Electronic Supplementary Information (ESI)

Self-assembled naphthalimide derivatives as efficient and low-cost electron extraction layer for n-i-p perovskite solar cells

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Supplementary Information

1. Materials and reagents

All chemicals and solvents used for synthesis are of reagent grade and were obtained from J&K Scientific, Adamas Reagent Co Ltd and so on. Other materials and solvents used for perovskite solar cell fabrication were purchased from TCI and Sigma-Aldrich.

2. Synthetic scheme

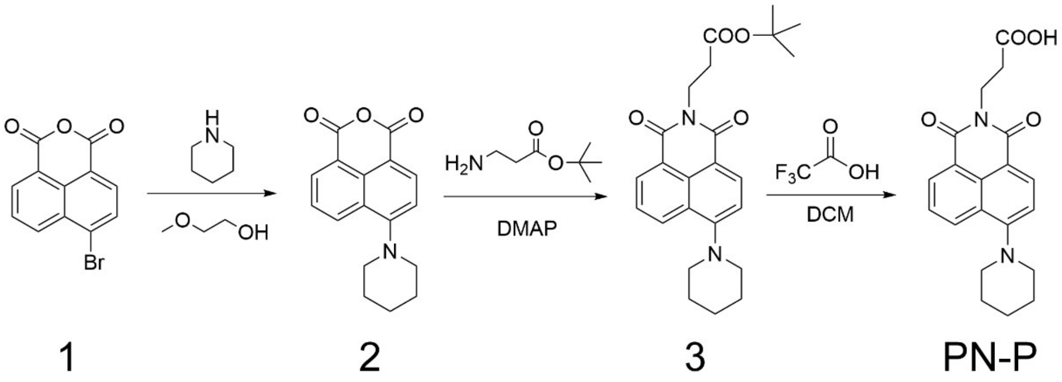


Figure S1. Synthetic route to compound **PN-P**.

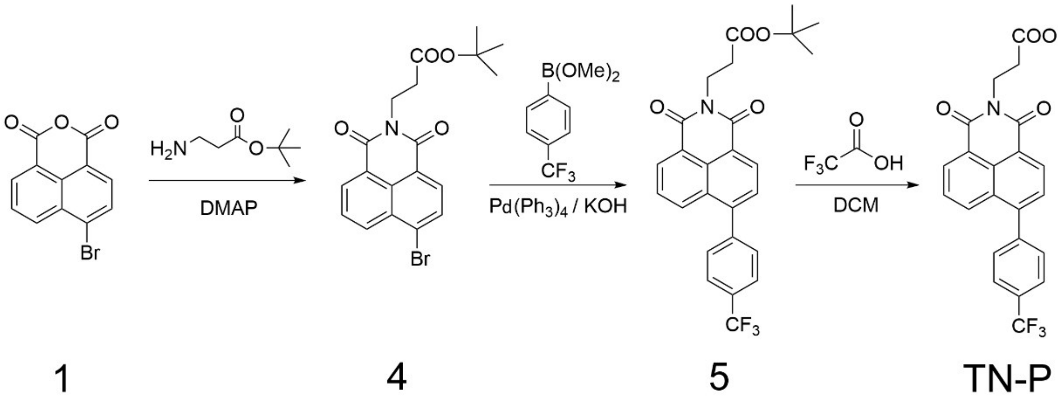
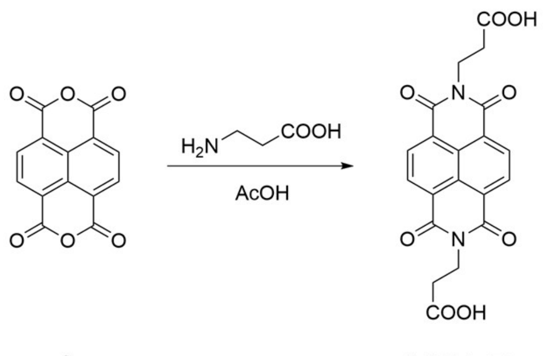


Figure S2. Synthetic route to compound **TN-P**.



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NDI-P

Figure S3. Synthetic route to compound **NDI-P**.

3. Synthesis

Synthesis of intermediate 2: 4-bromo-1,8-naphthalic anhydride (compound **1**, 2.0 g, 7.22 mmol) was dissolved in 2-methoxyethanol (25 ml), and piperidine (0.95 ml, 9.64 mmol) was added subsequently. The reaction mixture was stirred and heated to reflux at 125 ℃ for 12 h under nitrogen. After cooling to room temperature, ice water (60 ml) was added into the mixture. The precipitates was obtained using buchner funnel to filter the mixture and then purified by crystallization from ethanol. This yield **2** as a brown solid (1.2 g, 60%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.58-8.56 (m, 1H), 8.51-8.48 (d, J = 8.4 Hz, 1H), 8.45-8.42 (m, 1H), 7.73-7.68 (m, 1H), 7.21-7.18 (d, J = 8.4 Hz, 1H), 3.31-3.28 (t, J = 5.2 Hz, 4H), 1.93-1.87 (m, 4H), 1.79-1.73 (m, 2H).

Synthesis of intermediate 3: Compound **2** (370 mg, 1.32 mmol), β-alanine *tert*-butyl ester hydrochloride (292 mg, 1.61 mmol) and 4-dimethylaminopyridine (DMAP, 183 mg，1.50 mmol) were dissolved in ethanol (120 ml). The reaction mixture was stirred and heated to reflux at 80 ℃ for 20 h under argon. After that, the solvent was removed under reduced pressure and the residue was purified over silica gel using dichloromethane/petroleum ether (v/v, 2:1) as the eluent to yield **3** as a yellow product (300 mg. 52%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.58-8.55 (m, 1H), 8.51-8.48 (d, J = 8.1 Hz, 1H), 8.40-8.37 (m, 1H), 7.70-7.65 (m, 1H), 7.19-7.16 (d, J = 8.1 Hz, 1H), 4.46-4.41 (t, J = 7.4 Hz, 2H), 3.25-3.21 (t, J = 5.0 Hz, 4H), 2.70-2.65 (t, J = 7.4 Hz, 2H), 1.92-1.86 (m, 4H), 1.74-1.72 (m, 2H), 1.42 (s, 9H).

Synthesis of PN-P: Compound **3** (100 mg, 0.25 mmol) was dissolved in DCM (10 ml), then trifluoroacetic acid (0.57 ml，7.65 mmol) was added dropwise into the solution. After stirred overnight at room temperature, the reaction mixture was titrated to pH ≈ 5 using 1.5 M aqueous solution of Na_2CO_3 and extracted in separating funnel with dichloromethane (50 ml). The solvent was removed under reduced pressure and the residue was purified over silica gel using dichloromethane/methanol (v/v, 20:1) as the eluent. This gave **PN-P** as a bright yellow solid (75 mg, 85%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.59-8.57 (m, 1H), 8.52-8.49 (d, J = 8.2 Hz, 1H), 8.41-8.39 (m, 1H), 7.70-7.66 (m, 1H), 7.19-7.17 (d, J = 8.2 Hz, 1H), 4.52-4.48 (t, J = 7.6 Hz, 2H), 3.26-3.22 (t, J = 4.8 Hz, 4H), 2.85-2.81 (t, J = 7.6 Hz, 2H), 1.92-1.86 (m, 4H), 1.76-1.72 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ = 175.14, 164.52, 164.02, 157.60, 132.98, 131.28, 130.94, 130.03, 126.27, 125.38, 122.83, 115.51, 114.76, 54.55, 35.68, 32.45, 26.22, 24.34. HRMS: *m/z*; $[M+H]^+$, calcd for $C_{20}H_{21}N_2O_4$: 353.1501; found: 353.1499.

Synthesis of intermediate 4: 4-bromo-1,8-naphthalic anhydride (compound **1**, 1.0 g, 3.61 mmol), β-alanine *tert*-butyl ester hydrochloride (785 mg，4.32 mmol) and DMAP (504 mg, 4.12 mmol) were dissolved in ethanol (100 ml). The reaction mixture was stirred and heated to reflux at 80 ℃ for 20 h. After cooling to room temperature, the solvent in the mixture was removed under reduced pressure. The crude product was purified by column chromatography using ethyl acetate/petroleum ether (v/v, 1:4) as the eluent, yielding **4** as a white spumescent solid (1.01g, 70%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.67-8.65 (m, 1H), 8.59-8.57 (m, 1H), 8.43-8.41 (d, J = 7.8 Hz, 1H), 8.05-8.03 (d, J = 7.8 Hz, 1H), 7.87-7.83 (m, 1H), 4.46-4.43 (t, J = 7.6 Hz, 2H), 2.70-2.66 (t, J = 7.6 Hz, 2H), 1.42 (s, 9H).

