

1D Alignment of Co (II) Metalated Porphyrin – Napthalimide Based Self-Assembled Nanowires for Photocatalytic Hydrogen Evolution

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1. Experimental Details

1.1. Materials and Characterizations

The commercial reagents and chemicals were purchased from Sigma Aldrich. Analytical reagent grade solvents used for synthesis and distilled laboratory grade solvents were utilized for column chromatography. All the reactions were carried out under nitrogen or argon atmosphere and the apparatus were protected from ambient light. ¹H nuclear magnetic resonance (NMR) spectra of compounds recorded on a 400 MHz INOVA spectrometer using CDCl₃ as internal references. Matrix-assisted laser desorption ionization time-of-flight (MALDI–TOF) mass spectrometry performed on Shimadzu Biotech Axima Performance 2.9.3.20110624: Mode Reflectron-HiRes, Power: 85. FT-Infrared spectroscopic studies were performed with Bruker ALPHA II model by using KBr pellet for solid samples and liquid samples recorded on ZnSe crystal.

1.2. UV-visible and Fluorescence Measurement

Electronic absorption spectra of **PN1** - **PN5** were recorded on a Shimadzu (Model UV-3600) spectrophotometer. Steady-state fluorescence spectra of solutions were recorded on a Fluorolog-3 spectrofluorometer (Spex model, JobinYvon) at wavelength of excitation (λ_{exc}) = 470 nm. Fluorescence lifetime measurements of measured on a picoseconds time-correlated single photon (TCSPC) setup (Fluoro Log3-Triple Illuminator, IBH Horiba JobinYvon) employing a picoseconds light emitting diode laser (NanoLED, λ_{exc} = 440 nm). For all these analyses, **PN** Series were prepared in chloroform and measured in 1 cm cuvette at 25 °C.

1.3. Electrochemical Measurement

PC-controlled electrochemical analyser (CH Instruments, model CHI620C) was used to record cyclic voltammograms (CV) of **PN1** - **PN5** samples in chloroform solution at scan rate of 200 mV/s using 0.1 M tetrabutylammoniumhexafluorophosphate (NBu₄PF₆) supporting electrolyte. The working electrode is glassy carbon, standard calomel electrode (SCE) is reference electrode and platinum wire are an auxiliary electrode.

1.4. Theoretical calculations

PN1 - **PN5** were measured using density functional theory (Gaussian 09 program package) with B3LYP 6-31g (d,p) level theory. Here, we run the all DFT calculation by

placing a methyl group instead of long dodecyl and octyl-chains on both naphthalimide and porphyrin molecular systems respectively. HOMO/LUMO energy levels, frontier molecular orbitals and electrostatic potential (ESP) maps of the optimized structure were then generated using GaussView 5.0 and the formatted check files from the Gaussian 09 computation.

1.5. Electron Microscopic Studies

Transmission electron microscope (TEM) measurements were carried out using FEI (TECNAI G2 30 S-TWIN) with an accelerating voltage of 100 kV. Field Emission-Scanning electron microscopy (FE-SEM) measurements of aggregates performed using JSM 7610F JEOL without staining. For measurements, aggregates of **PN1** - **PN5** were prepared from the methanol vapour diffusion approach and drop casted on carbon coated copper grid and copper substrate directly without staining.

1.6. Electrochemical Impedance Spectroscopy (EIS):

Sample preparation for the experiments was achieved on conducting indium tin oxide (ITO) substrates that provide inert electrical contacts. Selective etching of indium tin oxide (ITO) glass slides (1 cm × 1 cm) was performed using 1 M HCl/Zn dust on a masked pattern to prefabricate two parallel electrodes set at a distance of ~1 mm apart. The samples were then deposited as thin films of the PN series (PN1- PN5), and their corresponding aggregates prepared at a concentration of 1×10^{-4} M in CHCl₃/MeOH on premasked substrate surfaces to achieve comparable and quantifiable cell geometry. Electrochemical impedance spectroscopy was performed on the deposited thin films employing a Zahner Zennium Electrochemical Workstation equipped with Thales operational software and coupled with a controlled heating chamber to carry out variable temperature measurements during heating. The measurements were carried out at different temperature settings from 25 to 65 °C with a stepwise increase in temperature of 10 °C. The temperature was measured with accuracy higher than ±0.1 °C using a K-type thermocouple placed in close proximity to the sample. The samples were equilibrated at each temperature for 1 h prior to acquiring the frequency sweep impedance data. The data were collected following a frequency sweep through 100–500 Hz at an alternating potential with a root-mean-square amplitude of ±10 mV across the open-circuit voltage (OCV) of the assembled cells. [1]

1.7. Photocatalytic experimental procedure:

1.7.1. Preparation of platinum titanium dioxide (PT): To enhance the better photocatalytic activity of H₂ production, 1 wt % Pt metal was deposited onto the surface of the catalysts by using the previously reported method. In a 100 mL round-bottomed flask, TiO₂ (1.0 g, Sigma-Aldrich anatase) was dispersed in 30 mL methanol. Aqueous solution of H₂PtCl₆ (0.25 mL, 8 wt% aqueous solution) was then added into the methanolic suspension of TiO₂ and the reaction mixture was irradiated using a 400 W xenon lamp for until gray color. The resultant Pt–TiO₂ composite of light gray colour was retrieved by centrifugation, washed three times with excess ethanol and dried under vacuum at 60 – 70 °C.

1.7.2. Preparation of dye adsorbed Pt/TiO₂ photocatalyst: The platinum loaded titanium dioxide was dispersed into the chloroform/methanol solution of **PN2** and the mixture was kept under stirring condition at 25 °C in the dark (covered with aluminium foil) for 24 h. After completion of the reaction, it was separated by centrifugation at 4000 rpm. Then filtered, washed with methanol and then dried under vacuum at 70 – 80 °C.

1.7.3. Photocatalytic experiments: Photocatalytic Hydrogen gas generation experiments were carried out in a custom-made photo reactor an external cooling jacket Pyrex glass system (130 ml) reactor with flat optical window of photo reactor fitted air with tight rubber septum at top of the loading photo reactor port. All experiments were carried over 20 mL aqueous suspension of 10 mg (0.010 g) photo catalyst containing 10 vol(%) of TEOA as sacrificial electron donor (SED). The solution was adjusted to the desired pH using 1(M) Muriatic acid (Hydrochloric acid). It was then air sealed with a rubber septum. Before light irradiation dissolved air was removed by 30 min high vacuum followed by purging of Nitrogen gas. Oriel instruments solar simulator equipped with 420W xenon arc lamp systems with AM1.5 cut-off filter as irradiation source was employed. Above filter can be easily replaced with any other wavelength cut-off filter to alter the radiation wavelength regime. Reaction vessel was kept away from 25 cm from the light source to ensure the one sun condition, as suggested by Oriel solar 85 simulator manual. Gas analysis was carried out by regular sampling after every hour, and the gas chromatograph (GC) equipped with thermochemical detector 90 (Agilent 7890) was employed for quantitative analysis. The turnover number (TON) is usually defined by the number of reacted molecules in comparison to the number of active sites. Typically, one hydrogen gas molecule would be produced when

two protons react with two electrons injected from the excited dyes Pt/TiO₂-PN2 respectively.^[2]

Therefore, the TON can be calculated according to equation (1).

$$TON = \frac{2 * \text{number of evolved H}_2 \text{ molecules}}{\text{Number of dye molecules adsorbed}} \quad (1)$$

The apparent quantum yields (AQY) are calculated according to the following equation (2).

$$AQY (\%) = \frac{\text{H}_2 \text{ molecules of evolved} * 2}{\text{incident photons}} \quad (\text{or}) \quad \frac{2X \text{ Rate}}{N} * 100 \quad (2)$$

Number of incident proton 'N'

$$N = \frac{E\lambda}{hc}$$

E=Nhν (according to plank equation)

$$\nu = \frac{c}{\lambda}$$

$$E = Nh\frac{c}{\lambda}$$

E = Incident light of radiation

$$E = 2.75 \times 10^{-3} \text{ joule}$$

λ=wave length of light (420 nm)

h = plank constant (6.626x10⁻³⁴js) or 6.626x10⁻²⁷ erg-s

c=speed of light (3x10⁸m/s) or 3x10¹⁰ cm/s

Surface area of reactor = (3*2) 6.0 cm²

Irradiation time=4 h

$$\frac{2.75 \times 10^{-3} \text{ j} \times 420 \times 10^{-9} \text{ m} \times 6.0 \text{ cm}^2 \times 4 \times 3600 \text{ s}}{6.626 \times 10^{-34} \text{ js} \times 3 \times 10^8 \text{ m/s}}$$

