Supporting Information

Perylene Diimide Architectures Based Electromechanical Sensors: A Systematic Experimental and Theoretical Framework for Comparative Analysis and Study of Transduction Mechanism

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Experimental section

The detailed synthetic procedure and characterization data have been described below:

N,N′-bis-(2,9-pentan-3-yl)-perylene-3,4,9,10- tetracarboxydiimide (PDI-1): A mixture of perylene bisanhydride (1 g, 2.5 mmol), 3-aminopentane (2 mL), and imidazole (4 g, 58.8 mmol) was stirred at 140 °C for 12 h. Then, the reaction mixture was cooled down to room temperature and ~150 mL of water. The red solid was collected, washed with water and brine until neutral, and dried in a vacuum. The final compound **PDI-1** was obtained as red power (yield: 47 %) was obtained. IR (KBr, cm^{-1}) 3641, 3411, 2956, 1700, 1655, 1596, 1340, 1252, 1198, 958, 805, 741 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm : 8.67 (d, *J* = 8.0 Hz 4H), 8.62 (d, J = 8.0 Hz, 4H), 5.11-5.03 (m, 2H), 2.32 – 2.23 (m, 4H), 2.00 – 1.90 (m, 4H), 0.93 (t, J = 7.5 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 164.1, 134.2, 130.3, 129.4, 126.2, 122.8, 57.7, 24.9, 11.3. LCMS m/z calcd. $C_{34}H_{30}N_2O_4$ $[M + H]^+$ 530.2, found 530.0.

N,N′-bis-(2,5-di-tert-butylphenyl)-perylene-3,4,9,10- tetracarboxydiimide (PDI-2): A mixture of perylene bisanhydride (2.0 g, 5.2 mmol) and excess 2,5-di-tert-Butylaniline (2.2 g) were taken in 15 mL of propionic acid under N_2 atmosphere, the reaction mixture was stirred and heated at 140 ºC for 8 h. After being cooled to room temperature, the resulting solution was poured into ~100 mL of water. The red solid was collected, washed with water, and brine until neutral, and dried in a vacuum. The crude product was purified by silica gel column chromatography (CH_2Cl_2/PE: 1:1 in v/v). The final compound, **PDI-2,** was obtained as an orange-red solid (yield: 35 %). IR (KBr, cm^{-1}) 3659, 3438, 2959, 1704, 1669, 1511, 1347, 1254, 1198, 967, 816, 672 cm^{-1}, ^{1}H NMR (400 MHz, $CDCl_3$) *δ* ppm: 8.78 (d, *J* = 8.0 Hz, 4H), 8.72 (d, *J* = 8.0 Hz, 4H), 7.61 (d, *J* = 8.6 Hz, 2H), 7.48 (m, *J* = 8.6 Hz, 2H), 7.06 – 7.01 (m, 2H), 1.34 (s, 18H), 1.31 (d, *J* = 2.2 Hz, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 164.3, 150.1 ,143.7, 135.0, 132.5, 131.8 , 129.8 , 128.8, 127.6 , 126.7 , 123.6 , 123.4 , 35.5 , 34.2 , 31.7. LCMS m/z calcd. $C_{52}H_{50}N_2O_4$ $[M + H]^+$ 766.3, found 766.0.

N,N′-bis-(1′-phenylethyl)-perylene-3,4,9,10- tetracarboxydiimide (PDI-3): Perylene bisanhydride (1.5 g, 3.6 mmol), freshly distilled 1-phenylethylamine (1.16 mL, 9.6 mmol) and 30 g of imidazole were introduced under an inert (N_2) atmosphere and the system was warmed up to 180 °C and stirred

for four h. The crude product was then cooled at room temperature. After cooling, ~200 mL of 2 M HCl was added, and the system was left overnight under vigorous stirring. The resulting dark-red solid was filtered off and washed thoroughly with distilled water until the washings' pH turned neutral. The crude product was purified by silica gel column chromatography (CH_2Cl_2/ethyl acetate = 20:1 in v/v). The pure compound **PDI-3** was obtained as red needle-shaped crystals (yield: 52 %). IR (KBr, cm^{-1}) 3523, 3441, 2927, 1692, 1596, 1333, 1255, 963, 748 cm^{-1}, ^1H NMR (400 MHz, $CDCl_3$) δ ppm: 8.63 (d, *J* = 8.0 Hz, 4H), 8.56 (d, *J* = 8.0 Hz, 4H), 7.56 – 7.52 (m, 4H), 7.37 – 7.32 (m, 4H), 7.26 - 7.24 (m, 2H), 6.57 (q, *J* = 7.1 Hz, 2H), 2.03 (d, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.7, 134.6, 131.8, 128.9, 128.3, 127.9, 127.5, 127.1, 127.0, 126.4, 124.5, 124.3, 123.6, 51.6, 51.1, 50.9, 39.5, 38.8, 33.7, 27.2, 26.9, 16.8, LCMS m/z calcd. $C_{40}H_{26}N_2O_4$ $[M + H]^+$ 598.2, found 598.0.

N,N′-bis-[2-(2,5-di-tert-butylphenyl)-9-(1-phenylethyl)]-perylene-3,4,9,10- tetracarboxydiimide (PDI-4): A mixture of perylene-3,4,9,10-tetracarboxylic dianhydride (1 g, 2.55 mmol), imidazole (13.5 g, 200 mmol), 1-phenylethylamine (370 mg, 3 mmol), and 2,5-Di-tert-butylaniline (637 mg, 3.1 mmol) was heated at 130 °C for 2 h. The crude product was purified by column chromatography (1:1 DCM/hexanes) to obtain pure **PDI-4** as a red solid (yield: 39%). IR (KBr, cm^{-1}) 3936, 3442, 3314, 2962, 1708, 1664, 1536, 1347, 1213, 975, 641 cm^{-1}, ^1H NMR (400 MHz, $CDCl_3$) δ ppm: 8.74 (d, *J* = 8.0 Hz, 2H), 8.66 – 8.63 (m, 3H), 8.62 – 8.59 (m, 3H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 7.1 Hz, 2H), 7.48 (m, 1H), 7.38 – 7.33 (m, 2H), 7.29 - 6.98 (m, 1H), 7.05 (d, *J* = 2.2 Hz, 1H), 6.61 – 6.54 (m, 1H), 2.04 (m, 3H), 1.34 (s, 9H), 1.30 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 164.4, 163.4, 150.1, 140.5, 134.9, 134.5 , 131.8, 131.7 , 131.6, 130.8, 128.8 , 127.7 , 127.2, 126.3 , 123.6, 123.1, 50.4 , 35.5, 34.2 , 31.2, 16.2. LCMS m/z calcd. $C_{46}H_{38}N_2O_4$ $[M + H]^+$ 682.3, found 682.0