Synthesis of intermediate 5: Compound **4** (304 mg, 0.76 mmol), 4-

trifluoromethylphenylboronic acid (192 mg, 1.01 mmol), $Pd(PPh_3)_4$ (116 mg, 0.10 mmol) and 2 M aqueous solution of K_2CO_3 (4 ml, 8.00 mmol) were added into tetrahydrofuran (30 ml). Then the closed system was filled with nitrogen immediately. The reaction mixture was stirred and heated to reflux at 85 °C for 12 h before being allowed to cool to room temperature. After that, the solvent was removed by rotary evaporation, and the mixture was dried in reduced pressure. Then organics was extracted in separating funnel using dichloromethane (100 ml). The obtained crude product was further purified over silica gel using dichloromethane/petroleum ether (v/v, 1:4) as the eluent to yield a white solid (290 mg, 83.7%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 8.68-8.66 (m, 2H), 8.18-8.16 (m, 1H), 7.84-7.82 (d, J = 8.0 Hz, 2H), 7.75-7.71 (m, 2H), 7.65-7.63 (d, J = 8.0 Hz, 2H), 4.51-4.47(t, J = 7,6 Hz, 2H), 2.73-2.69 (t, J = 7.6 Hz, 2H), 1.44 (s, 9H).

Synthesis of TN-P: Compound **5** (152 mg, 0.32 mmol) was dissolved in dichloromethane (6 ml), dropping trifluoroacetic acid (1 ml, 13.46 mmol) into the mixture and sealing the system. After stirred overnight at room temperature, the solvent was removed under reduced pressure and the residue was purified over silica gel using dichloromethane /methanol (v/v, 10:1) as the eluent. This gave **TN-P** as a white solid (117 mg, 89%). ^{1}H NMR (DMSO-d_6, 400 MHz, ppm): δ = 12.40 (br.s, 1H), 8.56-8.54 (m, 2H), 8.21-8.19 (m, 1H), 7.99-7.87 (d, J = 8.0 Hz, 2H), 7.88-7.86 (m, 2H), 7.81-7.79 (d, J = 8.0 Hz, 2H), 4.31-4.27 (t, J = 7.6 Hz, 2H), 2.64-2.60 (t, J = 7.6 Hz, 2H). ^{13}C NMR (DMSO-d_6, 100 MHz, ppm): δ = 172.43, 163.23, 163.00, 144.32, 142.33, 131.86, 130.88, 130.69, 130.26, 129.05, 128.20, 127.83, 125.65, 125.62, 122.84, 122.47, 121.95, 35.77, 32,13. HRMS: *m/z*; $[M-H]^-$, calcd for $C_{22}H_{14}F_3NO_4$: 412.0797; found: 412.0793.

Synthesis of NDI-P: 1,4,5,8-naphthalenetetracarboxylic acid anhydride (compound **6**, 1.55 g, 5.81 mmol), β-alanine (1.29 g, 14.41 mmol) were added into acetic acid (40 ml). The reaction mixture was then stirred and heated at 110°C for 12 h under nitrogen. After the reaction being allowed to cool to room temperature, ice water (50 ml) was added into the mixture. The mixture was filtered and the yellow colored precipitates were obtained to be recrystallized by ethanol. This yield **NDI-P** as a faint yellow solid (2.1 g, 90%). ^{1}H NMR (DMSO-d_6, 400 MHz, ppm): δ = 12.43 (br.s, 2H), 8.63 (s, 4H), 4.28-4.24 (t, J = 7.6 Hz, 2H), 2.65-2.61 (t, J = 7.6 Hz, 2H). ^{13}C NMR (DMSO-d_6, 100 MHz, ppm): δ = 172.36, 162.42, 130.34, 126.24, 126.02, 36.04, 31.93. HRMS: *m/z*; $[M-H]^-$, calcd for $C_{20}H_{13}N_2O_8$: 409.0672; found: 409.0676.

4. Perovskite solar cells fabrication

Preparing SA-EELs: We used indium tin oxide (ITO, 20mm×15mm×1.1mm, < 10 Ω per square) as substrates, which were washed with deionized water (30 min), ethanol (30 min), acetone (30 min) and isopropanol (15 min) in sequence via ultrasonic cleaning and then treated with ultraviolet ozone for 20 min. NPI compounds (**PN-P**, **TN-P**, **NDI-P**) were dissolved in dimethyl sulfoxide/isopropanol (v/v, 1:1) to prepare solutions (1×10^{-3} M) and kept stirring at 40°C for 2 h. Then cleaned ITO substrates were immersed in compound solutions for 6 h at 40°C. Next, these substrates were rinsed with ethanol to remove residual organics and then dried in drying oven for 30 min. After that, the substrates were stored in glovebox with nitrogen-filled to be ready for the next device fabrication. To be noted, SA-EEL/ITO that would be characterized in several measurements were prepared in this processes, and the devices based on bare ITO mentioned in the paper were fabricated with cleaned ITOs that hadn't been immersed in organic solution.

Device fabrication: Firstly, lead(II) iodide (PbI_2, 1.2 M) and methylammonium iodide (MAI, 1.2 M) were dissolved in anhydrous mixed solvent DMF/DMSO (v/v, 5:1). The mixture was stirred and heated at 50°C to prepare perovskite precursor solution. Perovskite films were then deposited onto SA-EEL substrates by one step “anti-solvent” method. Then the substrates were annealed at 100°C for 15 min. By the way, $MAPbI_3$ perovskite films characterized in this work were prepared on different substrates in same procedure. After that, the hole transporting layer (HTL) were prepared from *spiro*-OMeTAD solution in chlorobenzene (65 mM) by spin-coating at 3000 rpm for 25 s. In addition, the *spiro*-OMeTAD solution was added with *tert*-butylpyridine (TBP, 330 mol%), and tris(bis(trifluoromethylsulfonyl) imide) (Li-TFSI, 50% molar ratio to HTMs) as additives. Finally, the Au electrode was formed on the top of HTL with an average thickness of 40 nm by thermally evaporated under vacuum condition (1×10^{-5} Pa) .

5. Characterization and measurements

^1H NMR spectra were recorded on a Bruker AM 400 spectrometer with tetramethylsilane (TMS) as an internal standard. The high resolution mass spectrometry (HRMS) was performed using a Waters LCT Premier XE spectrometer. X-ray diffraction measurement was carried out using a RigakuD/MAX 2550 diffract meter. The steady state photoluminescence spectra (PL) were measured with a Horiba Fluoromax-4 fluorescence spectrometer. The UV-vis absorption spectra for all measurements in this paper were recorded with a Varian Cary 100 spectrophotometer. The time-resolved photoluminescence spectra (TRPL) were determined with the single photon counting technique by means of Edinburgh FLS890 spectrometer. SEM images were obtained by using a GeminiSEM 500 field emission scanning electron microscope. KPFM measurements were performed with a scanning probe microscope system (Agilent Technologies 5500) with an environmental enclosure to control acoustic and vibration noise. All the KPFM measurements were performed on the surfaces of the thin-film samples. We used Pt/Ir-coated Silicon-SPM-Sensors (Nanosensors PPP-EFM-20). The resonance frequency was ~85 kHz, the force constant was ~5 N/m and the oscillation amplitude was 30 nm. The CPD between the tip and the sample was measured by amplitude modulation KPFM (AM-KPFM) with the operating frequency of 15 kHz and the drive-offset of -3.0 V. Photocurrent density−voltage

($J-V$) curves of devices were measured by Keithley 2400 Source meter Instruments under standard AM 1.5 simulated solar irradiation (WXS-155S-10) with using a black metal mask, with aperture area of 0.09 cm^2. The IPCE spectra were measured by Newport-74125 system (Newport Instruments). The Ultraviolet Photoelectron Spectroscopy (UPS) were measured by SCIENTA 3000.

The cyclic voltammograms were carried out by using CHI660E electrochemical workstation (Chenhua Co. Ltd, Shanghai, China). These measurements were performed in 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF$_6$) as the supporting electrolyte in dimethylsulfoxide (dried and deoxygenated). A 3-electrode system was chosen for the electrochemical study (saturated calomel reference electrode, Pt wire as counter electrode, Glass carbon as working electrode). The ferrocene/ferrocenium (Fc/Fc$^+$) redox couple was used as an external potential reference, with a scan rate of 100 mV/s. The energy of the LUMO level of compounds were calculated from the following formulation: $E_{\text{LUMO}} = -(E_{1/2(\text{red.})} + 4.8 \text{ eV})$, for *n*-type materials.

6. Experimental data

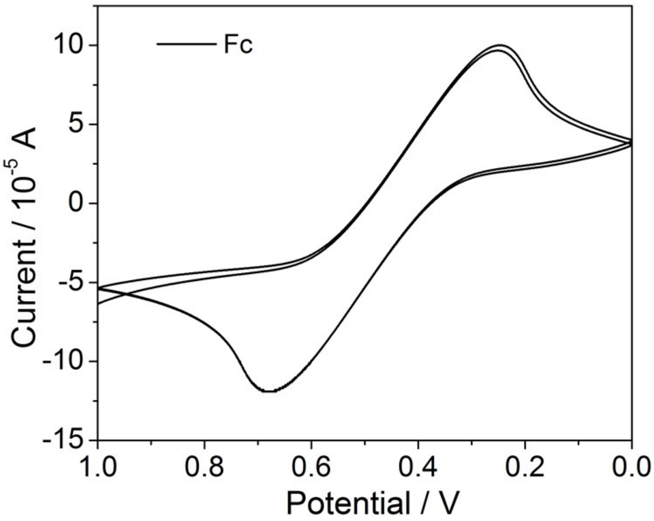


Figure S4. Cyclic Voltammograms of ferrocene as reference.

