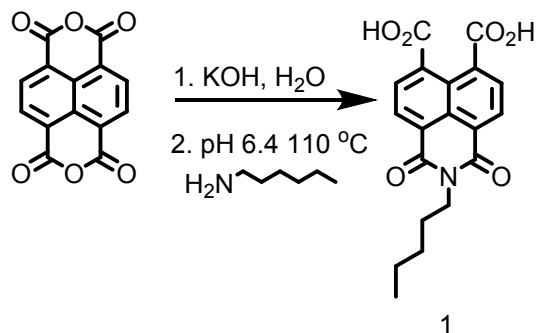


ESI for:

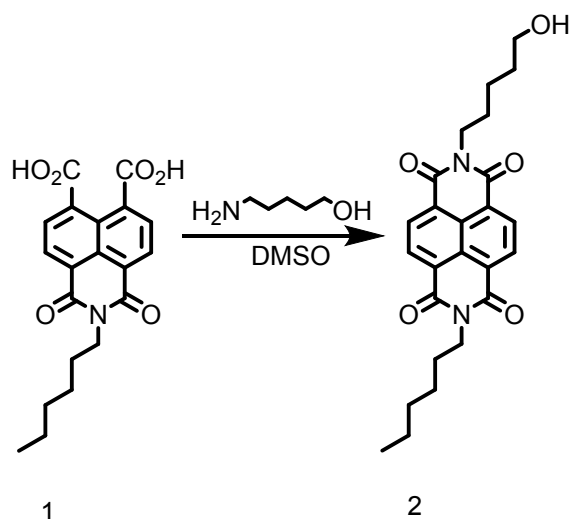
A Naphthalene Diimide Side-Chain Polymer as an Electron-Extraction Layer for Stable Perovskite Solar Cells

Khaled Al Kurdi, Declan McCarthy, David P. McMeekin, Sebastian O. Furer, Marie-Hélène Tremblay, Stephen Barlow, Udo Bach and Seth R. Marder

## Synthetic Details



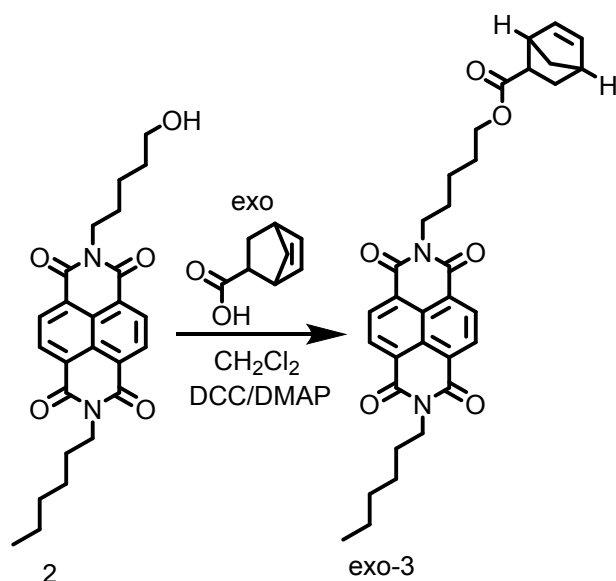
*N*-Hexyl-naphthalene-1,8-dicarbonyl-4,5-dicarboxylic acid (**1**) was synthesized according to a literature procedure.<sup>1</sup> The compound was isolated in 80% yield (4.8 g). Characterization by <sup>1</sup>H-NMR was consistent with the literature. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 13.58 (s, 2H), 8.55 (d, *J* = 7.6 Hz, 2H), 8.18 (d, *J* = 7.5 Hz, 2H), 4.03 (dd, *J* = 8.4, 6.6 Hz, 2H), 1.64 (p, *J* = 7.4 Hz, 2H), 1.38 – 1.28 (m, 2H), 1.32 – 1.26 (m, 2H), 0.86 (t, *J* = 7.2 Hz, 3H).



