Supporting Information

A novel small molecule based on Naphtho[1,2-b:5,6-b′]dithiophene benefits both fullerene and non-fullerene solar cells

Huan Li, Jin Fang, Jianqi Zhang, Ruimin Zhou, Qiong Wu, Dan Deng, Abdullah Adil Muhamman, Kun Lu, Xuefeng Guo and Zhixiang Wei

Materials and synthesis

All the solvents and common reagents were purchased from commercial resource. NDT was synthesized according to the previous work of our group and the pi-bridge 3T-CHO was acquired referring to the literatures.[1, 2] And the detailed synthetic processes of the other monomers and target small molecules were illustrated as follows.

NDTCHO

Monomer **NDT** (300 mg, 0.314 mmol) and monomer **3T-CHO** (455 mg, 0.785 mmol) were dissolved into anhydrous toluene (20 mL) in a three-neck flask. The solution was flushed with nitrogen for 20 min, and $Pd(PPh_3)_4$ (18 mg) was added into the solution quickly. Then, the solution was reacted at 110 °C for 24h under nitrogen protection. After cooling to room temperature, the toluene was removed under reduced pressure. The crude product was subsequently purified by column chromatography on silica gel (DCM/hexane = 1/1) to afford compound **3** as red solid. (357.5 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.84 (s, 2H), 7.83 (s, 2H), 7.75 (s, 2H), 7.64 (d, 2H), 7.15 (d, 2H), 7.05 (s, 2H), 6.94 (s, 2H), 6.90 (d, 2H), 2.90 (t, 4H), 2.75 (m, 8H), 1.68 (m, 10H), 1.50−1.30 (m, 56H), 1.00−0.89 (m, 24H). MALDI-TOF MS (m/z): 1626.23

NDTR

Monomer **NDTCHO** (163.6 mg, 0.1 mmol) and 3-ethylrhodanine (242 mg, 1.5 mmol) were dissolved in dry $CHCl_3$ (60 ml). After 3 drops of piperidine was added, the resulting solution was refluxed and stirred for 12 h under nitrogen. After cooling to room temperature, the reaction mixture was poured into water, and extracted several times with dichloromethane. The organic phases were combined, washed with brine, and dried over anhydrous magnesium sulfate. Then the solvent was removed under reduced pressure, and the crude product was purified by column chromatography on silica gel ($CHCl_3$) to yield NDTR as black solid (153.69 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.56 (d, 4H), 7.43 (s, 2H), 7.19 (d, 2H), 7.06 (d, 2H), 6.92 (s, 4H), 6.78 (s, 2H), 6.67 (s, 2H), 4.00 (m, 4H), 2.94 (m, 4H), 2.57 (m, 8H), 1.80 (m, 2H), 1.54−1.20 (m, 64H), 1.05−0.89 (m, 30H). MALDI-TOF MS (m/z): 1913.09