$$N = \text{m/s}$$

$$N = 5.02 \times 10^{20}$$

$$AQY(\%) = \frac{2X \text{ Rate}}{N} * 100 \quad (\text{or})$$

$$AQY \text{ or } AQE = \frac{n.R}{I} * 100$$

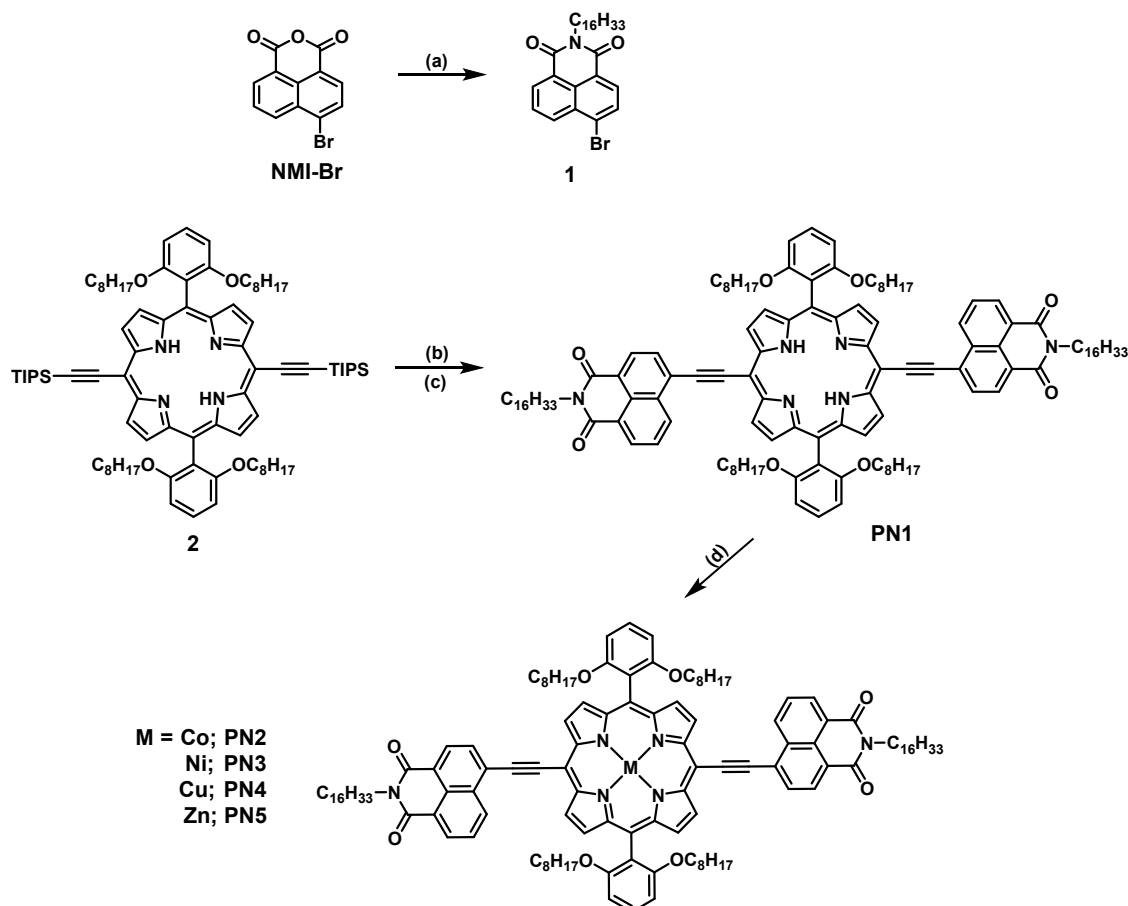
n = The number of electrons required for the reaction (it is equal to 2 for photocatalytic hydrogen generation).

R = Rate of hydrogen generation.

I = Number of incident photons

$$\text{TOF} = \frac{\text{TON}}{\text{reaction time}}$$

2. Synthesis of PN1 – PN5:



Scheme S1. Reagents and Conditions: (a) Hexadecylamine, ethanol, 70 °C, 12 h. (b) TBAF, THF, 0 °C. (c) **1**, Pd(dba)₃, AsPh₃, 50 °C, 12 h. (d) M(OAc)₂ and MCl₂ for cobalt metalation, DMF, 150 °C, 12 h.

2.1. Synthesis of bromo naphthalimide (1) : To a 50 mL ethanol solution of 4-Bromo-1, 8-naphthalic anhydride (1 g, 3.61 mmol), hexadecylamine (870 mg, 3.61 mmol) was added and refluxed for 12 h. Subsequently, the organic layer was washed with water and ethylacetate and dried over Na₂SO₄. The residue was subjected to column chromatography (silica gel : 60 – 120 mesh, Hexane/ EtOAc V/V:8/2) as an eluant to allow the isolation as an yellow coloured solid (yield : 70 %). ¹H NMR (500 MHz, CDCl₃) δ ppm: 8.65 (d, J = 7.3 Hz, 1H),

8.56 (d, $J = 9.5$ Hz, 1H), 8.41 (d, $J = 7.8$ Hz, 1H), 8.03 (d, $J = 7.9$ Hz, 1H), 7.84 (dd, $J = 7.9$ Hz, 1H), 4.16 (t, 2H), 1.77 – 1.67 (m, 2H), 1.46 – 1.18 (m, $J = 42.3, 24.3, 6.7$ Hz, 27H), 0.88 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ ppm: 163.62, 133.20, 132.01, 131.15, 130.64, 130.18, 129.02, 123.19, 122.33, 40.67, 31.96, 29.57, 28.12, 27.16, 22.72, 14.16. ESI-MS (m/z) = 500 (calculated mass = 499.21).

2.2 Synthesis of PN1: Compound **2** was prepared from previous reported procedure.^[3] To a anhydrous 5 mL THF solution of **2** (130 mg, 0.0929 mmol), TBAF (1 M) in THF (0.2 mL, 0.0929 mmol) added at 0 °C and stirred for 30 minutes under N_2 atmosphere. The mixture was quenched with H_2O and then extracted with CH_2Cl_2 . The organic layer was dried over anhydrous Na_2SO_4 and excess solvent was removed under reduced pressure. Further, the resultant intermediate (100 mg, 0.092 mmol) is added with **1** (184 mg, 0.368 mmol), $\text{Pd}_2(\text{dba})_3$ (16.47 mg, 0.018 mmol), AsPh_3 (5.508 mg, 0.018 mmol), THF (1 mL) and Et_3N (3 mL). The reaction mixture is stirred for 12 h at 50 °C and further cooled to room temperature followed by extraction with dichloromethane. The organic layer was washed with water and dried over Na_2SO_4 . The residue was subjected to column chromatography (silica gel : 60-120 mesh, Hexane/THF V/V:9/1) as an eluant to allow the isolation as green coloured solid (yield : 23 %). ^1H NMR (500 MHz, CDCl_3) δ 9.68 (d, $J = 4.6$ Hz, 4H), 9.33 (d, $J = 8.3$ Hz, 2H), 8.90 (d, $J = 4.5$ Hz, 4H), 8.77 (d, $J = 7.1$ Hz, 4H), 8.44 (d, $J = 7.5$ Hz, 2H), 8.04 – 8.00 (d, 2H), 7.73 (dd, $J = 8.5$ Hz, 2H), 7.03 (d, $J = 8.6$ Hz, 4H), 4.24 (m, $J = 7.8$ Hz, 4H), 3.89 (t, $J = 6.3$ Hz, 8H), 2.03 (m, $J = 13.0, 6.3$ Hz, 4H), 1.80 (m, $J = 15.3, 7.5$ Hz, 8H), 1.47 (m, $J = 15.2, 7.9$ Hz, 12H), 1.44 – 1.36 (m, 18H), 1.04 – 0.99 (m, 12H), 0.74 (m, $J = 14.7, 7.3$ Hz, 12H), 0.60 – 0.46 (m, 44H), 0.41 (t, $J = 7.3$ Hz, 12H), -1.71 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 164.02, 159.89, 132.27, 131.77, 129.63, 127.67, 127.67, 125.05, 123.27, 122.01, 119.37, 116.03, 105.14, 93.60, 68.72, 40.74, 31.98, 31.30, 29.76, 29.42, 28.55, 27.89, 27.27, 25.42, 22.75, 22.25, 14.18, 13.78. MALDI-TOF-MS (m/z) = 1862.63 (calculated mass = 1862). FT-IR (neat, cm^{-1}): 2921, 2853, 1695, 1657, 1585, 1459, 1353, 1243, 1157, 1092, 973, 784.

2.3. Synthesis of PN2 – PN5 : To obtain the metalation, various cobalt chloride (6.98 mg, 0.053 mmol), nickel acetate (8.01 mg, 0.053 mmol), copper acetate (7.01 mg, 0.053 mmol) and zinc acetate (7.01 mg, 0.053 mmol) were added in each DMF (30 mL) solution of **PN1** (100 mg, 0.053) and refluxed for 12 h at 150 °C. The resultant mixtures were extracted with DCM/water and dried over Na_2SO_4 . The residue was subjected to column chromatography

(silica gel : 60-120 mesh, Hexane/THF (9:1 v/v) to allow the isolation as green coloured **PN2 – PN5** solids (yield : 23 %).

PN2: MALDI-TOF-MS (m/z) = 1918. 158 (calculated mass = 1919.15). FT-IR (neat, cm^{-1}): 2921, 2852, 1698, 1658, 1585, 1519, 1455, 1352, 1240, 1092, 1000, 783.

