Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Highly Thermal-Stable Perylene-Bisimide Small Molecules as Efficient Electron-Transporting Materials for Perovskite Solar Cells

Weibo Yan, Zhaoxia He, Jingjing Jiang, Di Lu, Yuancai Gong, Wensheng Yang, Ruidong Xia, Wei Huang, Hao Xin*

Key Laboratory for Organic Electronics and Information Displays & Jiangsu Key Laboratory for Biosensors, Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), Nanjing University of Posts &Telecommunications, 9 Wenyuan Road, Nanjing 210023, China.

E-mail: iamhxin@njupt.edu.cn

1. Synthesis

***1.1.* The synthesis of PDI-Ph and PDI-PhCN was according to the literature.[1,2]**

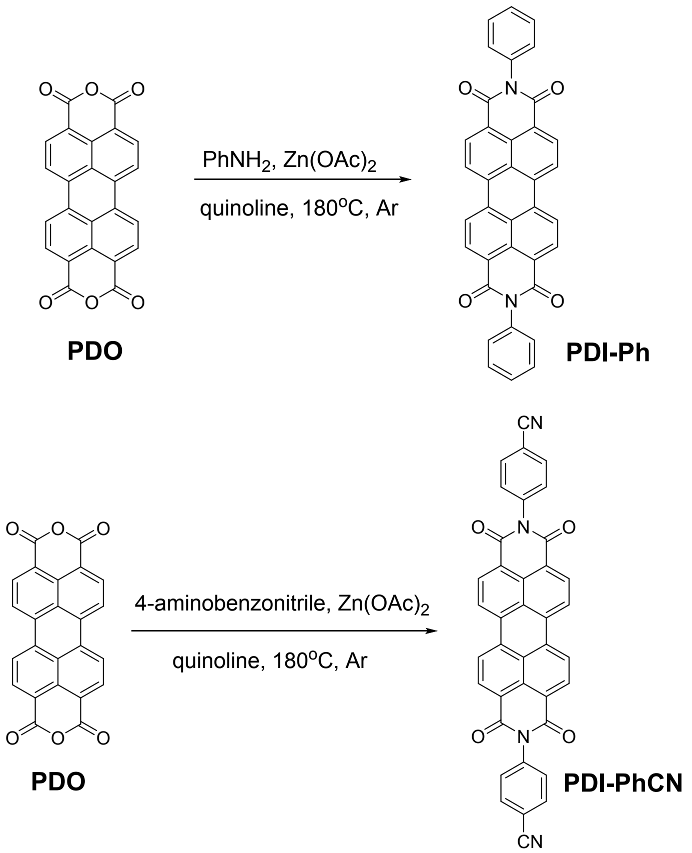

Figure S1. Synthetic route to PDI-based molecules, PDI-Ph and PDI-PhCN.