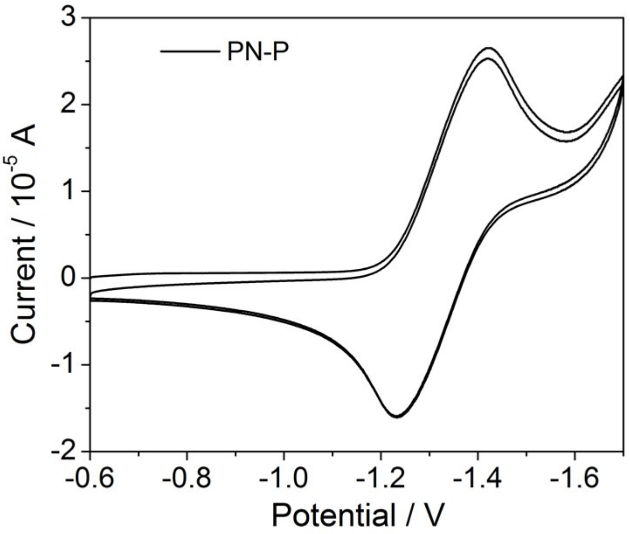


Figure S5. Cyclic Voltammograms of compound **PN-P** under repeated scan.

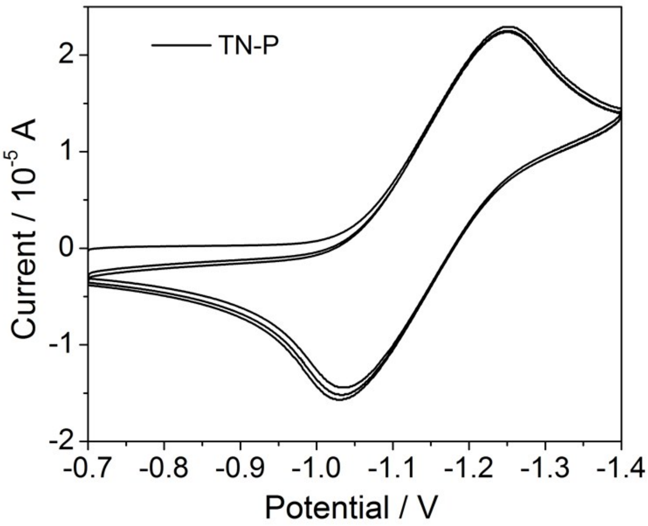


Figure S6. Cyclic Voltammograms of compound **TN-P** under repeated scan.

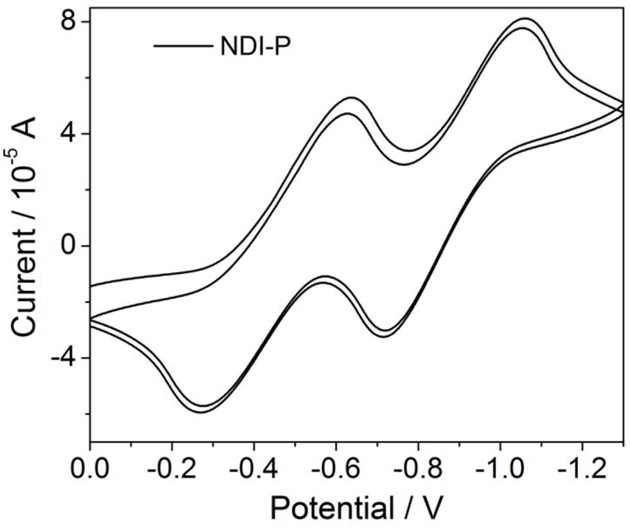


Figure S7. Cyclic Voltammograms of compound **NDI-P** under repeated scan.

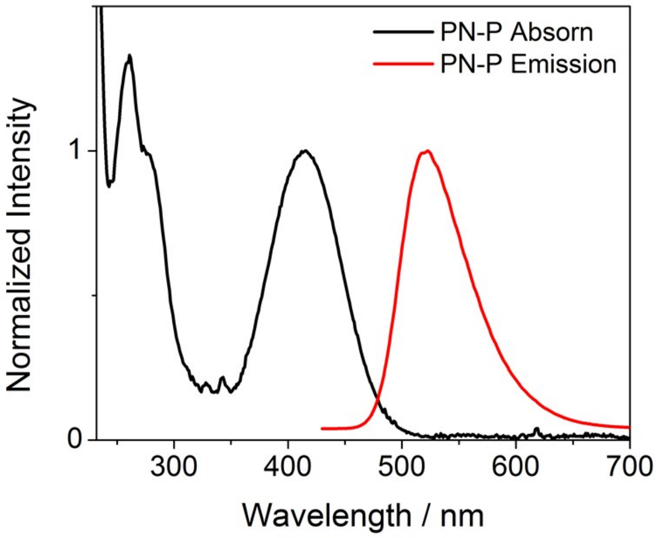


Figure S8. UV absorption and emission spectra of compound **PN-P** in DMSO.

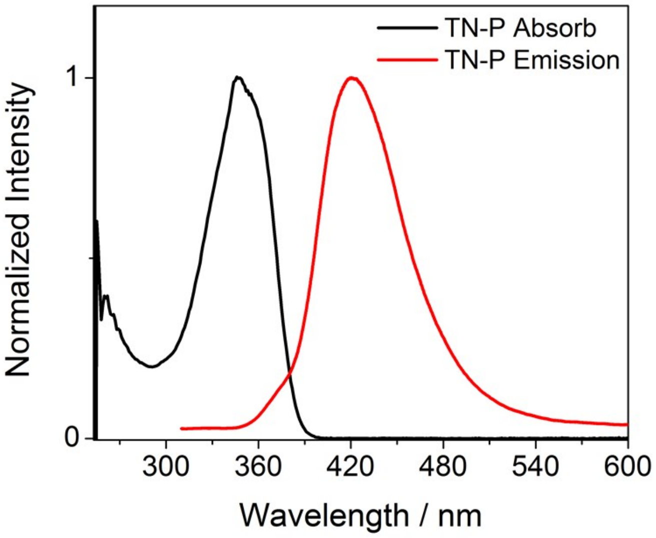


Figure S9. UV absorption and emission spectra of compound **TN-P** in DMSO.

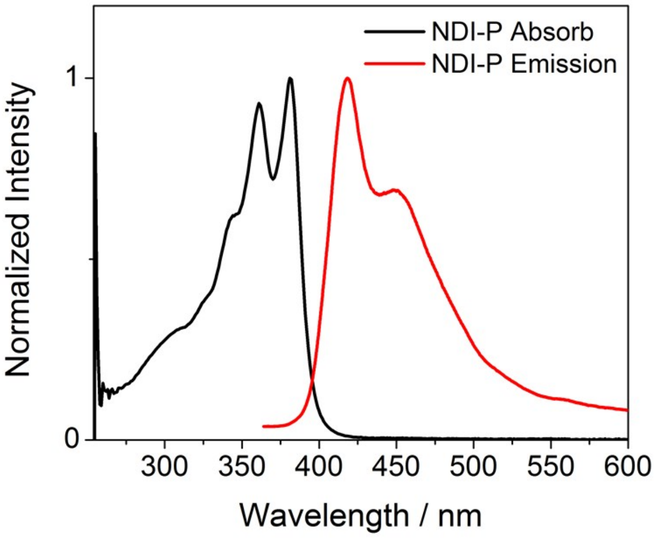


Figure S10. UV absorption and emission spectra of compound **NDI-P** in DMSO.

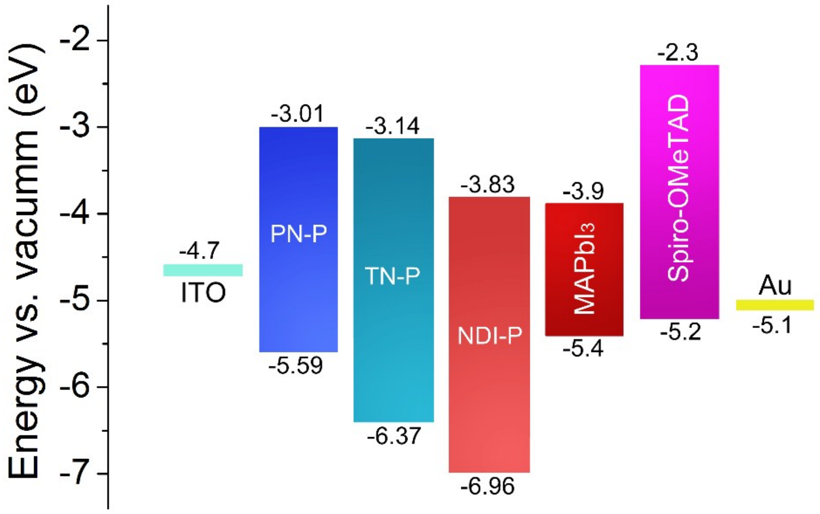


Figure S11. Energy level of different naphthalimide derivatives and other materials involved in this study.