PN3: ^1H NMR (500 MHz, CDCl_3) δ 9.68 (d, J = 4.6 Hz, 4H), 9.33 (d, J = 8.3 Hz, 2H), 8.90 (d, J = 4.5 Hz, 4H), 8.77 (d, J = 7.1 Hz, 4H), 8.44 (d, J = 7.5 Hz, 2H), 8.04 – 8.00 (d, 2H), 7.73 (dd, J = 8.5 Hz, 2H), 7.03 (d, J = 8.6 Hz, 4H), 4.24 (m, J = 7.8 Hz, 4H), 3.89 (t, J = 6.3 Hz, 8H), 2.03 (m, J = 13.0, 6.3 Hz, 4H), 1.80 (m, J = 15.3, 7.5 Hz, 8H), 1.47 (m, J = 15.2, 7.9 Hz, 12H), 1.44 – 1.36 (m, 18H), 1.04 – 0.99 (m, 12H), 0.74 (m, J = 14.7, 7.3 Hz, 12H), 0.60 – 0.46 (m, 44H), 0.41 (t, J = 7.3 Hz, 12H); ^{13}C NMR (101 MHz, CDCl_3) δ 163.50 (s), 162.94 (s), 158.59 (s), 143.14 (s), 131.76 (s), 131.59 (s), 130.71 (s), 129.06 (s), 127.35 (s), 126.61 (s), 122.20 (s), 120.65 (s), 104.32 (s), 67.76 (s), 39.67 (s), 30.93 (s), 30.31 (s), 28.49 (s), 27.67 (s), 27.18 (s), 26.21 (s), 24.34 (s), 21.69 (s), 21.24 (s), 13.12 (s), 12.77 (s). MALDI-TOF-MS (m/z) = 1918.354 (calculated mass = 1918.15). FT-IR (neat, cm^{-1}): 2920, 2852, 2177, 1695, 1657, 1583, 1456, 1351, 1241, 1091, 1001, 782.

PN4: MALDI-TOF-MS (m/z) = 1923.251 (calculated mass = 1923.15). FT-IR (neat, cm^{-1}): 2920, 2852, 1695, 1657, 1583, 1517, 1453, 1350, 1240, 1091, 999, 781.

PN5: ^1H NMR (500 MHz, CDCl_3); δ 9.68 (d, J = 4.6 Hz, 4H), 9.33 (d, J = 8.3 Hz, 2H), 8.90 (d, J = 4.5 Hz, 4H), 8.77 (d, J = 7.1 Hz, 4H), 8.44 (d, J = 7.5 Hz, 2H), 8.04 – 8.00 (d, 2H), 7.73 (dd, J = 8.5 Hz, 2H), 7.03 (d, J = 8.6 Hz, 4H), 4.24 (m, J = 7.8 Hz, 4H), 3.89 (t, J = 6.3 Hz, 8H), 2.03 (m, J = 13.0, 6.3 Hz, 4H), 1.80 (m, J = 15.3, 7.5 Hz, 8H), 1.47 (m, J = 15.2, 7.9 Hz, 12H), 1.44 – 1.36 (m, 18H), 1.04 – 0.99 (m, 12H), 0.74 (m, J = 14.7, 7.3 Hz, 12H), 0.60 – 0.46 (m, 44H), 0.41 (t, J = 7.3 Hz, 12H). ^{13}C NMR (101 MHz, CDCl_3); δ 159.93, 151.65, 151.10, 137.16, 133.15, 132.53, 132.03, 131.15, 130.46, 129.06, 128.79, 128.31, 126.97, 125.51, 124.73, 105.22, 68.71, 40.59, 31.67, 30.35, 29.40, 28.42, 27.74, 27.23, 25.32, 22.77, 22.51, 14.16. MALDI-TOF-MS (m/z) = 1924.206 (calculated mass = 1924.15). FT-IR (neat, cm^{-1}): 2918, 2850, 2169, 1693, 1653, 1581, 1504, 1453, 1349, 1242, 1089, 995, 775.

3. ¹H NMR Spectra of 1 and PN1 - PN5:

3.1. ¹H NMR of 1:

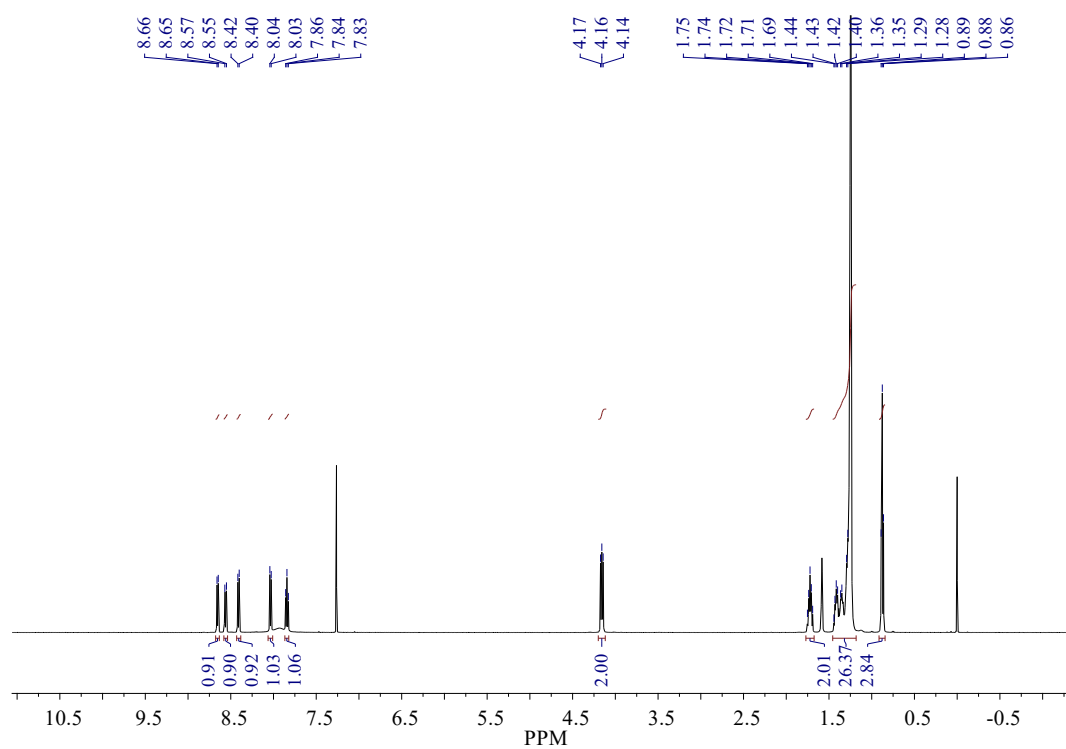


Fig. S1 ¹H NMR spectrum of NMI-Br

3.2. ¹H NMR of PN1:

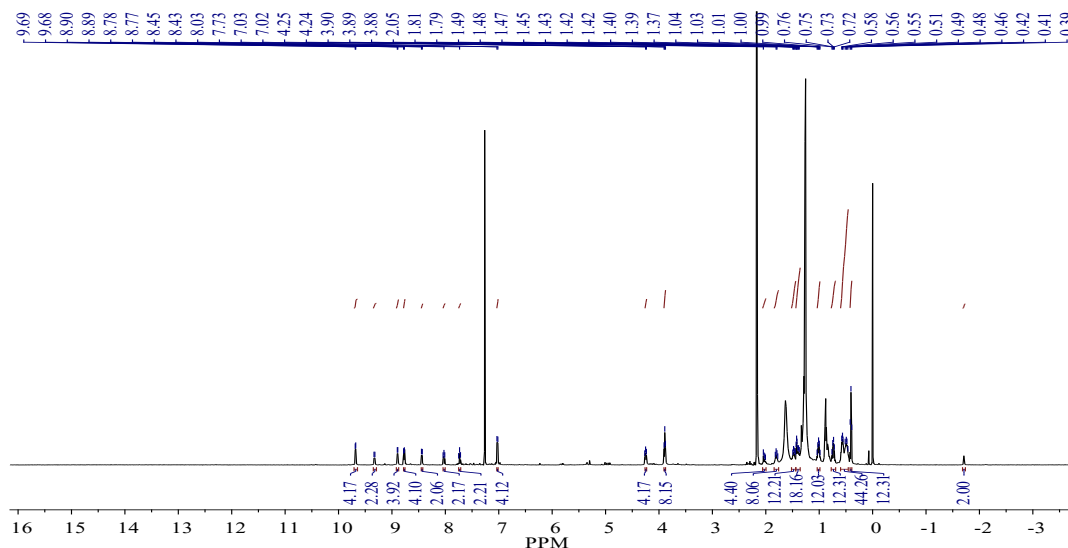


Fig. S2 ^1H NMR spectrum of PN1.