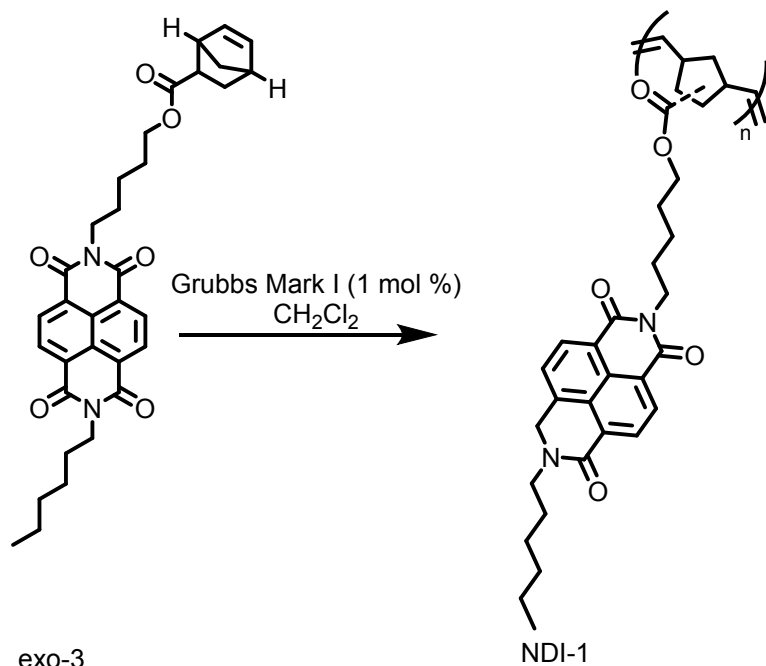
Compound **1** (1.00 g, 2.18 mmol) was weighed into a 25 mL two-neck round-bottomed flask and flushed with nitrogen. Dry DMSO (11 mL) was added followed by 5-amino-1-pentanol (0.284 g, 0.127 mmol) dissolved in 1.0 mL of anhydrous DMSO. The reaction solution was stirred at 130 °C overnight under nitrogen atmosphere. After cooling to room temperature, the dark brown solution was diluted with CHCl<sub>3</sub> (67 mL). The organic solution was washed with water (67 mL) twice and brine (33 mL), then dried over MgSO<sub>4</sub>. After filtering and removing the solvent under reduced pressure, the crude product was subjected to flash column chromatography: eluted with CH<sub>2</sub>Cl<sub>2</sub>/ethyl acetate/MeOH 69:30:1. This yielded a spongy-white solid, *N*-hexyl-*N'*-5-

<sup>1</sup> Liang, J.; Soucie, L. N.; Blechschmidt, D. R.; Yoder, A.; Gustafson, A.; Liu, Y., Aromatic Donor-Acceptor Interaction-Based Co(III)-salen Self-Assemblies and Their Applications in Asymmetric Ring Opening of Epoxides. *Org. Lett.* **2019**, *21*, 513-518

hydroxypentyl naphthalene-1,8:4,5-tetracarboximidecboximide in moderate yield (0.8 g, 65%).  $^1\text{H}$  NMR (500 MHz, Chloroform-*d*)  $\delta$  8.74 (d,  $J$  = 1.4 Hz, 4H), 4.24 – 4.15 (m, 4H), 3.67 (t,  $J$  = 6.4 Hz, 2H), 1.84 – 1.62 (m, 6H), 1.57 – 1.27 (m, 8H), 0.89 (t,  $J$  = 7.1 Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  162.82, 162.74, 130.92, 130.87, 126.62, 126.48, 62.64, 40.95, 40.71, 32.27, 31.43, 29.64, 27.97, 27.77, 26.68, 23.22, 22.49, 14.00. HRMS (ESI)  $m/z$  calculated for  $\text{C}_{25}\text{H}_{29}\text{N}_2\text{O}_5$  ( $\text{MH}^+$ ): 437.2071, found: 437.2063. Anal. Calcd for  $\text{C}_{25}\text{H}_{28}\text{N}_2\text{O}_5$ : C, 68.79; H, 6.47; N, 6.42. Found: C, 68.74; H, 6.73; N, 6.22.



