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Supplementary Information (SI)

Persistent Radical Anion Polymers Based on Naphthalenediimide and a Vinylene Spacer

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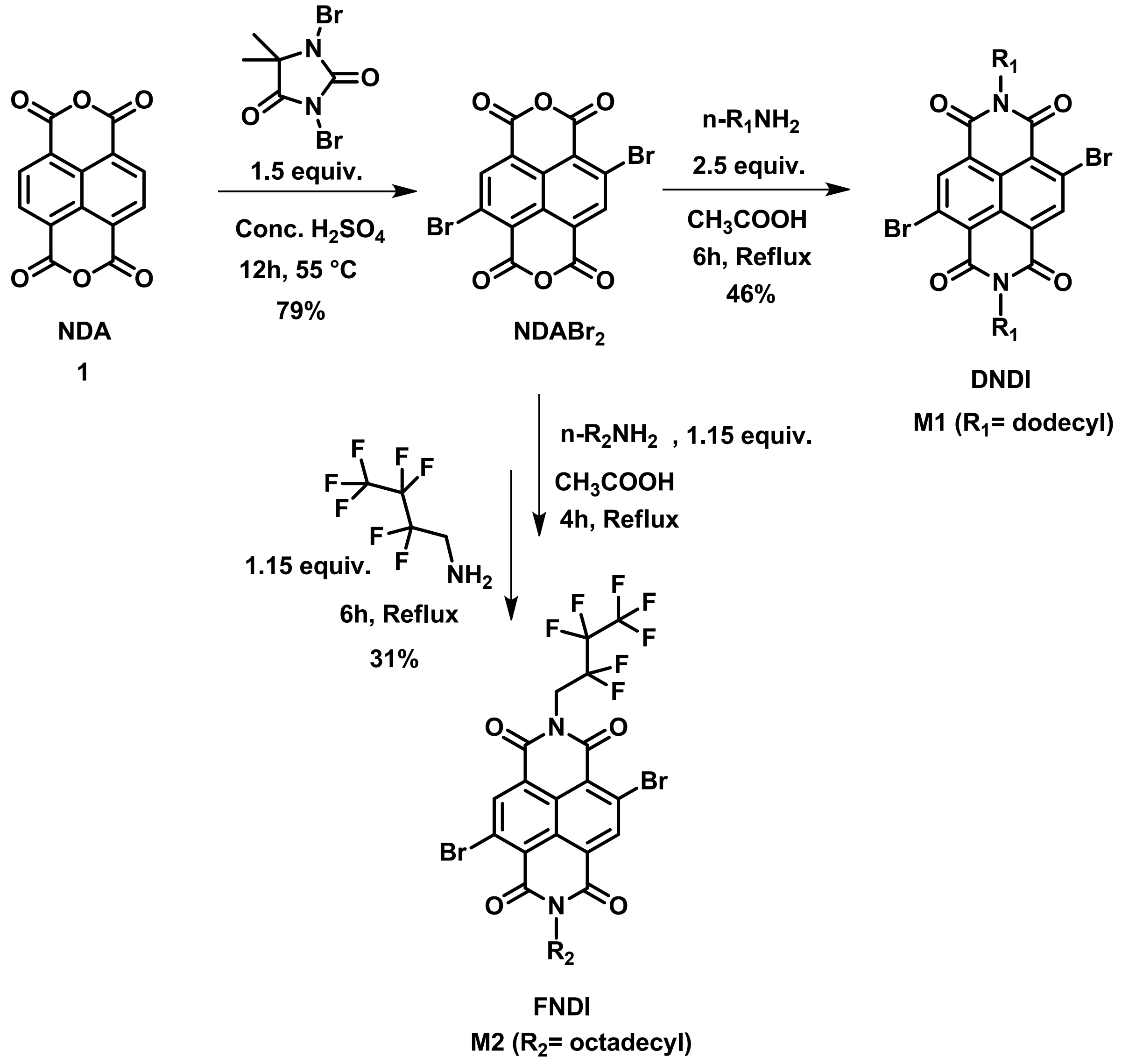


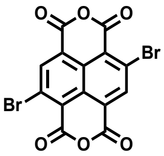
Scheme S1. Synthesis of NDI-based monomers **DNDI** and **FNDI**.

EXPERIMENTAL SECTION

Acetic acid, acetone, acetonitrile, chlorobenzene, chloroform, 1,4,5,8-naphthalenetetracarboxylic dianhydride (NDA), 1,3-Dibromo-5,5-dimethylhydantoin (DBH), ferrocene, *n*-dodecylamine, *n*-octadecylamine, 2,2,3,3,4,4,4-heptafluorobutylamine, hexane, methanol, tetrahydrofuran (THF), $Pd(PPh_3)_4$, tetrabutylammonium cyanide (TBACN), tetrabutylammonium perchlorate (TBAP), tetrakis(dimethylamino)ethylene (TDAE), trans-1,2-bis(tri-n-butylstannyl)ethylene, 1,2,4-trichlorobenzene (TCB), and toluene were purchased from commercial vendors and used as received unless otherwise stated. Toluene was dried by storage over 4 Å molecular drying sieves and degassed by sparging with N_2 for no less than one hour. ^1H NMR and ^{13}C NMR spectra were recorded on a 400 MHz Bruker Avance NMR spectrometer, ^{19}F NMR spectra were recorded on a 500 MHz Bruker Ascend NMR spectrometer. All the NMR spectra and chemical shifts were mentioned with respect to tetramethylsilane (TMS) internal standard in parts per million (δ scale). Gel permeation chromatography (GPC) analyses were performed on a HT-GPC, PL-GPC220, solvent: TCB, normal operating temperature: 135 °C. Absorption spectra were taken using a Shimadzu UV 3600 UV-Vis-NIR spectrometer. Polymer thin films for UV-Vis-NIR spectroscopy were prepared by spincasting onto ITO-coated glass slides from chlorobenzene solution. The electrochemical properties were performed by using a three electrode system on a CV-50W electrochemical analyser using a Pt disk (dia. 1.6 mm) and a platinum (Pt) wire as working electrode and as counter electrode respectively, with a reference electrode of Ag/AgCl. TBAP (0.1 M in N_2-purged dry acetonitrile) was utilised as the supporting electrolyte and ferrocene was used as an internal standard (the calculated half-wave potential for ferrocene/ferrocenium couple was found to be 0.32 V). Thermogravimetric study (TGA) was performed on a TGA Q50 instrument and differential scanning calorimetry (DSC) was performed on a DSC Q200 instrument. EPR spectra were collected at room temperature on a Bruker Elexsys E-500 at X-band. The two-terminal electronic devices were fabricated by vacuum depositing Au electrodes (100 nm) onto a clean glass substrate with a channel width and length at 5 mm and 165 µm, respectively, using a shadow mask. Solutions of a predetermined amount of polymer or polymer and TBACN in THF were dropcast onto these electrodes. Poling at a constant voltage was performed for a duration of time to ensure that the current measured was electronic and not ionic, and the final 30 measurements of current (the final 2.5 seconds of poling) were assumed to be the steady-state, electronic current for *I-V* characterization. All *I-V* characterization was carried out under ambient conditions at room temperature using Keithley 2440-5A SourceMeter. The film thicknesses were determined by profilimetry using a KLA Tencor Alpha-Step IQ Surface Profiler. DFT calculations were performed within the ωB97XD/6-31g(d,p) basis, with the geometry of each NDIV oligomer optimized with vinylene end groups on each end and all hydrocarbon side chains replaced with ethyl groups.

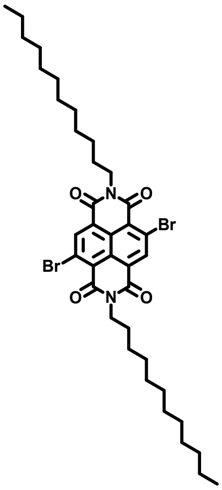
Synthesis

Synthesis of 2,6-Dibromo-1,4,5,8-naphthalenetetracarboxylic Dianhydride (NDABr$_2$).



