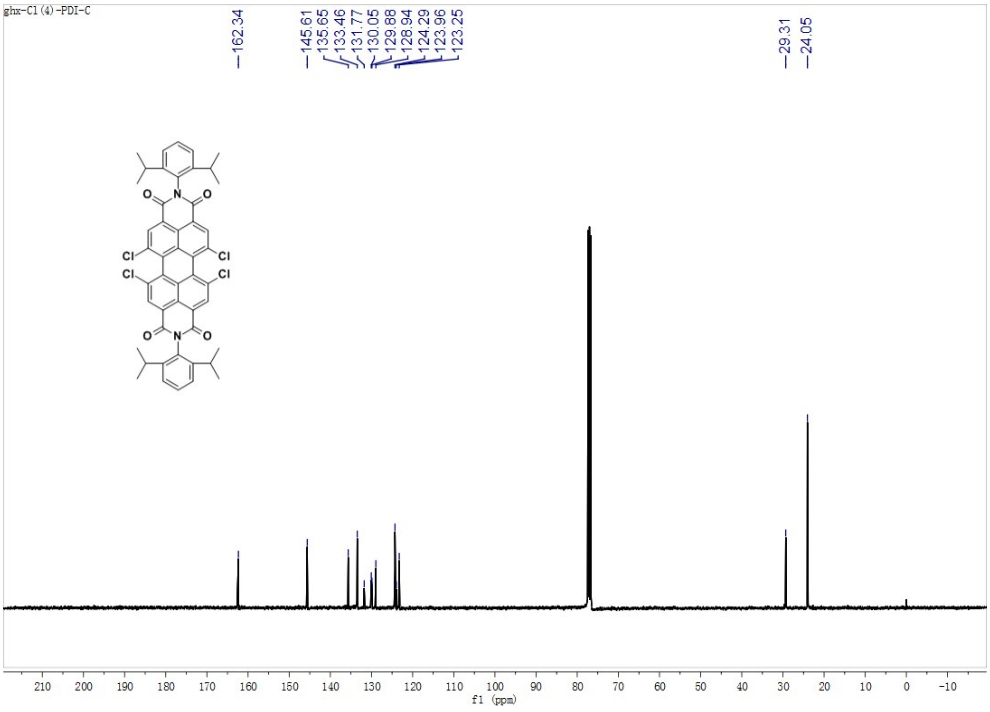
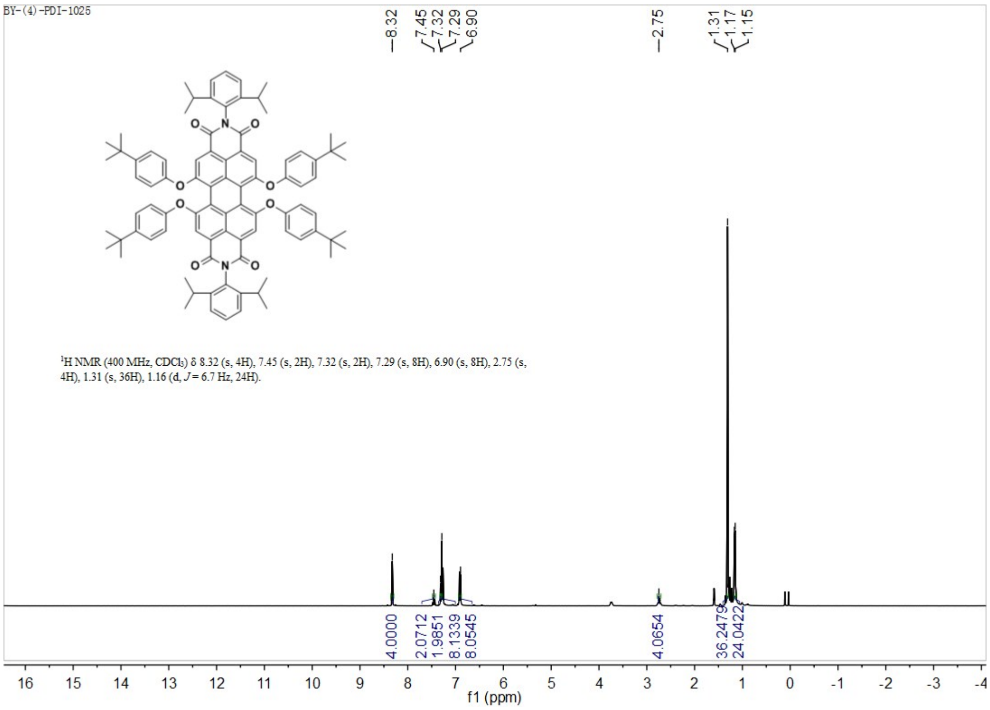


Figure S10. ^{13}C NMR spectrum of Cl$_4$-PDI (100 MHz, CDCl$_3$, 298K)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 4H), 7.45 (s, 2H), 7.32 (s, 2H), 7.29 (s, 8H), 6.90 (s, 8H), 2.75 (s, 4H), 1.31 (s, 36H), 1.16 (d, J = 6.7 Hz, 24H).

