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


**Supplemental Information:**

# Crosslinked and Dopant free Hole Transport Materials for Efficient and Stable Planar Perovskite Solar Cells

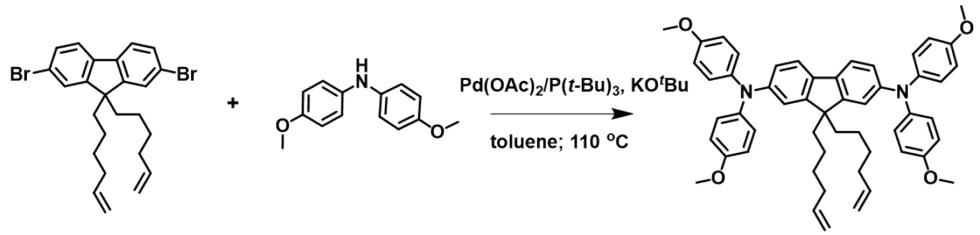
Yun Zhang,[a] Chun Kou,[b] Junjie Zhang,[a] Wenhua Li,[b,*] Yahui Liu,[b] Zhishan Bo[b,*] and Ming Shao[a, *]

a. Wuhan National Laboratory for Optoelectronics, Huazhong University of Science and Technology, Wuhan 430074, China.

b. Key Laboratory of Energy Conversion and Storage Materials, College of Chemistry, Beijing Normal University, Beijing 100875, China

c. College of Science, Beijing Jiaotong University, Beijing 1000444, China

**Material Synthesis:**




DH-MeO-FDPA

*Synthesis of DH-MeO-FDPA*

A mixture of 2,7-dibromo-9,9-di(hex-5-en-1-yl)-9H-fluorene (500 mg, 1.11 mmol), bis(4-methoxyphenyl)amine (640 mg, 2.79 mmol), potssium tert-butoxide (375 mg, 3.35 mmol) and toluene (10 mL) was placed in a Schlenk flask. The mixture was carefully degassed before and after $Pd(OAc)_2$ (25 mg, 0.11 mmol) and tri-tert-butyl phosphine (23 mg, 0.11 mmol) was added. After stirred and refluxed for 12 h, the reaction was stopped. After cooling to room temperature, water was added to quench the reaction. The mixture was extracted with ethyl acetate, the organic layer was dried over anhydrous $MgSO_4$. After filtration, the organic solvent was moved under reduced pressure. The residue was further purified by silica gel column chromatography to give DH-MeO-FDPA (780 mg, yield 89%) as pale yellow solid.

$^1H$ ($d_6$-DMSO, 400 MHz) $\delta$ : 7.43 (d, $J$ = 8.12 Hz, 2H), 6.83-6.94 (m, 18H), 6.70 (d, $J$ = 8.04 Hz, 2H), 5.58-5.65 (m, 2H), 4.83-5.19 (m, 4H), 3.70 (s, 12H), 1.51-1.81 (m, 8H), 1.03-1.07 (m, 4H), 0.59-0.61 (m, 4H).

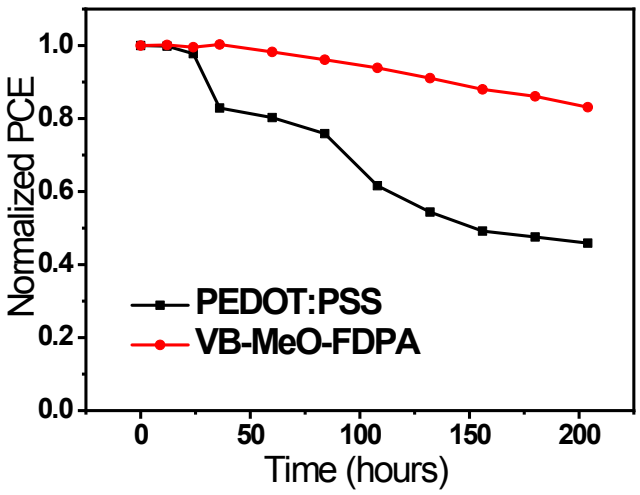



**Fig. S1** Stability date of unencapsulated perovskite devices with crosslinked VB-MeO-FDPA and PEDOT:PSS HTMs under continuous one sun illumination in a $N_2$ box