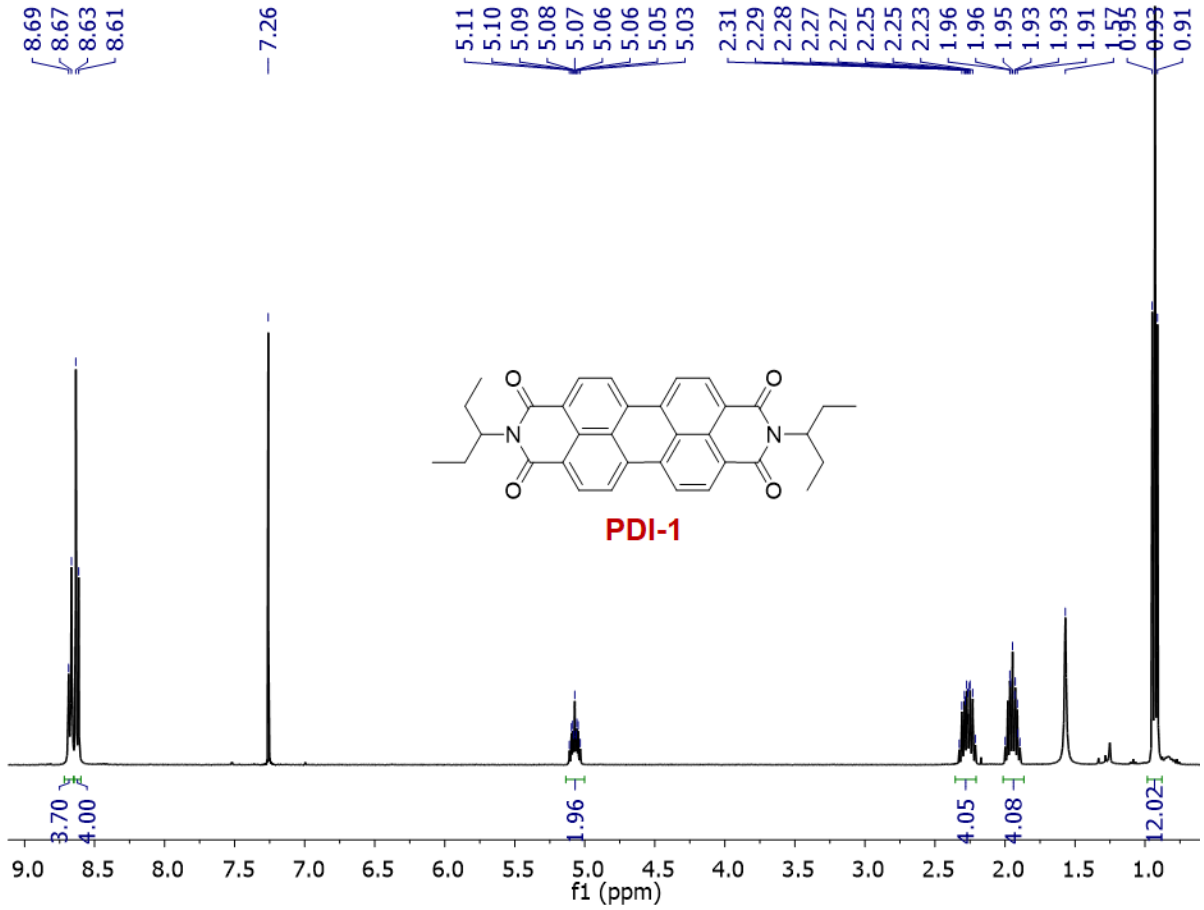

Figure S1. ^{1}H-NMR spectrum of **PDI-1** in $CDCl_3$ medium.

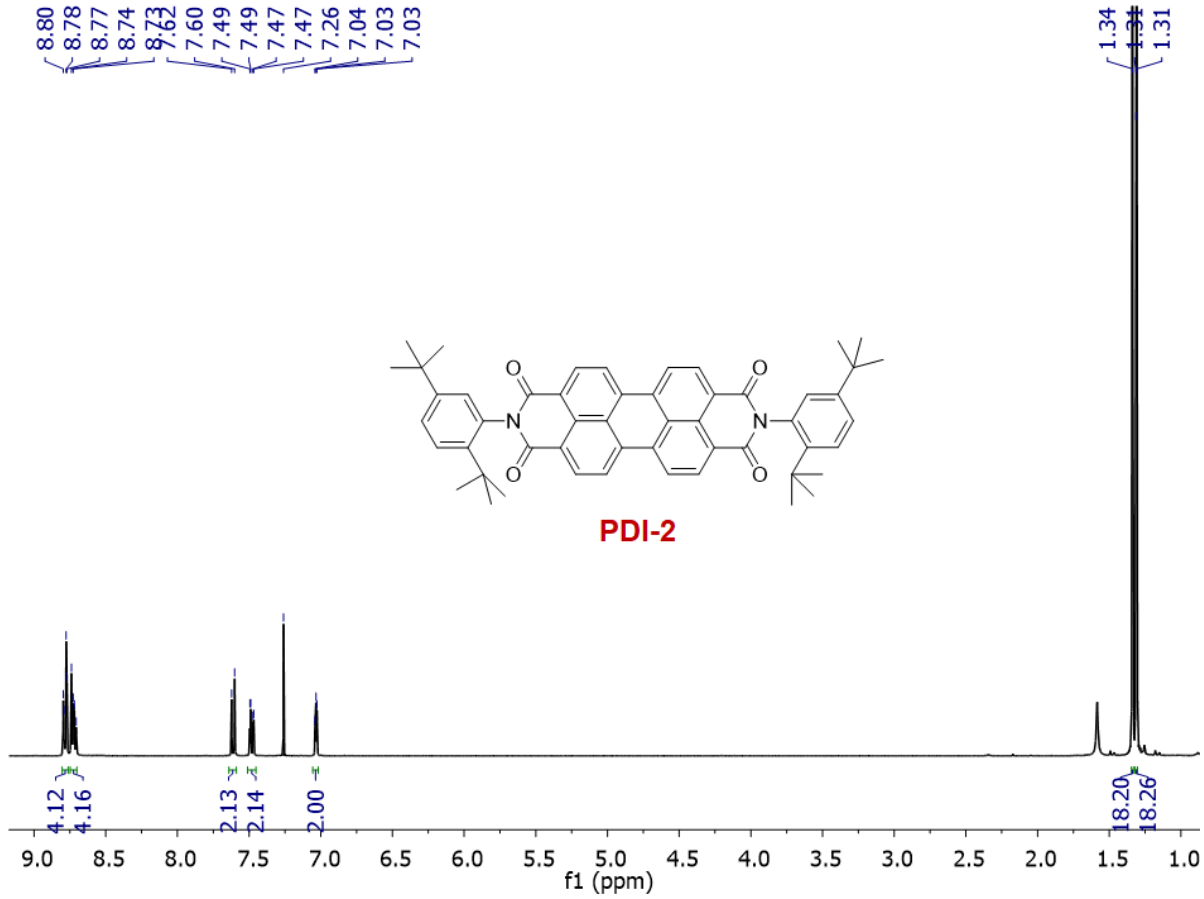

Figure S2. ^{1}H-NMR spectrum of **PDI-2** in $CDCl_3$ medium.