3.3. ^1H NMR of PN3

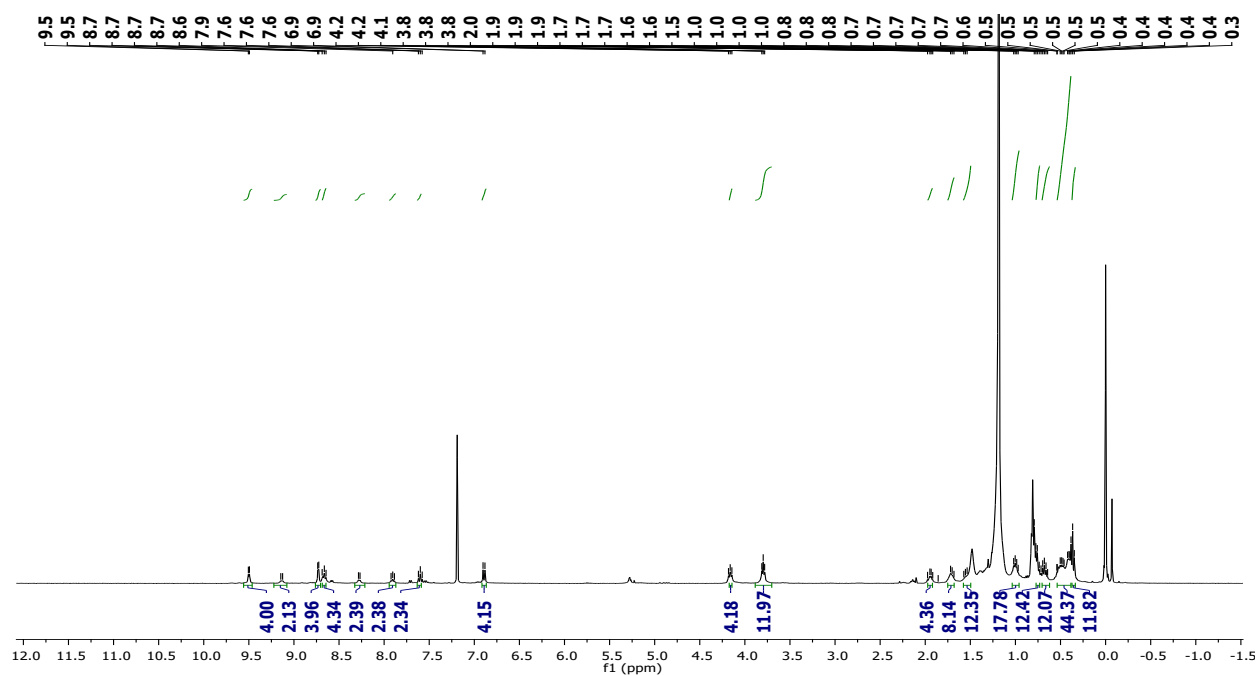


Fig. S3 ^1H NMR spectrum of PN3.

3.4. ^1H NMR of PN5

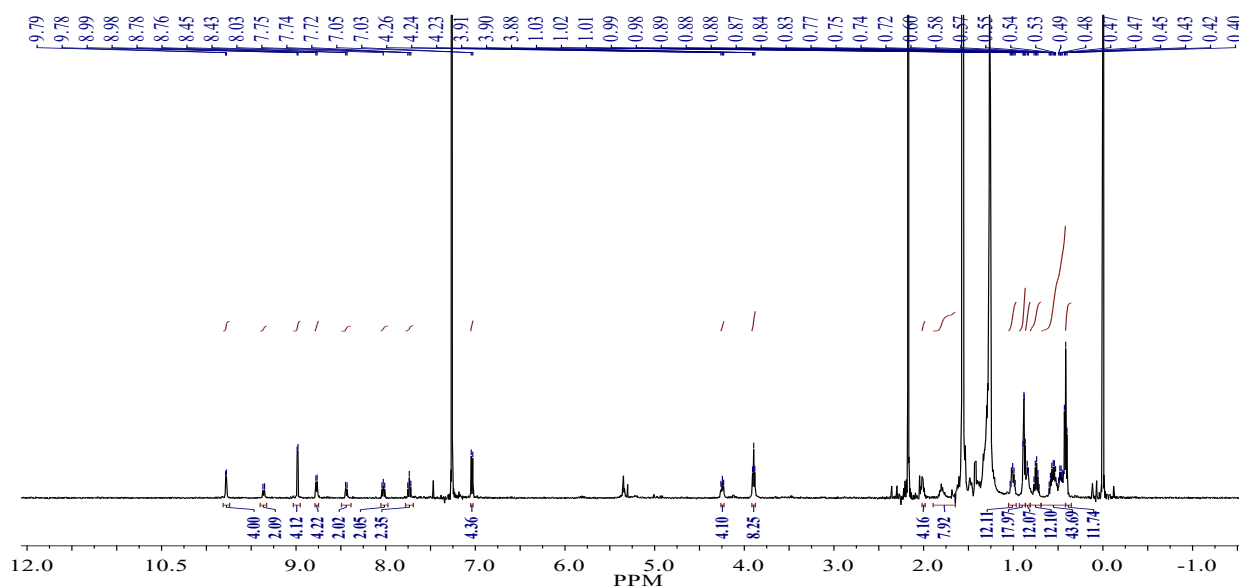


Fig. S4 ^1H NMR spectrum of **PN5**.