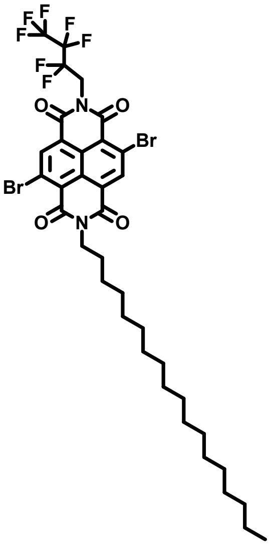
NDABr$_2$ was prepared in a modified version of the previously reported procedure.[1] In a single-necked RB flask, NDA (1.34 g, 5 mmol) was stirred at room temperature in concentrated sulfuric acid (15 mL) for 5 min. DBH (2.14 g, 7.5 mmol) was added in portion wise over a period of 40 min at room temperature. The resulting brown solution was stirred at 55 °C for 12 h. In order to precipitate the solid, the mixture was poured over crushed ice. Filtration of the precipitated solid was done, further washed with water (100 ml) followed by methanol (100 ml) then dried in vacuum to obtain NDABr$_2$ which was used for next steep without farther purification (1.68 g, 79 %). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ 8.78 (s, 2H).

Synthesis of *N, N′*-bis(*n*-dodecyl)-2,6-dibromo-1,4,5,8-naphthalenedicarboximide (DNDI).



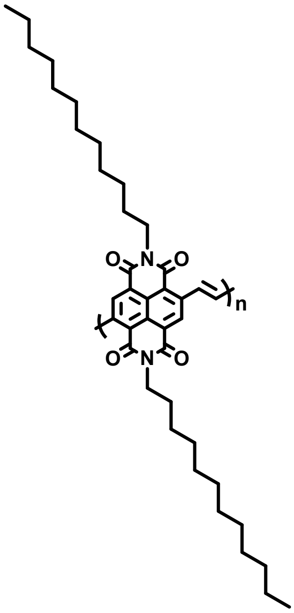
A mixture of NDABr$_2$ (423 mg, 1 mmol), *n*-dodecylamine (462 mg, 2.5 mmol), and acetic acid (20 mL) was stirred at 90 °C under N$_2$ atmosphere for 8 hours. The mixture was cooled to room temperature followed by addition of 80 ml of cold water. A yellow precipitate formed upon cooling and was separated by gravity filtration, washed with 100 ml of methanol and dried under vacuum. Final purification was done by column chromatography eluting with hexane/chloroform (60 : 40) to obtain **DNDI** as a yellow solid (350 mg, 46%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.99 (s, 2H), 4.18 (t, J = 7.6 Hz, 4H), 1.78−1.68 (m, 4H), 1.44−1.34 (m, 8H), 1.30−1.22 (m, 28H), 0.89−0.85 (m, 6H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 160.76, 160.73, 139.07, 128.32, 127.73, 125.36, 124.10, 41.62, 31.91, 29.62, 29.61, 29.56, 29.51, 29.34, 29.29, 27.90, 27.08, 22.69, 14.11.

Synthesis of *N*-(2,2,3,3,4,4,4-heptafluorobutyl)-*N*'-octadecyl-2,6-dibromo-1,4,5,8-naphthenedicarboximide (FNDI).



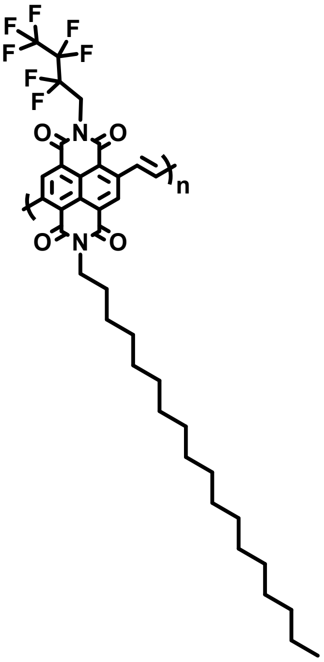
A mixture of $NDABr_2$ (423 mg, 1 mmol), *n*-octadecylamine (309 mg, 1.15 mmol), and acetic acid (20 mL) was stirred at 90 °C under N_2 atmosphere for 4 hours before 2,2,3,3,4,4,4-heptafluorobutylamine (228 mg, 1.15 mmol) was added to the same reaction mixture at the same temperature and stirred for another 6 hours. The mixture was cooled to room temperature followed by addition of 80 ml of cold water. A precipitate that formed upon cooling was separated by gravity filtration, washed with 50 ml of methanol and dried under vacuum. Final purification was done by column chromatography eluting with hexane/chloroform (40 : 60) to obtain **FNDI** as a greenish yellow solid (266 mg, 31%). ^1H NMR (400 MHz, $CDCl_3$): δ 9.04 (s, 1H), 9.02 (s, 1H), 5,03 (t, $J = 15.2$ Hz, 2H), 4.19 (t, $J = 7.6$ Hz, 2H), 1.77−1.71 (m, 2H), 1.45−1.34 (m, 4H), 1.34−1.26 (m, 26H), 0.90–0.85 (m, 3H). ^{19}F NMR (500 MHz, $CDCl_3$): δ −80.41 (t, 3F), −115.85 (m, 2F), −127.60 (br, 2F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.63, 160.51, 160.29, 139.79, 139.15, 129.45, 128.36, 127.90, 127.80, 125.89, 124.79, 124.35, 123.36, 41.71, 38.80, 31.91, 29.69, 29.65, 29.63, 29.57, 29.51, 29.35, 29.27, 27.88, 27.06, 22.68, 14.11,

Synthesis of PDNDIV



DNDI (76 mg, 0.10 mmol), and trans-1,2-bis(tri-n-butylstannyl)ethylene (61 mg, 0.1 mmol) were added to 3 mL of dry toluene in a two-necked 25 ml round-bottom flask under nitrogen. The solution was purged with nitrogen for 10 min. Then, $Pd(PPh_3)_4$ (5.8 mg, 5 mol %) was added to the solution and the mixture was refluxed for 12 h. The crude reaction mixture was then precipitated in 30 ml methanol and collected by gravity filtration, after which the resulting solution was subjected to Soxhlet extraction with methanol, acetone, and hexane as washing solvents. A final chloroform extraction resulted in a deep red colored solution, which was then reprecipitated from 10 ml methanol and dried under a vacuum to yield reddish black polymer **PDNDIV** (40 mg, yield 61%). ^1H NMR (400 MHz, $CDCl_3$): δ 9.19 (br, 2H) 8.93 (br, 2H), 4.20 (br, 4H), 1.83−1.69 (br, 4H), 1.40−1.15 (br, 36H), 0.94−0.76 (br, 6H).

Synthesis of PFNDIV



FNDI (86 mg, 0.10 mmol), and trans-1,2-bis(tri-n-butylstannyl)ethylene (61 mg 0.1 mmol) were added to 4 mL of dry toluene in a two-necked 25 ml round-bottom flask under nitrogen. The solution was purged with nitrogen for 15 min. Then, $Pd(PPh_3)_4$ (5.8 mg, 5 mol %) were added to the solution and the mixture was refluxed for 12 h. The crude reaction mixture was then precipitated in 40 ml methanol and collected by gravity filtration. The resulting solution was subjected to Soxhlet extraction with methanol, acetone, and hexane as washing solvents. A final chloroform extraction resulted in a deep red colored solution, which was then reprecipitated from 10 ml methanol and dried under a vacuum to yield reddish black polymer **PFNDIV** (54 mg, yield 73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.21 (br, 2H) 8.91 (br, 2H), 5.07 (br, 2H), 4.21 (br, 2H), 1.74 (br, 2H), 1.48−1.10 (br, 30H), 0.99−0.76 (br, 3H).