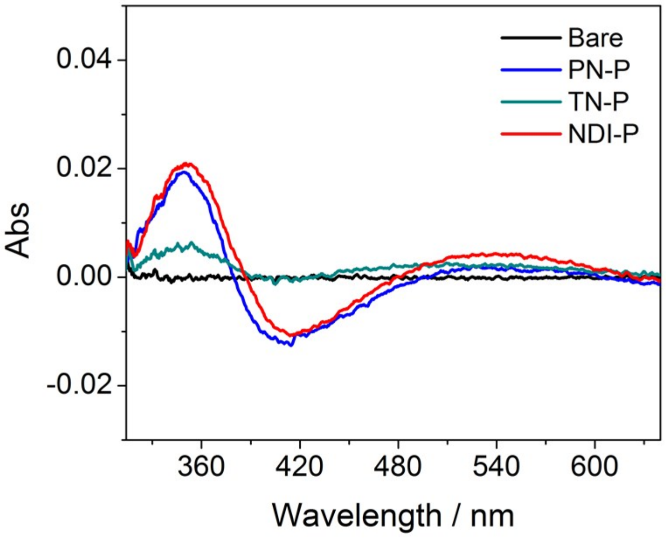


Figure S12. UV absorption spectra of ITO glasses with or without different SA-EELs.

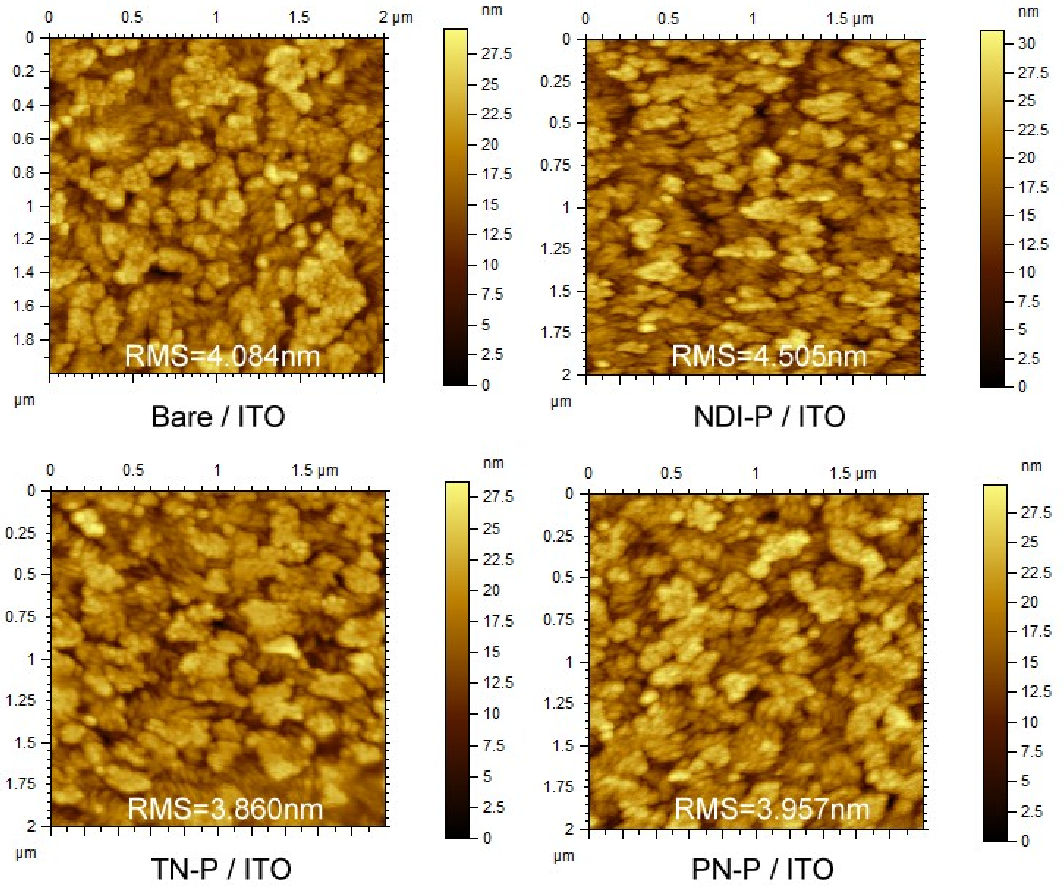


Figure S13. Topographical AFM images of ITO glasses with or without different SA-EELs. (RMS, short for root mean square (roughness), computes the standard deviation for the height distribution of a sample surface)

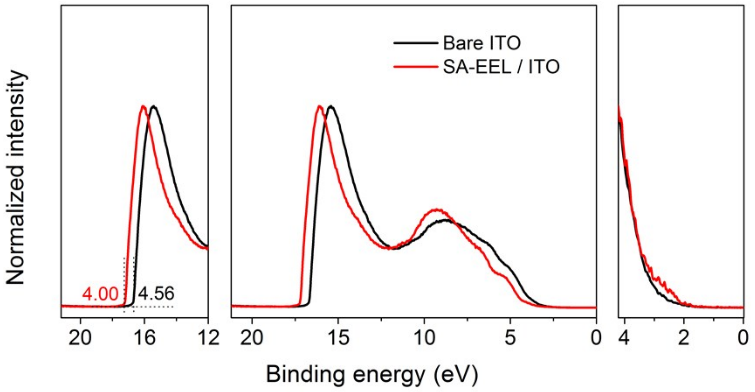


Figure S14. UPS spectra of bare ITO and SA-EEL/ITO samples. The work function of ITO reduced from -4.56 eV to -4.00 eV after surface modification with self-assembled molecular EEL.

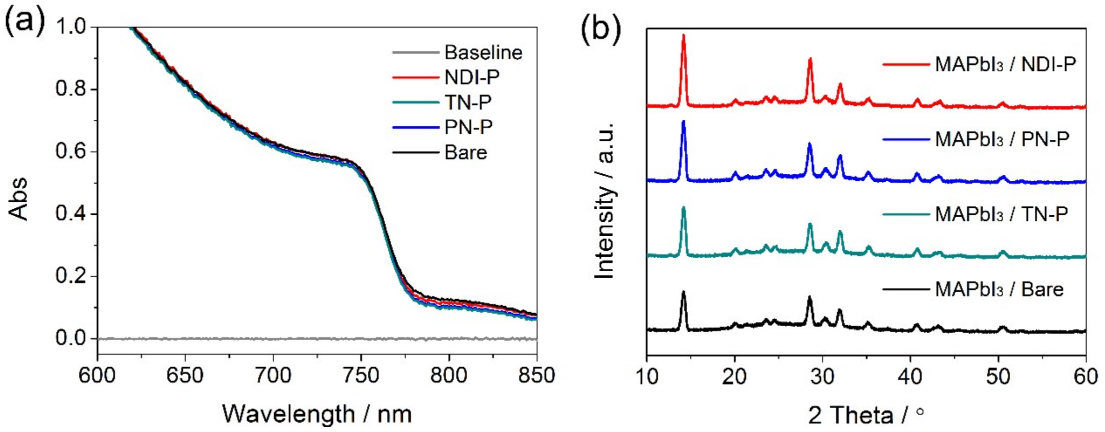


Figure S15. UV absorption spectra (a) and XRD data (b) of $MAPbI_3$ films deposited on ITO glasses with or without different SA-EELs.