Figure S11. ^{1}H NMR spectrum of PDI **4** (400 MHz, $CDCl_3$, 298K)

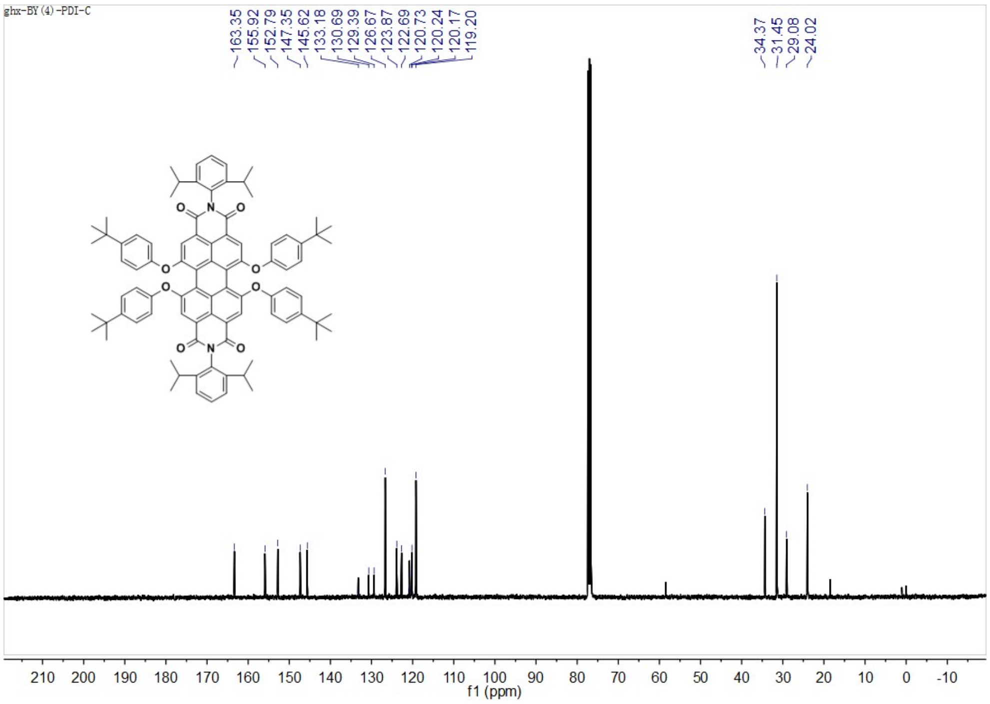


Figure S12. ^{13}C NMR spectrum of PDI **4** (100 MHz, $CDCl_3$, 298K)