Compound (**2**) (0.99 g, 2.26 mmol) was added along with *exo*-5-norbornenecarboxylic acid (0.41 g, 2.94 mmol) to an oven-dried 50 mL two-necked round-bottomed flask equipped with a stirring bar. The flask was then fitted with a septum and purged and refilled with nitrogen 3 times. Then approximately 15 mL of dry dichloromethane were added via a cannula and the mixture was stirred until dissolved. Then, in a separate vial under inert atmosphere, *N,N'*-dicyclohexylcarbodiimide (DCC) (0.51 g, 2.48 mmol) and 4-dimethylaminopyridine (DMAP) (0.019 g, 0.16 mmol) were dissolved in 5 mL of dry dichloromethane. The resulting solution was added to the reaction mixture via a syringe. The reaction was stirred overnight under  $\text{N}_2$  and monitored by TLC. The product was purified by removing the methylene chloride under reduced pressure and then the solid was triturated with MeOH. The crude product was collected by vacuum filtration then purified by flash chromatography (5% ethyl acetate in dichloromethane as eluent) to yield compound **3** (1.1 g, 88%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.76 (s, 4H), 6.16 – 6.05 (m, 2H), 4.26 – 4.15 (m, 4H), 4.10 (t,  $J$  = 6.5 Hz, 2H), 3.01 (s, 1H), 2.89 (s, 1H), 2.20 (dd,  $J$  = 10.0, 4.4 Hz, 1H), 1.95 – 1.68 (m, 4H), 1.74 (s, 5H), 1.51 (s, 2H), 1.43 (d,  $J$  = 7.7 Hz, 2H), 1.34 (td,  $J$  = 7.2, 6.1, 4.0 Hz, 6H), 0.94 – 0.85 (m, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  162.87, 138.04, 135.75, 131.00, 130.95, 126.72, 126.55, 64.20, 46.63, 46.35, 43.18, 41.63, 40.68, 31.50, 30.32, 28.42, 28.04, 27.71, 26.75, 23.54, 22.56, 14.06. HRMS (ESI)  $m/z$  calculated for  $\text{C}_{33}\text{H}_{36}\text{N}_2\text{NaO}_6$  [ $(\text{M}+\text{Na})^+$ ]: 579.2466, found: 579.2452. Anal. Calcd for  $\text{C}_{33}\text{H}_{36}\text{N}_2\text{O}_6$ : C, 71.20; H, 6.52; N, 5.03. Found: C, 70.92; H, 6.55; N, 5.03.



Compound **3** (0.20 g, 0.36 mmol) was added to an oven-dried round-bottomed flask equipped with a stirring bar. The flask was sealed then evacuated and refilled with nitrogen three times. The solid was dissolved in anhydrous dichloromethane (8 mL) under  $\text{N}_2$ . "First generation" Grubbs initiator (18.4 mg, 0.0036 mmol) was added to a separate vial, purged and refilled with nitrogen three times, then dissolved in dichloromethane (1.0 mL). The resulting solution was added to the reaction mixture via syringe. The reaction mixture was stirred under nitrogen atmosphere for 12 h. The reaction was quenched by the addition of excess ethyl vinyl ether. The crude polymer was precipitated upon addition to stirring methanol solution. The solid was isolated by vacuum filtration. The resulting solid was dissolved in dichloromethane and precipitated in MeOH and once again isolated by vacuum filtration. The solid was then redissolved in dichloromethane and treated with a mixture of 10 mL of deionized  $\text{H}_2\text{O}$  and 10 mL of 35% by weight  $\text{H}_2\text{O}_2$ . The heterogeneous mixture was stirred for 20 min in air then moved to separatory funnel where the aqueous layer was extracted twice with dichloromethane. The organic layers were combined, dried over sodium sulfate, and the solvent was removed under reduced pressure. Polymer **NDI-1** was isolated as a faintly green-colored solid (0.147 g, 73%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.68 (s, 4H), 5.5-5.1 (m, 2H), 5, 4.16 (s, 4H), 4.08 (s, 2H), 3.0-2.45 (m, 3H), 2.0 (d, 2H), 1.73 (s, 7H), 1.44 (d, 4H), 1.35 (s, 4H), 1.19 (s, 1H), 0.91 (d,  $J = 6.9$  Hz, 3H). Anal. Calcd for  $\text{C}_{33}\text{H}_{36}\text{N}_2\text{O}_6$ : C, 71.20; H, 6.52; N, 5.03. Found: C, 69.26; H, 6.46; N, 5.03. GPC analysis in  $\text{CHCl}_3$ :  $M_n = 13.3$  kDa,  $M_w/M_n = 1.3$  DP = 23.