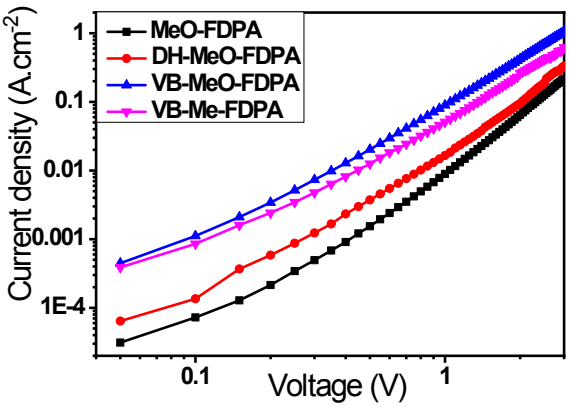



**Fig. S2** Current density-voltage (J–V) characteristics of hole-only devices with the structure of ITO/PEDOT:PSS/HTMs/$MoO_3$/Ag

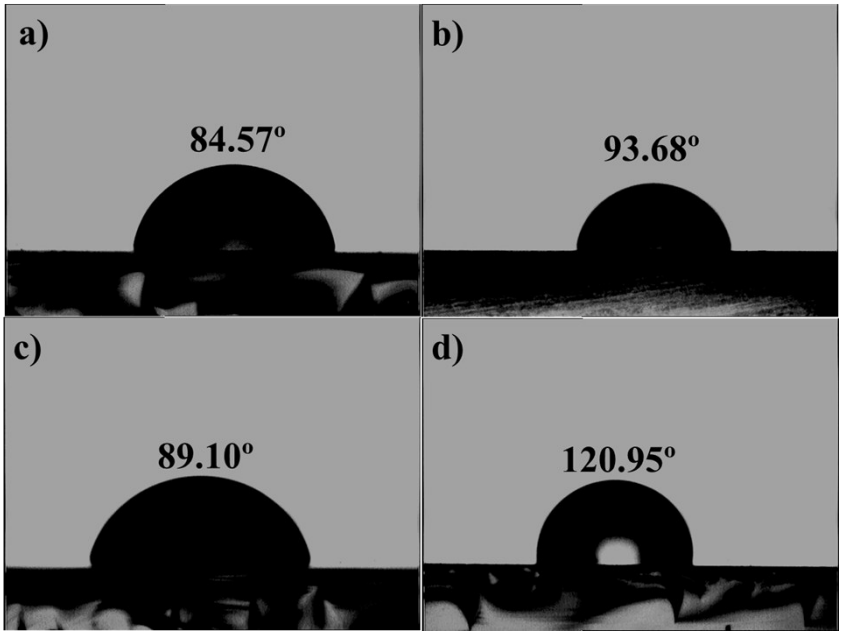



**Fig. S3** Contact angles of water on four HTMs a) MeO-FDPA, b) DH-MeO-FDPA, c) VB-MeO-FDPA and d) VB-Me-FDPA

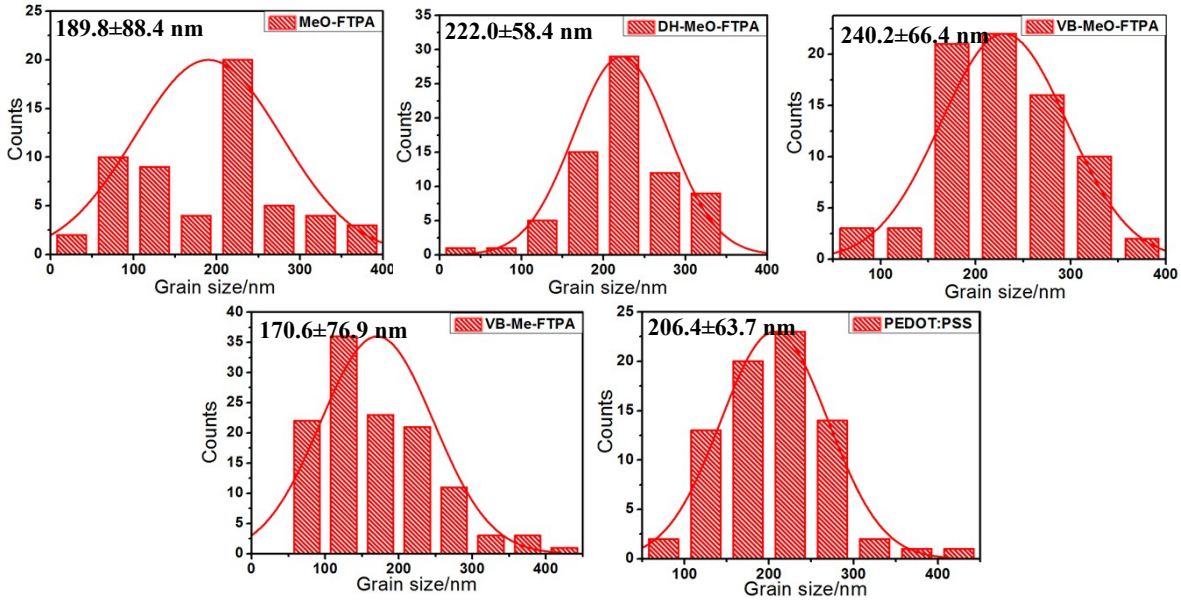



**Fig. S4** Statistic results of perovskite grain size coated on different hole transport layers.

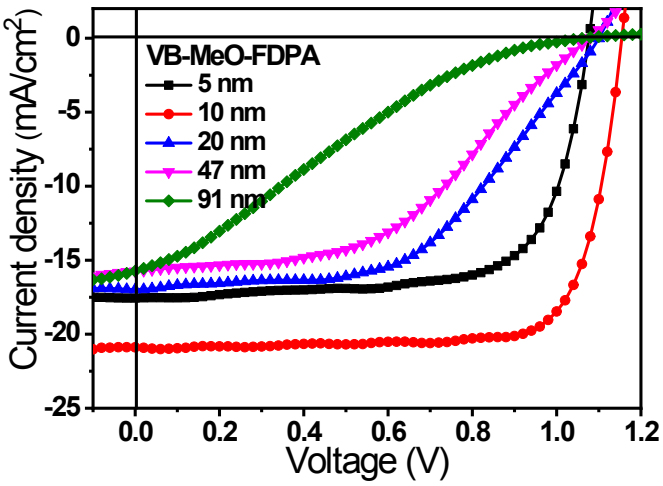



**Fig. S5** J-V curves of perovskite devices with various thickness of crosslinked HTM(VB-MeO-FDPA)

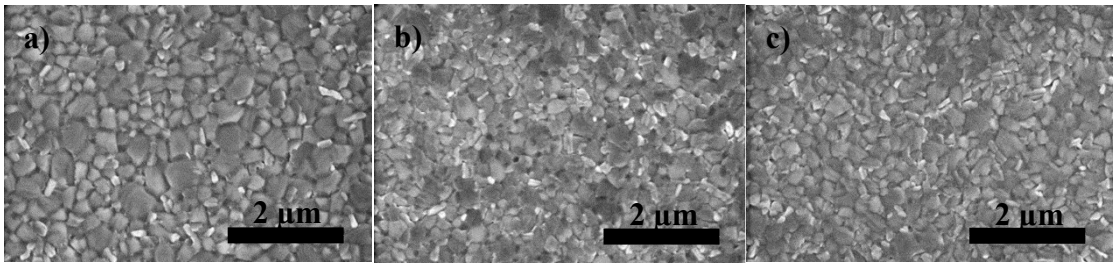