3. ESI Mass Spectra of PDIs 1-4

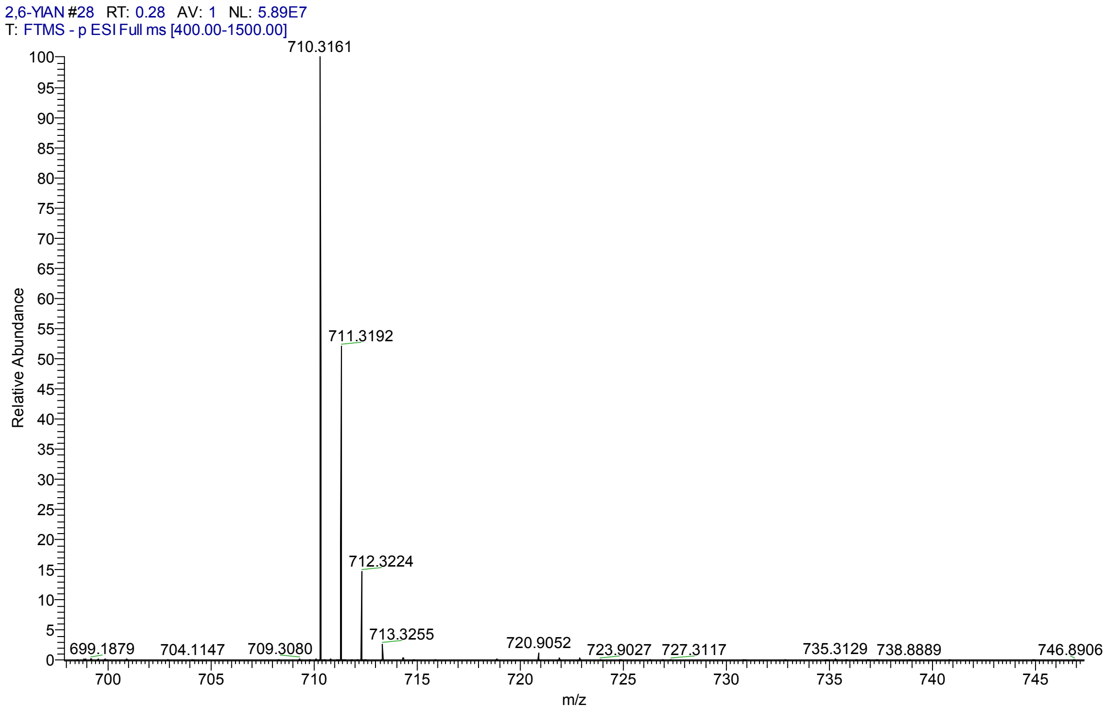


Figure S13. ESI mass spectrum of PDI **1** in CH_2Cl_2

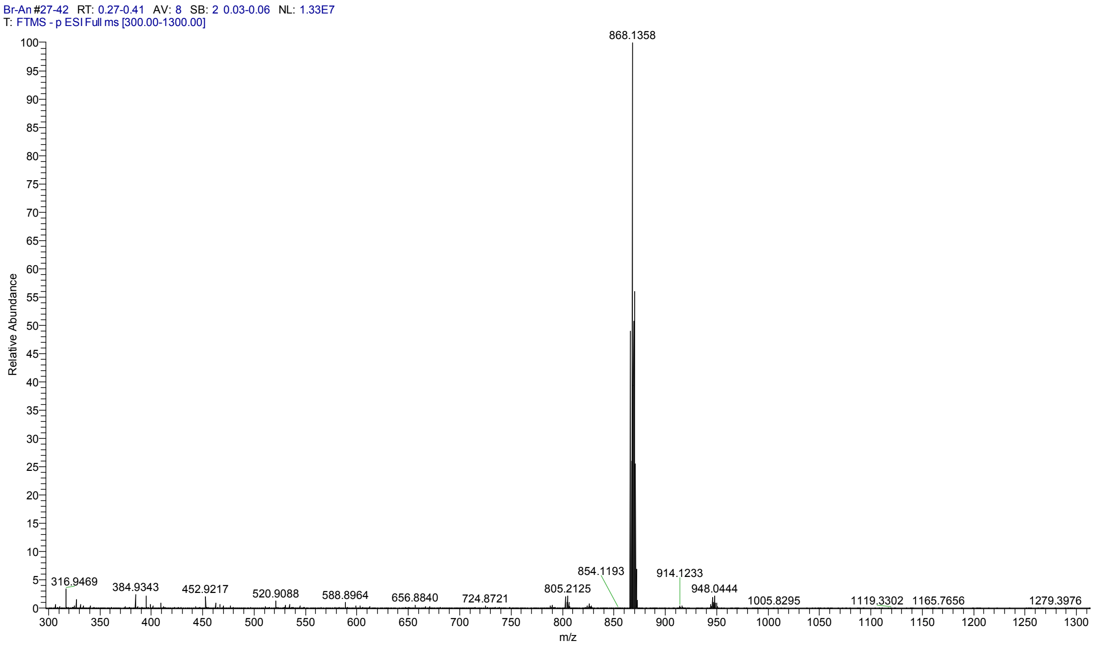


Figure S14. ESI mass spectrum of Br_2-PDI in CH_2Cl_2

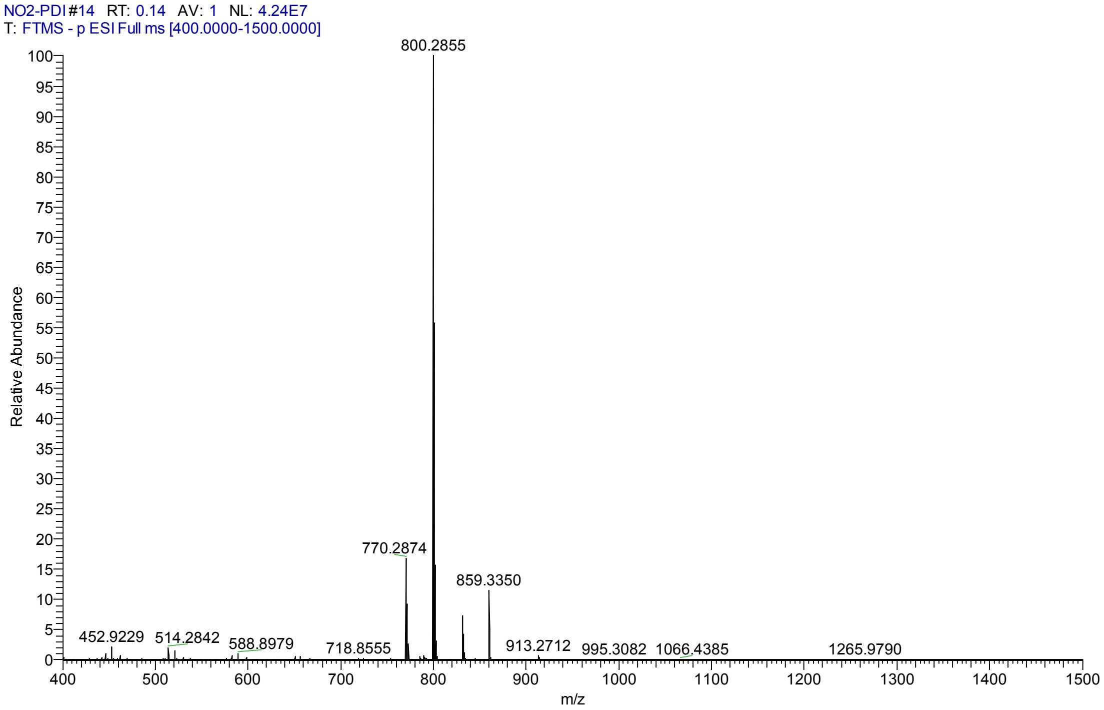


Figure S15. ESI mass spectrum of PDI **2** in CH_2Cl_2

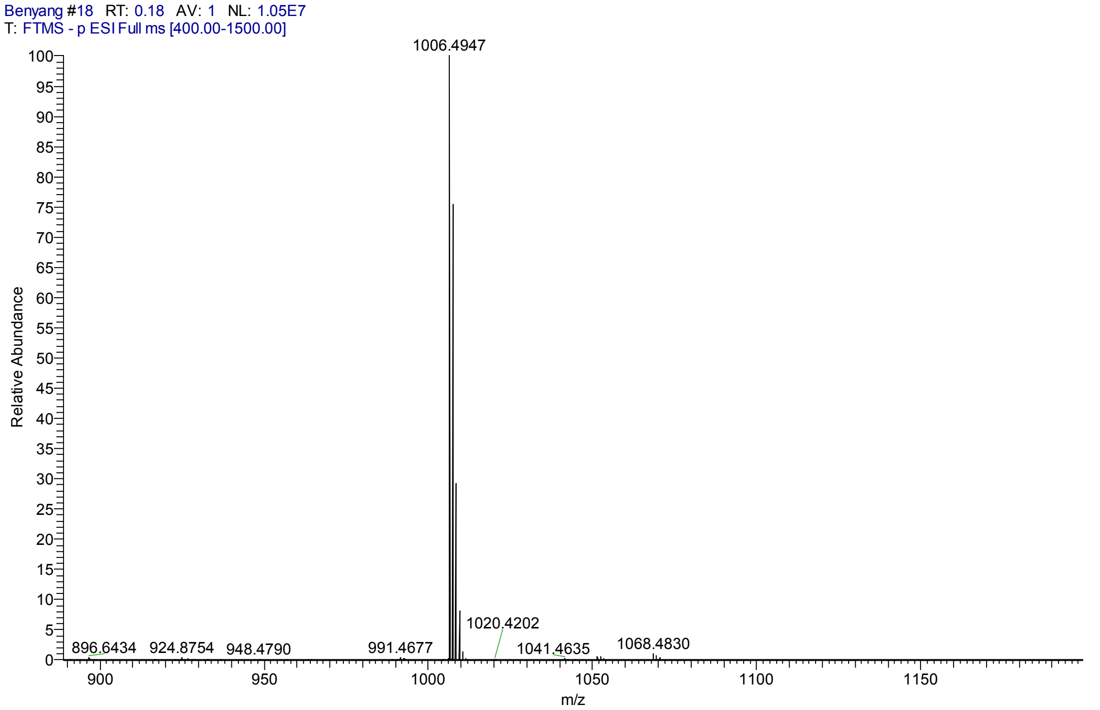


Figure S16. ESI mass spectrum of PDI **3** in CH_2Cl_2

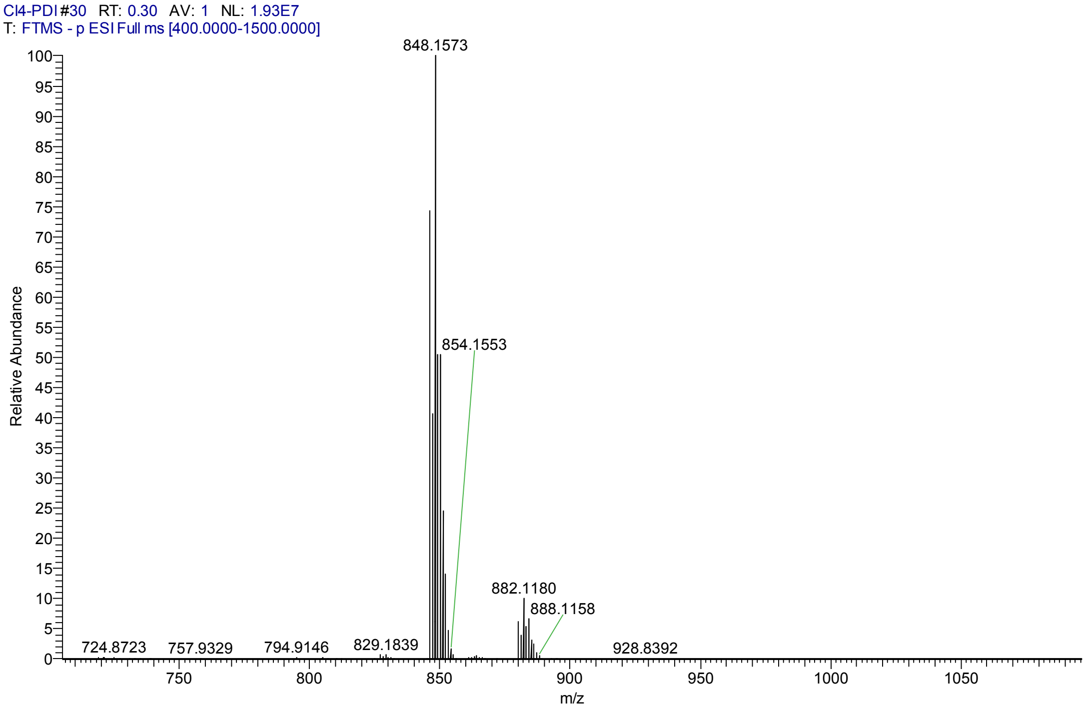


Figure S17. ESI mass spectrum of Cl_4-PDI in CH_2Cl_2

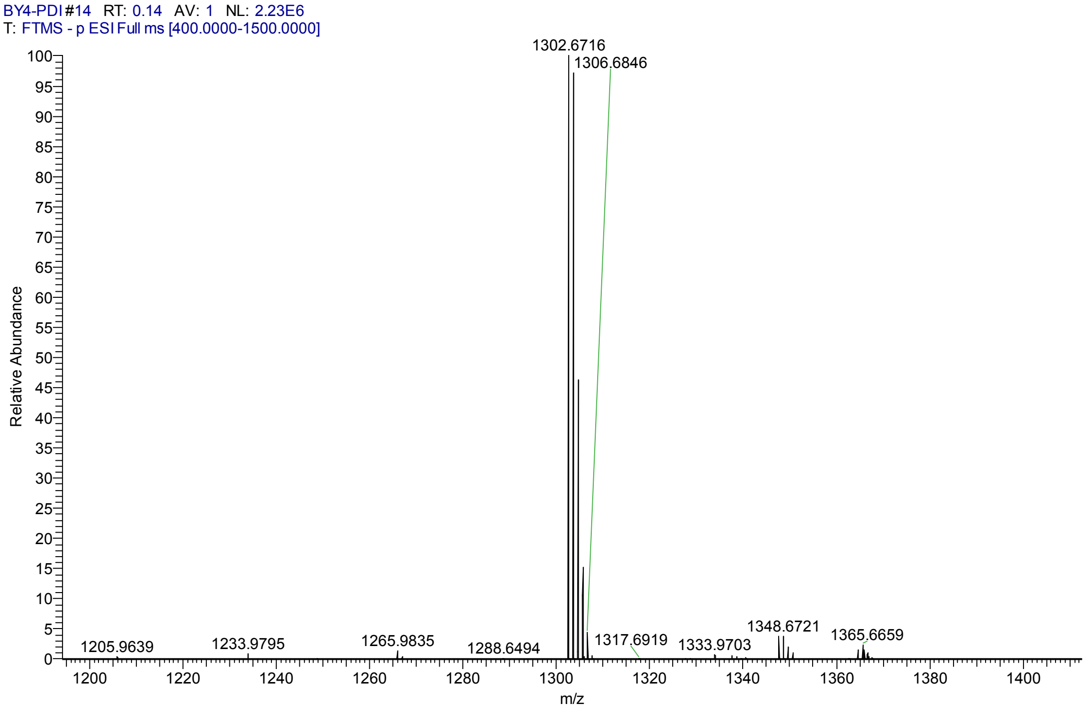


Figure S18. ESI mass spectrum of PDI **4** in CH_2Cl_2

4. Molecular Packing of PDI 3

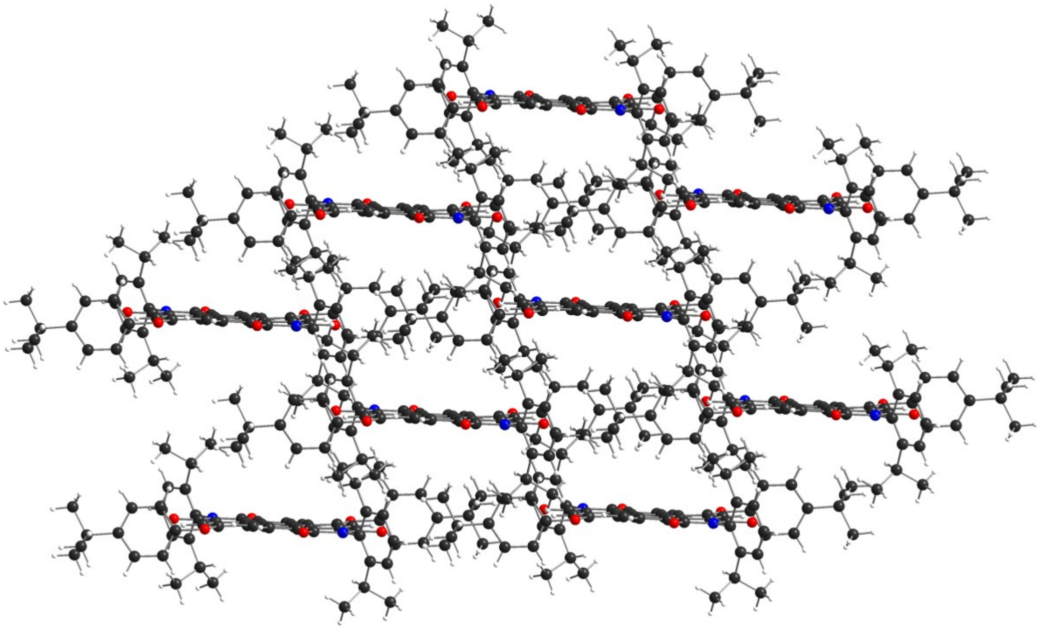
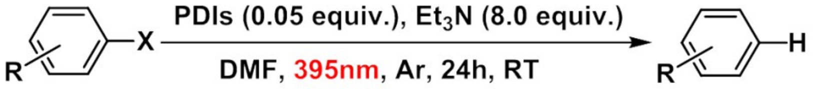


Figure S19. Molecular packing of PDI **3** viewed along *c* axis