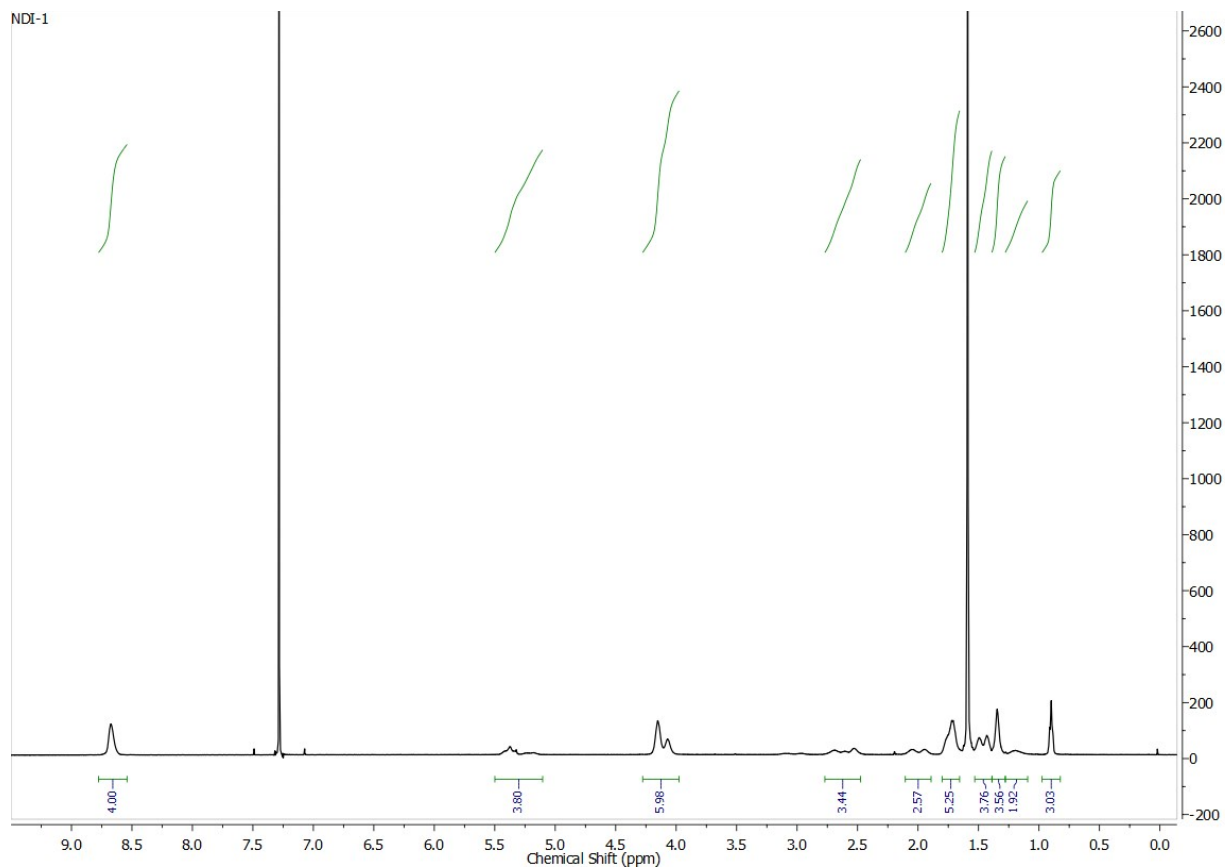


Figure S1.  $^1\text{H}$  NMR spectrum of NDI-1.

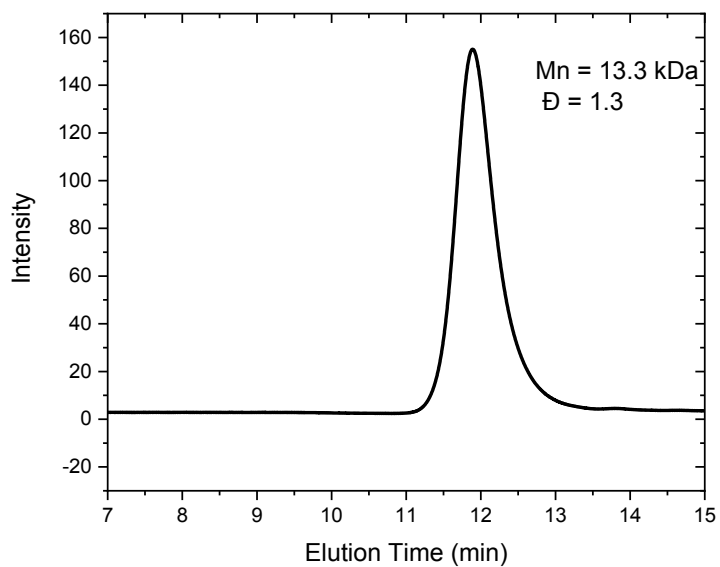


Figure S2. GPC for NDI-1.

