

Supporting Information to the New Journal of Chemistry

Structural symmetry-breaking of perylene diimide acceptor at N-position for enhanced photovoltaic performance

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Table of the contents

1. General information
2. Material synthesis
3. Thermal Gravimetric Analysis (TGA)
4. DFT calculation
5. UV-vis in solution and Cyclic voltammograms (CVs)
6. The photovoltaic performance of the devices
7. The relationship between photocurrent (J_{ph}) and effective voltage (V_{eff})
8. 1H and ^{13}C NMR spectra
9. MALDI-TOF Mass Spectrum

1. General information

All chemical reactions were conducted in oven-dried or flame-dried glassware. A homo-built flow photochemical reactor was used to synthesize the **MBI-PDI2** with Au Light CEL-LB70 as the light source. All the chemicals and starting materials were purchased from commercial sources without further treatment unless specially noted. The commercially available polymer donor PM6 was purchased from Solarmer Materials Int. with a MW over 40000 and a PDI of 1.8-2.0. Compounds perylene diimide, monobromoperylene diimide and perylene diimide dimer were synthesized according to literature procedures.

^1H NMR and ^{13}C NMR spectra were measured on Bruker DRX 500 or Varian Mercury plus-400. MALDI-TOF Mass spectrum was measured with AB Sciex 5800. UV-Vis spectrum was recorded on Shimadzu UV-1800. Cyclic voltammograms (CVs) were obtained on CHI660E electrochemical workstation. A three-electrode one-compartment cell containing a solution of the analyte and supporting electrolyte (tetrabutylammonium, $([\text{NBu}_4]\text{PF}_6)$, 0.1M) in CH_2Cl_2 was utilized. A 500 μm diameter platinum-disk working electrode, a platinum-wire counter electrode, and an Ag/AgCl reference electrode were used. The atomic force microscope (AFM) images were recorded by a Dimension Icon AFM (Bruker).

Thermogravimetric analysis (TGA) was carried out on a tainstruments SDT Q-600 under a nitrogen atmosphere at a heating rate of 10 $^\circ\text{C}/\text{min}$.

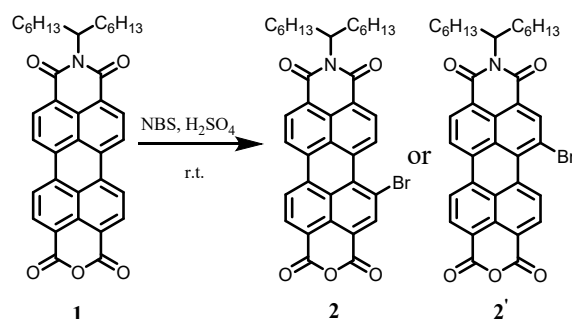
In order to reduce the computational costs, it is reasonable to replace the long $\text{C}_{13}\text{H}_{27}$ side chain attached to each imide N with a single H atom. The geometry optimizations of **MBI-PDI2** and **PDI2** were performed using the density functional theory (DFT) combining with the Perdew, Burke and Ernzerhof (PBE) functional and the Pople's 6-31G(d) basis set. Choosing this level is a result of the compromise between the computational accuracy and the costs, because of the large size of these two molecules, of which consist of around 350 atoms. Frequency analysis were then performed to confirm the geometry stability without imaginary frequency. All calculations were carried on the Gaussian16 quantum chemistry package. The HOMOs and LUMOs of these two molecules were obtained by using the Multiwfn program and visualized *via* the VMD package.

Device fabrication: The inverted devices were fabricated with the structure of indium tin oxide (ITO)/ zinc oxide (ZnO)/ active layer/ molybdenum oxide (MoO_3)/ silver (Ag). The pre-patterned (sheet resistance, 15 Ω/sq) ITO-glass substrates were sequentially cleaned in ultrasonic bath with detergent (Alconox Inc.), de-ionized water, acetone and isopropanol. The oven-dried substrates were then treated by an oxygen plasma (180 W) for 5 min. The ZnO precursor solution (110 mg/mL) was prepared by dissolving 0.22 g zinc acetate

dihydrate ($\text{ZnAc}_2 \cdot 2\text{H}_2\text{O}$) in 2 mL 2-methoxyethanol and 0.056 mL ethanol amine and then stirred for at least 24h before use. The solution was filtered with polyether sulfone (PES) filters. The ZnO precursor solution was spin-cast onto ITO substrate with spinning rate of 5000 rpm for 30s and the thickness was ~ 32 nm. The as-cast film was then annealed in ambient circumstance upon 150°C for 60 min to form a compact ZnO layer. The blend solutions of PM6: MBI-PDI2 and PM6: PDI2 (D/A ratio, 1:1.5, weight ratio) mixtures were all processed with chlorobenzene (CB) with an identical concentration of 15 mg mL^{-1} . 1,8-diiodooctane (DIO) and 1-chloronaphthalene (CN) was added to the active layer solution at different volume fractions of the solution. All these solutions were heated at 60°C and stirred overnight (or 100°C for 3h) to obtain well-mixed blend solutions. The active layer thicknesses of these three devices were carefully optimized through spinning rate variation (1200, 1500, 1800, 2000 and 2500 rpm). And, the spinning duration was fixed at 30s. The active layers were thermal annealed at 80, 90, 100, 110 and 120°C in glove box for 10 min to get rid of residual solvent. A MoO_3 (8 nm) layer and an Ag layer (100 nm) electrode were sequentially deposited by thermal evaporation using a shadow mask under a vacuum of $<1.0 \times 10^{-4}$ pa. The effective device area, defined by the overlap region of ITO and Ag electrodes, was 0.0625 cm^2 .

The $J-V$ measurements were conducted under AM 1.5G illumination at 100 mW cm^{-2} using an AAA solar simulator (SP94023A-SR1, NEWPORT). The illumination intensity was calculated with a standard photovoltaic cell (91150V) which incorporated with a quartz window (1000P072). External quantum efficiency (EQE) was determined by an EQE system (Zolix, China). The film thicknesses were determined on Bruker DektakXT Stylus Profiling System.