5. Photocatalytic Properties of PDIs1-4

Table S1: Reduction of various aryl halides by PDIs **1**-**4** under the radiation of 395nm light, wherein the conversion rates were determined by GC with internal standards. n.d. = not detected



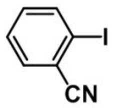
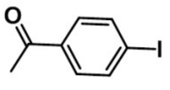
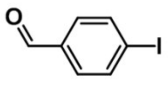
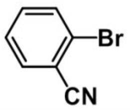
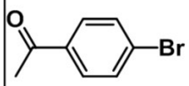
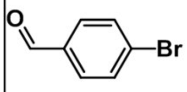
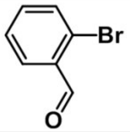
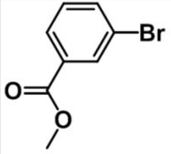
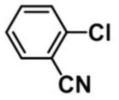
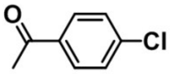
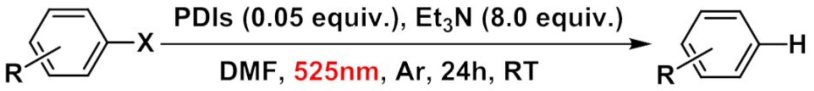
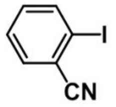
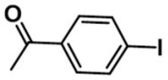