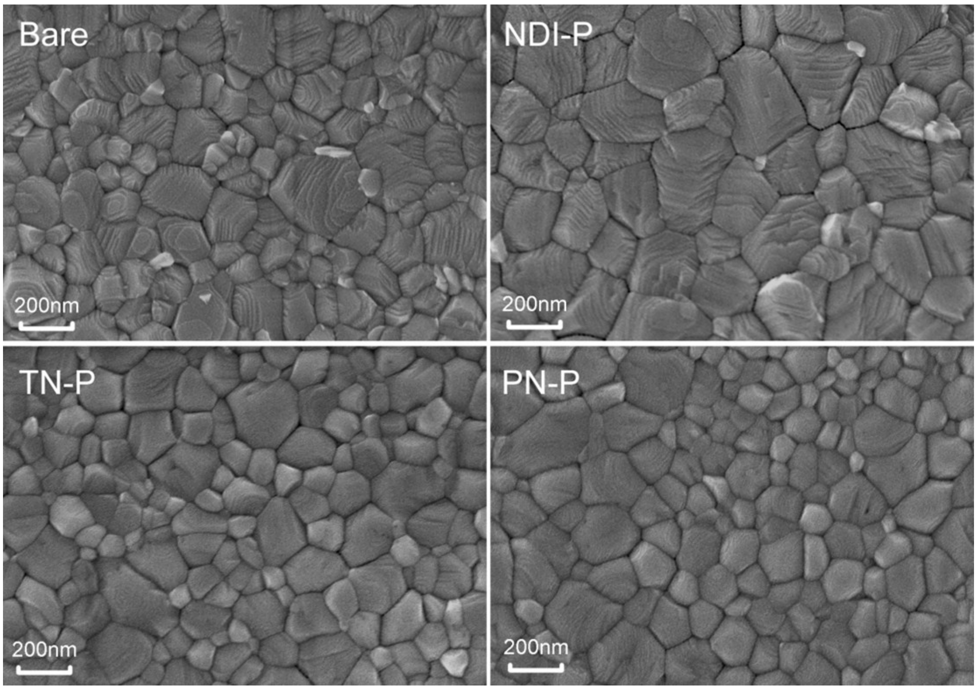


Figure S16. Top-view SEM images of $MAPbI_3$ films grown on ITO glasses with or without different SA-EELs

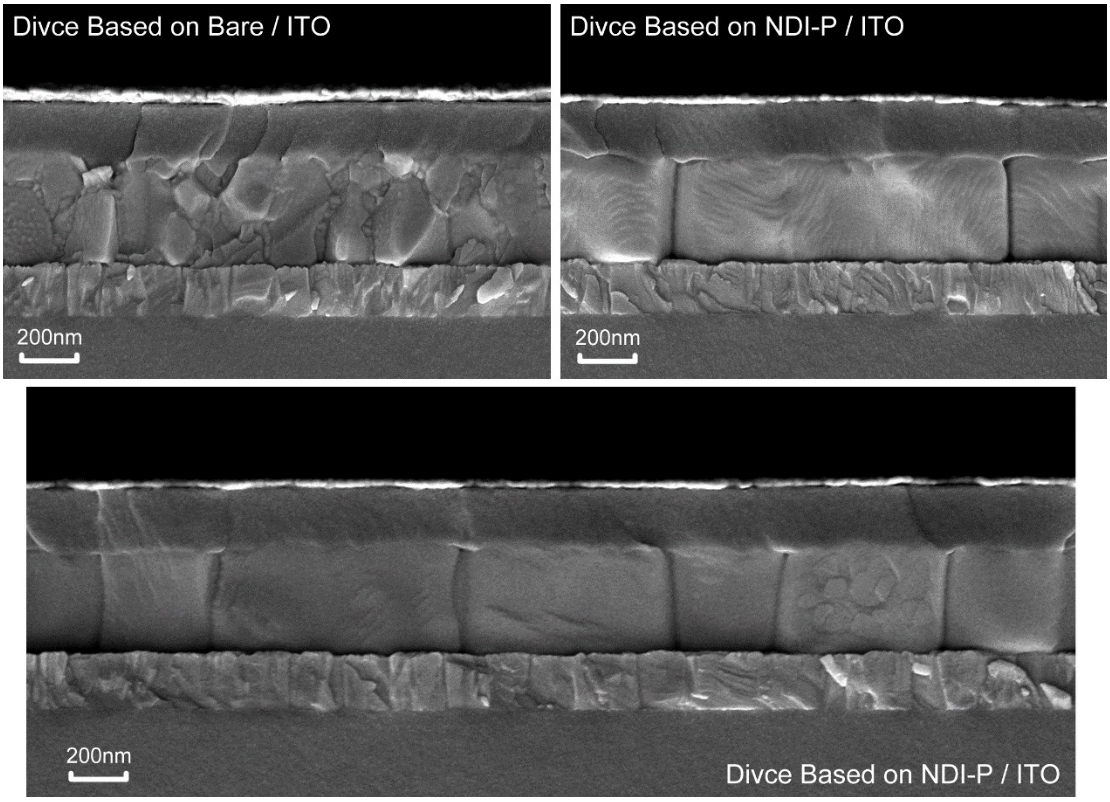


Figure S17. Cross-section SEM image of the complete device based on bare ITO and NDI-P based SA-EEL.

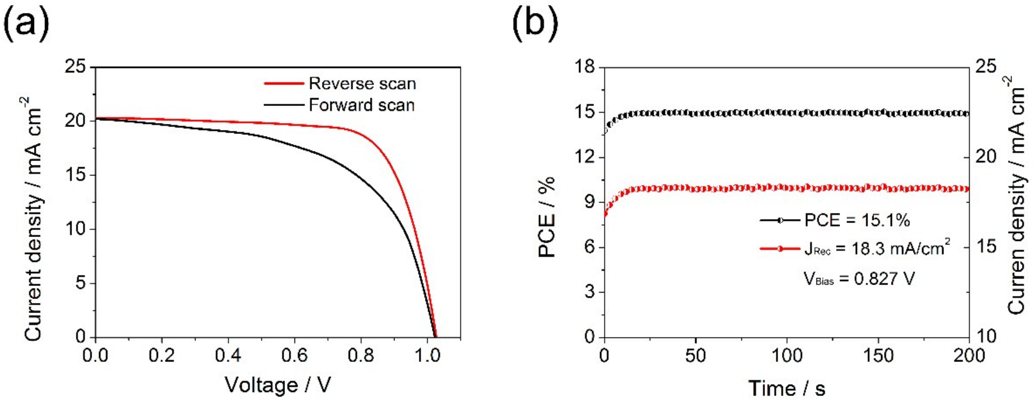


Figure S18. (a) The evaluation of hysteresis to a **NDI-P** based device. (b) The PCE tracking of a **NDI-P** based device under continuous illumination, with recording the current density at an applied bias of 0.827 V nearing to the maximum power point.

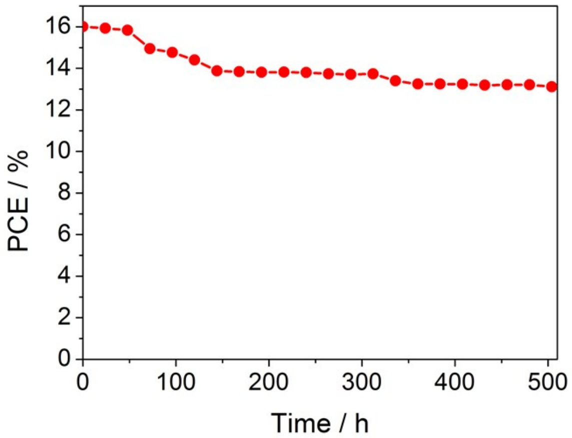


Figure S19. Stability of the un-encapsulated **NDI-P** based PSC device stored in a dry cabinet (RH = 20%, temperature at 25 ^{o}C).

Table S1. Photophysical and electrochemical properties of **PN-P**, **TN-P** and **NDI-P**.

Compound	λ_{max}[a] [nm]	λ_{em}[b] [nm]	E_g[c] [eV]	E_{LUMO}[d][eV]	E_{HOMO}[e] [eV]
PN-P	260 416	523	2.58	-3.01	-5.59
TN-P	348	419	3.23	-3.14	-6.37
NDI-P	360 381	418	3.13	-3.83	-6.96

[a] Absorption maximum in DMSO solution. [b] Peak values of emission spectra in DMSO solution. [c] E_g was calibrated from the intersection wavelength of normalized emission and absorption spectra by 1240/λ. [d] The E_{LUMO} was obtained in DMSO with ferrocene (-4.8 eV vs.vacuum) as an external reference. [e] Calculated by E_{LUMO} - E_g.

Table S2. Photovoltaic parameters of typical $MAPbI_3$ PSCs (0.09 cm^2) with or without different SA-EELs in reverse scan (Fig. 4a).

PSCs	J_{sc} [mA cm^{-2}]	V_{oc} [V]	FF [%]	PCE [%]	R_s [Ω]	R_{sh} [Ω]
Bare	8.45	0.32	36.65	0.91	118.43	666.88
PN-P	10.23	0.76	69.68	5.45	11.40	4401.56
TN-P	10.93	0.94	52.94	5.41	157.74	2506.36
NDI-P	20.57	1.05	73.98	16.01	15.70	7840.23

Table S3. Time-resolved PL decay fitting parameters.