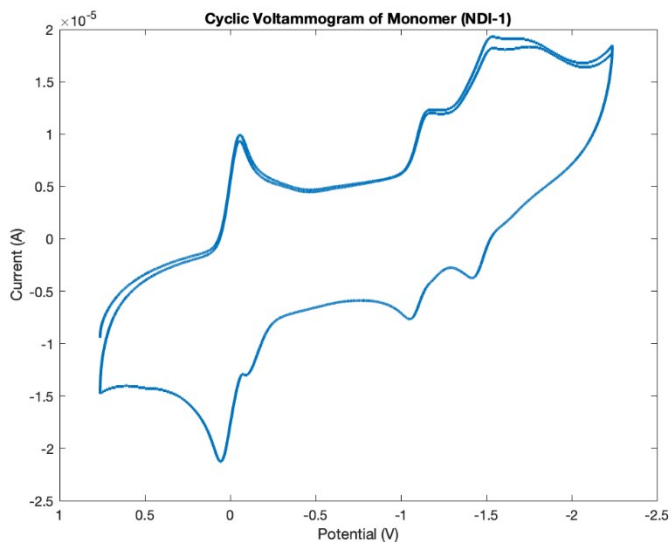


Figure S3. Cyclic Voltammogram of monomer of NDI-1 in DCM. (0.1 M  $\text{NBu}_4\text{PF}_6$  in dichloromethane, with internal  $\text{FeCp}_2$ ). The first and second half-wave potentials are seen at  $-1.11$  and  $-1.48$  V respectively vs.  $\text{FeCp}_2^{+/0}$ .

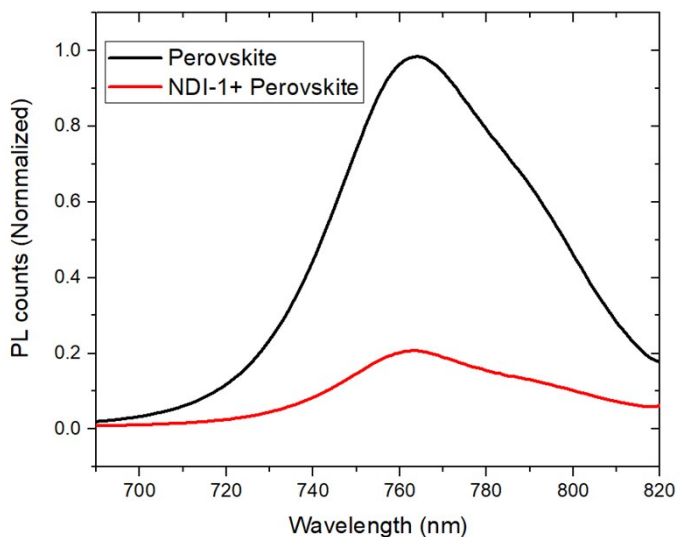


Figure S4. PL spectra of perovskite on bare glass, and perovskite on top of NDI-1