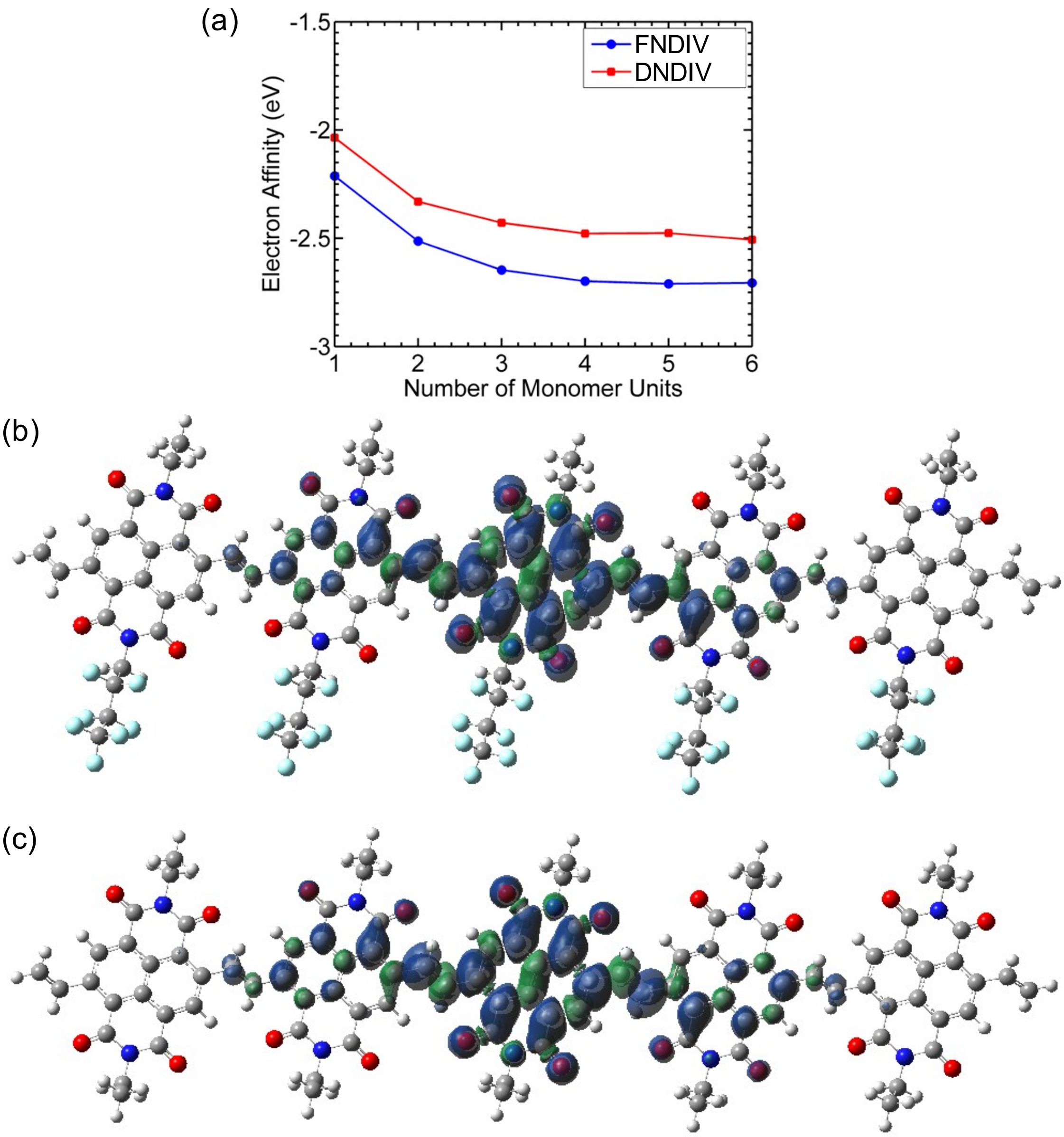


Figure S1. (a) DFT calculated electron affinity of **DNDIV** and **FNDIV** oligomers modelled with increasing naphthalene diimide units. (b) Optimized geometry and molecular orbital spin density difference plots including positive spin density (green orbital) and negative spin density (blue orbital) for the 5-mer of **[FNDIV]**$^{\bullet-}$ and (c) **[DNDIV]**$^{\bullet-}$.

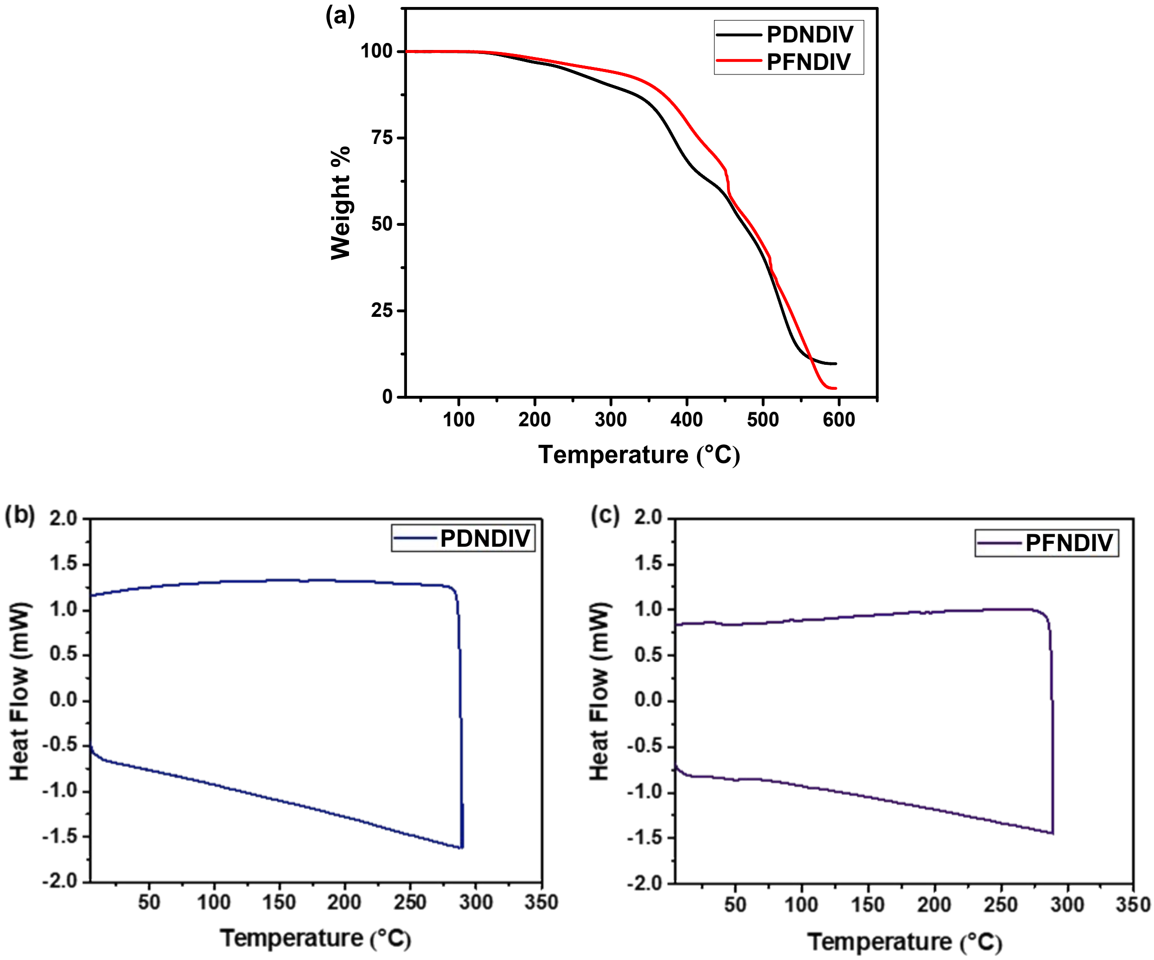


Figure S2. (a) TGA thermograms of **PDNDIV** and **PFNDIV** (b) DSC plots of **PDNDIV**, (c) DSC plots of **PFNDIV** at heating rate of 10 °C min^{-1} under a N_2 atmosphere.