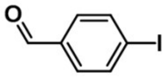
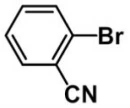
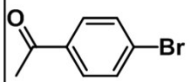
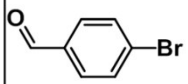
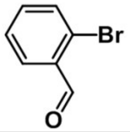
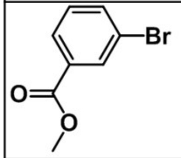
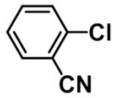
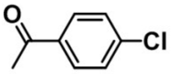
PDIs / substrates	PDI **1**	PDI **2**	PDI **3**	PDI **4**
	**40.3%**	**n.d.**	**58.3%**	**49.3%**
	**48.6%**	**n.d.**	**59.9%**	**48.8%**
	**42.4%**	**n.d.**	**60.2%**	**49.7%**
	**36.3%**	**n.d.**	**52.1%**	**46.3%**
	**39.4%**	**n.d.**	**55.5%**	**45.5%**
	**40.9%**	**n.d.**	**57.3%**	**46.7%**
	**37.4%**	**n.d.**	**43.3%**	**44.9%**
	**36.4%**	**n.d.**	**60.0%**	**50.9%**
	**31.4%**	**n.d.**	**48.3%**	**40.2%**
	**35.7%**	**n.d.**	**50.4%**	**41.6%**