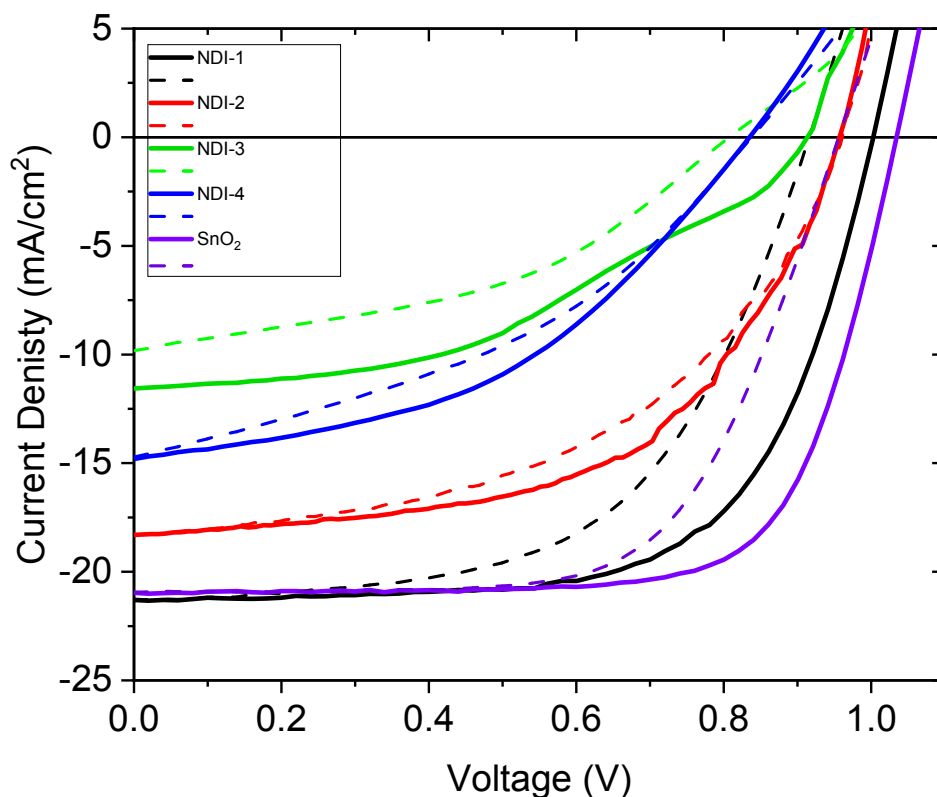


Figure S5. Forward (dashed) and reversed JV curves of champion devices with different ETMs.

Table 1. Average forward and reverse scan photovoltaic parameters.

Material		$V_{OC}$ (V)	$J_{SC}$ (mA cm <sup>-2</sup> )	Fill Factor (%)	PCE (%)
SnO <sub>2</sub>	forward	0.97 (±0.04)	20.6 (±0.3)	62 (±6)	13.0 (±1.6)
	reverse	0.99 (±0.02)	20.9 (±0.4)	73 (±1.3)	15.0 (±0.5)
NDI-1	forward	0.92 (±0.05)	20.5 (±0.2)	55 (±5)	10.7 (±2)
	reverse	0.98 (±0.02)	21.1 (±0.2)	62 (±2.1)	12.8 (±0.6)
NDI-2	forward	0.91 (± 0.06)	14.7 (± 2.9)	42 (± 8)	6.0 (± 2)
	reverse	0.94 (± 0.04)	15.2 (± 2.6)	47 (± 6)	6.7 (± 1.6)
NDI-3	forward	0.75 (± 0.03)	10.01 (± 2.0)	40 ((± 3.2)	3.0 (± 0.5)
	reverse	0.79 (± 0.06)	11.0 (± 2.0)	41 (± 3.7)	3.6 (± 0.7)
NDI-4	forward	0.74 (± 0.06)	11.1 (± 1.0)	40 (± 1.5)	3.4 (± 0.3)
	reverse	0.79 (± 0.02)	12.6 (± 1.8)	42 (± 2.4)	4.3 (± 0.9)