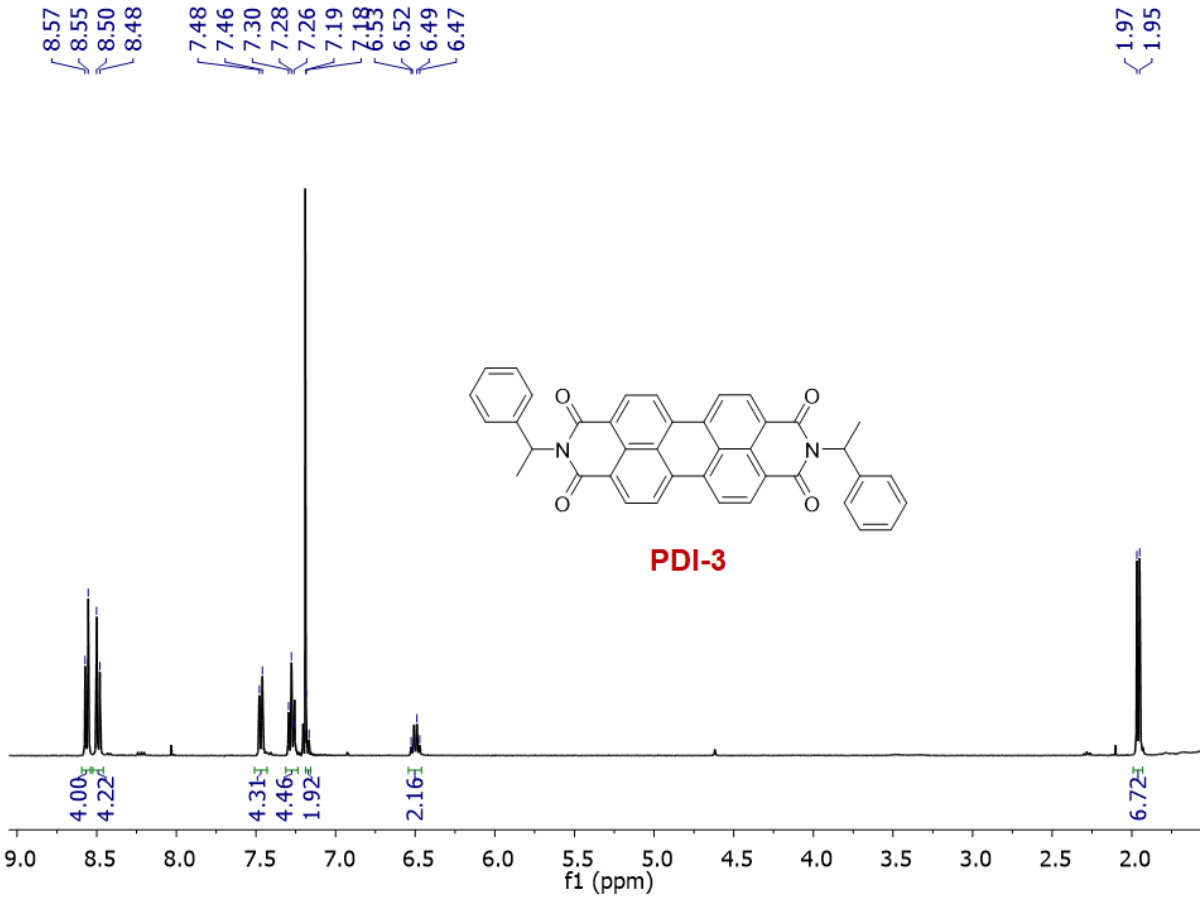

Figure S3. ^{1}H-NMR spectrum of **PDI-3** in $CDCl_3$ medium.