4. ^{13}C NMR Spectra of **1 and PN1 - PN5:**

4.1. ^{13}C NMR of **1**

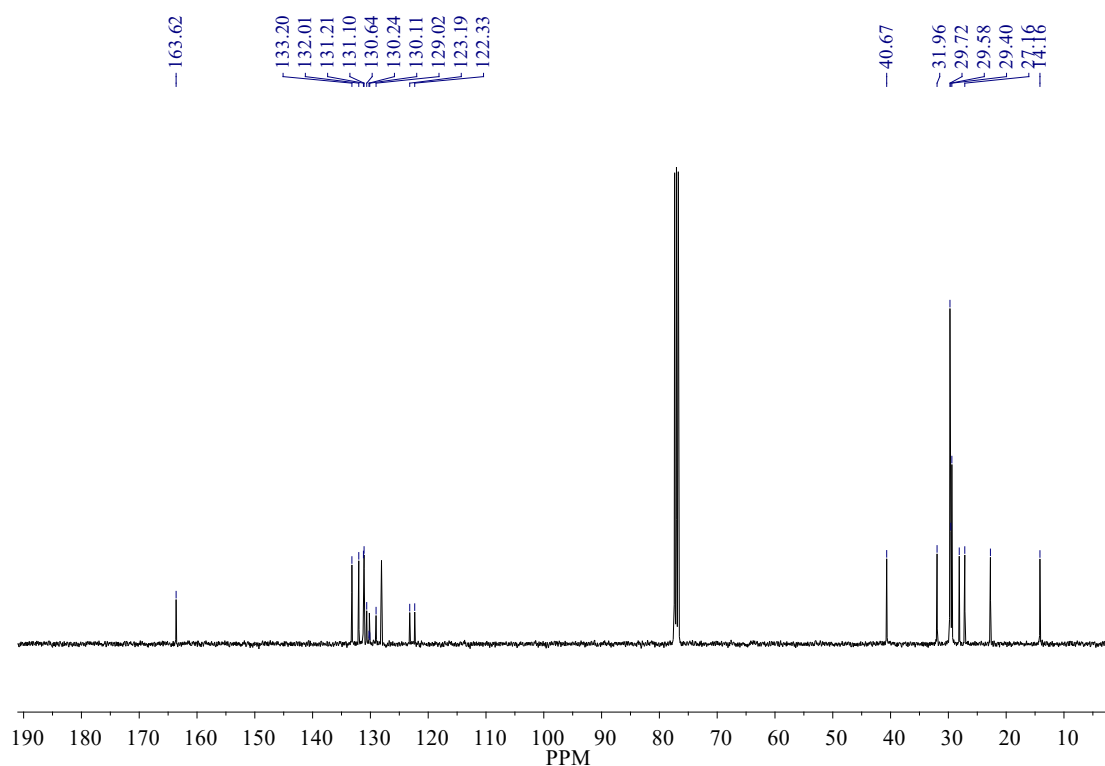


Fig. S5 ^{13}C NMR of **1**

4.2. ^{13}C NMR of PN1

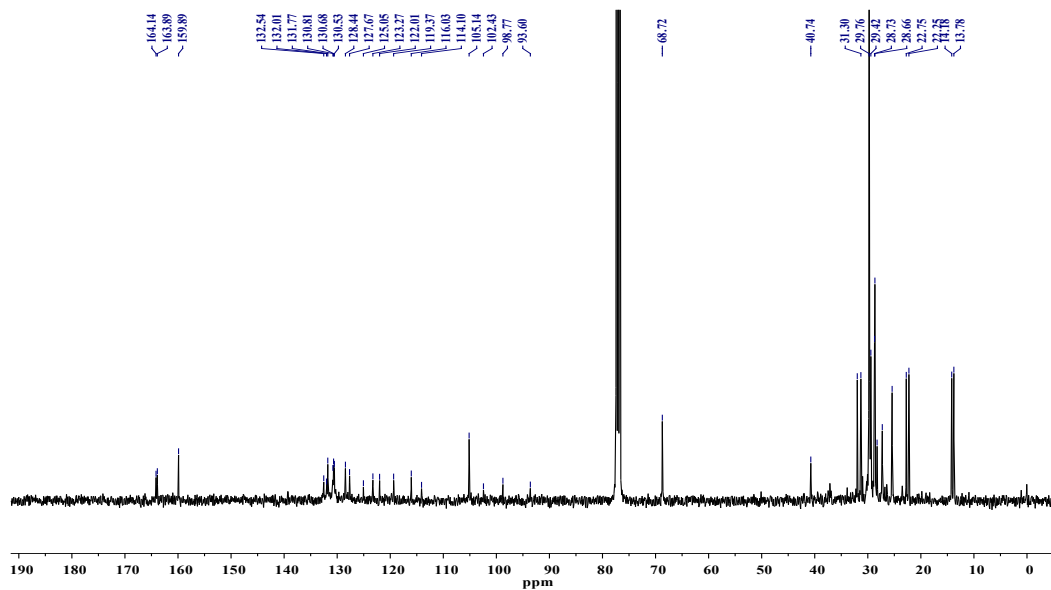


Fig. S6 ^{13}C NMR of PN1

4.3. ^{13}C NMR of PN3

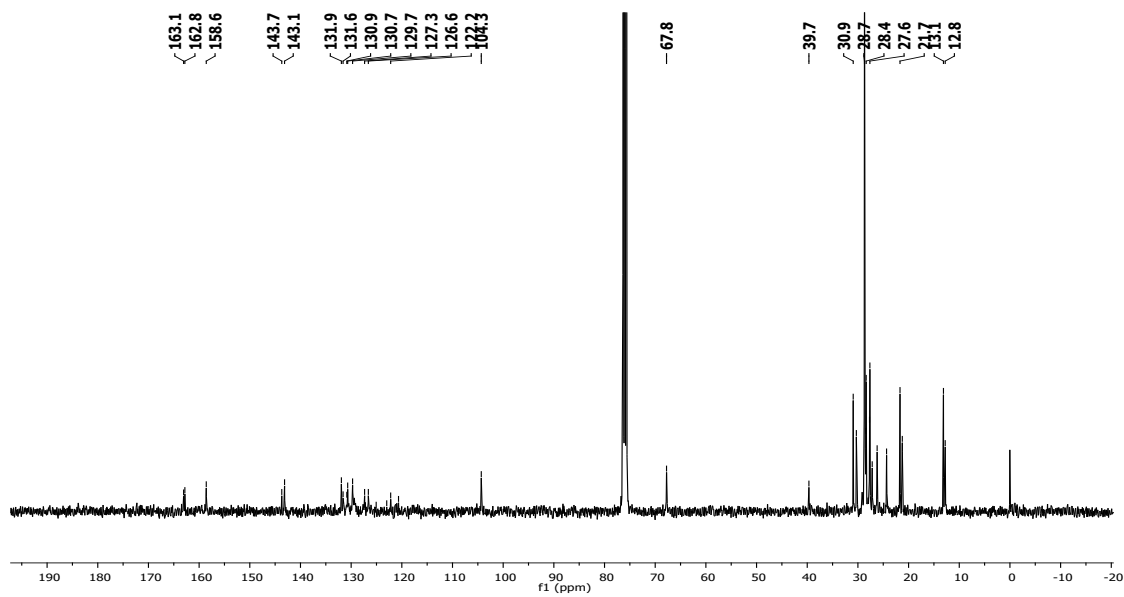


Fig. S7 ^{13}C NMR of PN3

4.4. ^{13}C NMR of PN5

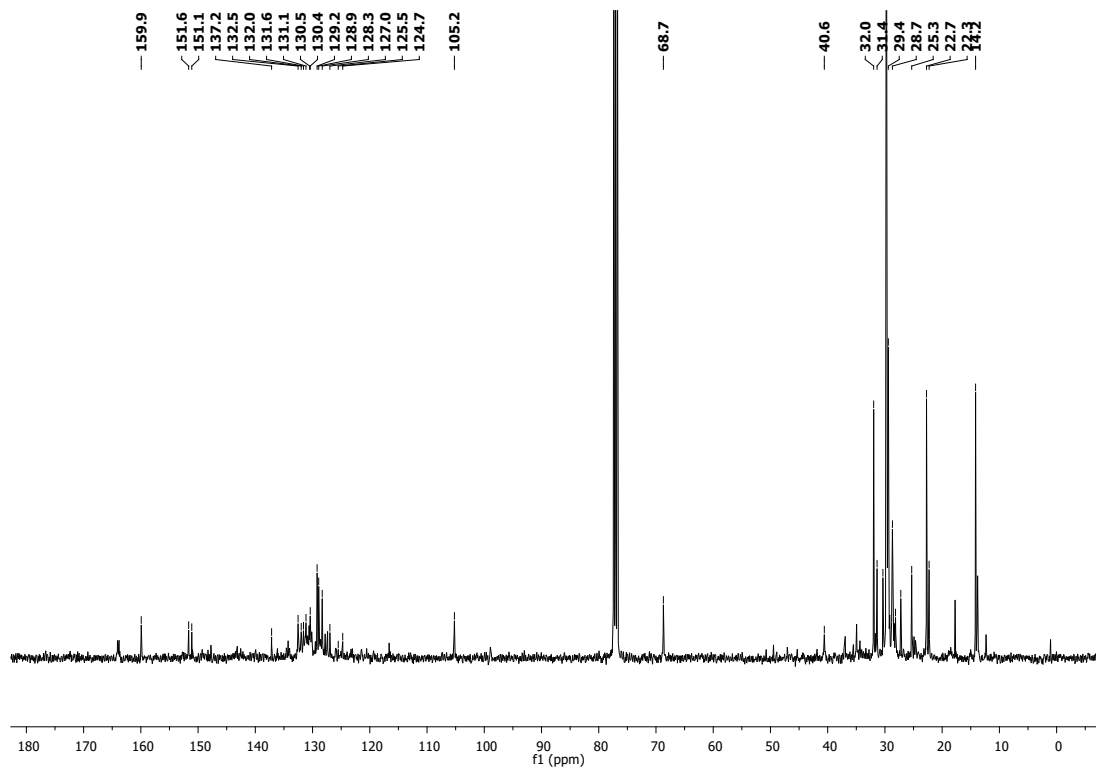


Fig. S8 ^{13}C NMR of PN5.

5. MALDI-TOF-MS spectra of PN1- PN5:

5.1. MALDI-TOF-MS of PN1:

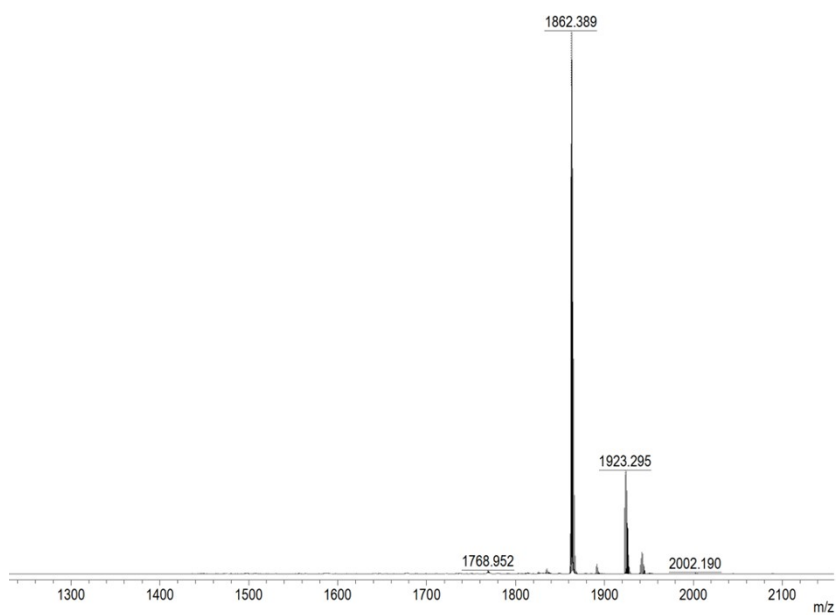


Fig. S9 MALDI-TOF-MS of PN1.

5.2. MALDI-TOF-MS of PN2

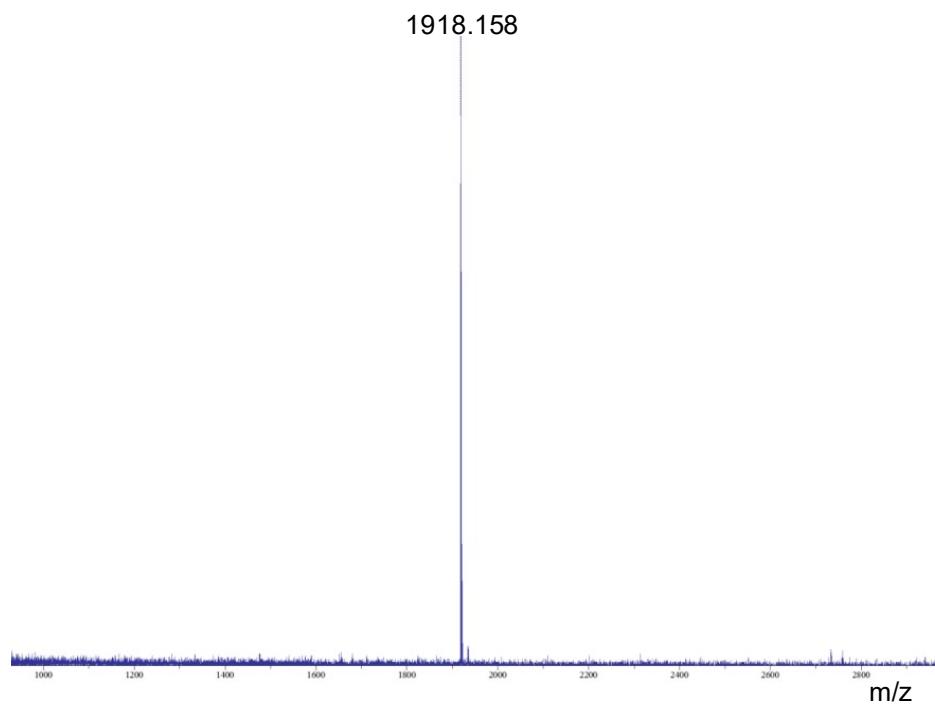


Fig. S10 MALDI-TOF-MS of **PN2**.