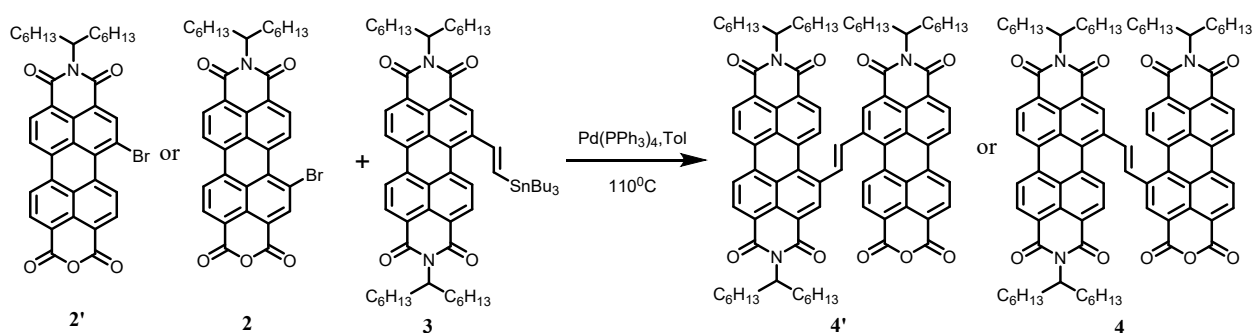
2. Material synthesis



Scheme S1 Synthetic route of 2/2'

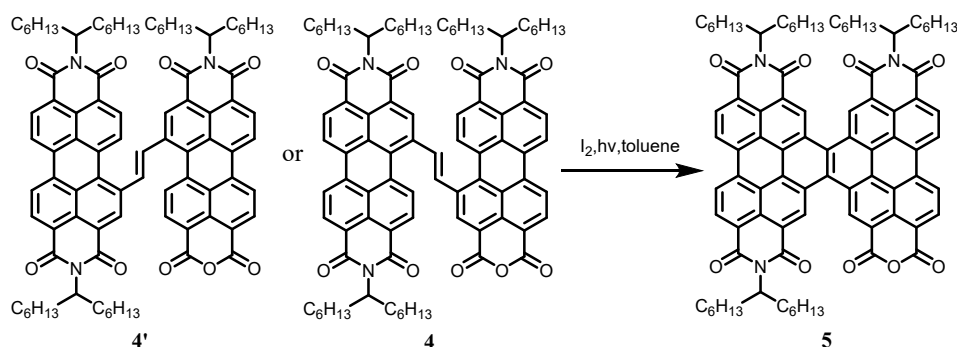
1 (8 g, 13.96 mmol) was dissolved in 15 mL concentrated sulfuric acid in a 100 mL round bottom flask, and 7.45 g of N-bromobutanamide (NBS) was added for several times. Then it was stirred at room

temperature. After 1 h, the mixture was poured into 200 mL of ice water. Then the precipitate was collected by vacuum filtration, washed with water, dried, and purified by column chromatography on silica gel (petroleum ether/CH₂Cl₂, 1:1 to 1:3, v/v) to afford **2/2'** as a red solid (4.08 g, 45%). ¹H NMR (500 MHz, CDCl₃): δ 9.74 (d, J = 8.2 Hz, 1H), 8.89 (s, 1H), 8.69 (s, 1H), 8.64-8.54 (m, 4H), 5.14 (s, 1H), 2.28-2.15 (m, 2H), 1.92-1.79 (m, 2H), 1.39-1.16 (m, 18H), 0.83 (s, 7H). ¹³C NMR (126 MHz, CDCl₃): δ 159.90, 159.58, 159.34, 158.73, 140.84, 135.71, 135.37, 135.33, 135.30, 133.08, 133.03, 132.67, 131.04, 130.09, 128.85, 128.81, 128.79, 128.02, 127.99, 127.27, 127.10, 124.63, 123.93, 123.88, 123.07, 122.03, 120.60, 119.17, 118.96, 118.63, 118.48, 77.29, 77.04, 76.79, 55.17, 54.98, 32.34, 32.28, 31.76, 29.21, 29.19, 26.92, 26.90, 22.59, 14.06. MS (MALDI-TOF): [M+H]⁺ calculated for 652.170; found 651.678.



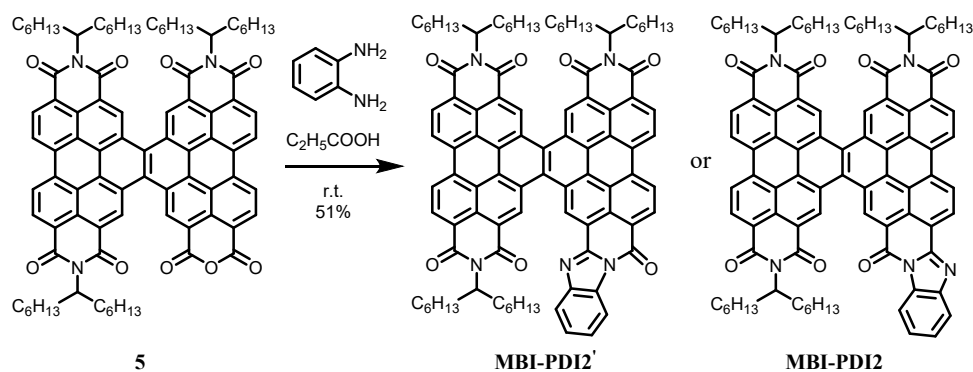
Scheme S2 Synthetic route of **4/4'**

To a mixture of **2/2'** (2 g, 3.071 mmol), **3** (3.95 g, 3.686 mmol), Pd(PPh₃)₄ (106 mg, 0.009 mmol) in a 100 mL flask, degassed toluene (40 mL) was added. The reaction was performed at 110 °C for 12 h under nitrogen. The solvent was removed using vacuum rotary evaporator and purified by column chromatography on silica gel (petroleum ether/CH₂Cl₂, 1:1 to 1:3, v/v) to afford **4/4'** as a purple solid (4.15 g, 70%). ¹H NMR (500 MHz, CDCl₃): δ 8.92 (d, J = 21.8 Hz, 2H), 8.86 -8.65 (m, 11H), 8.60 (d, J = 7.1 Hz, 1H), 8.16 (d, J = 19.7 Hz, 2H), 5.18 (s, 3H), 2.24 (s, 6H), 1.85 (s, 6H), 1.62 (d, J = 25.5 Hz, 7H), 1.40 – 1.14 (m, 54H), 0.80 (d, J = 6.7 Hz, 18H). ¹³C NMR (126 MHz, CDCl₃): δ 164.48, 163.38, 159.97, 159.76, 159.61, 136.35, 136.11, 135.17, 134.73, 134.58, 134.44, 133.80, 133.36, 133.24, 132.62, 130.80, 130.32, 130.23, 129.06, 128.62, 127.93, 127.60, 127.29, 123.97, 123.85, 123.75, 123.05, 77.30, 77.05, 76.79, 54.97, 54.82, 32.37, 32.34, 31.77, 31.75, 29.26, 29.24, 29.20, 26.99, 26.96, 26.93, 22.61, 22.57, 14.06, 14.03.