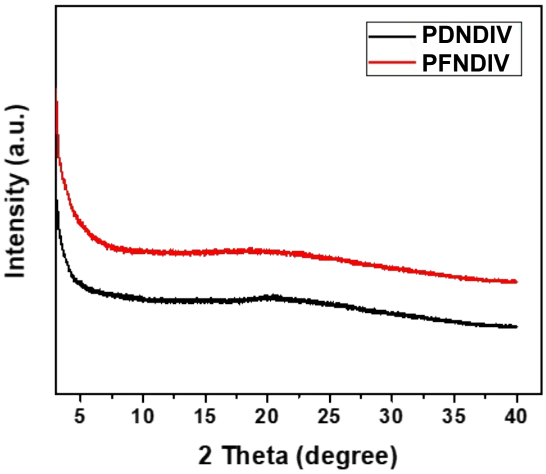


Figure S3. XRD patterns of **PDNDIV** and **PFNDIV** at rt.

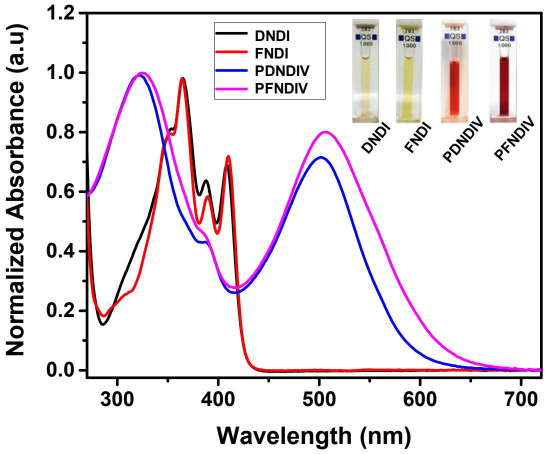


Figure S4. Comparison of UV-Vis spectrum of monomers and polymers in chloroform. Inset Colour photographs of monomers and polymers.

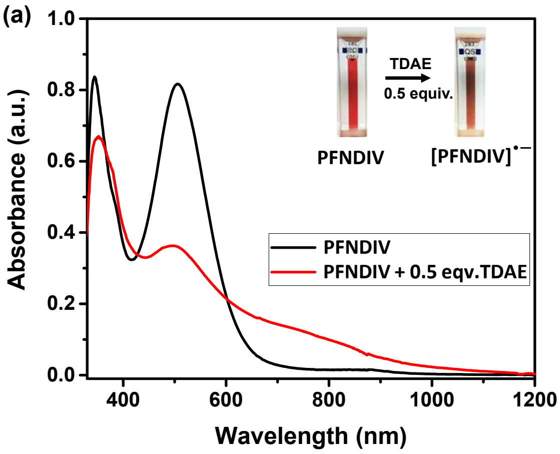


Figure S5. UV–Vis–NIR spectroscopic changes of **PFNDIV** in THF with TDAE dopant, inset TDAE induced colorimetry.

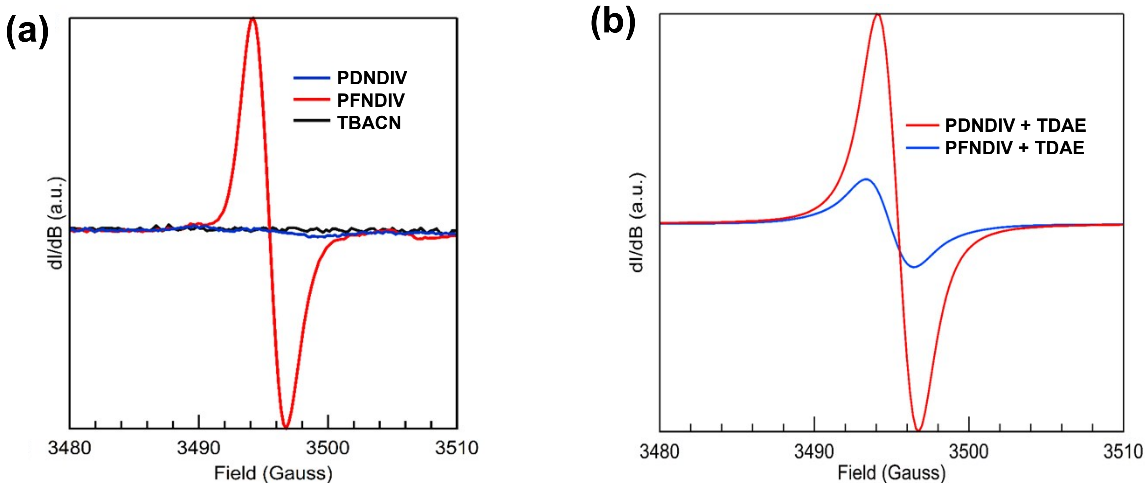


Figure S6. (a) Control EPR spectra of **PDNDIV**, **PFNDIV** and TBACN, in THF. (b) EPR spectrum of **[PDNDIV]**$^{\bullet-}$ and **[PFNDIV]**$^{\bullet-}$ in THF (TDAE induced).

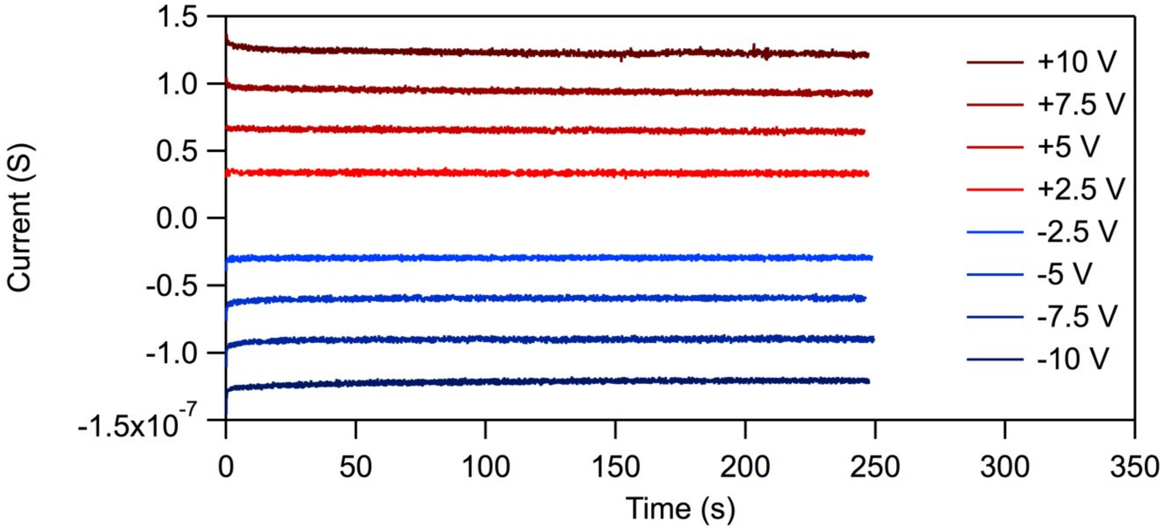


Figure S7. Current response of **[PFNDIV]**$^{\bullet-}$ to a constant applied voltage over time.