***1.2.* Synthesis of dibromo-perylene diimide (PDI-PhCN-2Br and PDI-PhCN-4Br):[3-5]**

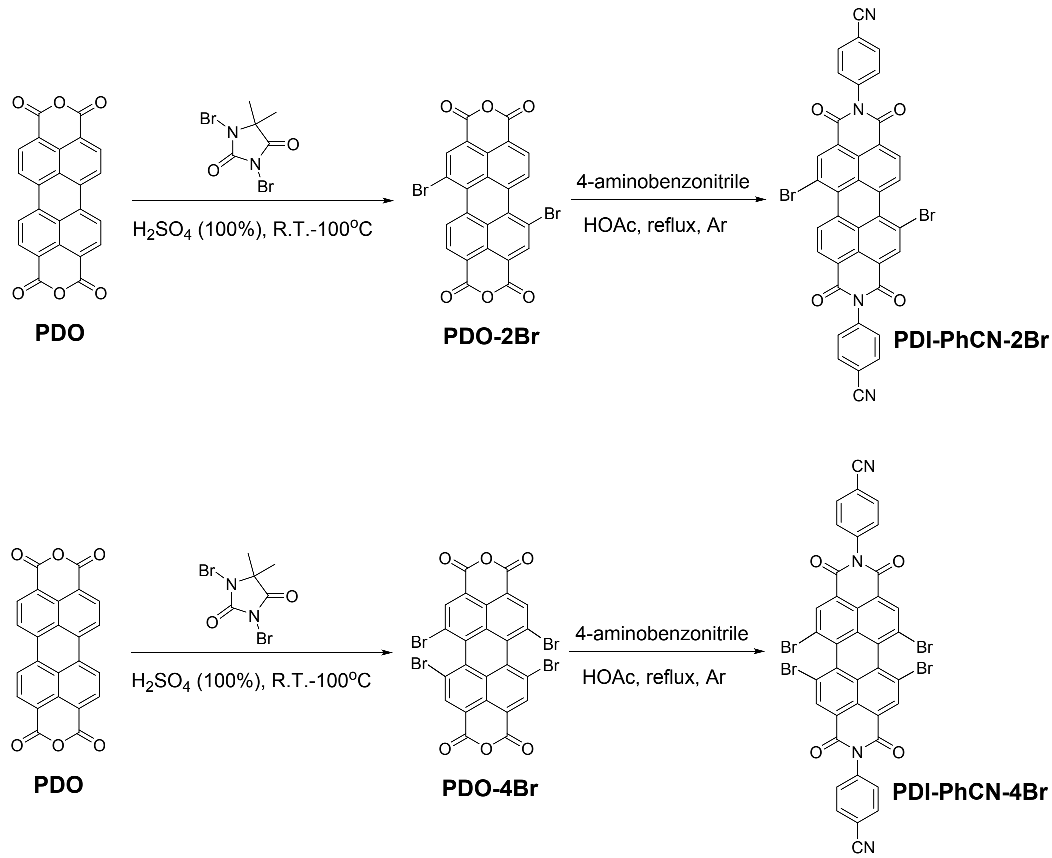

Figure S2. Synthetic route to PDI-based molecules, PDI-PhCN-2Br and PDI-PhCN-4Br .

Compound PDO (3.92 g, 10 mmol) was added into H_2SO_4 (100%) [H_2SO_4(98%)+ H_2SO_4(20%SO_3)] (50 mL), and stirred at room temperature for 4 h. Then 1,3-dibromo-5,5-dimethylhydantoin (3.43 g, 12 mmol) was added slowly in batches. After complete addition, the mixture was stirred at room temperature for 12 h and then 100 ^{o}C for 6 h. The solution was slowly added into ice water, and the red solid was obtained by filtration. After drying, all crude product PDO-2Br and 4-aminobenzonitrile (4.72 g, 40 mmol) were directly into glacial acetic acid (250 mL), and then refluxed for 48h. The solution was poured into ethanol (300 mL) to precipitate. The purplish red solid was obtained by filtration and drying. At last, the crude product was purified through high vacuum sublimation (350 ^{o}C, $8*10^{-4}$ Pa) to get the red solid 2.30 g with a yield of 34.3%. ^{1}H NMR (400 MHz, DMSO-d6): δ [ppm] = 9.50 (br, 2H) 8.79-8.69 (4H, m), 8.09 (4H, d, J2 = 8.8 Hz), 7.70 (4H, d, J = 8.8 Hz). MS (MALDI-TOF) calcd. for [$C_{38}H_{14}Br_2N_4O_4$]: 750.36; found for $[M+H]^+$: 751.70.

Compound PDO (3.92 g, 10 mmol) was added into H_2SO_4 (100%) [H_2SO_4(98%)+ H_2SO_4(20%SO_3)] (50 mL), and stirred at room temperature for 4h. Then 1,3-dibromo-5,5-dimethylhydantoin (6.86 g, 24 mmol) was added slowly in batches. After complete addition, the mixture was stirred at room temperature for 12 h and then 100 ^{o}C for 6 h. The solution was slowly added into ice water, and the red solid was obtained by filtration. After drying, all crude product PDO-4Br and 4-aminobenzonitrile (4.72 g, 40 mmol) were directly into glacial acetic acid (250 mL), and then refluxed for 48 h. The solution was poured into ethanol (300 mL) to precipitate. The purplish red solid was obtained by filtration and drying. At last, the crude product was purified through high vacuum sublimation (320 ^{o}C, $8*10^{-4}$ Pa) to get the red solid 2.75 g with a yield of 30.3%. ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.89 (s, 4H), 7.90 (4H, d, J2 = 8.4 Hz), 7.48 (4H, d, J = 8.4 Hz). MS (MALDI-TOF) calcd. for [$C_{38}H_{12}Br_4N_4O_4$]: 903.76; found for $[M+H]^+$: 904.13.