Scheme S3 Synthetic route of **5**

4/4' (2 g, 0.148 mmol) was dissolved in 800 mL toluene in a 1000 mL round bottom flask, and 500 mg of I₂ was added. The mixture was repeatedly pumped through the home-built flow light reactor with a retention time of 3 hours. The solvent was removed using vacuum rotary evaporator and the crude residue was washed with methanol to remove excessive iodine. The crude red solid was then purified with silica gel column using petroleum CH₂Cl₂ as eluent. And the final product of **5** was obtained as a red solid (1.79 g, 90%). ¹H NMR (500 MHz, CDCl₃): δ 10.30 (d, J = 31.3 Hz, 4H), 9.48 (t, J = 8.8 Hz, 4H), 9.31-9.11 (m, 4H), 5.30 (s, 3H), 2.33 (s, 6H), 1.96 (s, 6H), 1.30 (d, J = 53.1 Hz, 51H), 0.82 (s, 18H). ¹³C NMR(126 MHz, CDCl₃): δ 164.96, 163.63, 160.26, 136.21, 135.60, 133.98, 133.16, 131.84, 129.19, 127.51, 127.36, 127.20, 126.97, 126.49, 126.42, 126.25, 126.12, 126.03, 125.22, 124.58, 124.44, 124.29, 124.23, 124.06, 119.22, 118.07, 77.28, 77.03, 76.78, 55.22, 32.44, 31.77, 31.75, 29.26, 29.22, 27.05, 27.02, 22.61, 22.58, 14.06, 14.03. MS (MALDI-TOF): [M+H]⁺ calculated for 1348.700; found 1348.915.



Scheme S4 Synthetic route of **MBI-PDI2/MBI-PDI2'**

The condensation of compound **5** (1 g, 0.742 mmol) with 1, 2-diaminobenzene (96 mg, 0.89 mmol) in 15 mL propanoic acid at room temperature led to target compound. After adding water to the reaction mixture, precipitation was filtered. The crude products were purified by silica gel column chromatography with dichloromethane as eluent and lead to purple-back solid mixture **MBI-PDI2/MBI-PDI2'** (0.53 g, 51%). ¹H NMR (500 MHz, CF₃COOD): δ 10.86 (s, 1H), 10.42 (s, 3H), 9.90 (d, J = 8.3 Hz, 1H), 9.83 (s, 1H), 9.69 (d, J = 8.4 Hz, 3H), 9.51-9.29 (m, 3H), 9.03 (d, J = 8.3 Hz, 1H), 7.92 (d, J = 52.7 Hz, 3H), 5.53 (s, 3H), 2.39 (d, J = 69.2 Hz, 6H), 2.14 (d, J = 45.3 Hz, 6H), 1.77-1.05 (m, 49H), 0.84 (d, J = 40.5 Hz, 16H). ¹³C NMR (126 MHz, CF₃COOD): δ 167.45, 167.15, 166.87, 166.54, 166.31, 166.19, 165.93, 162.40, 162.06, 161.71, 161.36, 137.38, 135.08, 134.68, 133.96, 132.93, 132.00, 130.77, 129.73, 129.01, 128.76, 127.72, 127.31, 127.27, 127.01, 126.75, 126.28, 125.76, 125.05, 124.80, 124.13, 123.93, 123.41, 117.77, 115.52, 113.27, 111.02, 57.54, 57.39, 32.29, 32.26, 31.99, 31.47, 28.90, 28.71, 26.77, 26.73, 22.18, 22.02, 12.50. MS (MALDI-TOF): [M+H]⁺ calculated for 1421.750; found 1421.628.

3. Thermal Gravimetric Analysis (TGA)

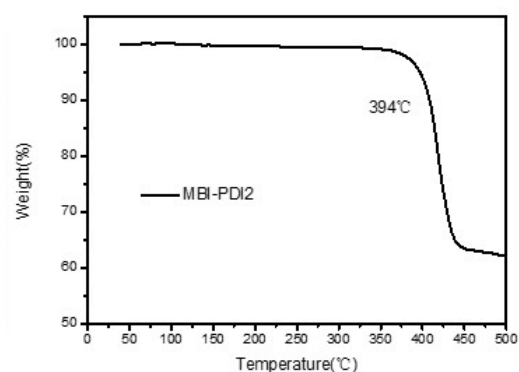


Figure S1. (a) Thermogravimetric analysis (TGA) result of **MBI-PDI2** with a heating rate of 10 °C/min under nitrogen.

4. DFT calculation

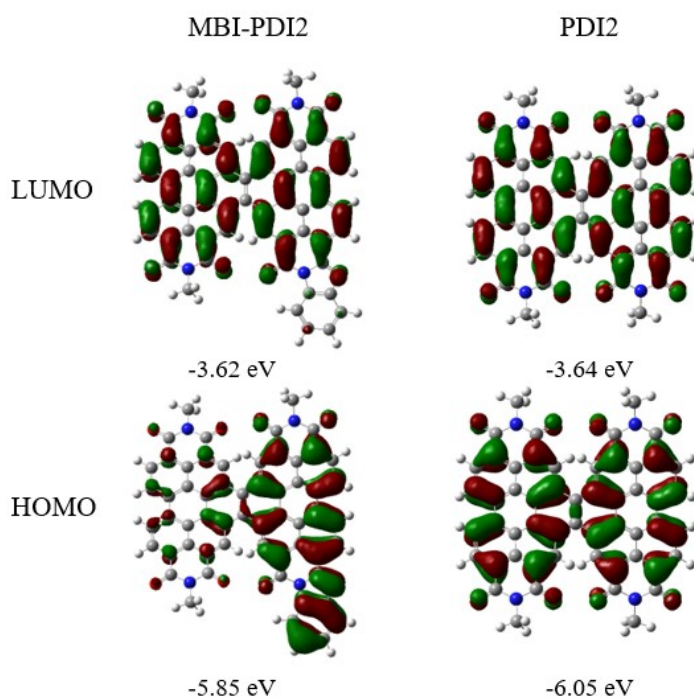


Figure S2. HOMOs and LUMOs of **MBI-PDI2** and **PDI2**.