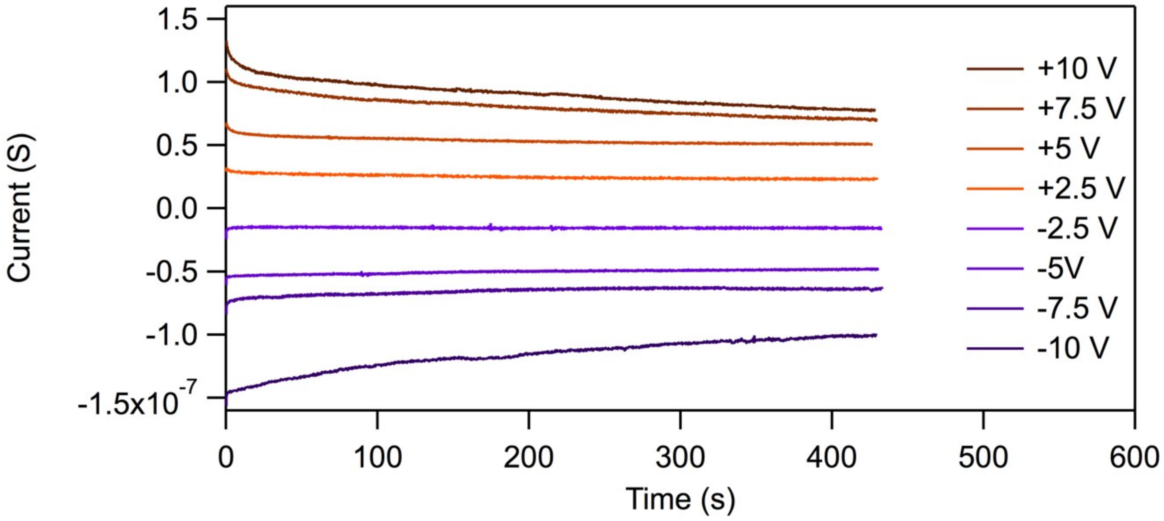


Figure S8. Current response of **[PDNDIV]**$^{\bullet-}$ to a constant applied voltage over time.

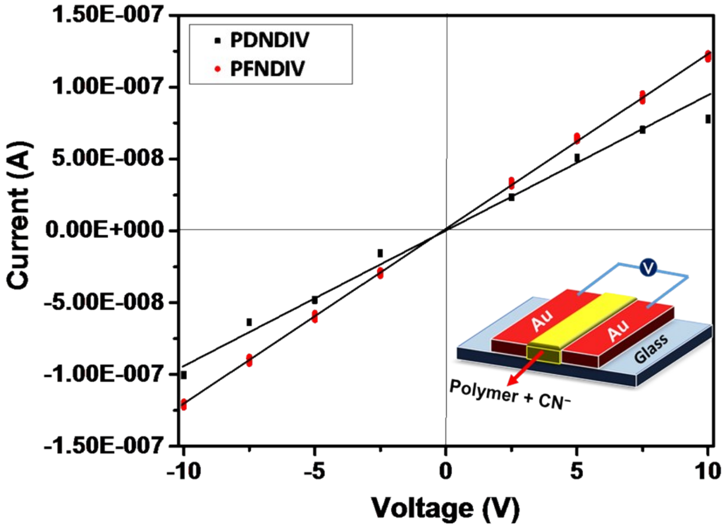
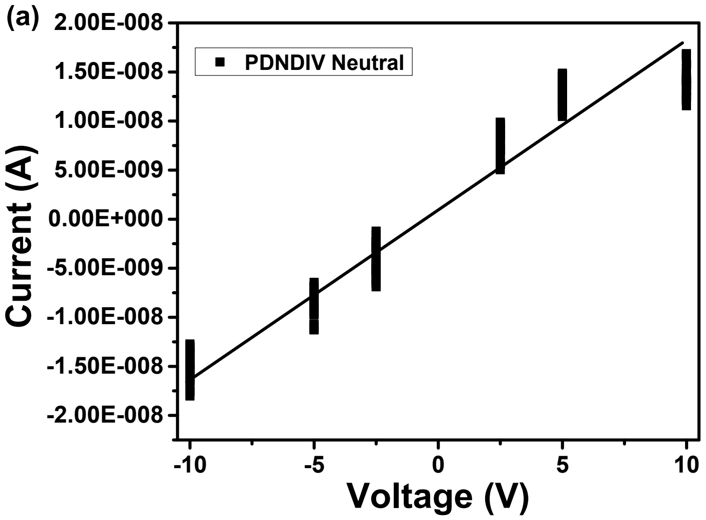


Figure S9. *I*-*V* curves of **[PDNDIV]**$^{\bullet -}$ and **[PFNDIV]**$^{\bullet -}$ doped using TBACN.



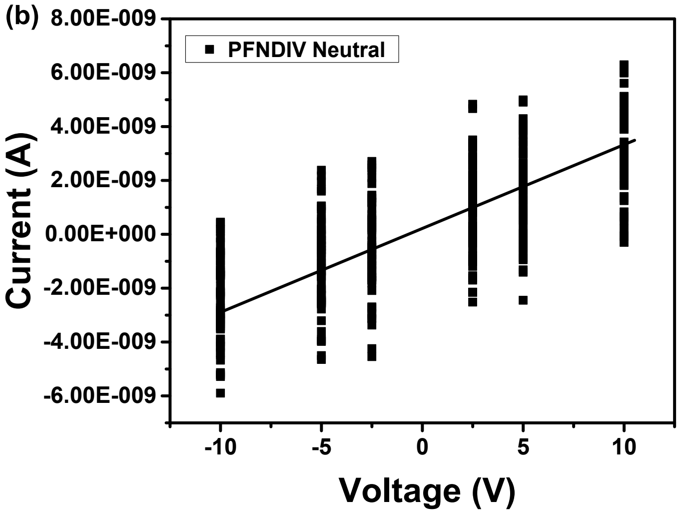


Figure S10. *I*-*V* curves of **PDNDIV** (a) and **PFNDIV** (b) in absence of any dopant.

Table S1. Conductance, Conductivity, and Film Thickness of PDNDIV and PFNDIV in Presence of TBACN.

Polymer	Equivalents of TBACN	Conductance (S)	Conductivity (S cm^{-1})	Thickness (µm)
PDNDIV	**0.0**	**1.64×10^{-9}**	**3.49×10^{-8}**	**15.5**
PDNDIV	**4.0**	**9.01×10^{-9}**	**6.98×10^{-7}**	**4.26**
PFNDIV	**0.0**	**2.76×10^{-10}**	**2.61×10^{-8}**	**3.48**
PFNDIV	**1.0**	**1.22×10^{-8}**	**3.28×10^{-7}**	**12.2**