5.3. MALDI-TOF-MS of PN3:

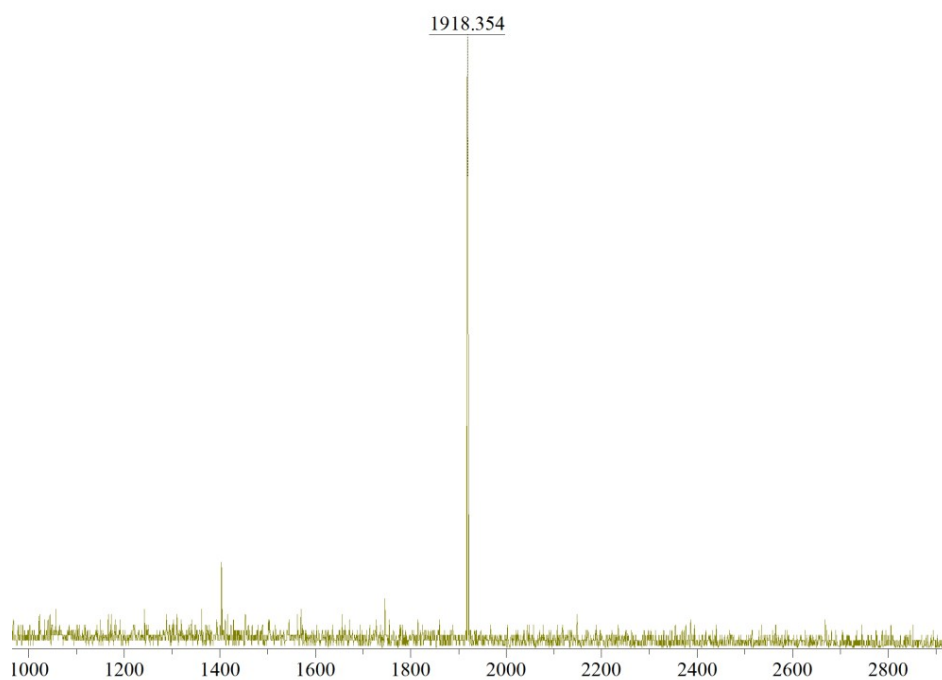


Fig. S11 MALDI-TOF-MS of **PN3**.

5.4. MALDI-TOF-MS of PN4

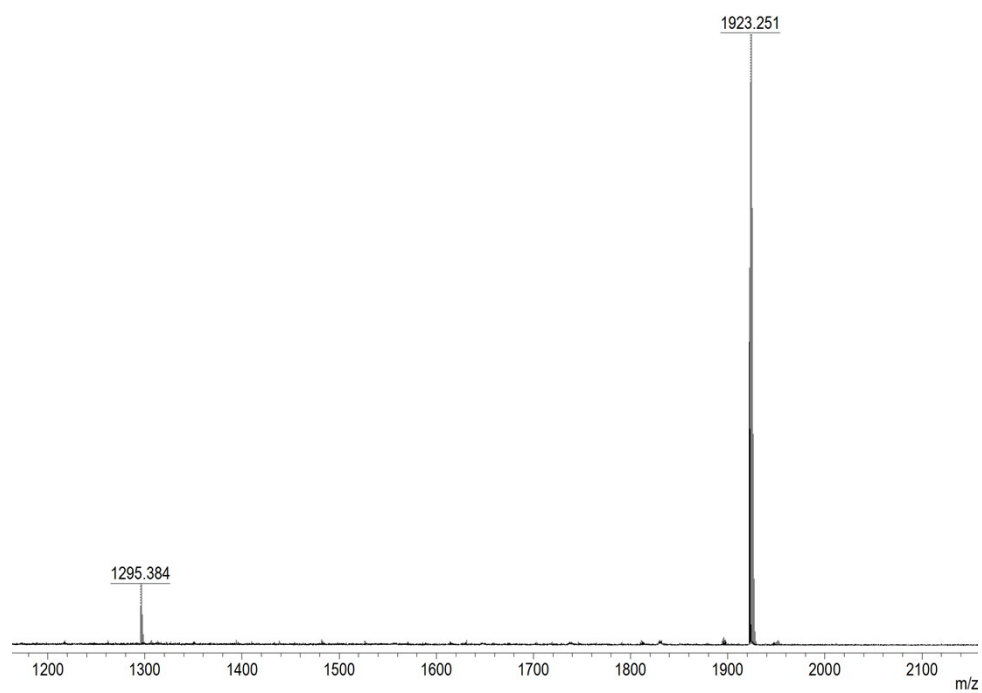


Fig. S12 MALDI-TOF-MS of PN4.

5.5. MALDI-TOF-MS of PN5:

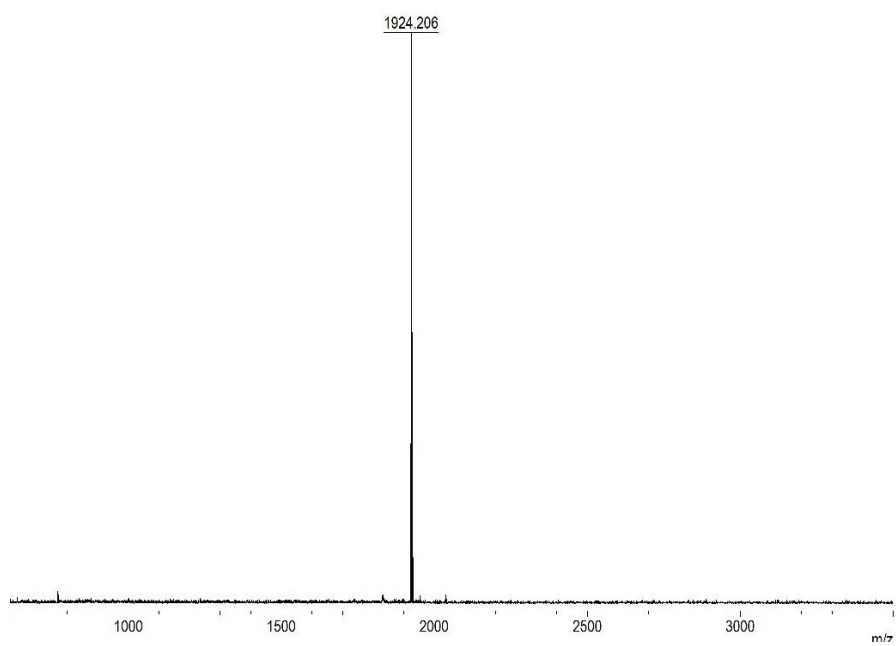


Fig. S13 MALDI-TOF-MS of PN5.

6. Optical and electrochemical spectral data of PN1 – PN5:

Table S1. UV-visible absorption, emission, lifetime and electrochemical spectral data of PN1 – PN5.

Samples	λ_{\max} (nm)	λ_{Ems} (nm)	τ (ns)	χ^2	Relative Population (%)	Oxidation Potentials	Reduction Potentials
PN1	467, 621,706	713	$\tau_1 = 1.5$ $\tau_2 = 6.2$	0.986	B1 = 33.76 B2 = 66.24	0.93	-1.40, -1.10, -0.96
PN2	472, 643	-	-	-	-	0.77	-1.28, -0.94, -0.78
PN3	476, 635	685	$\tau_1 = 1.2$ $\tau_2 = 1.3$	1.445	B1 = 86.49 B2 = 13.51	0.90	-1.353, -0.97
PN4	472, 653	-	-	-	-	0.93	-1.40, -1.06
PN5	471, 668	685	$\tau_1 = 1.3$ $\tau_2 = 7.6$	1.004	B1 = 95.92 B2 = 4.08	0.84, 1.14	-1.43, -1.17,

7. UV-visible absorption spectra of PN3 – PN5 at aggregated state:

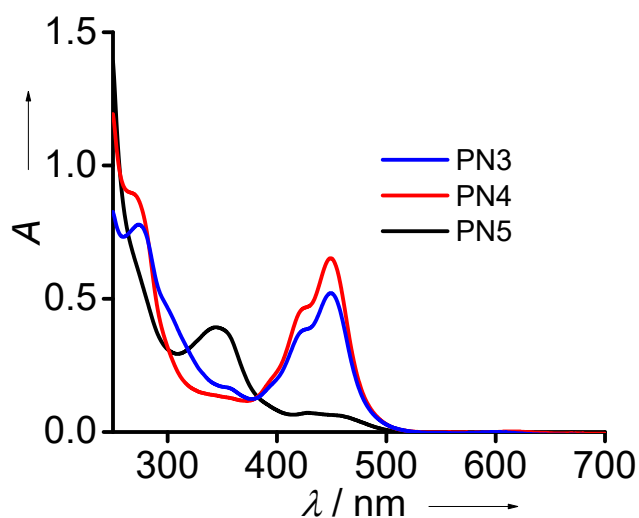


Fig. S14 a) UV-visible optical absorption spectra of PN3 – PN5 aggregates.