Table S2: Reduction of various aryl halides by PDIs **1**-**4** under the radiation of 525nm light, wherein the conversion rates were determined by GC with internal standards

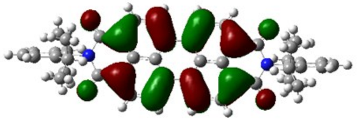
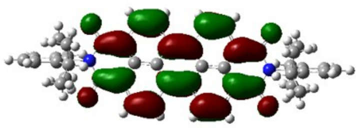
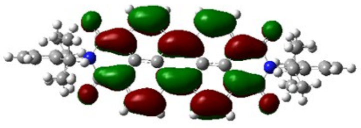
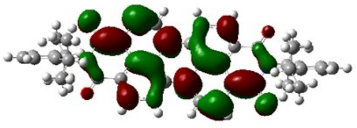
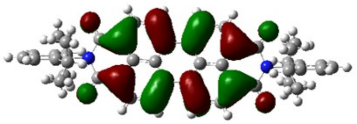
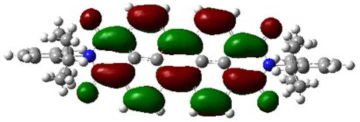
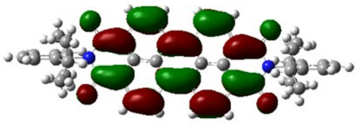
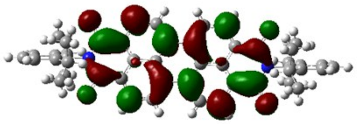
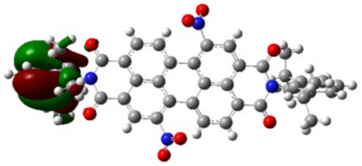
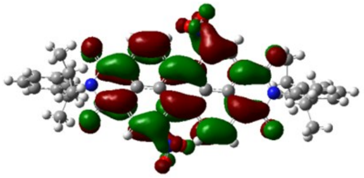
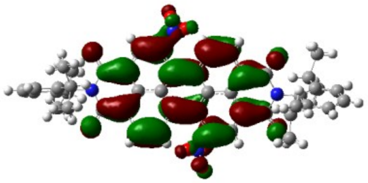
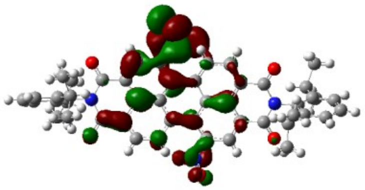


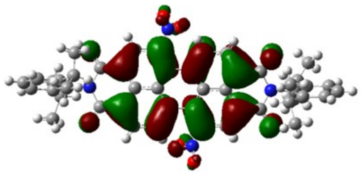
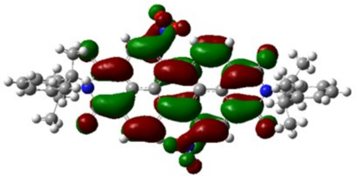
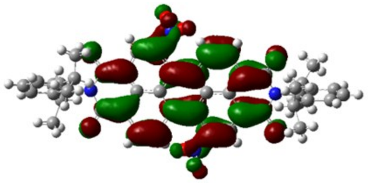
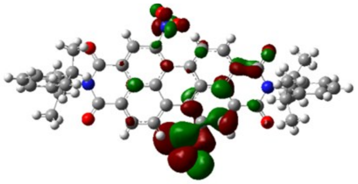
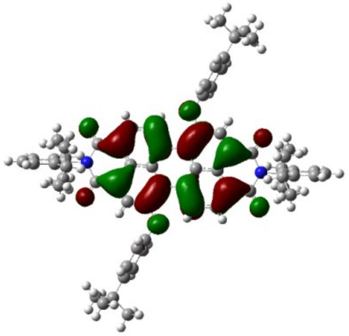
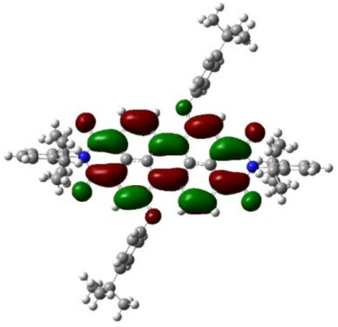
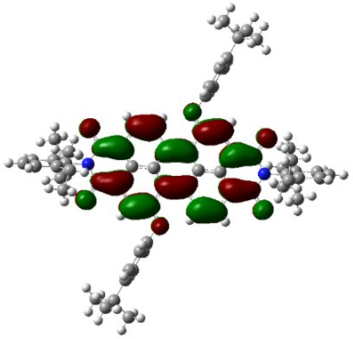
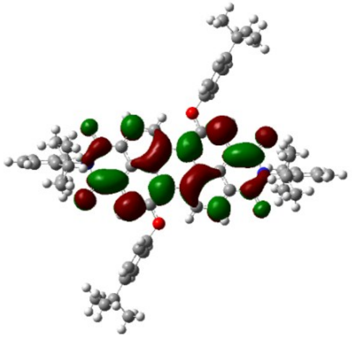
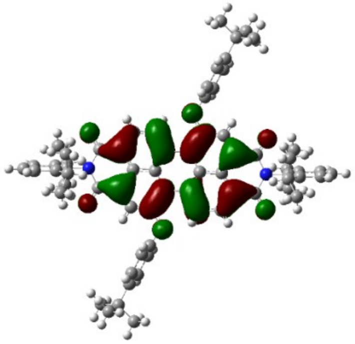
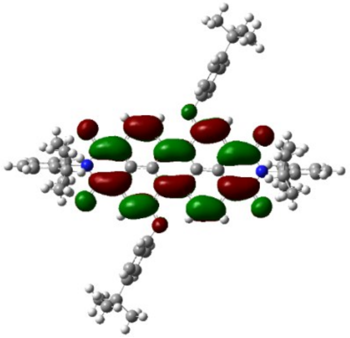
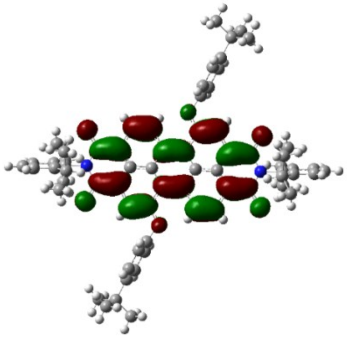
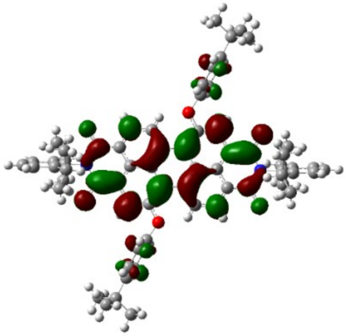
PDIs substrates	PDI **1**	PDI **2**	PDI **3**	PDI **4**
	**43.2%**	**5.21%**	**71.6%**	**50.7%**
	**45.1%**	**4.12%**	**76.2%**	**52.4%**
	**46.5%**	**5.36%**	**69.5%**	**53.3%**
	**41.5%**	**n.d.**	**62.8%**	**48.7%**
	**40.4%**	**n.d.**	**71.9%**	**49.0%**
	**42.3%**	**n.d.**	**68.3%**	**47.3%**
	**40.9%**	**n.d.**	**65.9%**	**45.1%**
	**46.7%**	**4.87%**	**75.4%**	**52.4%**
	**36.6%**	**n.d.**	**58.6%**	**45.1%**
	**38.3%**	**n.d.**	**59.4%**	**45.1%**