2. Calculation

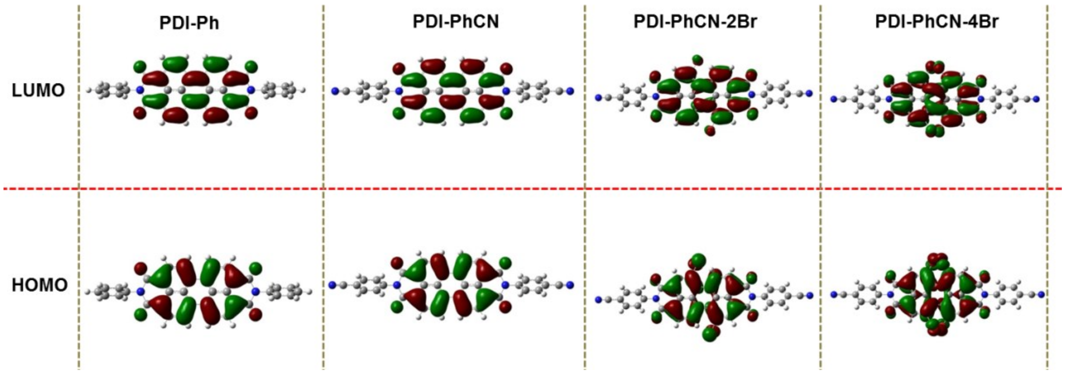

Figure S3. The density distribution of electron cloud for these four PDI-molecules were calculated by density functional theory (DFT) with B3LYP/6-31G(d) basis set.

3. Mobility of electron-transporting material (ETM)

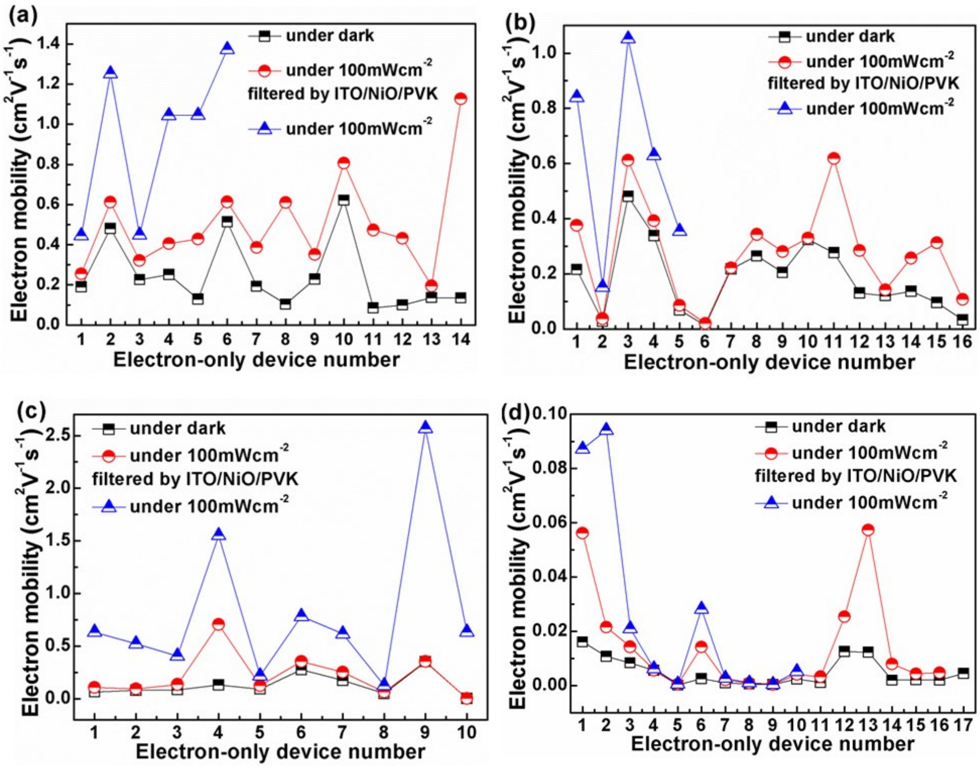

Figure S4. J-V curves of the ETM films (a) PDI-Ph, (b) PDI-PhCN, (c) PDI-PhCN-2Br, (d) PDI-PhCN-4Br measured from their electron-only devices with a structure of ITO/ZnO/ETM/LiF/Al,. The solid lines are the curve fittings using SCLC model. The thickness of the films are 108 nm, 98 nm, 77 nm, and 75 nm, respectively, as given in Table 2.