5. UV-Vis in solution and Cyclic voltammograms (CVs)

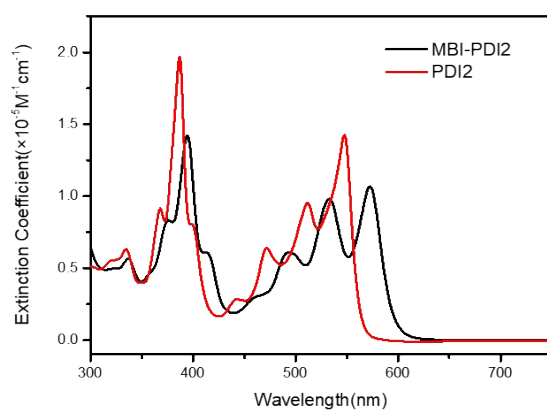


Figure S3. UV-Vis absorption spectra for **MBI-PDI2** and **PDI2** in the CHCl_3 solutions of a concentration of 5.0×10^{-6} M.

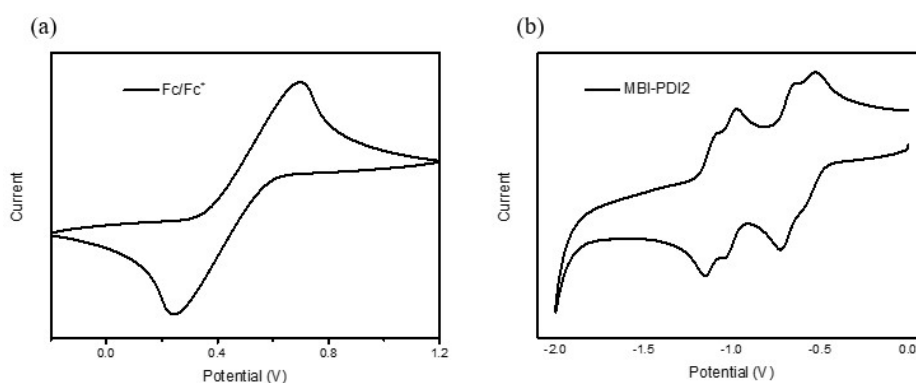


Figure S4. Cyclic voltammograms (CVs) for (a) Fc/Fc^+ , (b) **MBI-PDI2**.

5. The photovoltaic performance of the devices

Table S1. The detailed photovoltaic performance of **MBI-PDI2** and **PDI2** blend with two donors.

Device	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
PBDB-T:PDI2	0.882 ± 0.005	8.94 ± 0.24	43.5 ± 1.6	3.47 ± 0.15
	(0.888)	(9.21)	(45.0)	(3.69)
PBDB-T:MBI-PDI2	0.768 ± 0.006	10.36 ± 0.31	54.7 ± 1.9	4.59 ± 0.09
	(0.774)	(10.74)	(56.6)	(4.70)
PTB7-Th:PDI2	0.792 ± 0.005	13.51 ± 0.38	49.7 ± 2.1	5.57 ± 0.18
	(0.798)	(13.92)	(51.8)	(5.76)
PTB7-Th:MBI-PDI2	0.728 ± 0.007	14.60 ± 0.13	59.8 ± 1.2	6.55 ± 0.06

(0.735)

(14.74)

(61.1)

(6.62)

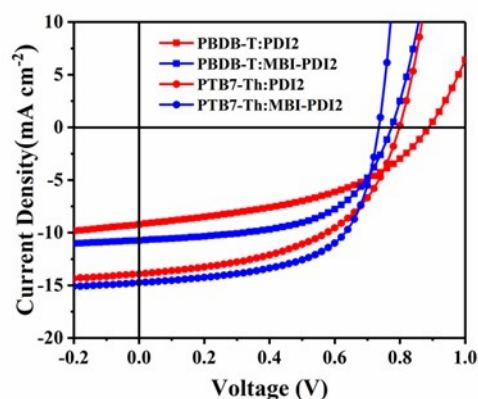


Figure S5. J - V curves of **MBI-PDI2** and PDI2 blend with two donors

Table S2. Optimization of the inverted devices additive ratios for **MBI-PDI2**-based blend films under illumination of AM 1.5G, 100 mW cm⁻².

Additive	wt%	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
DIO	0.5%	0.941	9.76	63.3	5.81
	1%	0.942	9.59	64.0	5.78
	1.5%	0.929	9.60	63.2	5.64
	2%	0.930	9.55	63.1	5.61
CN	0.5%	0.943	10.63	56.1	5.62
	1%	0.936	11.21	57.3	6.01
	1.5%	0.937	10.90	57.6	5.88
	2%	0.933	10.60	57.7	5.70

Table S3. Optimization of the inverted devices annealing temperature for **MBI-PDI2**-based blend films under illumination of AM 1.5G, 100 mW cm⁻².

TA	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
80°C	0.938	10.70	64.1	6.43
90°C	0.948	11.92	62.1	7.02

100°C	0.938	11.94	63.6	7.13
110°C	0.936	10.22	65.6	6.27

7. The relationship between photocurrent (J_{ph}) and effective voltage (V_{eff})

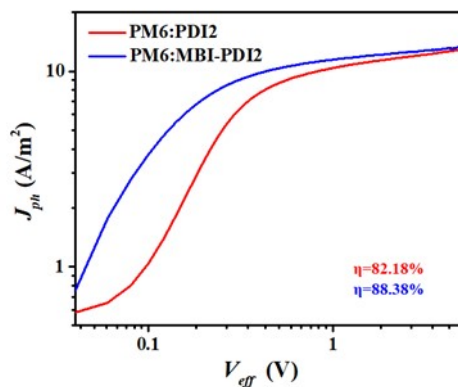


Figure S6. The saturated photocurrent versus effective voltage (J_{ph} - V_{eff}) curves of the OSCs based on PM6:PDI2 and PM6:MBI-PDI2.