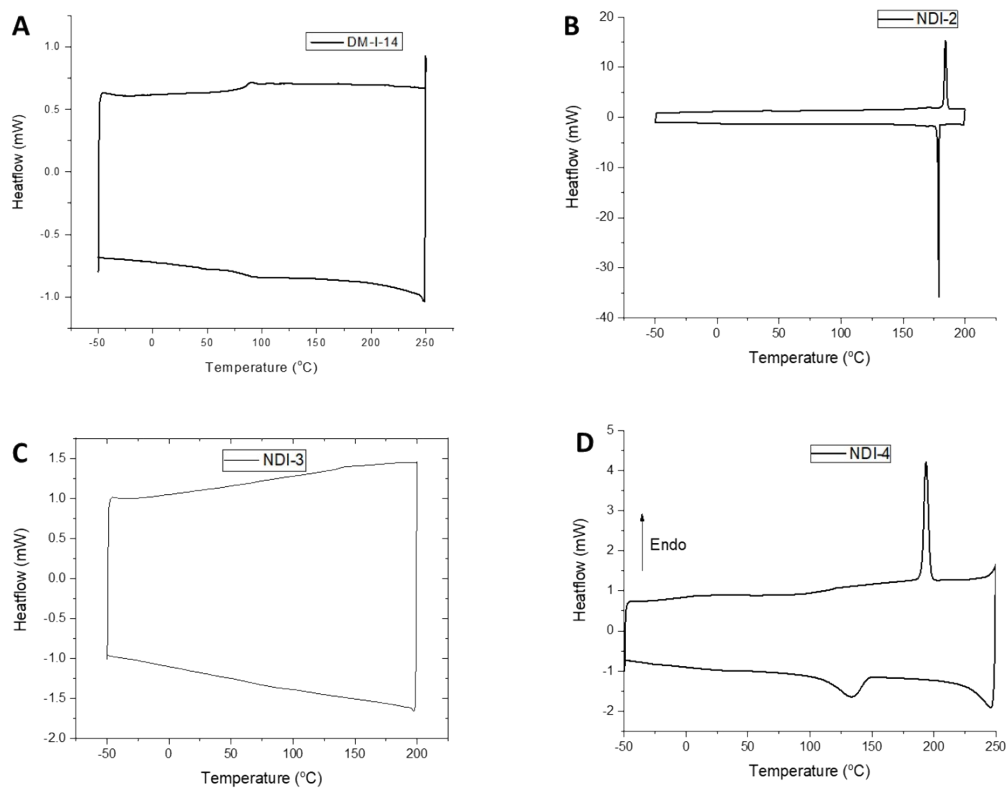


Figure S6. Second heating and cooling cycles of DSC for all NDI molecules studied.

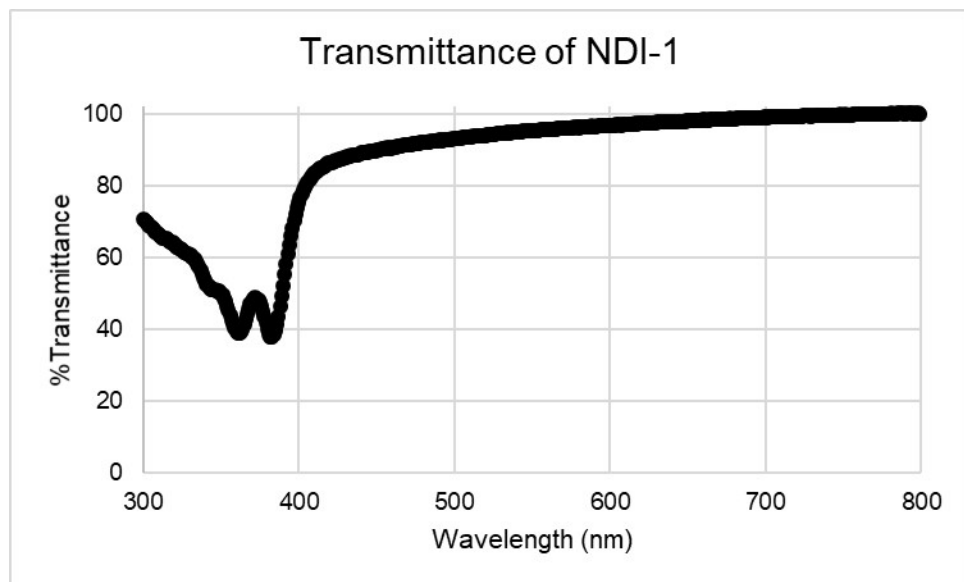


Figure S7. Transmittance of NDI-1 film (30 nm thickness).