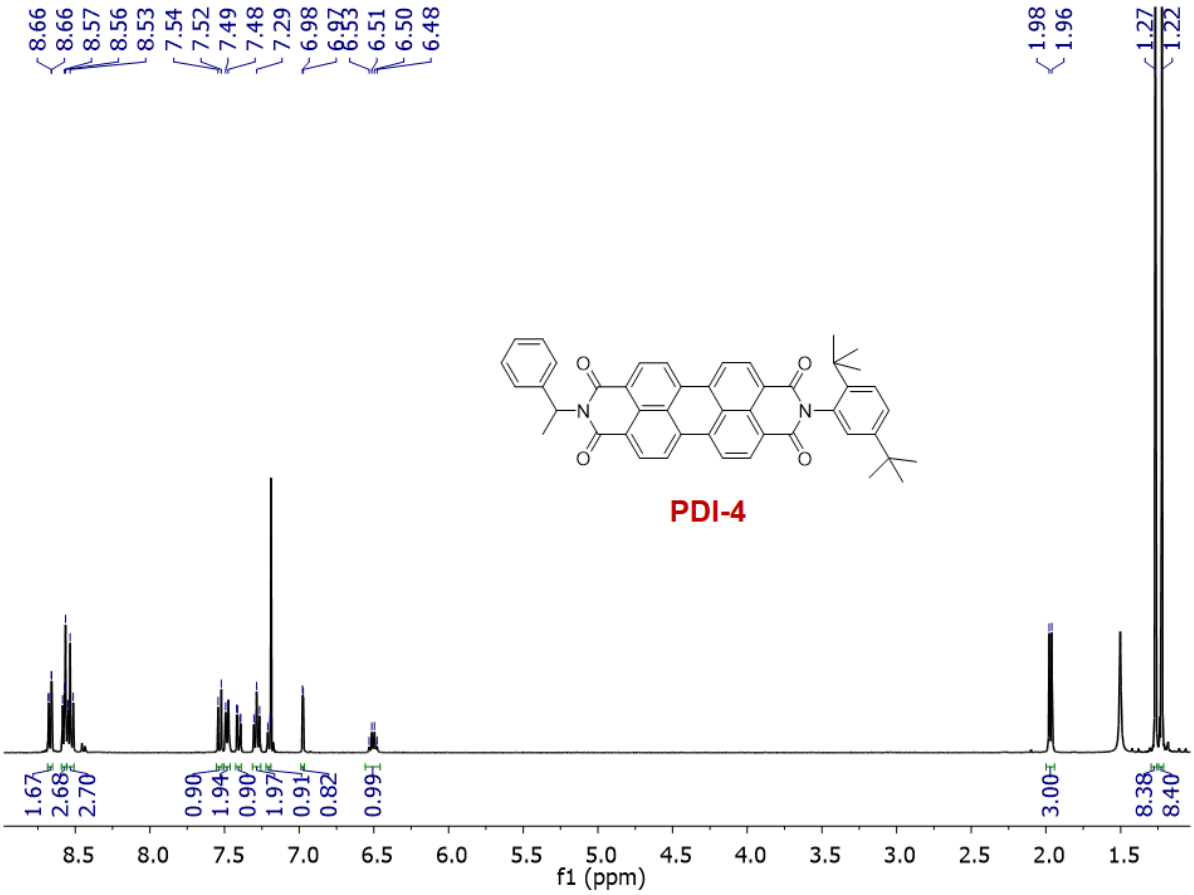

Figure S4. ^{1}H-NMR spectrum of **PDI-4** in $CDCl_3$ medium.

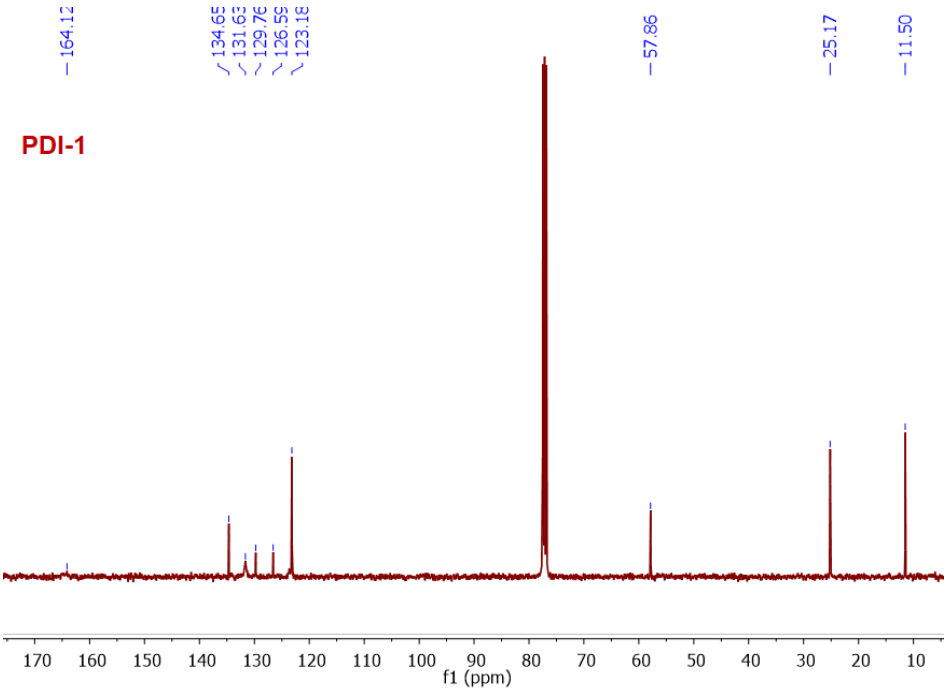

Figure S5. ^{13}C-NMR spectrum of **PDI-1** in $CDCl_3$ medium.

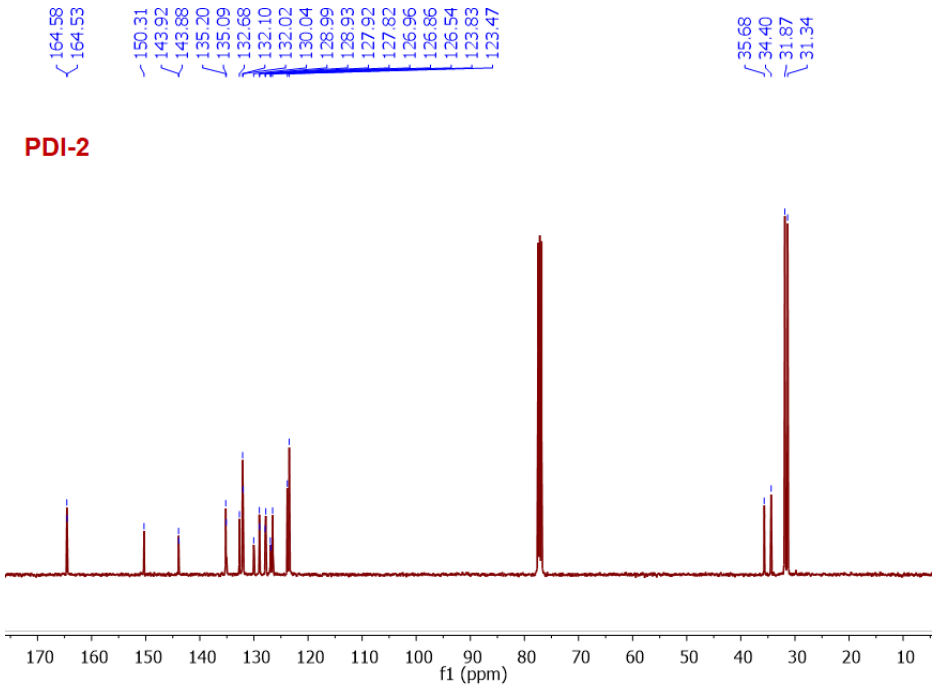

Figure S6. ^{13}C-NMR spectrum of **PDI-2** in $CDCl_3$ medium.