8. 1H and ^{13}C NMR spectra

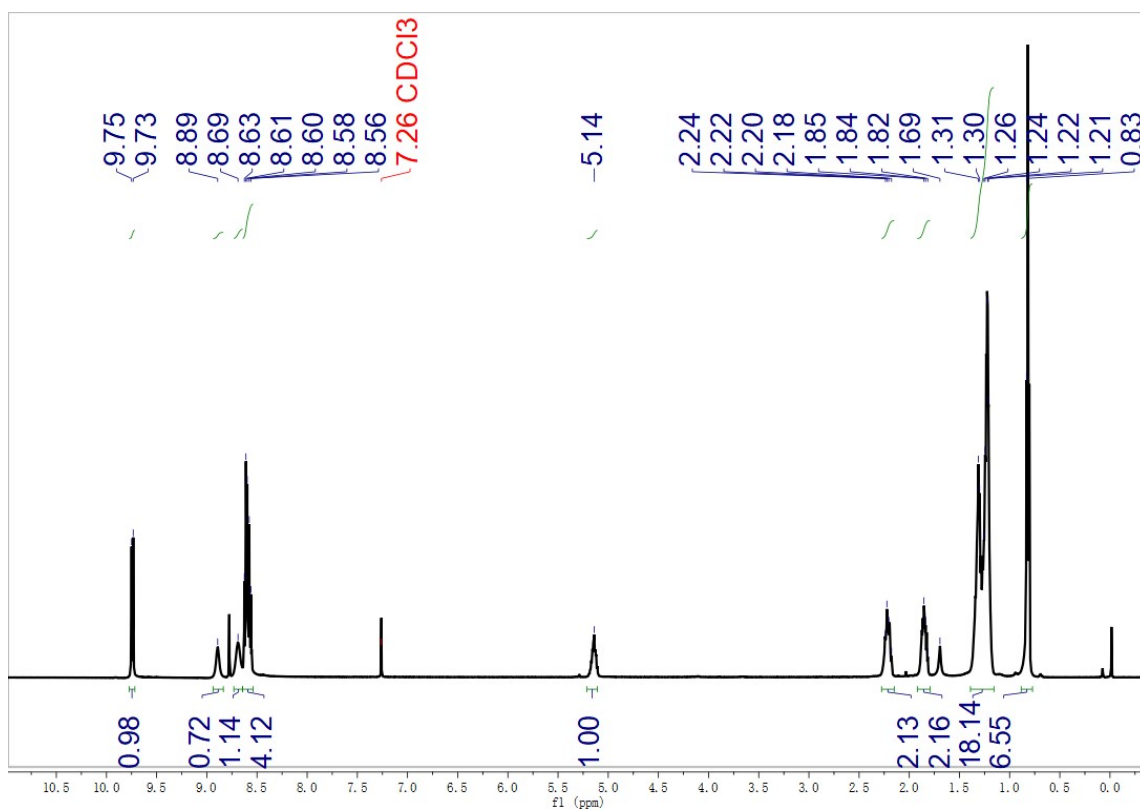


Figure S7. 1H NMR spectra for 2/2'

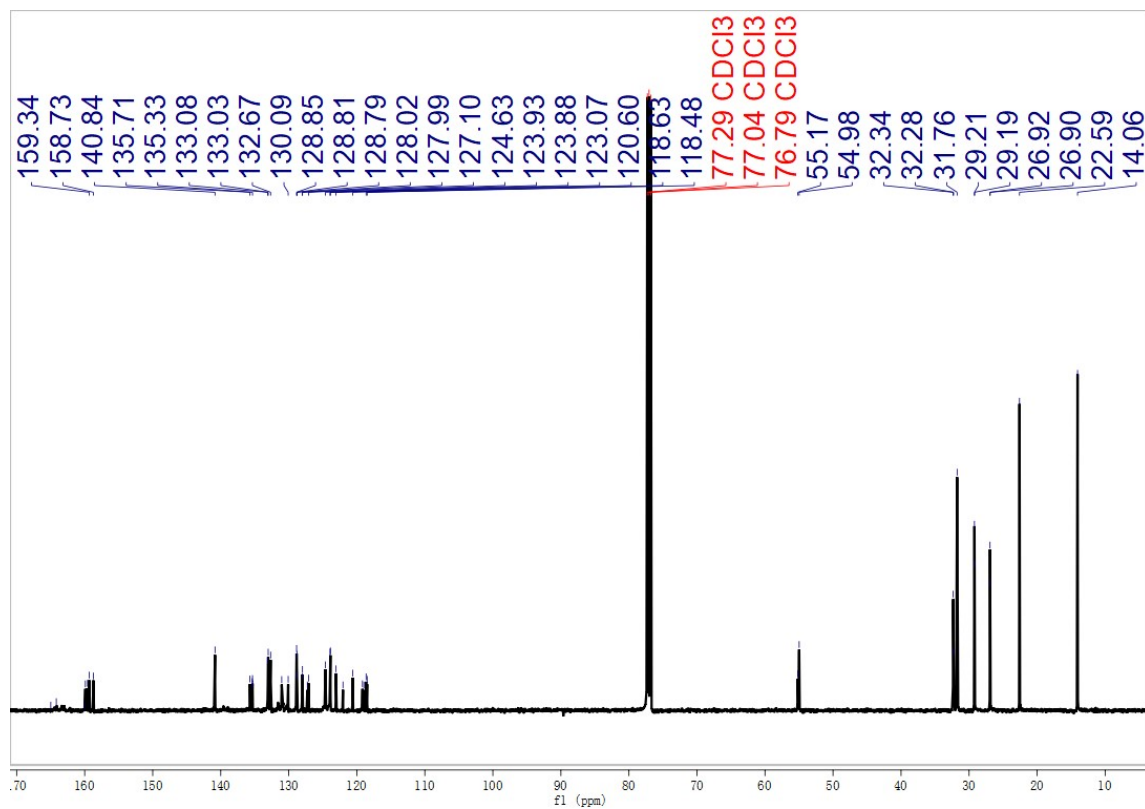


Figure S8. ^{13}C NMR spectra for 2/2'