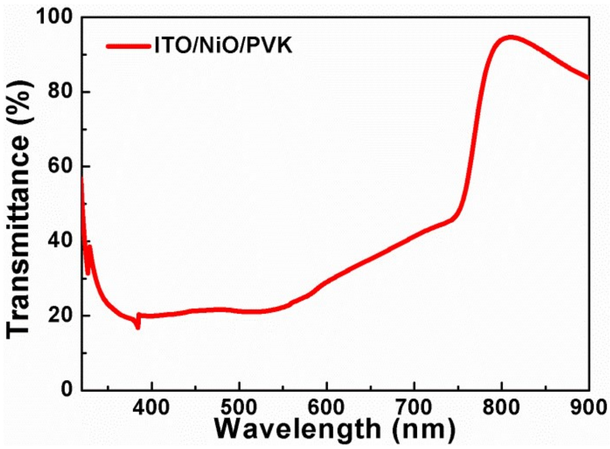

Figure S5. Transmittance of the ITO/NiO_x/PVK(PVK=perovskite $MAPbCl_xI_{3-x}$) film.

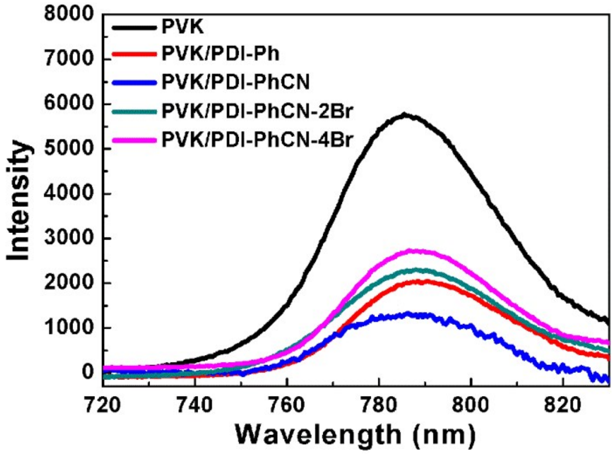

Figure S6. Photoluminescence of pristine PVK ($MAPbCl_xI_{3-x}$), PVK/PDI-Ph, PVK/PDI-PhCN, PVK/PDI-PhCN-2Br and PVK/PDI-PhCN-4Br films with exciting light (420 nm) irradiating from PDI-molecule side.

4. Device performance

Table S1. Device performance parameters for perovskite solar cells based on PDI-Ph as single electron-transporting material (ETM) under AM 1.5G Illumination (100 $mWcm^{-2}$). The average value was calculated from ~50 devices.

Thickness of PDI-Ph (nm)	V_{OC} (V)	J_{SC} ($mAcm^{-2}$)	FF (%)	η_{avg} (%)	η_{max} (%)
30	0.82±0.04	18.3±1.9	65.3±0.5	9.84±1.10	10.99
25	0.84±0.04	18.8±1.2	63.9±0.6	10.2±0.67	10.87
20	0.84±0.06	17.7±1.4	60.9±1.6	8.71±1.70	10.41
15	0.75±0.03	14.6±1.1	53.0±2.1	5.84±0.51	6.35

Table S2. Device performance parameters for perovskite solar cells based on PDI-PhCN as single electron transporting material (ETM) under AM 1.5G Illumination (100 $mWcm^{-2}$). The average value was calculated from ~50 devices.

Thickness of PDI-PhCN (nm)	V_{OC} (V)	J_{SC} ($mAcm^{-2}$)	FF (%)	η_{avg} (%)	η_{max} (%)
30	0.92±0.04	20.5±2.0	62.8±8.6	11.28±1.37	12.65
25	0.93±0.04	21.9±1.4	65.8±5.9	13.10±1.50	14.60
20	0.89±0.03	21.2±1.8	61.3±5.5	11.38±1.17	12.55
15	0.88±0.02	18.7±1.2	51.0±1.0	8.20±1.71	9.91

Table S3. Device performance parameters for perovskite solar cells based on PDI-PhCN-2Br as single electron transporting material (ETM) under AM 1.5G Illumination (100 $mWcm^{-2}$). The average value was calculated from ~50 devices.