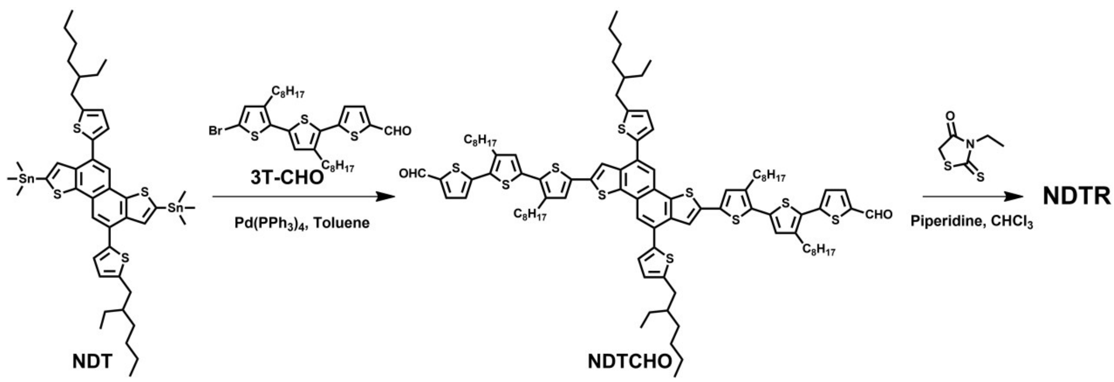

Figure S1. The synthesis route of small molecule **NDTR.**

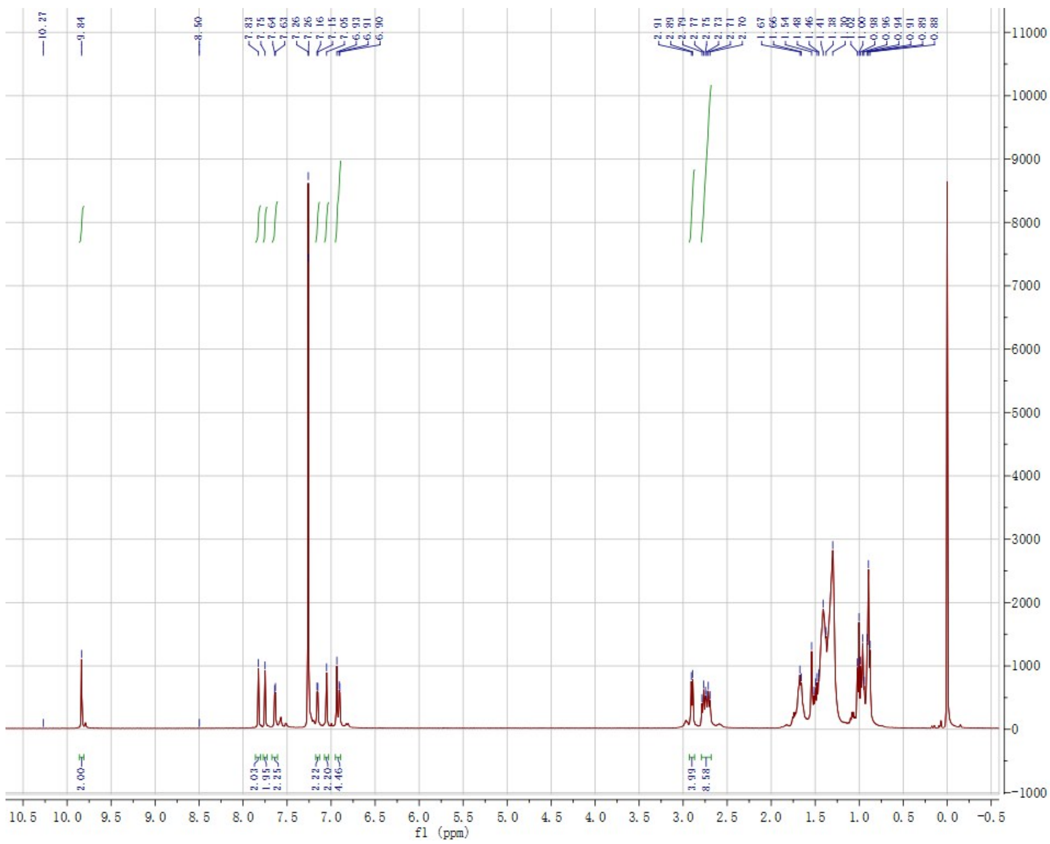

Figure S2. ^{1}H-NMR spectrum of **NDTCHO** in $CDCl_3$.