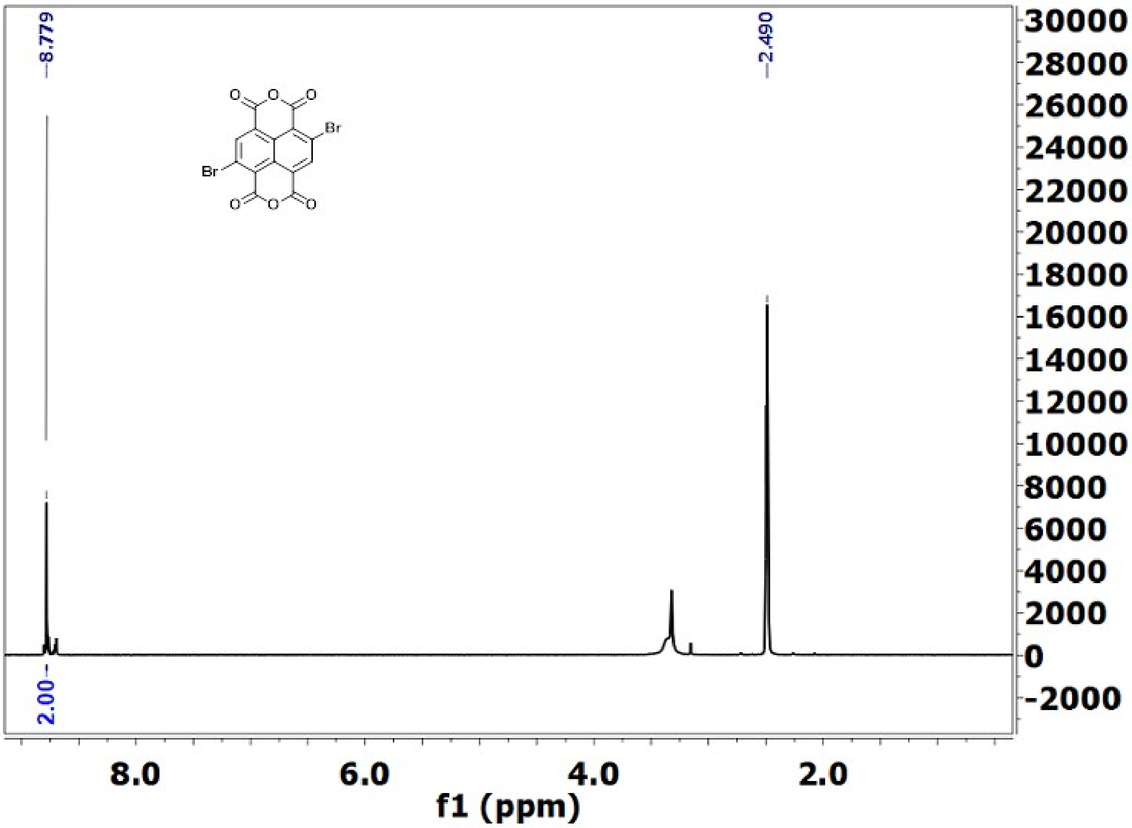


Figure S11. ^{1}H NMR of compound **NDABr$_2$**.

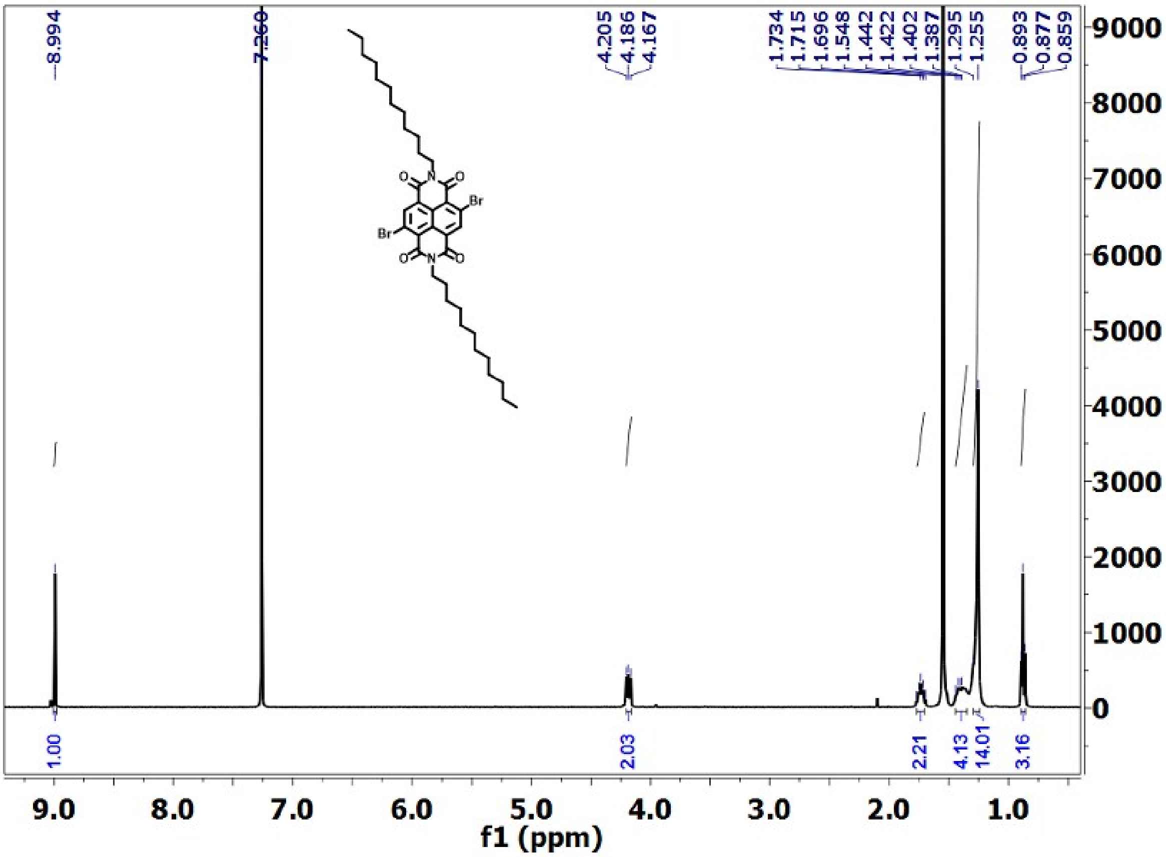


Figure S12. ^{1}H NMR of compound **DNDI**.

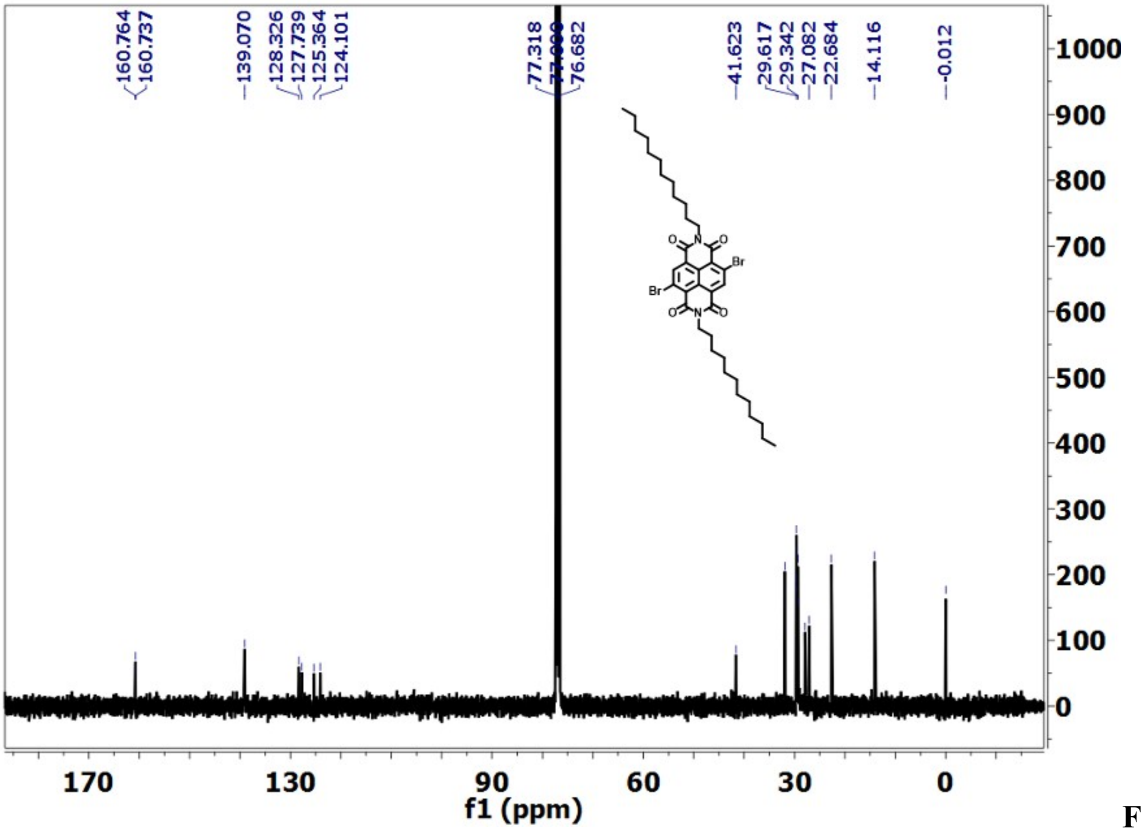


Figure S13. ^{13}C NMR of compound **DNDI**.