8. FT-IR spectra of PN1 – PN5 :

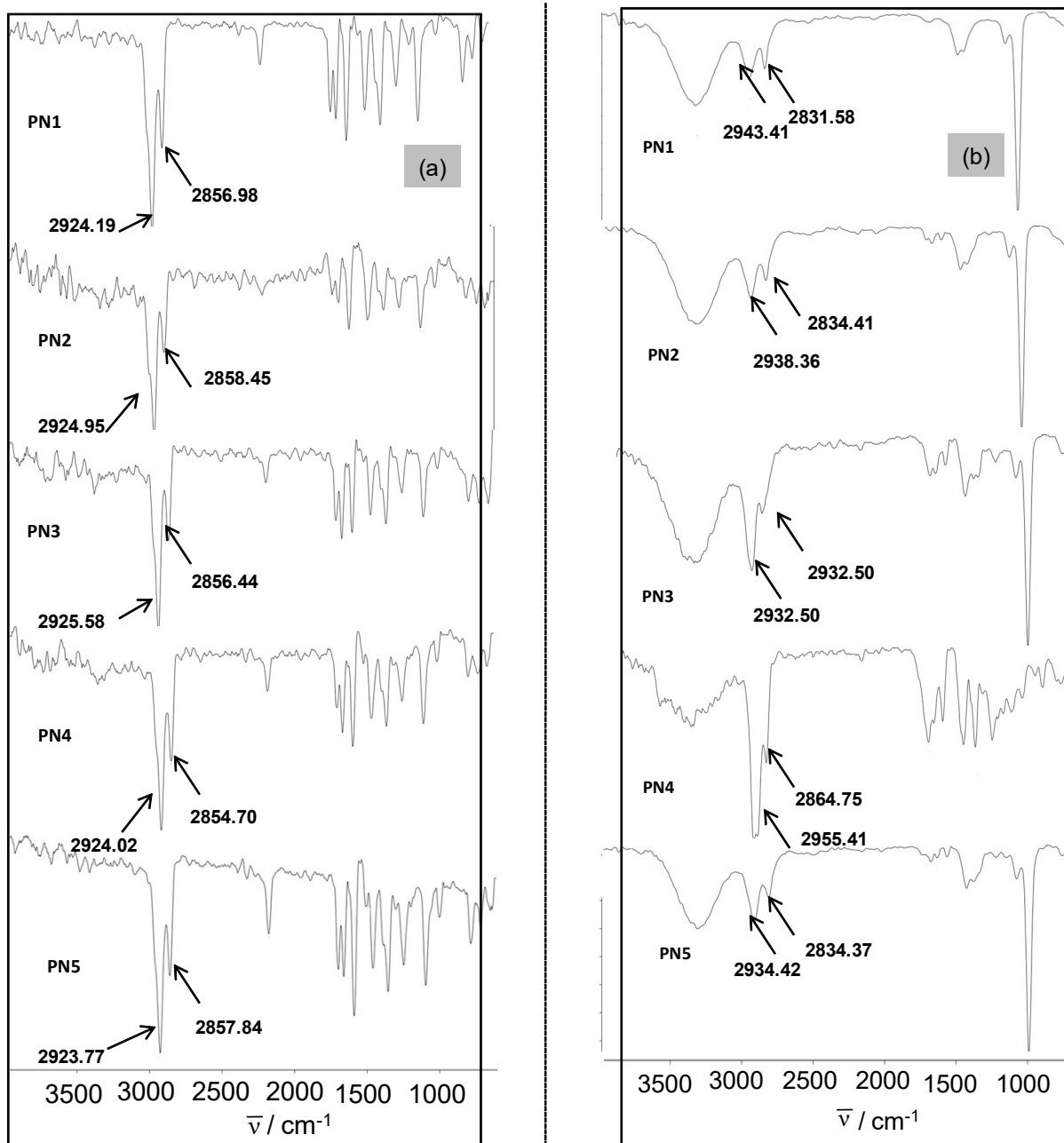


Fig. S15 FT-IR analysis of **PN3 – PN5** in chloroform (a) and aggregates recorded in methanol (b).

9. PXRD spectra of **PN3 – PN5**:

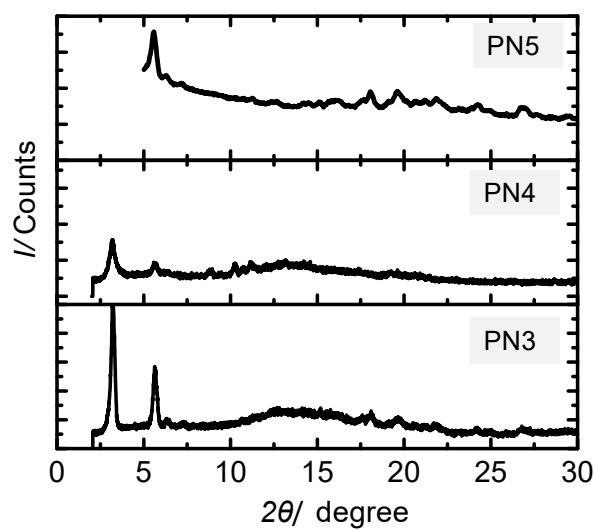


Fig. S16 Powder x-ray diffraction analysis of PN3 – PN5.

10. Electron microscopic images and Diffraction analysis of PN3 PN5:

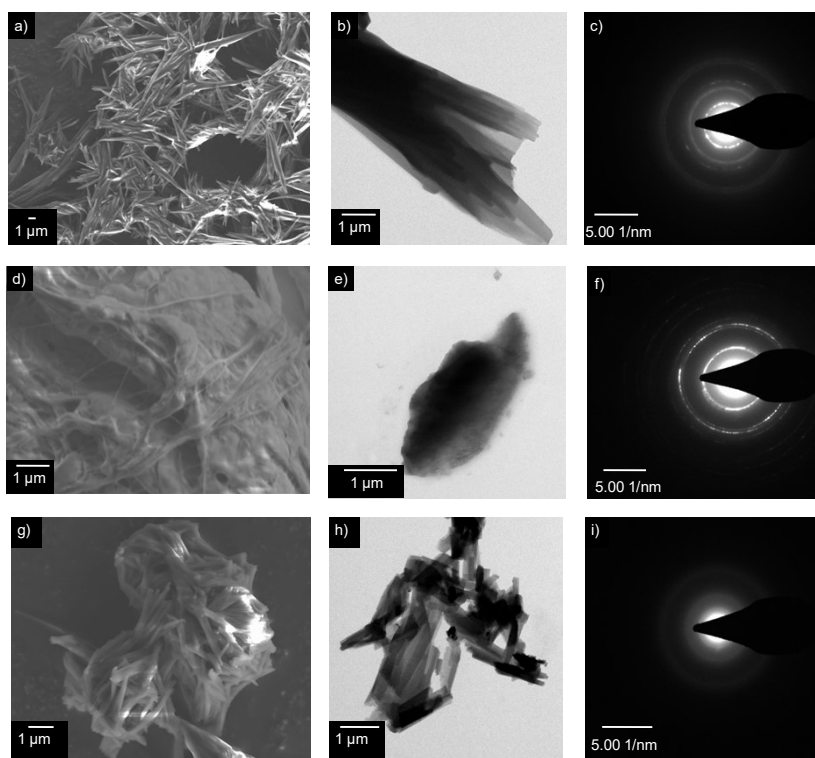


Fig. S17 (a,b) SEM, TEM images and corresponding electron diffraction analysis of (a,b,c) PN3, (d,e,f) PN4 and (g,h,i) PN5 aggregates at concentration of 1×10^{-4} M at 25 °C.

11. Electrochemical Impedance analysis of PN1 PN5:

11.1. ECI spectral data of PN2:

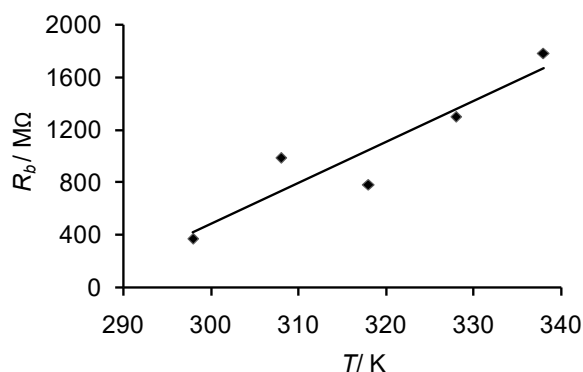


Fig. S18 Graph represents the resistance against variations in temperature from 25 °C to 65 °C (298 – 338 K) of **PN2**.