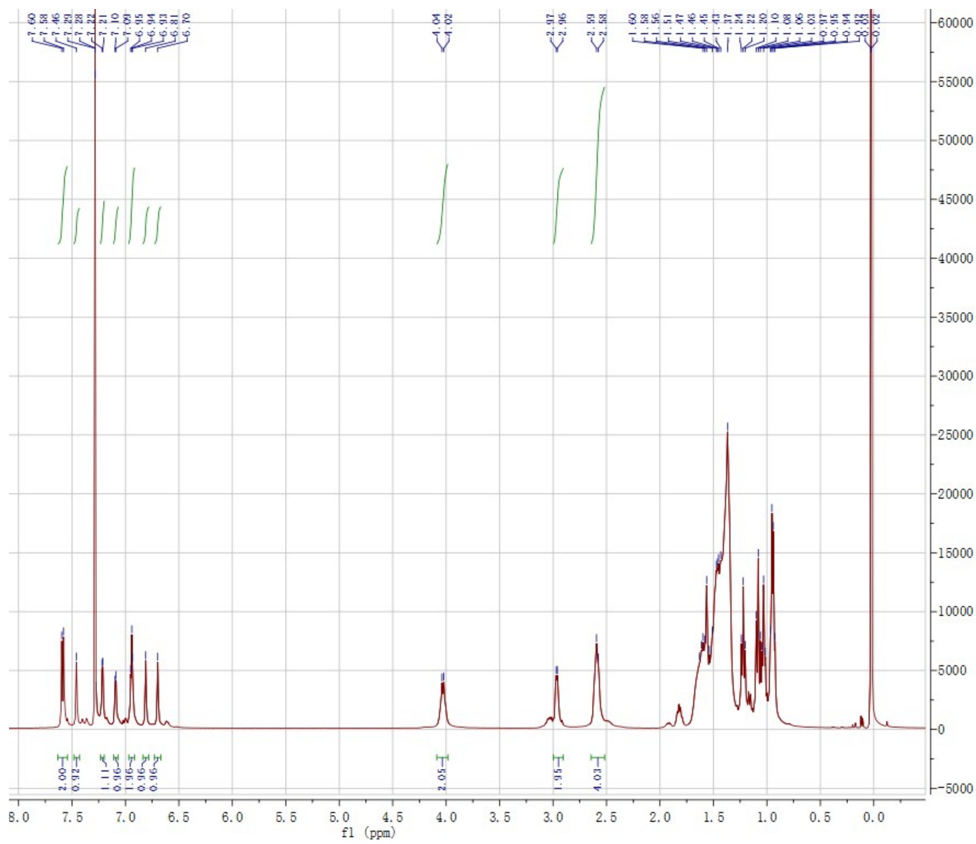

Figure S3. ^{1}H-NMR spectrum of **NDTR** in $CDCl_3$**.**

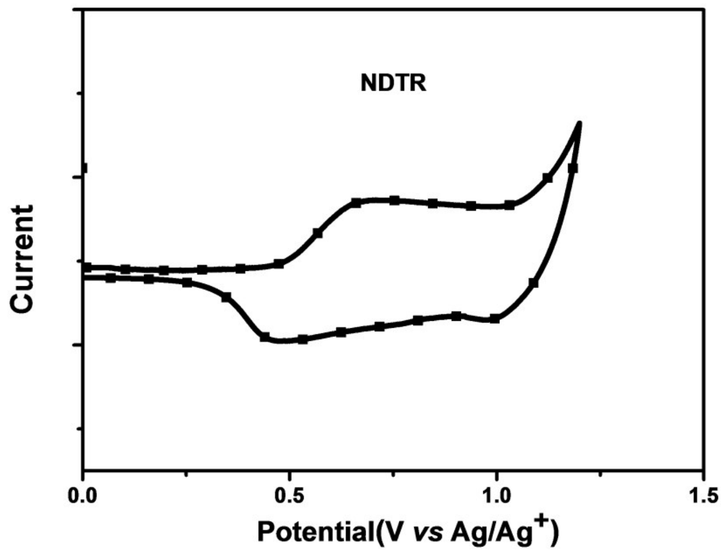

Figure S4. Electrochemical cyclic voltammetry curve of the NDTR film measured in 0.1 mol L^{-1} Bu_4NPF_6 acetonitrile solutions

Table S1. Photovoltaic performance of NDTR:$PC_{71}BM$ based conventional devices with different D:A ratios and additives.