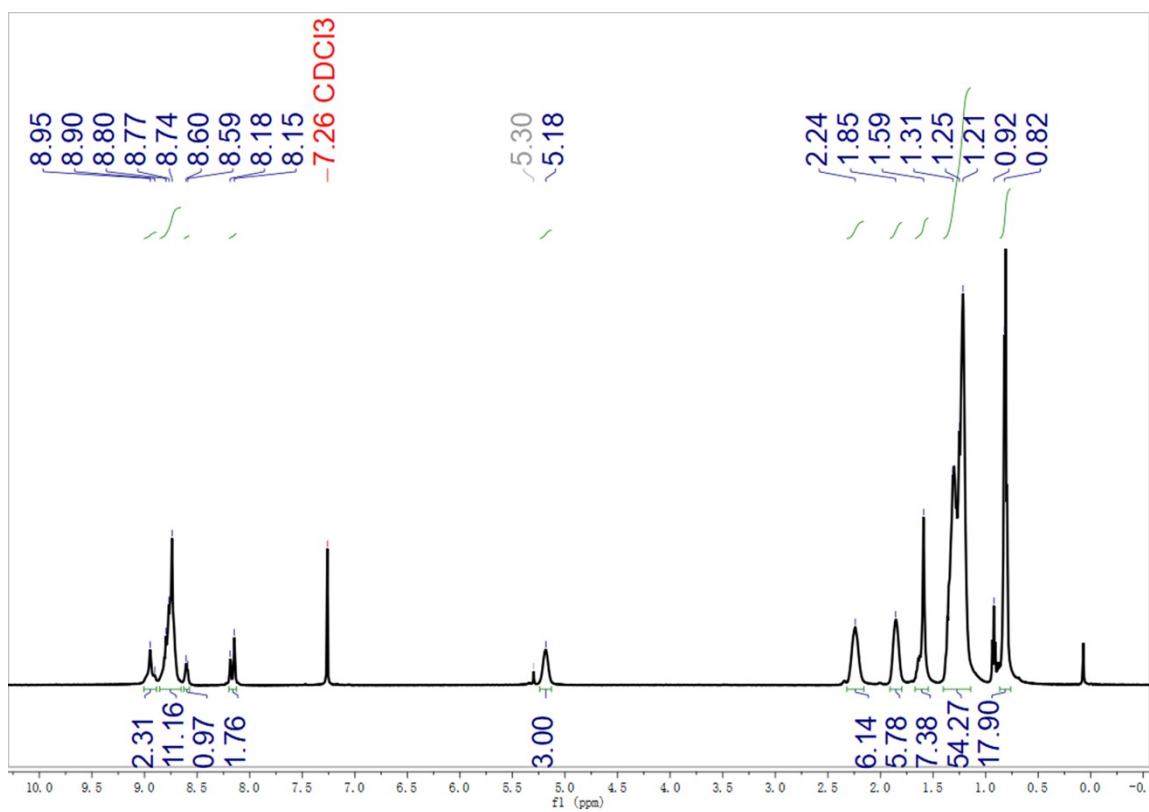


Figure S9. ^1H NMR spectra for 4/4'

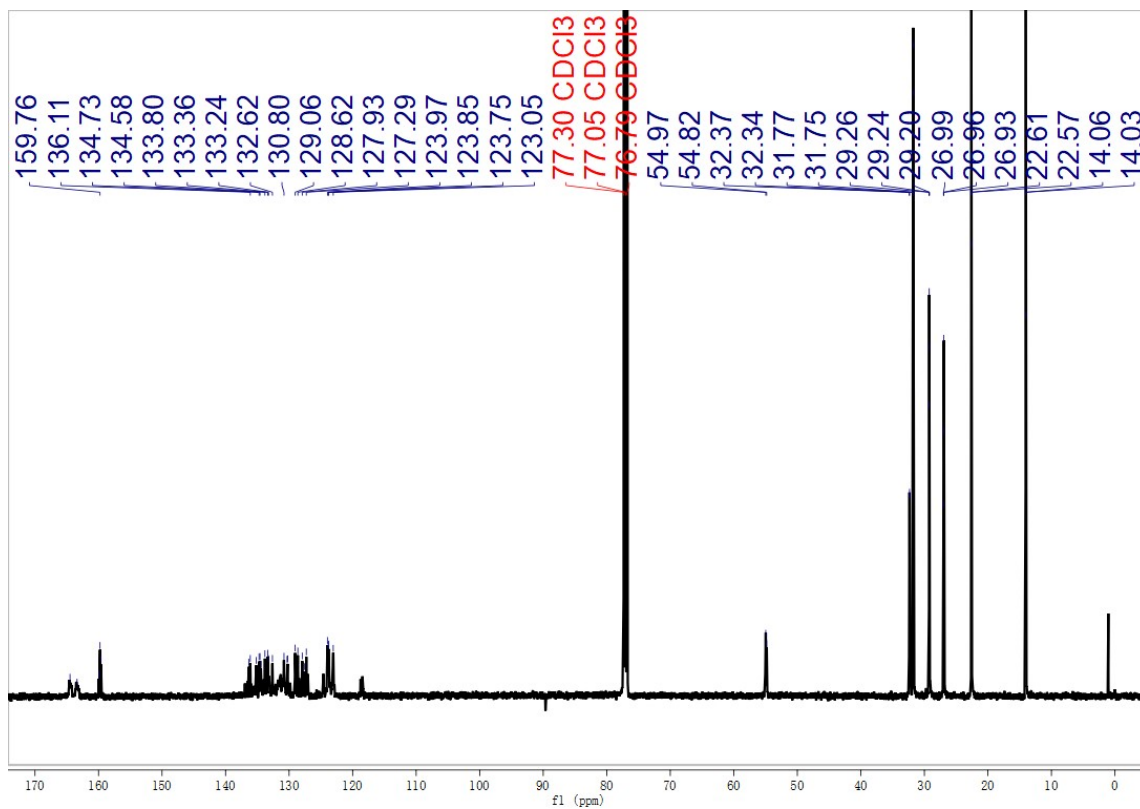


Figure S10. ^{13}C NMR spectra for 4/4'