Sample	A_1 (%)	Life time τ_1 (ns)	A_2 (%)	Life time τ_2 (ns)	A_3 (%)	Life time τ_3 (ns)
Perovskite/ITO	5.39	2.28	94.61	48.12	/	/
Pero/**PN-P**/ITO	0.47	3.24	11.42	40.05	56.72	29.72
Pero/**TN-P**/ITO	0.52	2.83	43.00	97.17	/	/
Pero/**NDI-P**/ITO	1.40	13.33	21.02	86.67	/	/

7. ^{1}H-NMR, ^{13}C-NMR and HRMS of synthesized compounds

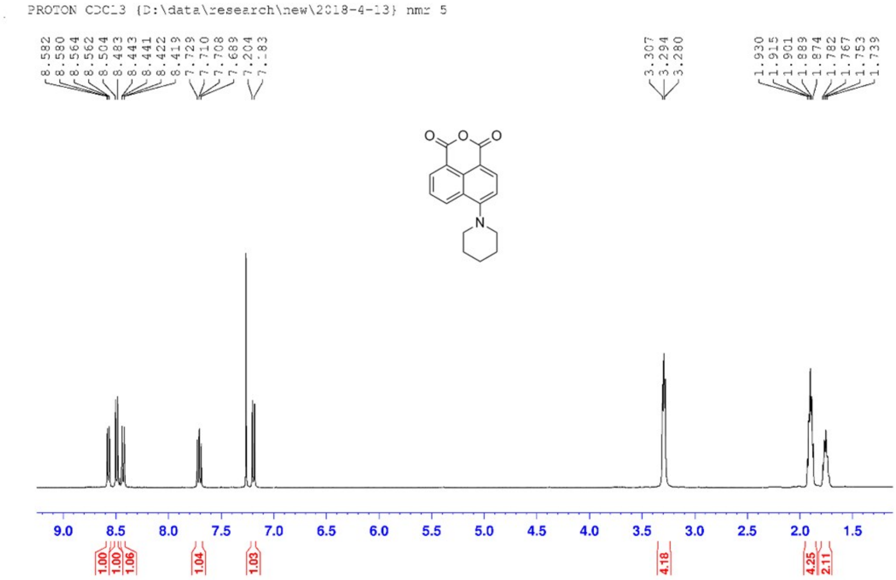


Figure S20. ^{1}H-NMR spectrum of **2** in CDCl$_3$.

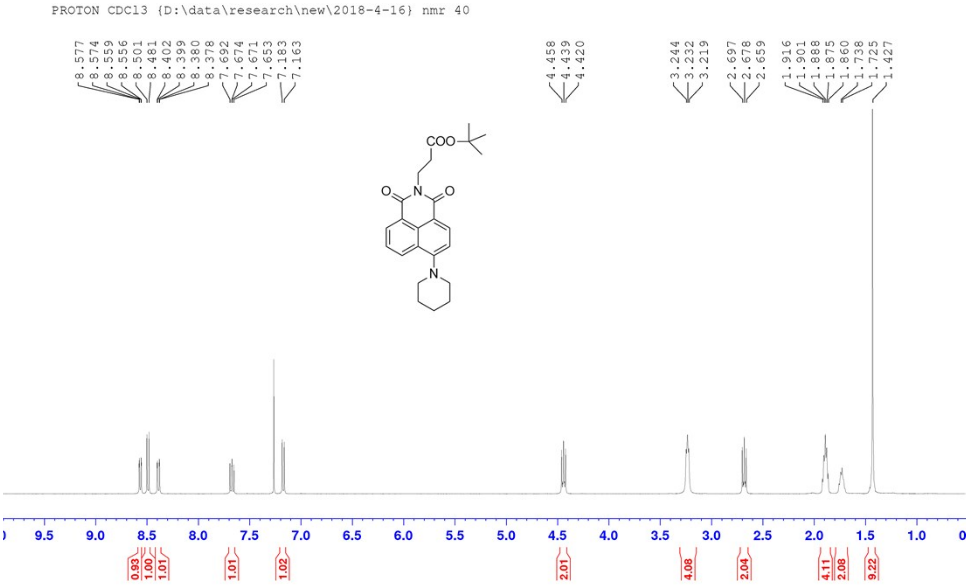


Figure S21. ^{1}H-NMR spectrum of **3** in CDCl$_3$.

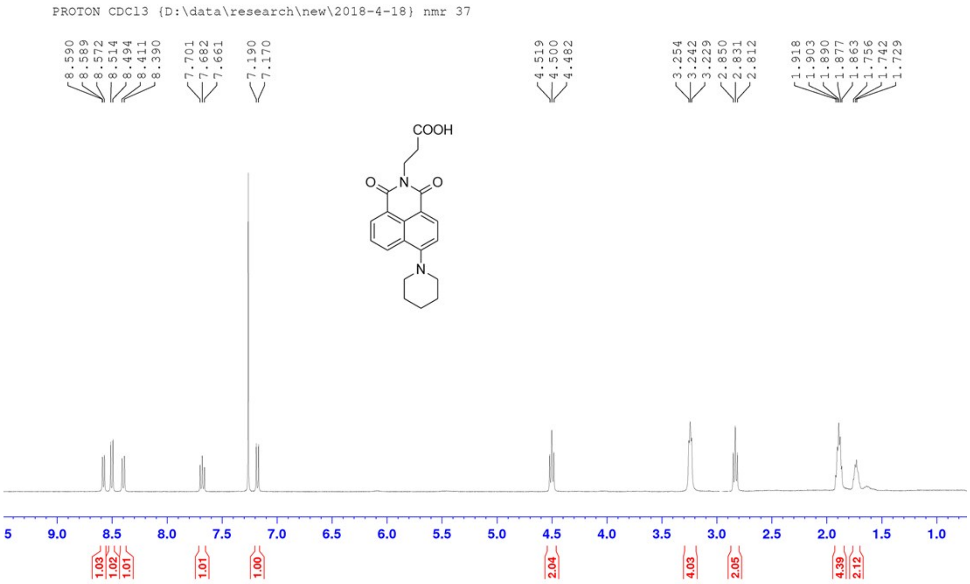


Figure S22. ^{1}H-NMR spectrum of **PN-P** in $CDCl_3$.

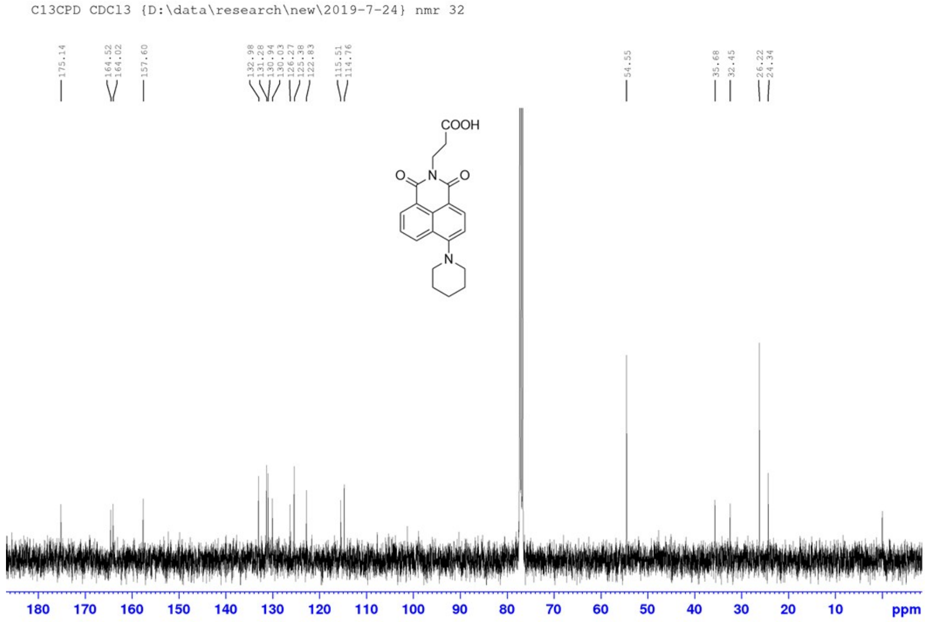


Figure S23. ^{13}C-NMR spectrum of **PN-P** in $CDCl_3$.

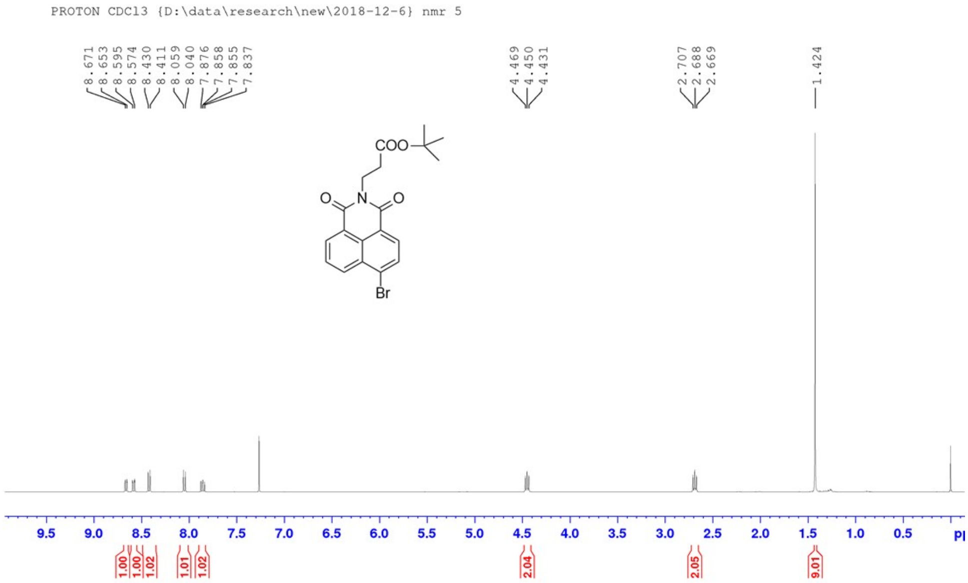


Figure S24. ^{1}H-NMR spectrum of **4** in $CDCl_3$.