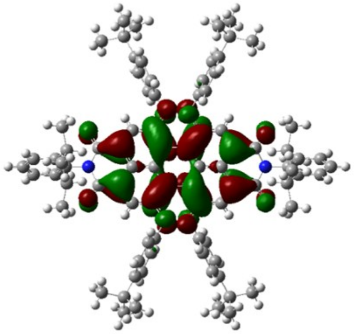
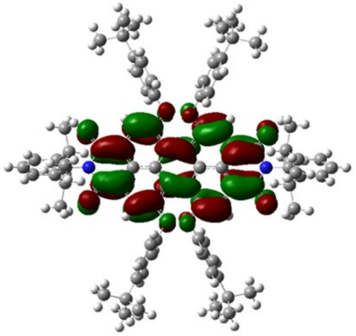
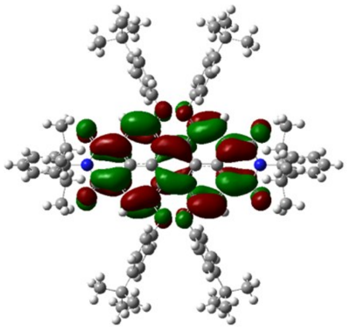
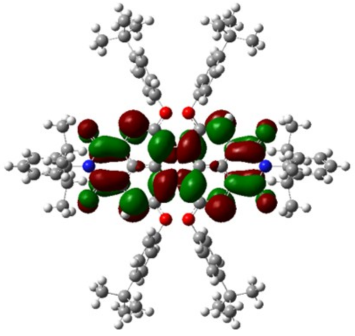
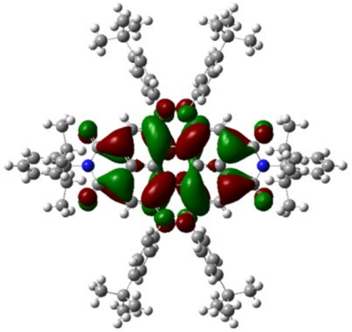
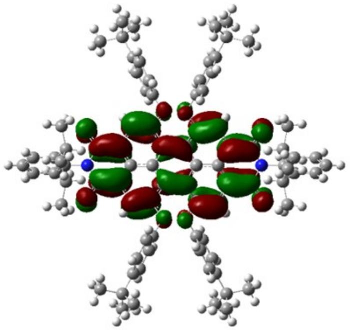
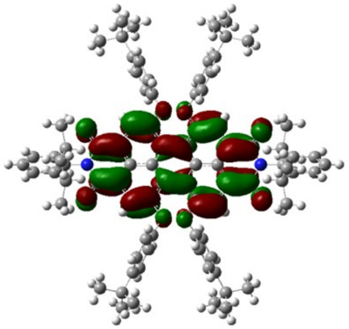
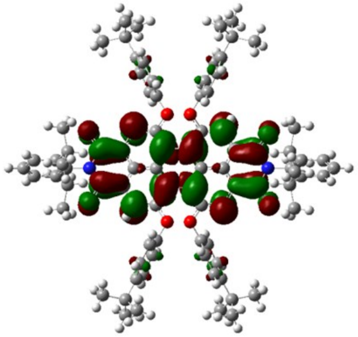
6. Theoretical Calculations of PDIs 1-4

The Gaussian 09 suit of programs is used to carry out all the DFT calculations. [S2] Geometry optimizations of PDIs **1-4** have been performed using the DFT hybrid functional B3LYP with the 6-21G basis set, then the electron density map for the final geometries have been calculated at B3LYP/6-31G(d,p) level.[S3, S4] The obtained ground-state and excited-state HOMO and LUMO orbits as well as orbital energies of PDIs **1-4** and their radical anions are listed as Table S3.