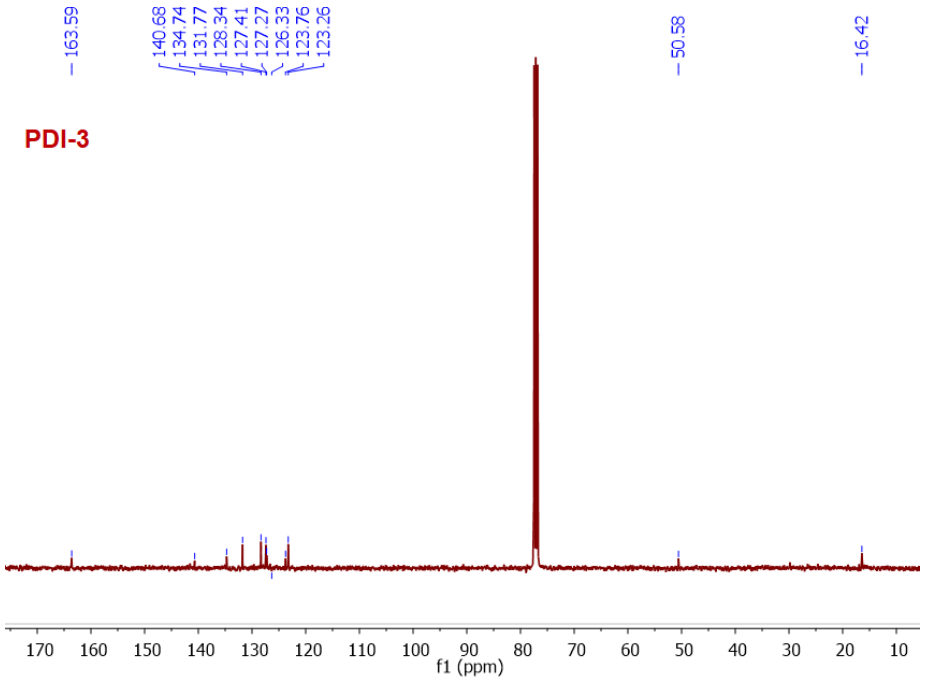

Figure S7. ^{13}C-NMR spectrum of **PDI-3** in $CDCl_3$ medium.

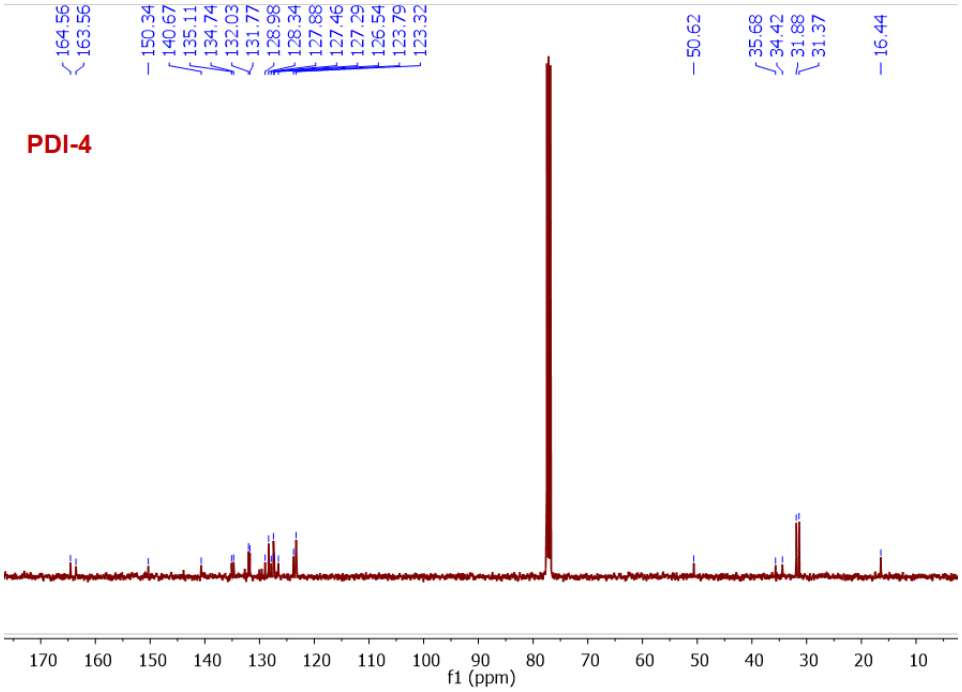

Figure S8. ^{13}C-NMR spectrum of **PDI-4** in $CDCl_3$ medium.