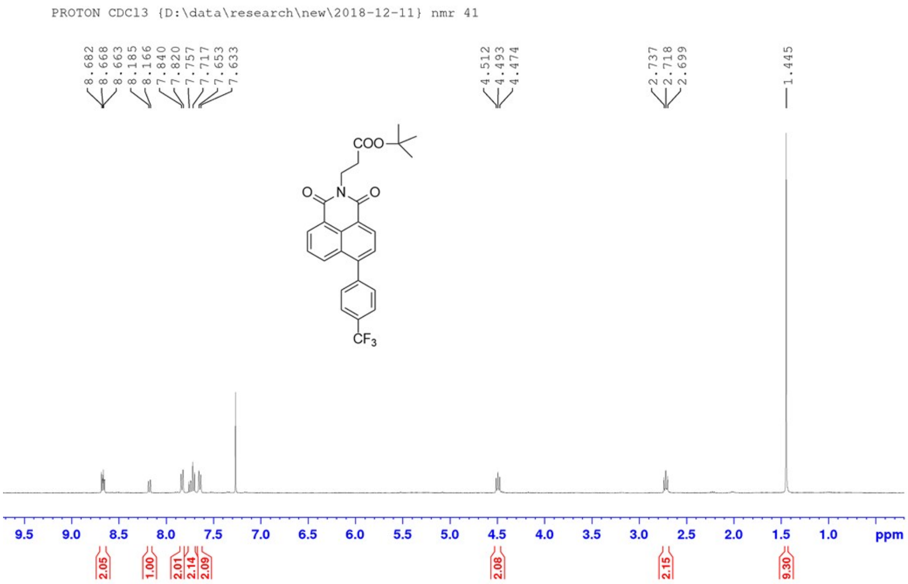


Figure S25. ^{1}H-NMR spectrum of **5** in $CDCl_3$.

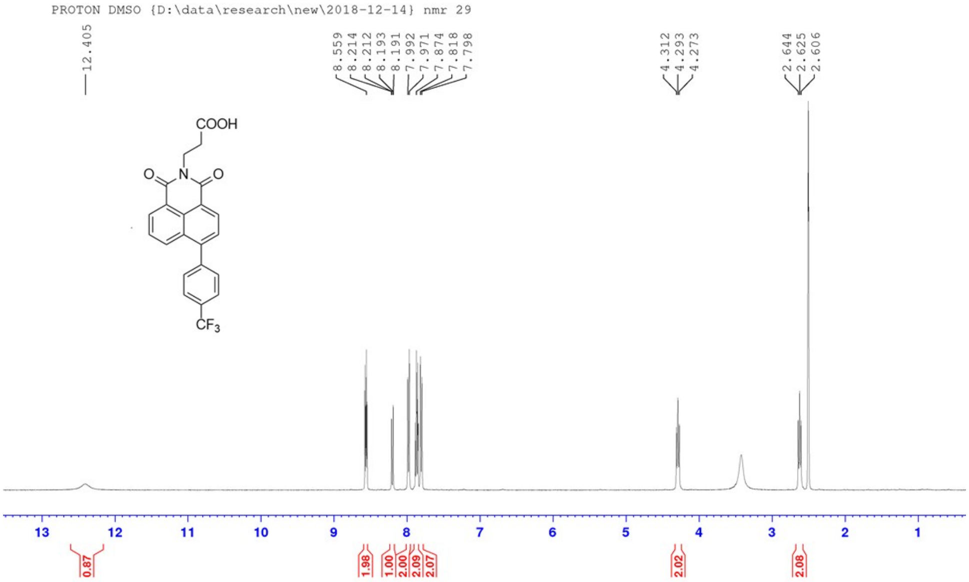


Figure S26. ^{1}H-NMR spectrum of **TN-P** in DMSO-d_6.

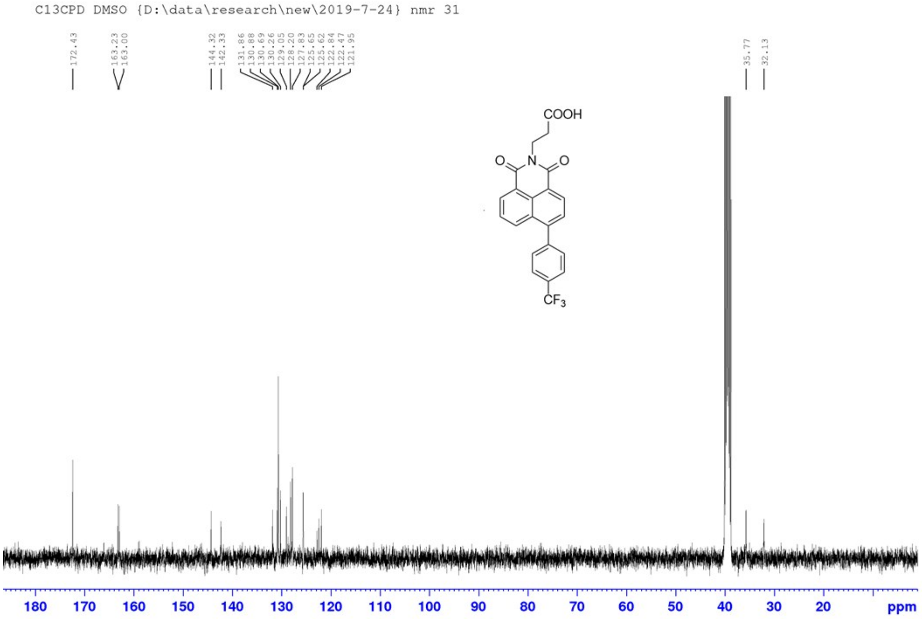


Figure S27. ^{13}C-NMR spectrum of **TN-P** in DMSO-d_6.

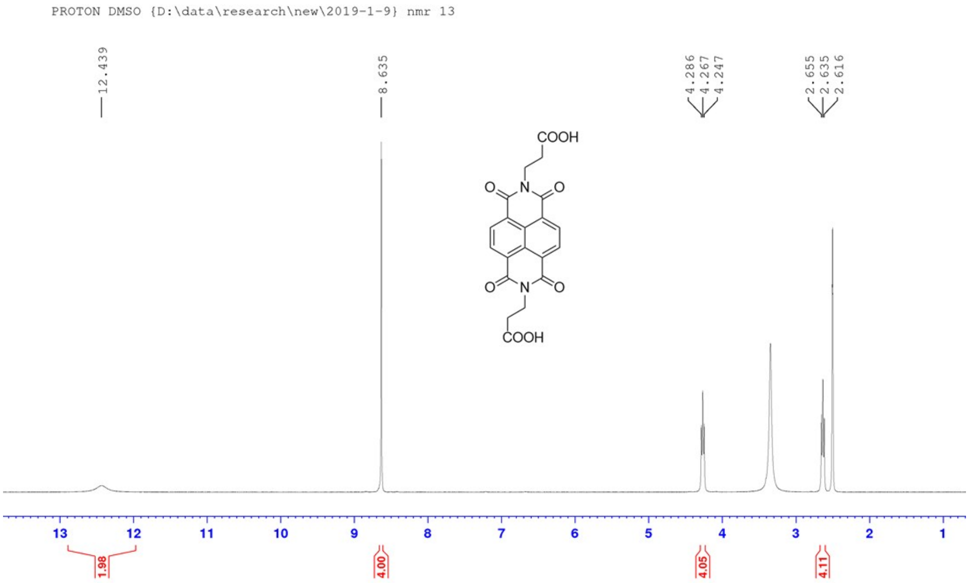


Figure S28. ^{1}H-NMR spectrum of **NDI-P** in DMSO-d_6.