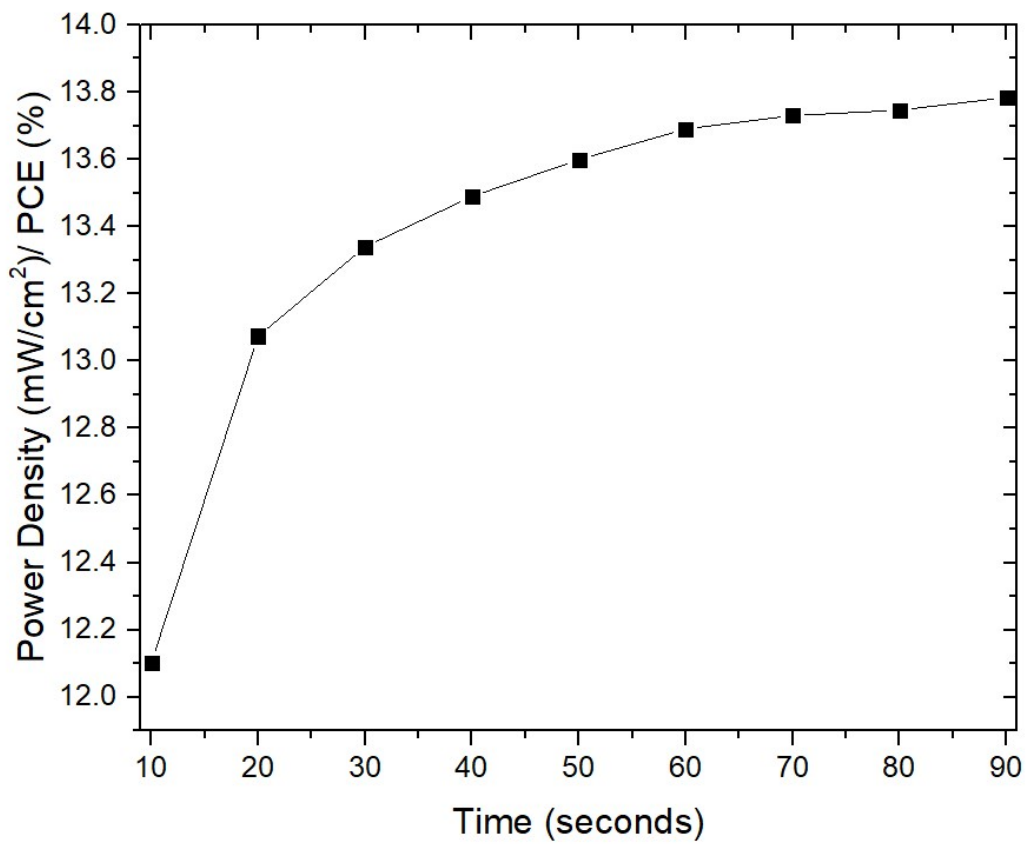


Figure S8. Evolution of MPPT vs. time for device with NDI-1 as the electron transport material.

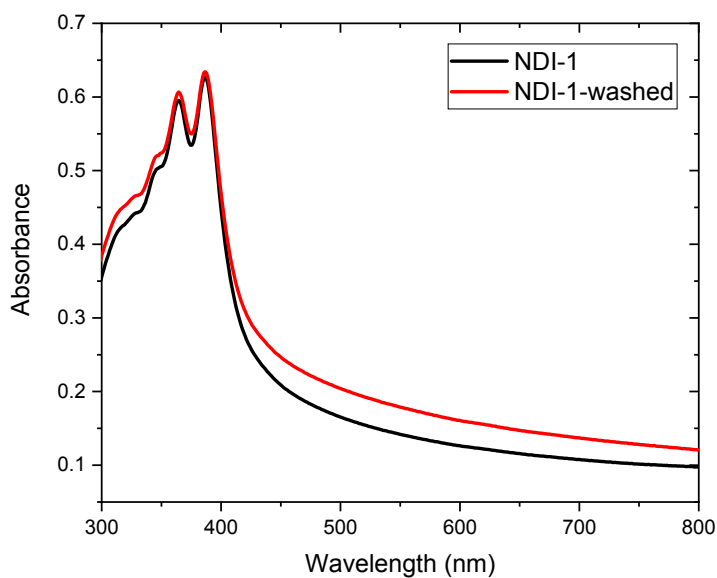


Figure S9. UV-vis of NDI-1 before and after washing with DMF. Films (1 cm<sup>2</sup>) were drop casted from toluene (5 mg/mL) then washed with DMF (~ 0.4 mL) and dried with nitrogen gas upon spinning off the DMF.

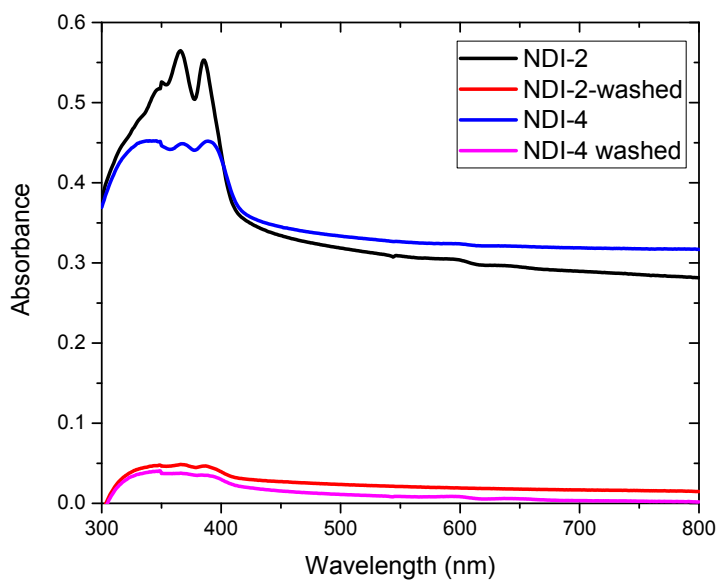


Figure S10. UV-vis of sample NDI small molecule films. Films (1 cm<sup>2</sup>) were drop casted from toluene (5 mg/mL) then washed with DMF (~ 0.4 mL) and dried with nitrogen gas upon spinning off the DMF.