D:A ratio	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)	Additives
1:0.4	0.89	7.51	57.73	3.86	None
1:0.6	0.90	7.23	67.29	4.36	None
1:0.6	0.88	9.32	62.52	5.13	0.5%CP
1:0.6	0.94	10.34	65.60	6.36	0.2%DPE
1:0.6	0.93	9.99	64.68	6.01	0.5%DPE
1:0.6	0.90	8.95	56.12	4.50	1%DPE
1:0.6	0.86	10.02	41.43	3.57	2%DPE
1:0.8	0.90	7.47	60.57	4.02	None
1:0.8	0.92	10.99	73.60	7.45	0.2%CP
1:0.8	0.93	11.79	70.28	7.73	0.2%CP and DPE
1:0.8	0.93	11.42	72.79	7.75	0.2%DPE
1:0.8	0.94	9.30	60.81	5.29	0.5%DPE
1:1	0.90	6.77	61.18	3.75	None
1:1.5	0.87	5.26	64.98	2.83	None
1:2	0.85	4.75	58.50	2.38	None

Table S2. Photovoltaic performance of NDTR:IDIC based conventional devices with different D:A ratios and thermal annealing temperatures.

D:A ratio	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)	TA temperature ℃
1:1	0.87	8.58	41.40	3.08	No
1:1	0.89	10.18	45.48	4.10	80
1:1	0.88	9.83	46.74	4.06	100
1:1	0.89	12.07	49.87	5.37	120
1:1.2	0.88	9.43	48.98	4.06	120
1:0.8	0.89	13.20	56.60	6.60	120
1:0.6	0.89	12.22	59.48	6.51	120

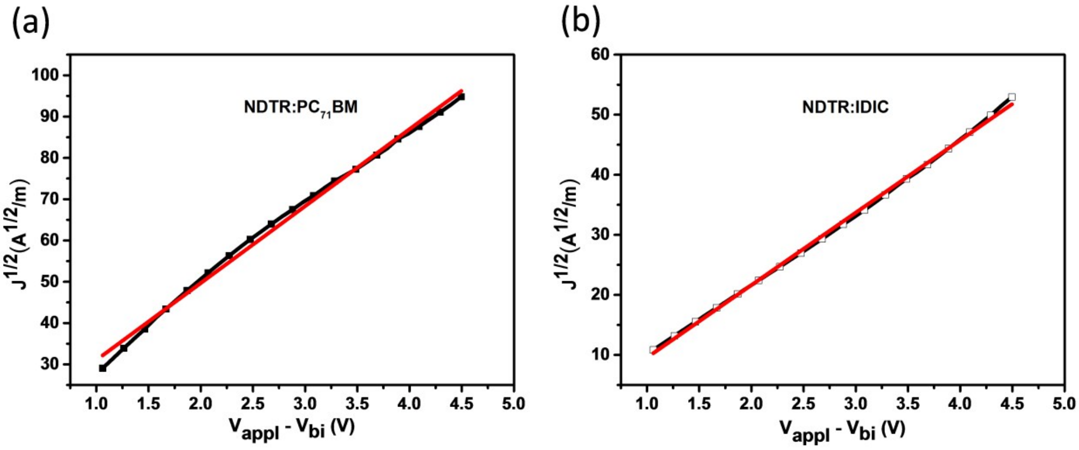

Figure S5. The corresponding $J^{1/2}$-V curves for hole-only devices composed of donor/acceptor in the dark.