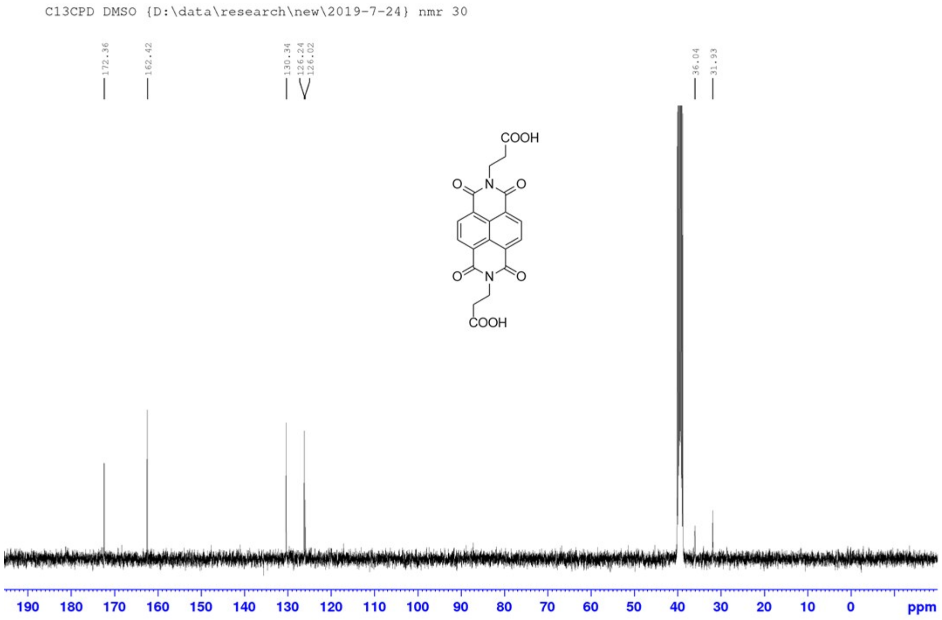
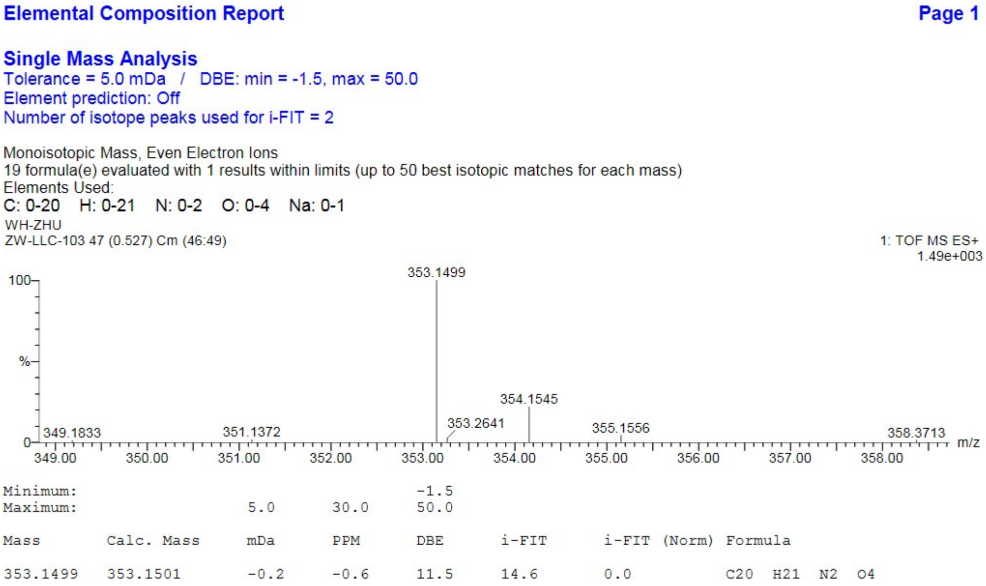


Figure S29. ^{13}C-NMR spectrum of **NDI-P** in DMSO-d_6.



Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

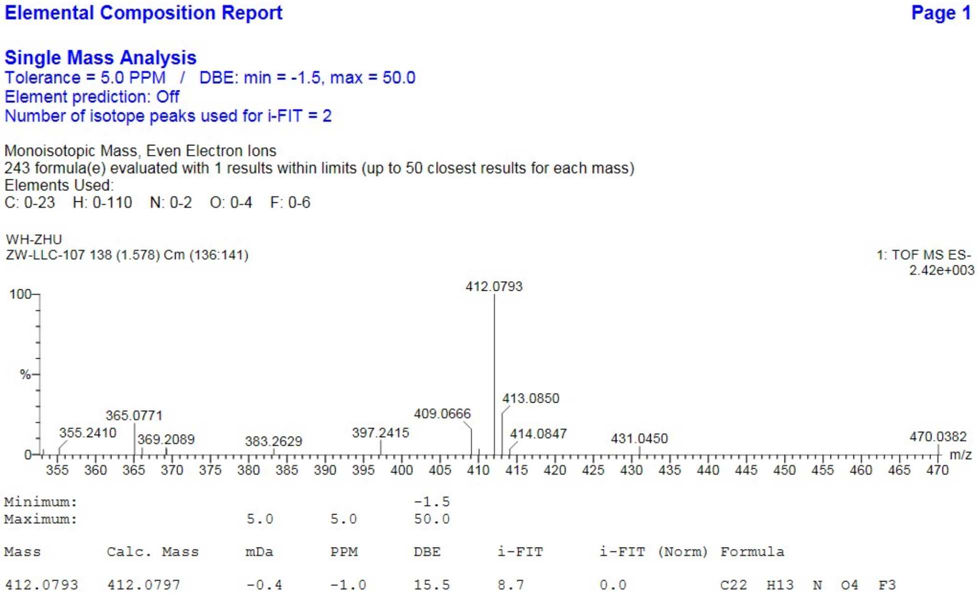
Monoisotopic Mass, Even Electron Ions
19 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-20 H: 0-21 N: 0-2 O: 0-4 Na: 0-1
WH-ZHU
ZW-LLC-103 47 (0.527) Cm (46:49)

```
Minimum:                                  -1.5
Maximum:                5.0       30.0    50.0

Mass       Calc. Mass   mDa       PPM     DBE      i-FIT     i-FIT (Norm) Formula

353.1499   353.1501     -0.2      -0.6    11.5     14.6      0.0          C20  H21  N2  O4
```

Figure S30. High resolution mass spectrometry of compound **PN-P**.



Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
243 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-23 H: 0-110 N: 0-2 O: 0-4 F: 0-6

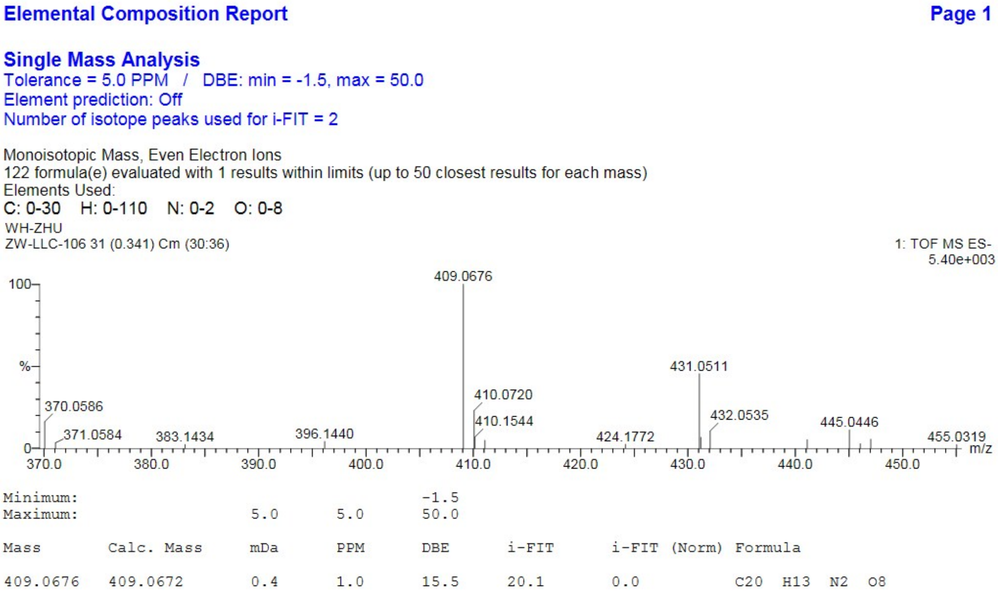
WH-ZHU
ZW-LLC-107 138 (1.578) Cm (136:141)

```
Minimum:                                  -1.5
Maximum:                5.0       5.0     50.0

Mass       Calc. Mass   mDa       PPM     DBE      i-FIT     i-FIT (Norm) Formula

412.0793   412.0797     -0.4      -1.0    15.5     8.7       0.0          C22  H13  N  O4  F3
```

Figure S31. High resolution mass spectrometry of compound **TN-P**.



Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
122 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-30 H: 0-110 N: 0-2 O: 0-8
WH-ZHU
ZW-LLC-106 31 (0.341) Cm (30:36)

```
Minimum:                                     -1.5
Maximum:                      5.0      5.0    50.0

Mass       Calc. Mass    mDa      PPM      DBE      i-FIT      i-FIT (Norm) Formula

409.0676   409.0672      0.4      1.0      15.5     20.1       0.0          C20  H13  N2  O8
```

Figure S32. High resolution mass spectrometry of compound **NDI-P**.