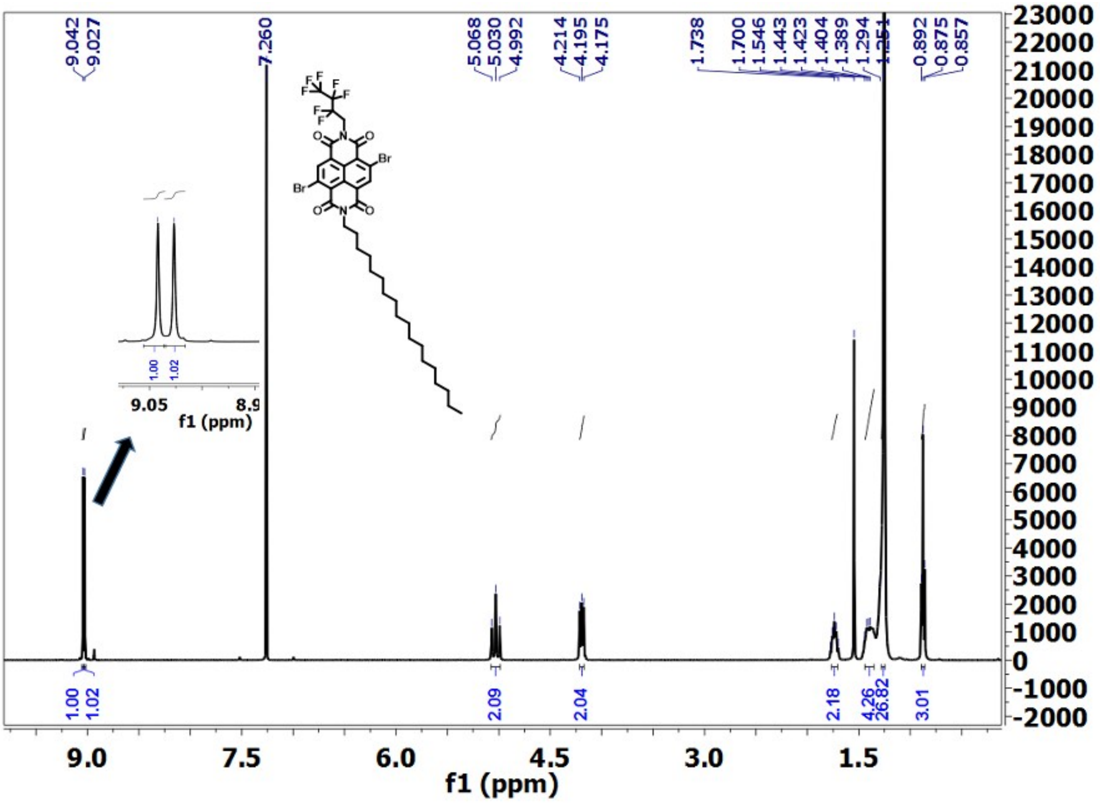


Figure S14. ^{1}H NMR of compound **FNDI**.

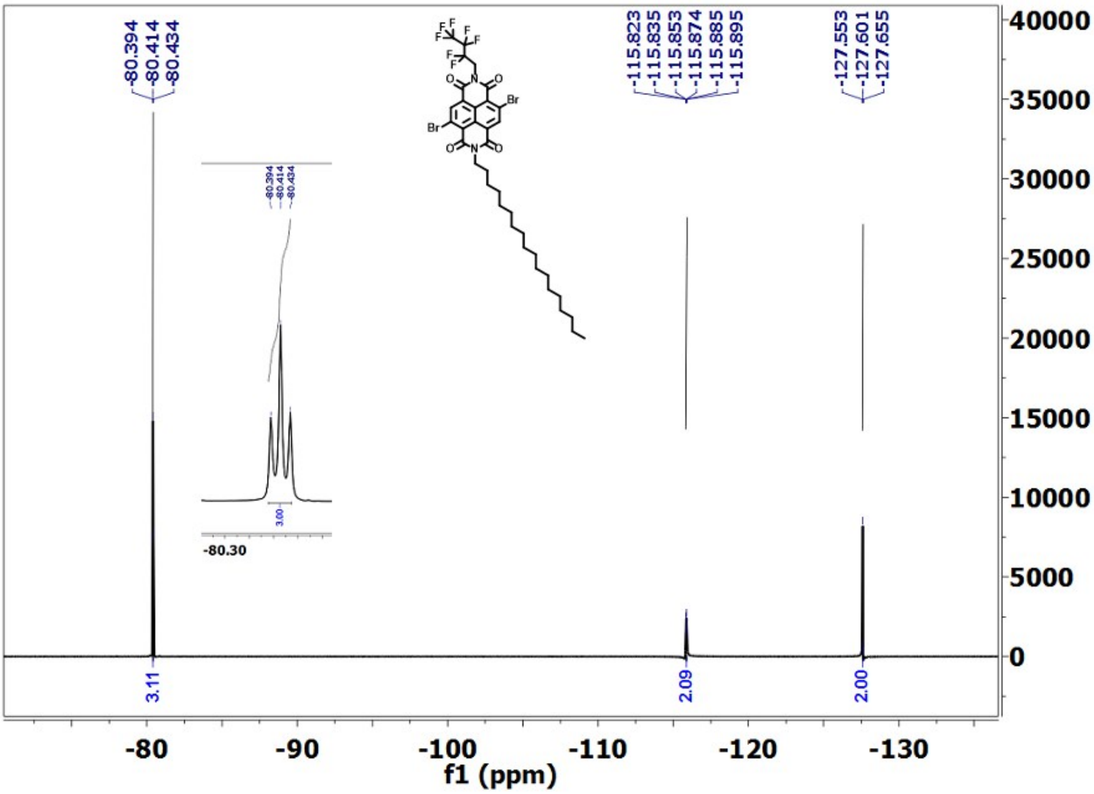


Figure S15. ^{19}F NMR of compound **FNDI**.