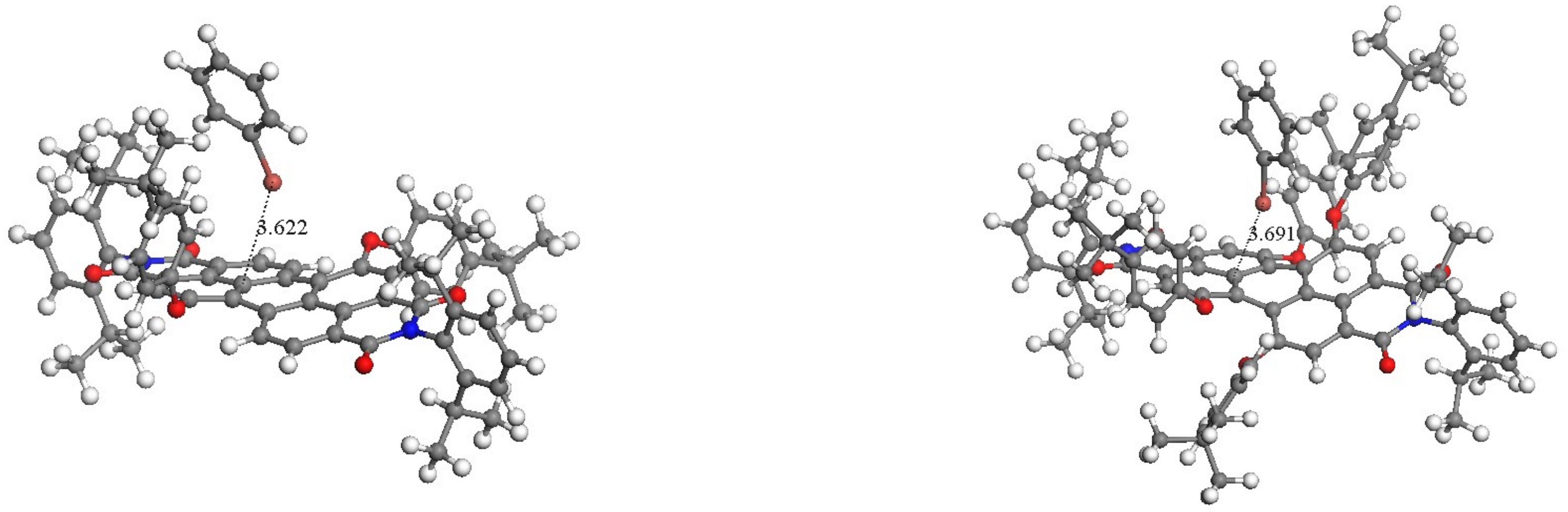
Table S3**：** The ground-state and excited-state HOMO and LUMO orbits and energies of PDIs **1-4** and their radical anions

PDIs	Energies(eV)	Ground States		Excited States	
		HOMO	LUMO	SOMO-1	SOMO-2
PDI **1**	Neutral				
		-5.98	-3.43	-4.49	-2.05
	Radical Anion				
		-2.52	0.00	-1.02	1.23
PDI **2**	Neutral				
		-6.32	-4.02	-5.06	-2.97

	Radical Anion				
		-3.30	-0.68	-1.68	0.09
PDI **3**	Neutral				
		-5.42	-2.98	-3.99	-1.83
	Radical Anion				
		-2.25	0.19	-0.81	1.21

PDI **4**	Neutral				
		-5.09	-2.76	-3.73	-1.88
	Radical Anion				
		-2.12	0.23	-0.75	1.02

To check the bay-substituents steric effect of PDIs on their interacting with the reaction substrates, the bromobenzene was model molecule and its interactions with PDIs **3** and **4** have been calculated by using the Gaussian 09, where geometry optimizations were also performed using the DFT hybrid functional B3LYP with the 6-21G basis set, then the electron density map for the final geometries were calculated at B3LYP/6-31G(d,p) level. As shown in Figure S20, the central PDI scaffolds of both PDIs **3** and **4** are found to be exposed to the model molecule bromobenzene, and thus possess considerately strong lone pair-π interactions with the distances between Br atoms and π-planes of 3.622 and 3.691Å. Accordingly, the bay-substituents steric effect of PDIs **3** and **4** on their photocatalytic performances towards the reductive dehalogenation of aryl halides is supposed to be rather limited.



E_b= 0.2221eV

E_b=0.3073eV

Figure S20. The calculated molecular interactions between PDI **3** and bromobenzene (left) as well as those between PDI **4** and bromobenzene (right)

7. References

[1] (a) Dubey R.K., Westerveld N., Grozema F.C., Sudhölter E. J. R., Jager W. F., *Org. Lett.*, **2015**, *17*, 1882-1885; (b) Dubey R. K., Westerveld N., Sudhölter E. J. R., Grozema F. C., Jager W. F., *Org. Chem. Front.*, **2016**, *3*, 1481-1492.

[2] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, revision A.1; Gaussian, Inc.: Wallingford, CT, 2009

[3] Becke, A. D.; Density-functional thermochemistry. III. The role of exact exchange, *J. Chem. Phys.*, **1993**, *98*, 5648-5652.

[4] Lee, C.; Yang, W.; Parr, R. G., Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density, *Phys. Rev. B*, **1998**, *37*, 785-789.