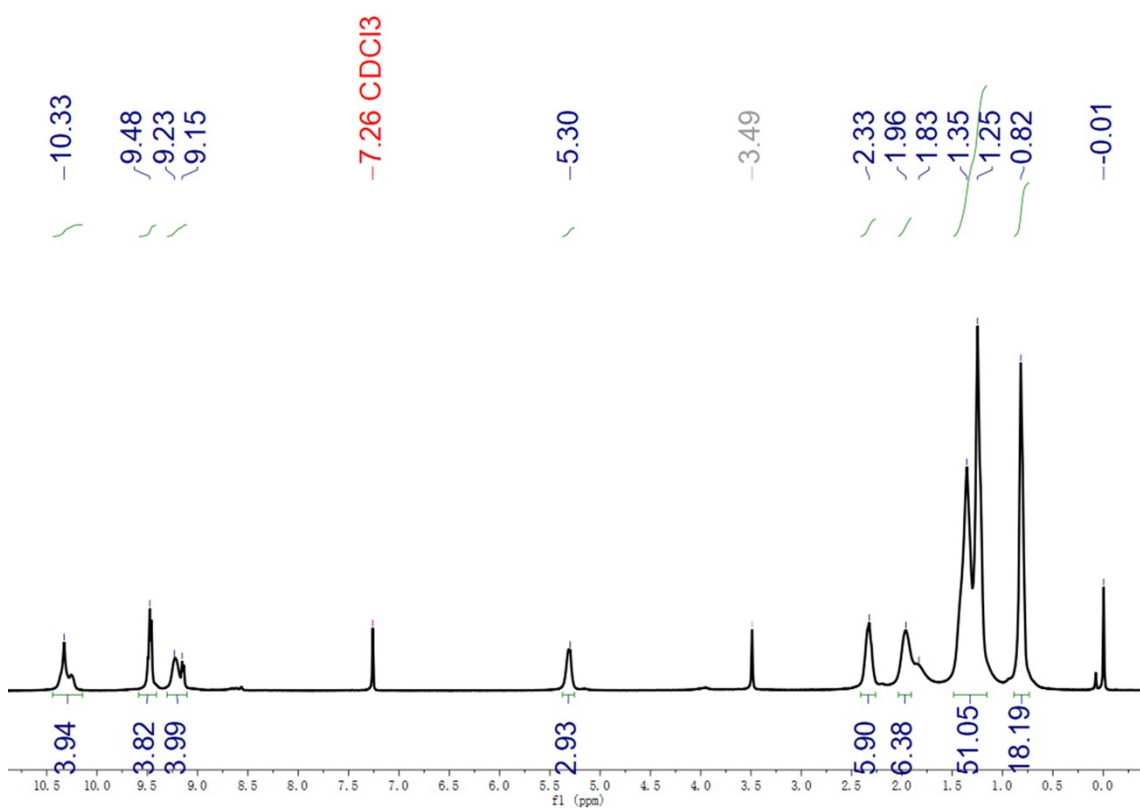


Figure S11. ^1H NMR spectra for 5

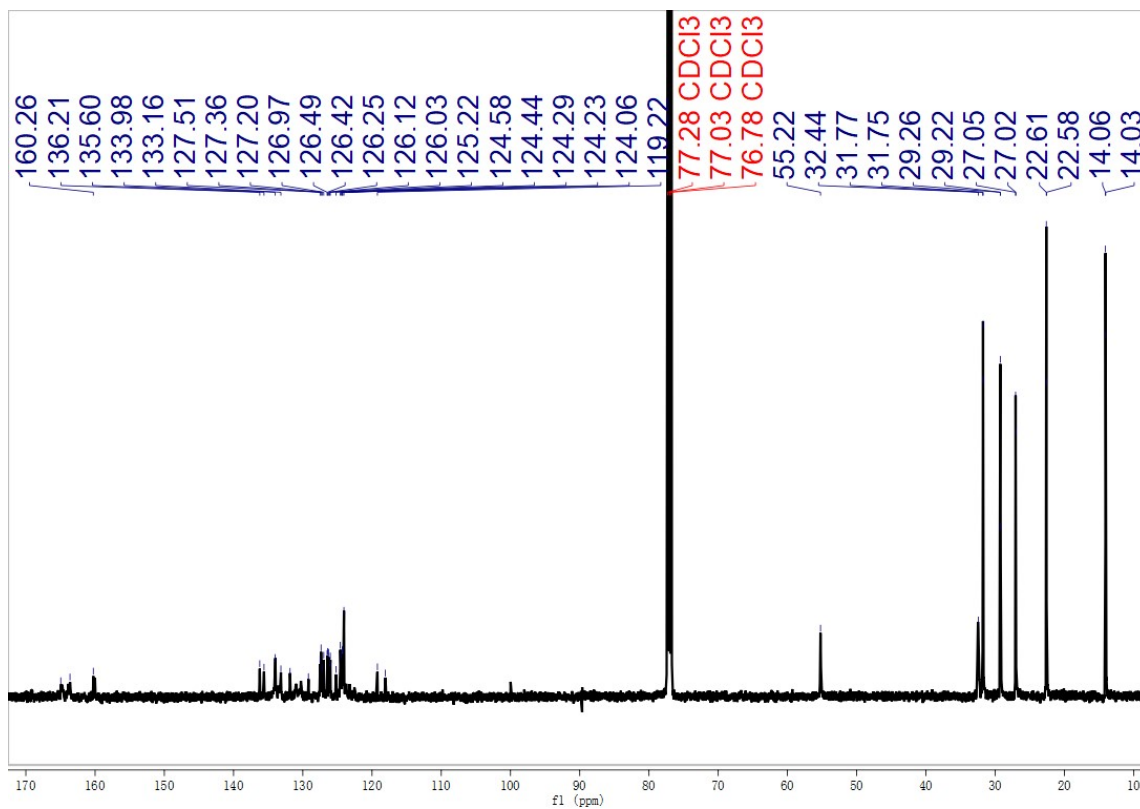


Figure S12. ¹³C NMR spectra for 5

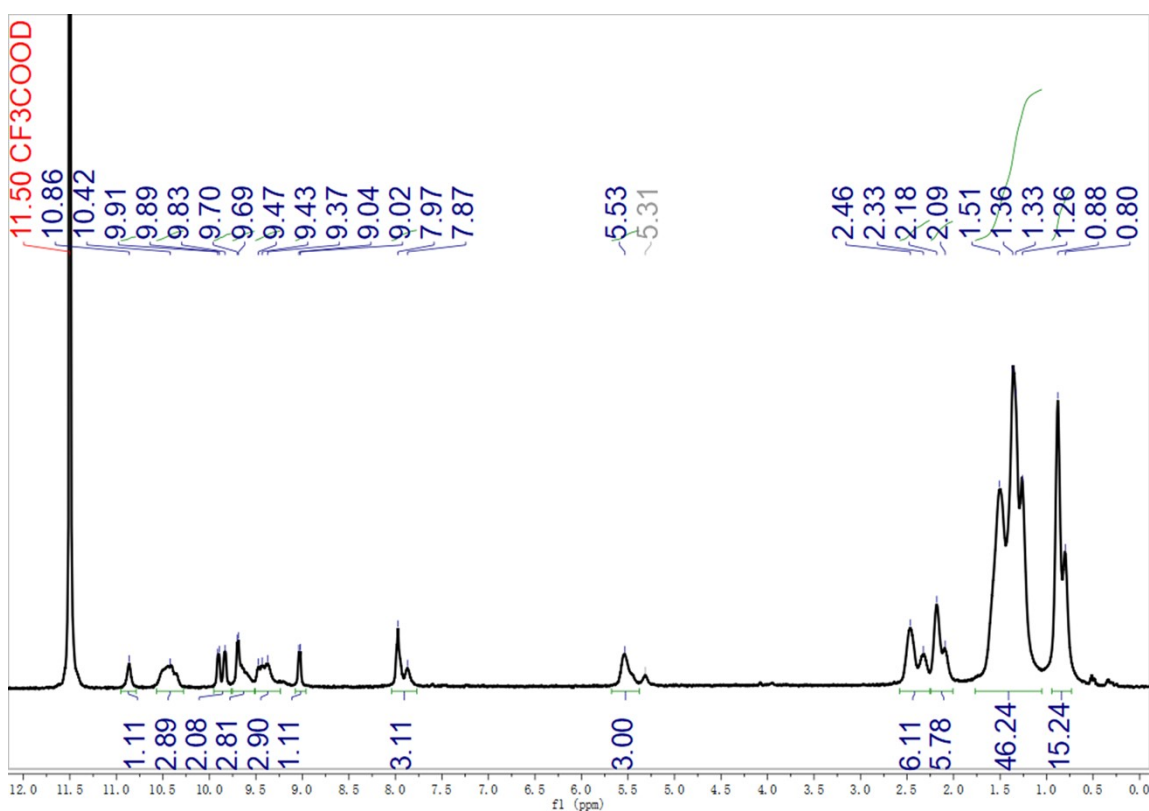


Figure S13. ¹H NMR spectra for MBI-PDI2/MBI-PDI2'