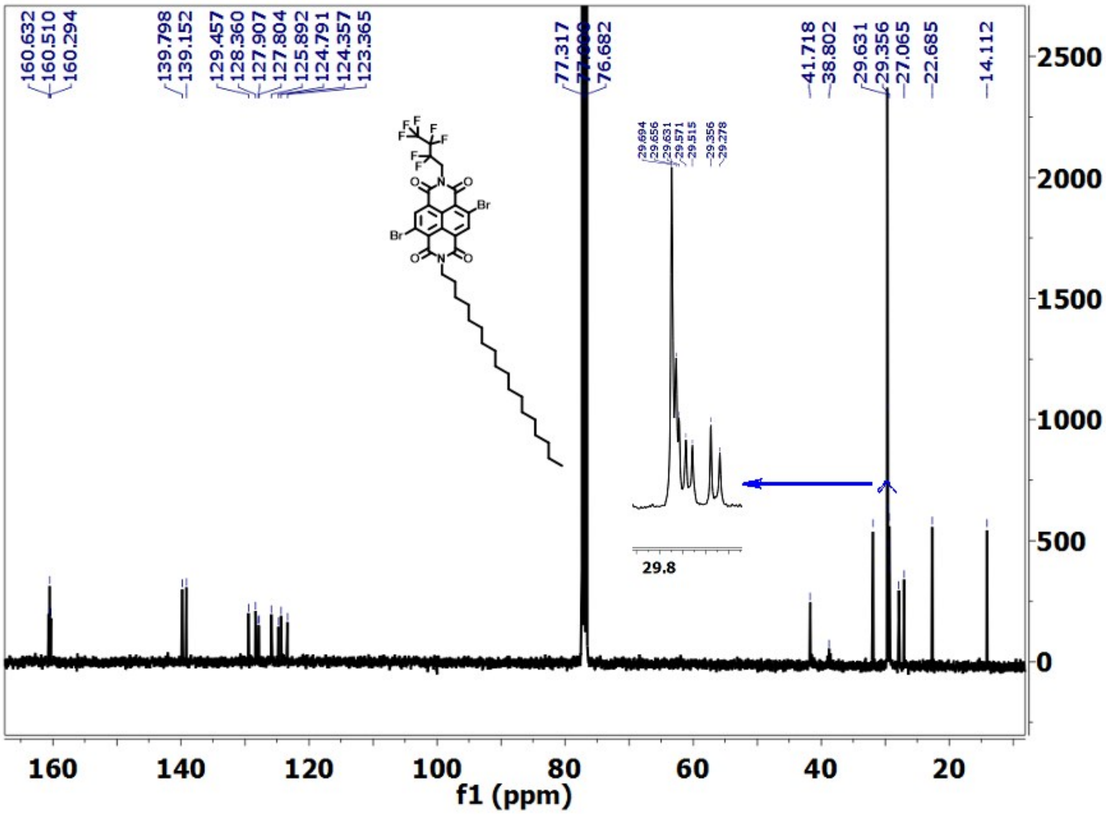


Figure S16. ^{13}C NMR of compound **FNDI**.

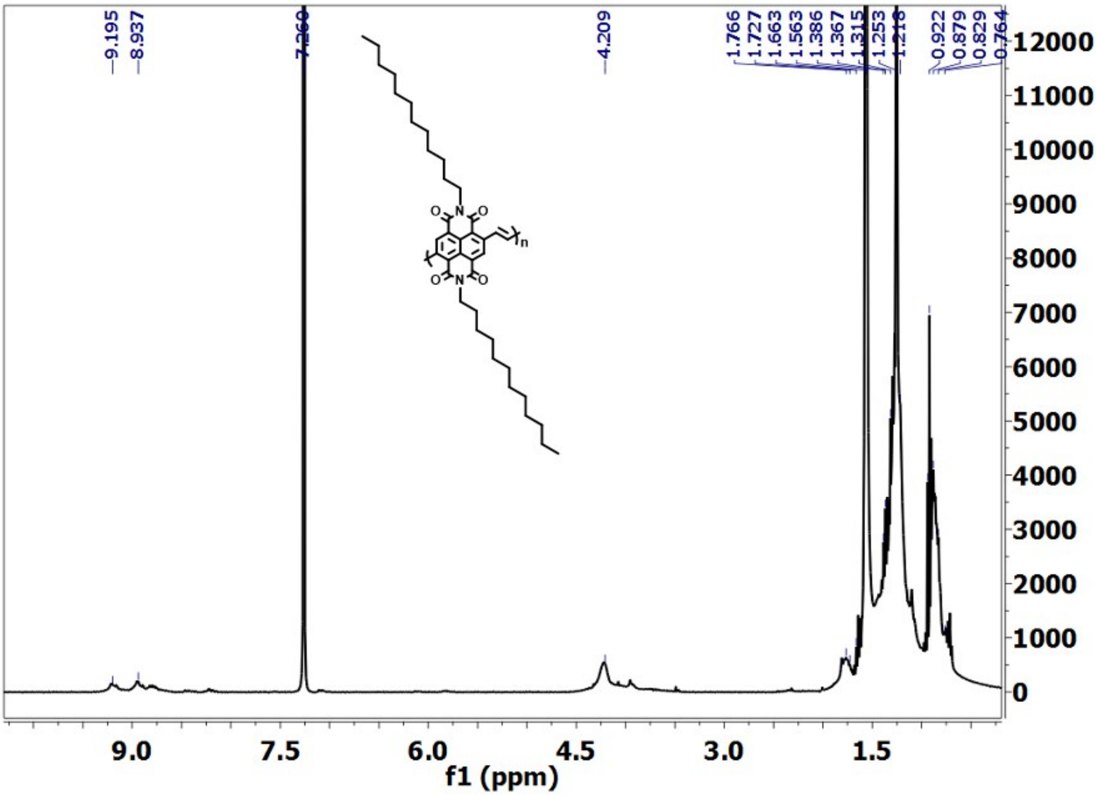


Figure S17. ^{1}H NMR of **PDNDIV**.

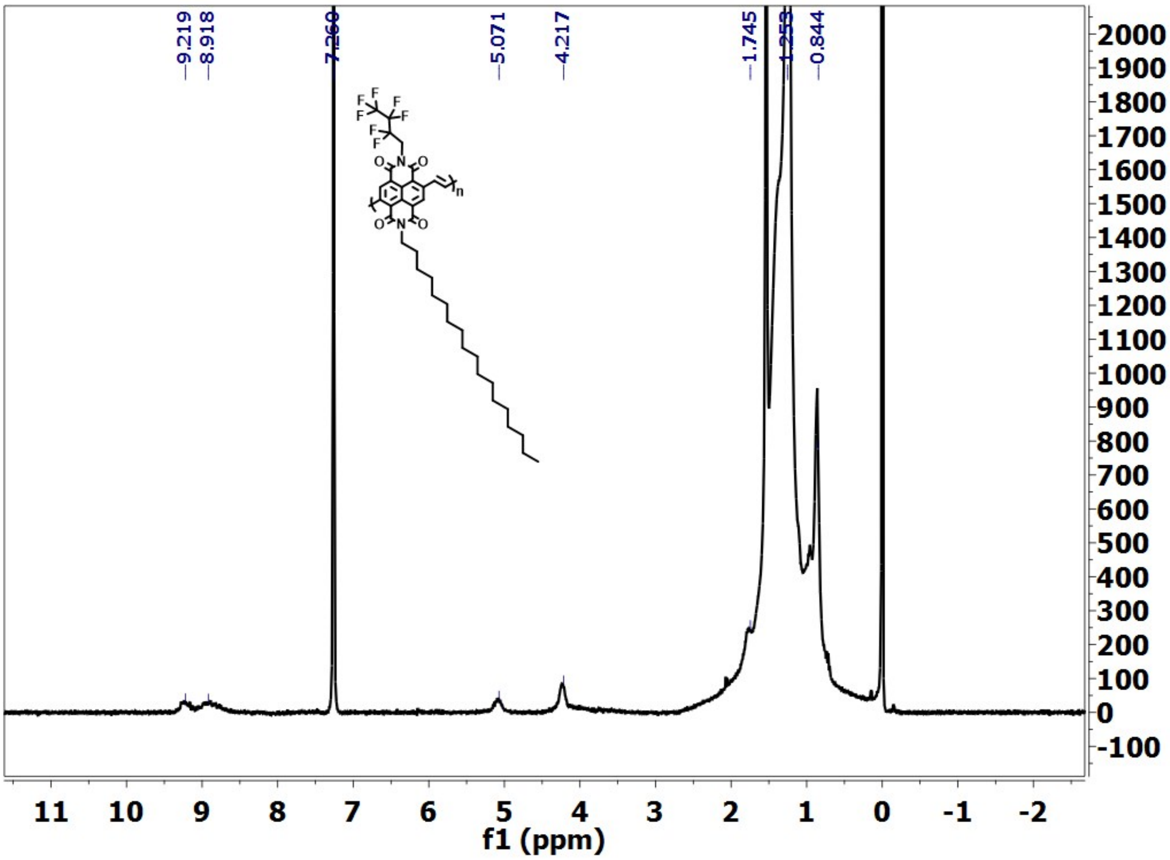


Figure S18. ^{1}H NMR of **PFNDIV**.

Reference:

1. Sasikumar, M.; Suseela, Y. V.; Govindaraju, T., Dibromohydantoin: A Convenient Brominating Reagent for 1,4,5,8-Naphthalenetetracarboxylic Dianhydride. *Asian Journal of Organic Chemistry* **2013,** *2* (9), 779-785.