11.2. ECI spectra of PN1:

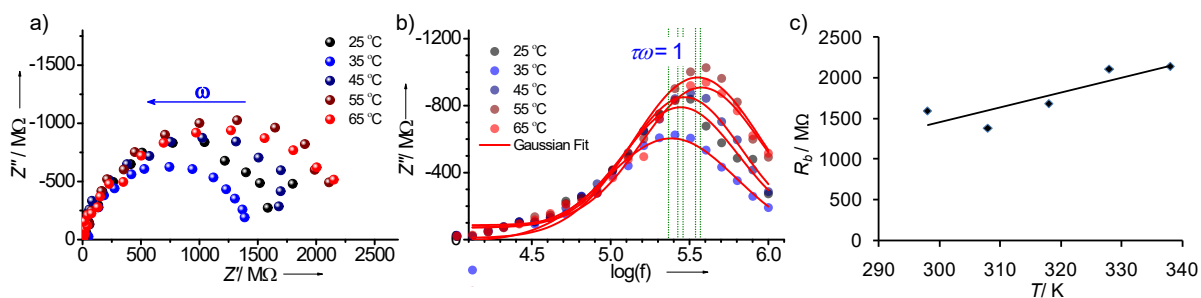


Fig. S19 Electrochemical impedance spectral data of **PN1**. (a) Temperature dependent Nyquist plot of **PN1** from 25 °C to 65 °C (b) Temperature dependent changes of logarithmic frequency vs Imaginary impedance. (c) Temperature in Kelvin against bulk resistance.

11.3. ECI spectra of PN3:

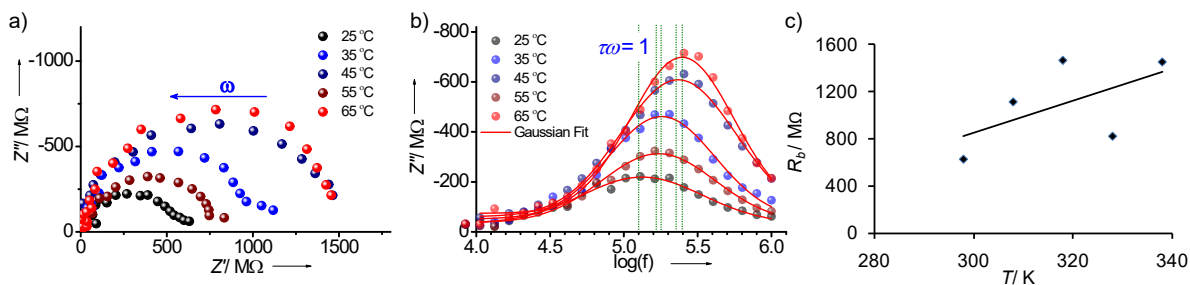


Fig. S20 Electrochemical impedance spectral data of of **PN3**. (a) Temperature dependent Nquist plot of **PN3** from 25 °C to 65 °C (b) Temperature dependent changes of logarithmic frequency vs Imaginary impedance. (c) Temperature in Kelvin against bulk resistance.

11.4. ECI spectra of PN4:

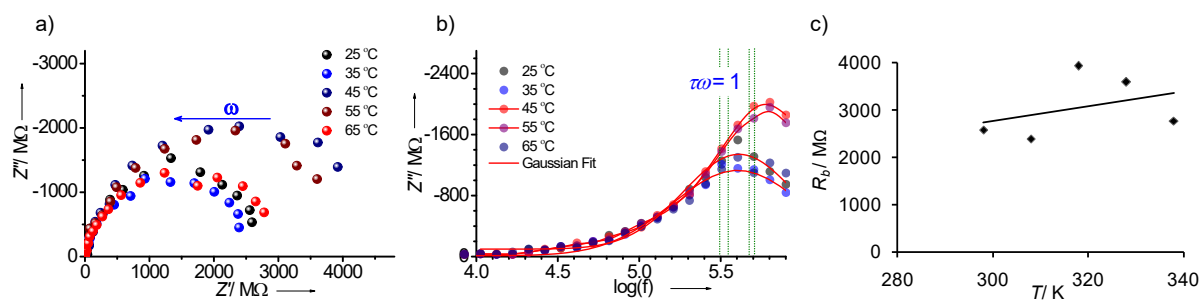


Fig. S21 Electrochemical impedance spectral data of of **PN4**. (a) Temperature dependent Nquist plot of **PN4** from 25 °C to 65 °C (b) Temperature dependent changes of logarithmic frequency vs Imaginary impedance. (c) Temperature in Kelvin against bulk resistance.

11.5. ECI spectra of PN5:

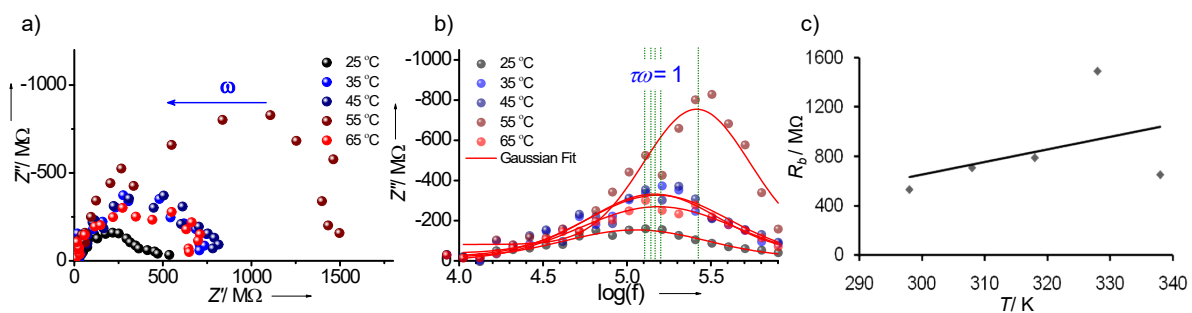


Fig. S22 Electrochemical impedance spectral data of of **PN5**. (a) Temperature dependent Nyquist plot of **PN5** from 25 °C to 65 °C (b) Temperature dependent changes of logarithmic frequency vs Imaginary impedance. (c) Temperature in Kelvin against bulk resistance.


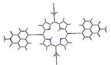
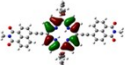
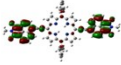
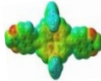

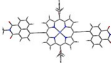
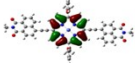
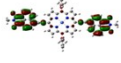
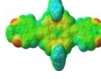

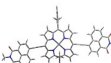
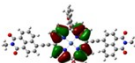
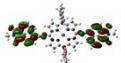
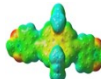

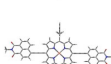
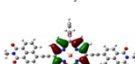
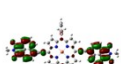
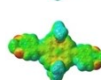

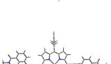
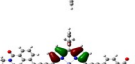
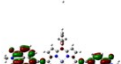
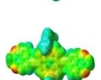
11.6. Summary of electrochemical impedance data of PN1 – PN5:

Table S2. Electrochemical impedance spectroscopy data of **PN1 – PN5**; where, R_b = bulk resistance; σ = specific conductivity, τ_b = the bulk relaxation time and C_b = bulk capacitance and estimated for the sample at the corresponding temperature.

T(C)	R_b (M Ω)	1/ R_b	σ (S/cm)	fp (MHz)	τ_b (μ s)	C_b (nf)
PN1						
25	1592.97	0.0006	0.008	0.32	50.0	0.31
35	1383.58	0.0007	0.009	0.25	64.3	0.46
45	1684.07	0.0005	0.007	0.32	49.2	0.29
55	2106.75	0.0004	0.006	0.39	39.9	0.19
65	2140.63	0.0004	0.005	0.40	39.7	0.18
PN2						
25	372.80	0.0026	0.033	0.11	1.41	3.7
35	986.44	0.0010	0.012	0.20	0.96	0.80
45	784.71	0.0012	0.015	0.16	0.78	1.23
55	1300.16	0.0007	0.009	0.25	63.1	0.48
65	1780.94	0.0005	0.007	0.40	39.7	0.22
PN3						
25	624.57	0.0016	0.020	0.18	84.5	1.36
35	1112.29	0.0008	0.011	0.20	77.4	0.69
45	1465.98	0.0007	0.008	0.25	62.4	0.42
55	820.08	0.0012	0.015	0.17	94.2	0.11
65	1452.12	0.0006	0.008	0.27	58	0.40
PN4						
25	2584.98	0.0003	0.004	0.32	49.4	0.19
35	2391.69	0.0004	0.005	0.26	60.6	0.25
45	3936.90	0.0002	0.003	0.51	31.4	0.07
55	3593.64	0.0002	0.003	0.50	31.7	0.08
65	2767.16	0.0004	0.004	0.32	49.8	0.17
PN5						
25	544.79	0.0018	0.022	0.13	1.23	2.27
35	708.11	0.0014	0.017	0.17	93.9	1.33
45	789.16	0.0012	0.015	0.20	77.7	0.98
55	1490.13	0.0006	0.008	0.31	50	0.33
65	651.94	0.0015	0.019	0.12	1.25	1.92

12. Theoretical calculations data of PN1 – PN5:

Table S3. Optimized structures, HOMO-1 and LUMO+1 energy diagrams/values and ESP data of PN1 – PN5.

Samples	Optimized Structures		HOMO-1 (eV)	LUMO+1 (eV)	ESP		
	Top view	Side view					
PN1				5.43		2.48	
PN2				5.30		2.48	
PN3				5.31		2.48	
PN4				5.33		2.48	
PN5				5.35		2.47	

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