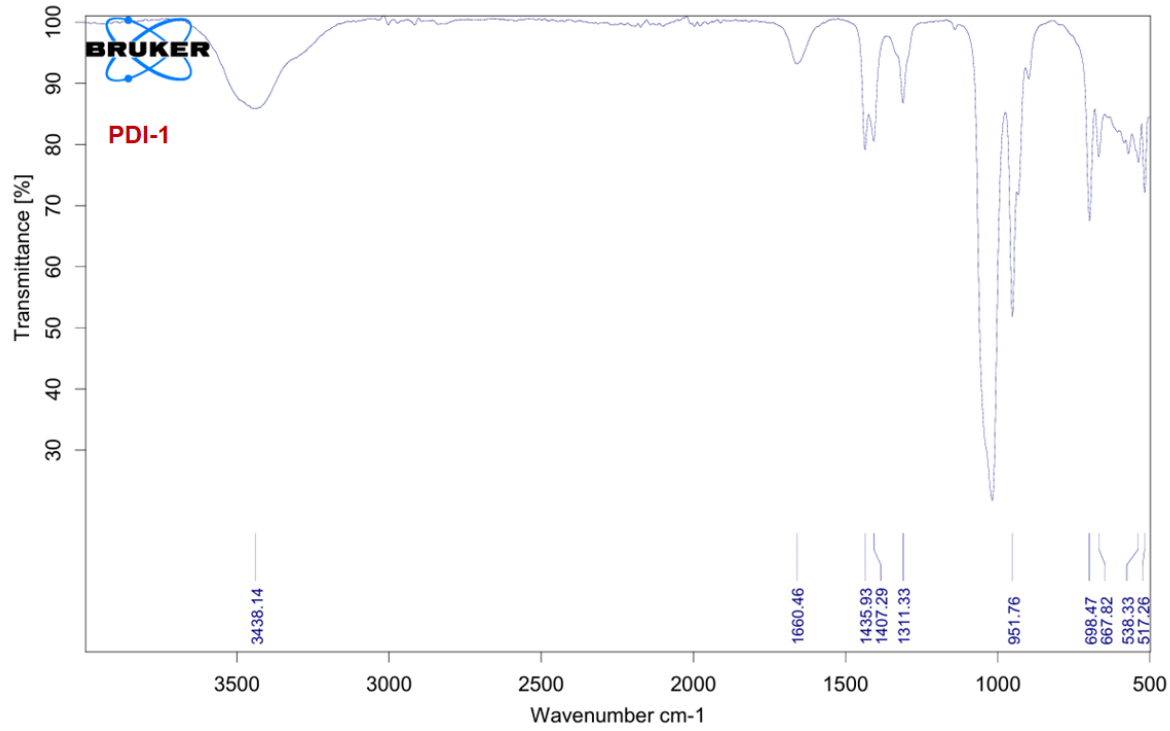

Figure S9. FTIR spectrum of **PDI-1**

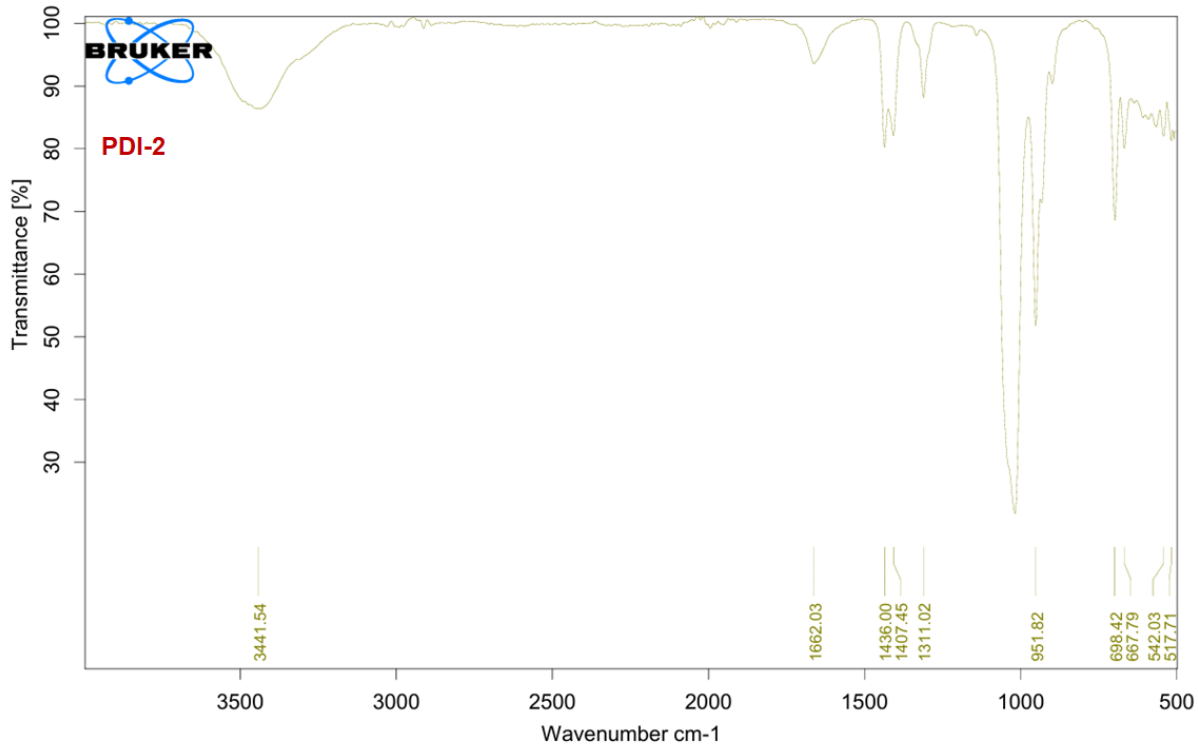

Figure S10. FTIR spectrum of **PDI-2**

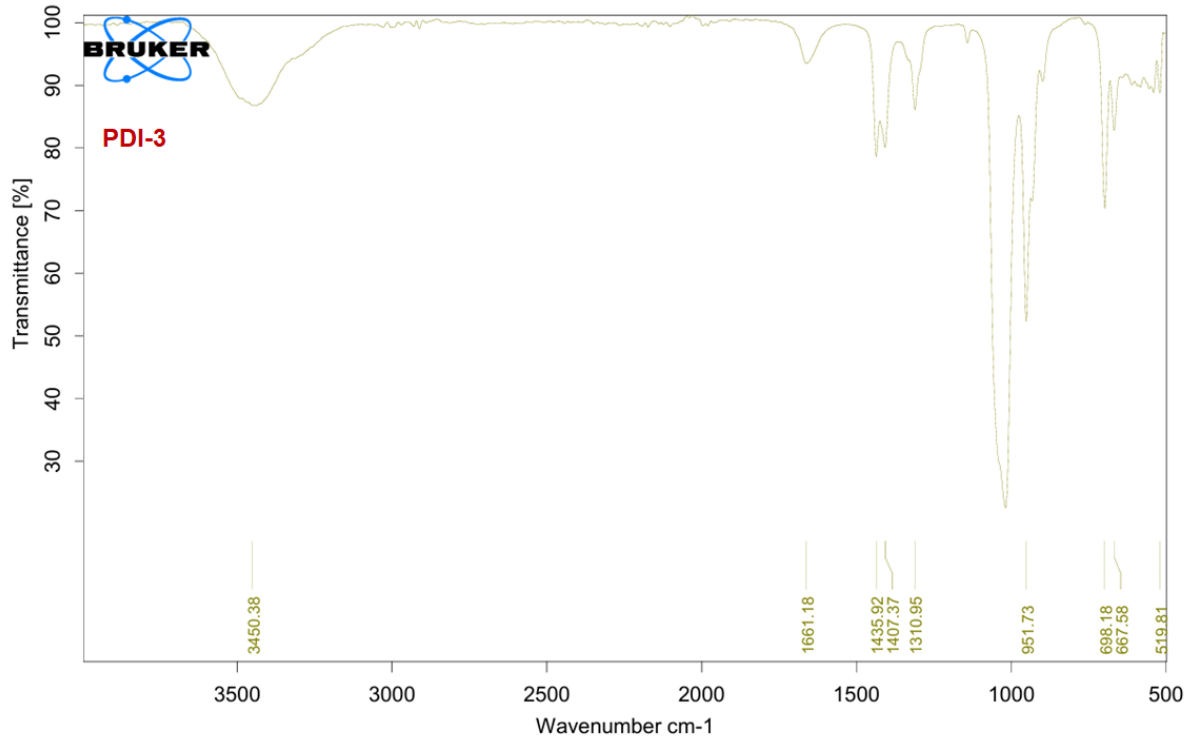

Figure S11. FTIR spectrum of **PDI-3**

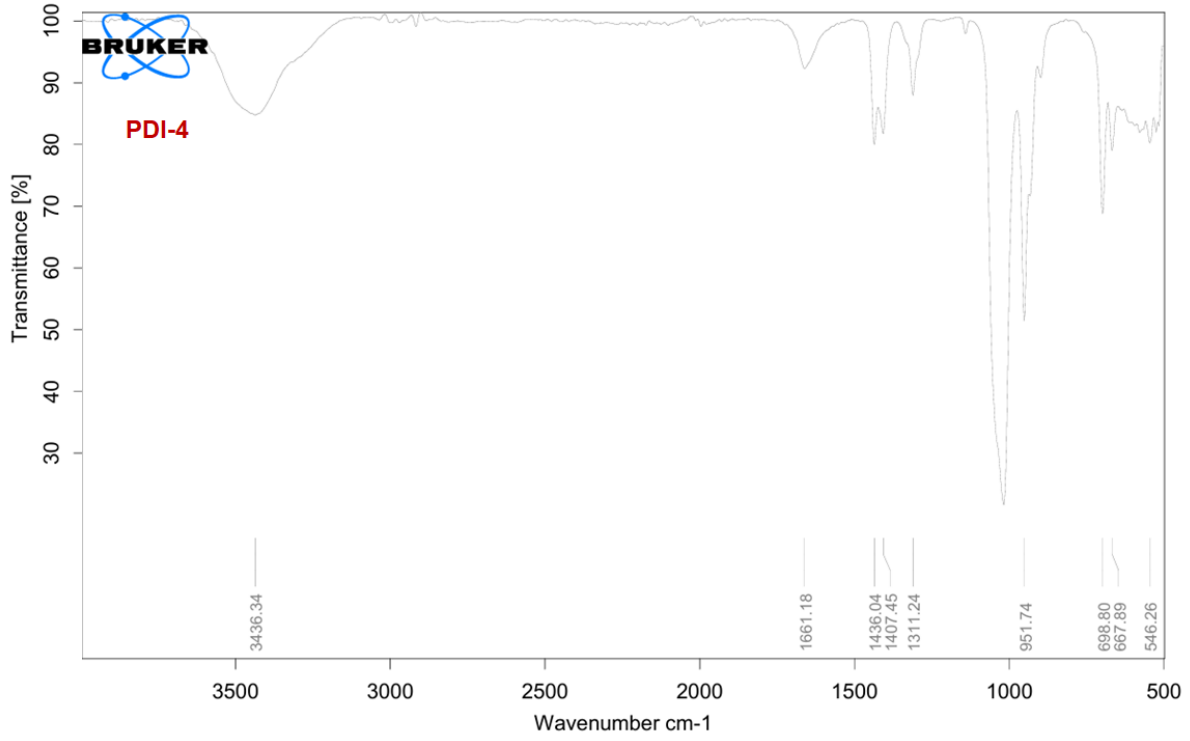

Figure S12. FTIR spectrum of **PDI-4**

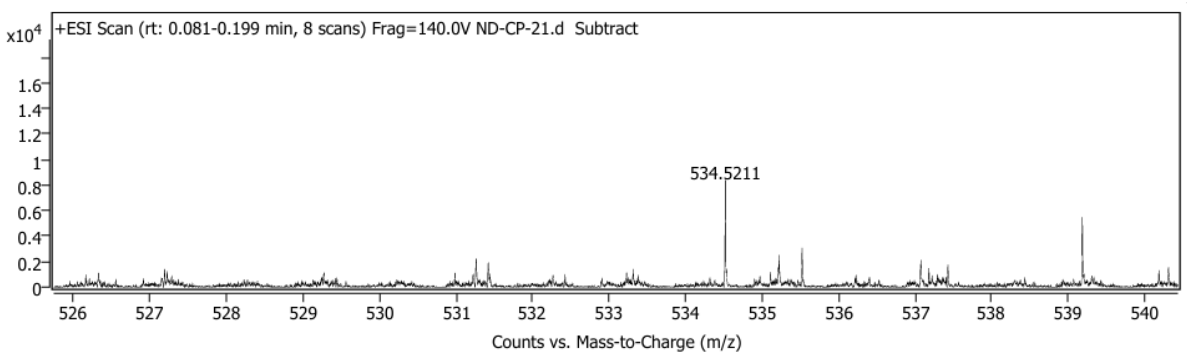

Figure S13. HRMS spectra of **PDI-1**

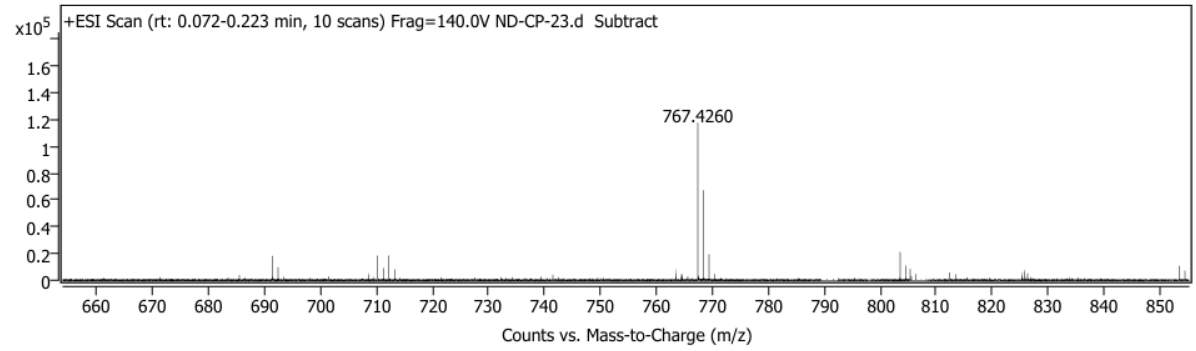

Figure S14. HRMS spectra of **PDI-2**

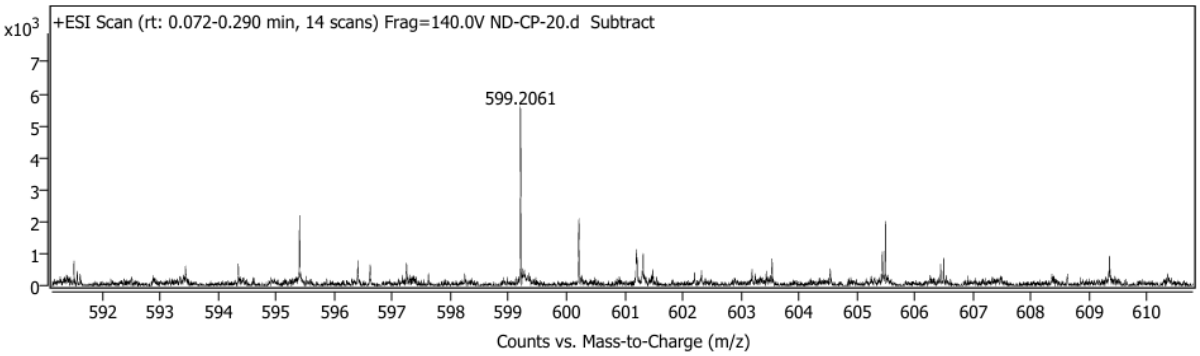

Figure S15. HRMS spectra of **PDI-3**

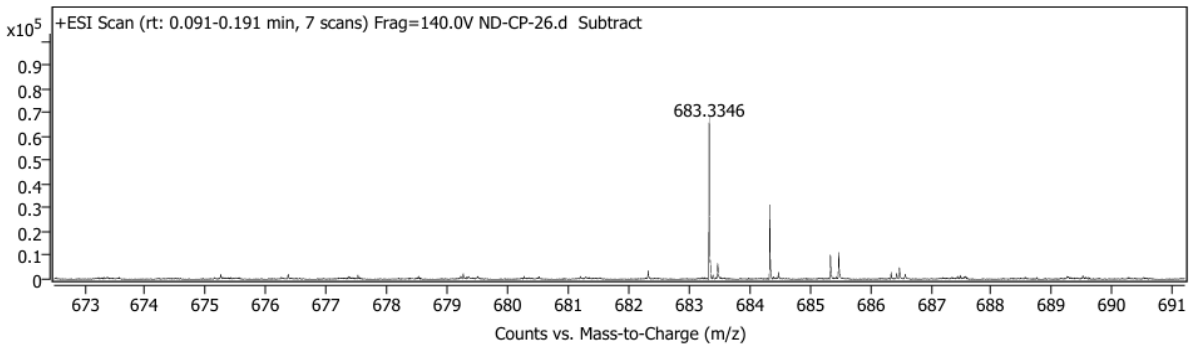

Figure S16. HRMS spectra of **PDI-4**