**Fig. S6** SEM images of perovskite films deposited on different HTMs a) PEDOT:PSS, b) VB-MeO-FDPA and c) PEDOT:PSS/ VB-MeO-FDPA bilayer.

**Table. S1** Summarization of the PL decay time for perovskite films with different HTLs.

| HTLs | | Perovskite | PEDOT:PSS | MeO-FDPA | DH-MeO-FDPA | VB-MeO-FDPA | VB-Me-FDPA |
|---|---|---|---|---|---|---|---|
| PL lifetime /ns | $\tau_1$ | 56.70 | 48.75 | 44.64 | 28.38 | 13.87 | 37.31 |
| | $\tau_2$ | 13.27 | 15.15 | 15.84 | 13.17 | 5.08 | 10.49 |

**Table. S2** Photovoltaic performance of PSCs with VB-MeO-FDPA treated at different crosslinking Temperature

| Crosslinking Temp (℃) | $J_{sc}$ (mA/cm$^2$) | $V_{oc}$ (V) | FF (%) | PCE (%) |
|---|---|---|---|---|
| RT | 5.4 | 0.78 | 19.4 | 0.8 |
| 100 | 12.6 | 1.01 | 50.2 | 6.4 |
| 140 | 17.9 | 0.96 | 64.5 | 11.1 |
| 160 | 20.9 | 1.15 | 77.5 | 18.7 |
| 200 | 19.8 | 1.09 | 74.0 | 16.0 |