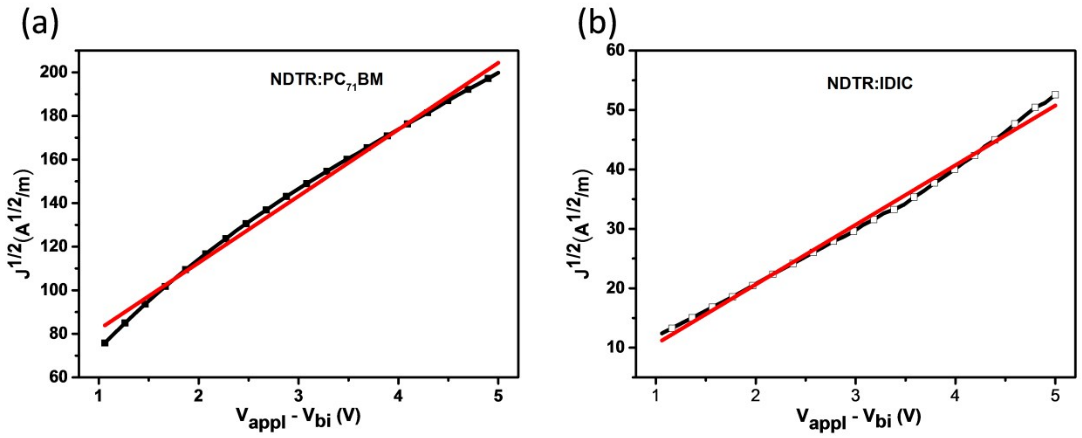

Figure S6. The corresponding $J^{1/2}$-V curves for electron-only devices composed of donor/acceptor in the dark.

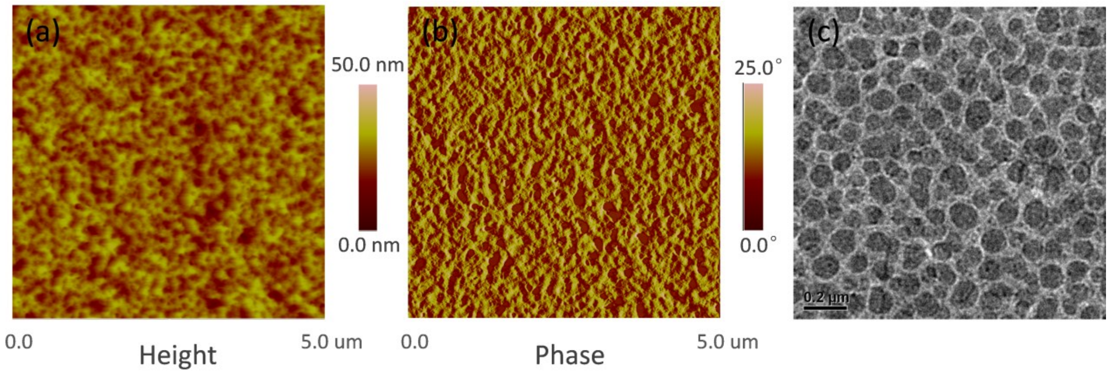

Figure S7. The AFM and TEM images of NDTR:$PC_{71}BM$ system without DPE as additive.

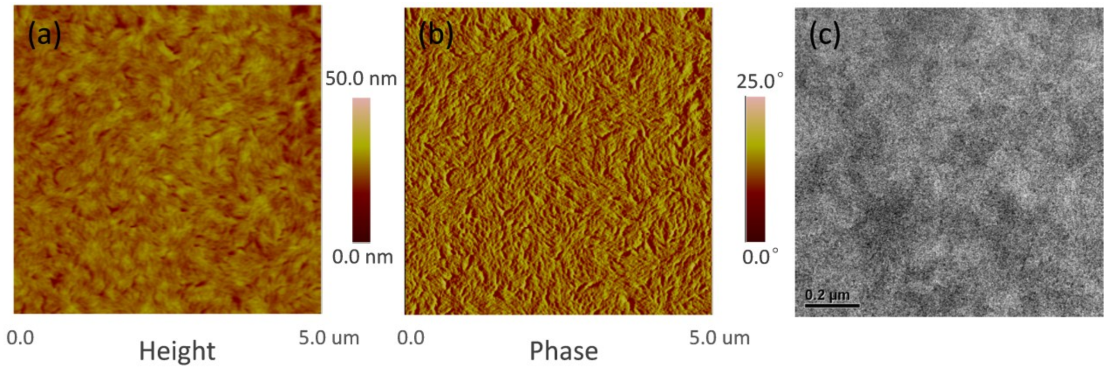

Figure S8. The AFM and TEM images of NDTR:IDIC system without thermal annealing (TA).

References

1. X. Zhu, J. Fang, K. Lu, J. Zhang, L. Zhu, Y. Zhao, Z. Shuai and Z. Wei, *Chem. Mater.*, 2014, **26**, 6947-6954.
2. R. J. Kumar, J. M. MacDonald, T. B. Singh, L. J. Waddington and A. B. Holmes, *J. Am. Chem. Soc.*, 2011, **133**, 8564-8573.