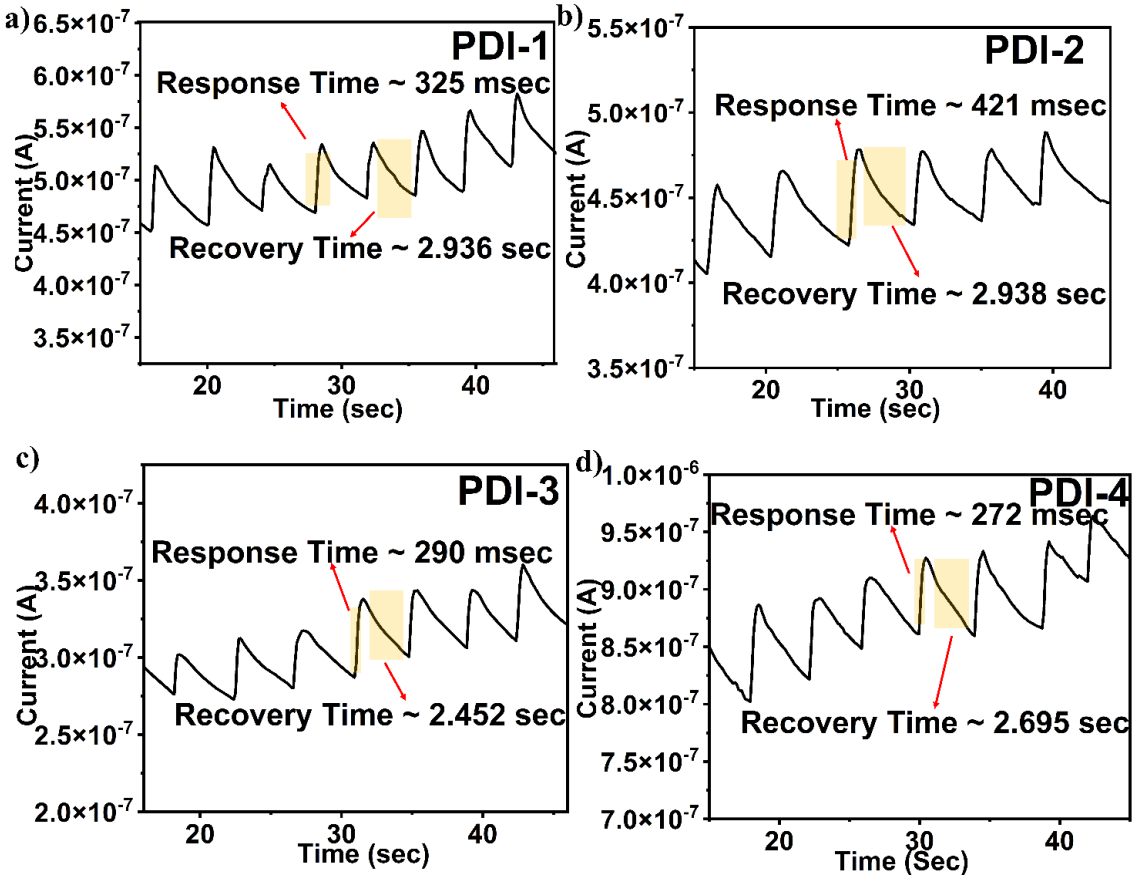

Figure S17: The fabricated PDI-based breath sensors' Response and recovery times.

Table. S1: Comparison between the PDI-based sensor with sensors reported in the existing literature

Material	Substrate	Deposition Technique	Range of Detection	Pressure Sensitivity	Theoretical Validation using DFT	Reference
C-PPy@MF	3D-macroporous melamine foam	ultrasonic irradiation	1-90 kPa	2 kPa^{-1}	No	[1]
Elastic microstructured conducting polymer (EMCP) with polypyrrole interconnects	-	-	>1kPa	<0.4 kPa^{-1}	No	[2]
Polypyrrole (PPy) with Fe^{3+} arrays	Cellulose paper	In-situ growth with PPy vapors	>75Pa	1.09 kPa^{-1}	No	[3]
PDMS with sodium bicarbonate	ITO coated PET	Drop casting	0.33-250 kPa	0.01 kPa^{-1}	No	[4]
$PtSe_2$	Polyimide	CVD, Photolithography, followed by a Reactive Ion etching process	-	1.64 10^{-3} $mbar^{-1}$	Yes	[5]
3D conductive network (Polyaniline filler with silk fibroin and poly (lactic-co-glycolic acid))	ITO coated glass	Doctor-blade coating	0-165.3 kPa	2.54 kPa^{-1}	No	[6]
Perylene diimide (PDI-1, PDI-2, PDI-3, and PDI-4)	Cellulose paper	Vacuum filtration	1.477-3.185 kPa	0.315, 1.266, 0.749, 2.120 kPa^{-1}	Yes	This work

References:

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