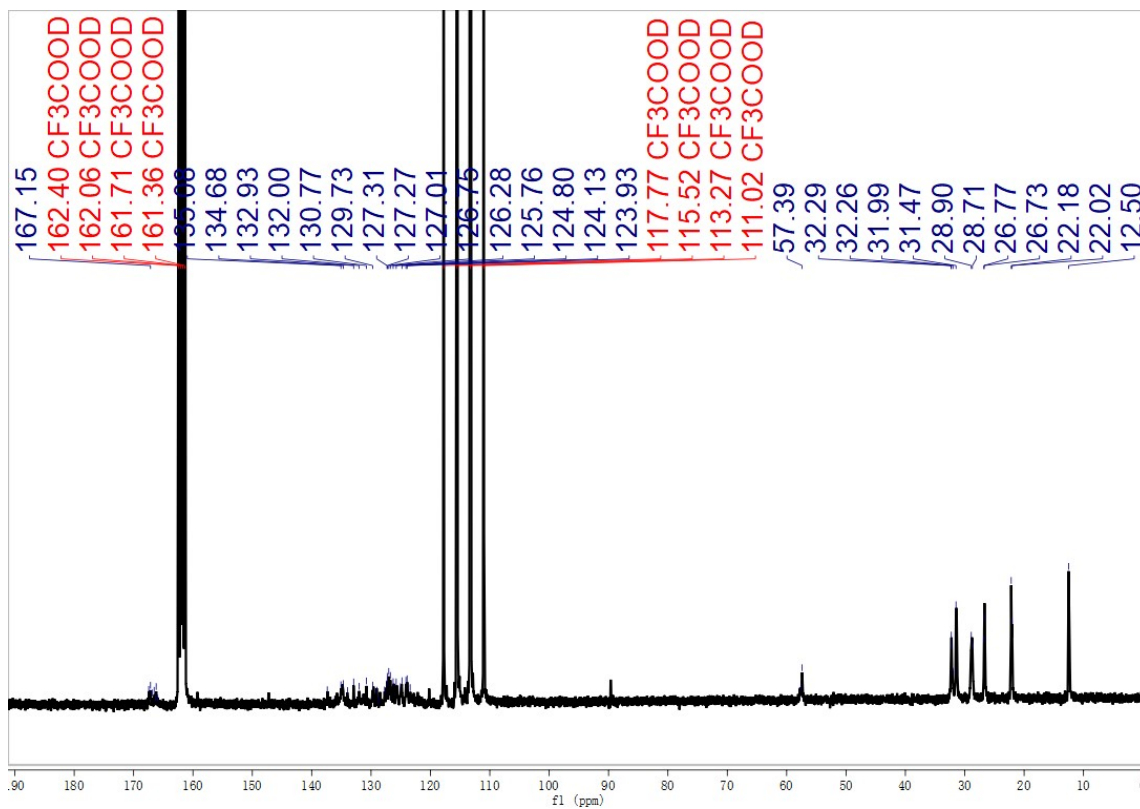


Figure S14. ^{13}C NMR spectra for **MBI-PDI2/MBI-PDI2'**

8. MALDI-TOF Mass Spectrum

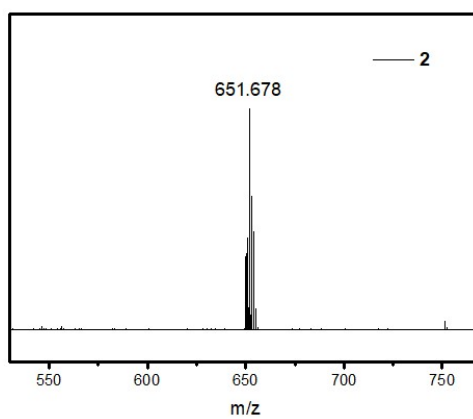


Figure S15. MALDI-TOF Mass Spectrum for **2**. MS (MALDI-TOF): $[\text{M}+\text{H}]^+$ calculated for 652.170; found 651.678.

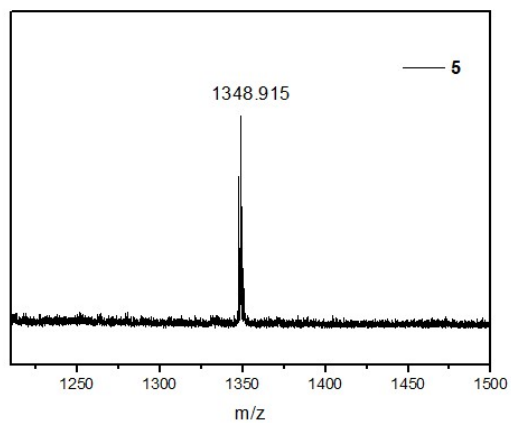


Figure S16. MALDI-TOF Mass Spectrum for **5**. MS (MALDI-TOF): $[M+H]^+$ calculated for 1348.700; found 1348.915.

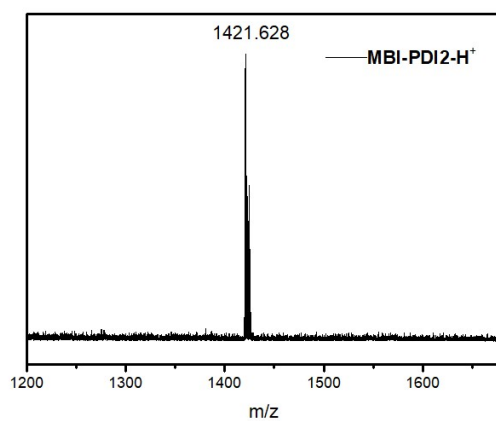


Figure S17. MALDI-TOF Mass Spectrum for **MBI-PDI2**. MS (MALDI-TOF): $[M+H]^+$ calculated for 1421.750; found 1421.628.