Thickness of PDI-PhCN-2Br (nm)	V_{OC} (V)	J_{SC} ($mAcm^{-2}$)	FF (%)	η_{avg} (%)	η_{max} (%)
30	0.84±0.06	18.6±1.9	61.2±7.4	9.55±0.89	10.44
25	0.83±0.05	21.8±2.9	67.2±4.0	11.60±1.10	12.70
20	0.84±0.05	21.1±2.1	61.8±6.0	10.82±0.83	11.65
15	0.83±0.06	19.3±1.9	49.6±6.5	8.50±1.45	9.95

Table S4. Device performance parameters for perovskite solar cells based on PDI-PhCN-4Br as single electron transporting material (ETM) under AM 1.5G Illumination (100 $mWcm^{-2}$). The average value was calculated from ~50 devices.

Thickness of PDI-PhCN-4Br (nm)	V_{OC} (V)	J_{SC} ($mAcm^{-2}$)	FF (%)	η_{avg} (%)	η_{max} (%)
30	0.83±0.04	18.8±1.3	40.6±4.2	6.72±0.98	7.70
25	0.87±0.04	19.4±1.8	40.2±4.4	6.98±0.73	7.71
20	0.83±0.04	19.5±1.3	39.6±3.3	6.41±0.70	7.11
15	0.87±0.05	18.4±1.5	24.6±2.4	4.04±0.44	4.48

Table S5. Device performance parameters for perovskite solar cells based on PDI-Ph(25nm)/BCP as bilayer electron transporting material (ETM) under AM 1.5G Illumination (100 $mWcm^{-2}$). The average value was calculated from ~50 devices.

Thickness of BCP (nm)	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	η_{avg} (%)	η_{max} (%)
10	0.94±0.03	21.2±1.8	61.9±3.7	12.3±1.20	13.5
7	0.91±0.04	21.7±1.9	67.7±6.5	13.3±1.65	15.0
4	0.87±0.06	20.3±2.1	65.9±5.1	11.4±1.30	12.7

Table S6. Device performance parameters for perovskite solar cells based on PDI-PhCN(25nm)/BCP as bilayer electron transporting material (ETM) under AM 1.5G Illumination (100 $mWcm^{-2}$). The average value was calculated from ~50 devices.

Thickness of BCP (nm)	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	η_{avg} (%)	η_{max} (%)
10	1.04±0.03	21.6±1.4	70.7±4.9	15.8±0.80	16.6

7	1.02±0.04	22.4±1.3	73.4±5.3	17.4±1.40	18.8
4	1.00±0.02	22.2±1.0	66.4±2.9	14.8±1.20	16.0

4. Reference

(1) A. Rademacher, S. Märkle and H. Langhals, Lösliche Perylen-Fluoreszenzfarbstoffe rnit Hoher Photostabilität. *Chem. Ber.* 1982, **115**, 2927-2934.

(2) W. E. Ford, H. Hiratsuka and P. V. Kamat, Photochemistry of 3,4,9,10-Perylenetetracarboxyllc Dianhydride Dyes. 4. Spectroscopic and Redox Properties of Oxidized and Reduced Forms of the Bis(2,5-di-tert-butylphenyl)imide Derivative. *J. Phys. Chem.* 1989, **93**, 6692-6696.

(3) X. Sun, W. Qiu, D. Wei, M. Tang and L. Guo, Synthesis and Photophysical Properties of Novel Phthalocyanine–Perylenediimide–Phthalocyanine Triad and Phthalocyanine–Perylenediimide Dyads. *RSC Adv.* 2014, **4**, 25616-25624.

(4) U. Rohr, C. Kohl, K. Müllen, A. van de Craats and J. Warman, Liquid Crystalline Coronene Derivatives. *J. Mater. Chem.* 2001, **11,** 1789-1799.

(5) M. Sasikumar, Y. V. Suseela and T. Govindaraju, Dibromohydantoin: A Convenient Brominating Reagent for 1,4,5,8-Naphthalenetetracarboxylic Dianhydride. *Asian J. Org. Chem.* 2013, **2**, 779-785.