Electronic Supplementary Material (ESI) for Materials Advances.

Efficient furan-bridged dibenzofulvene-triphenylamine hole transporting materials for perovskite solar cells

Nan Wu[a1], Xianfu Zhang[a1], Xuepeng Liu[a*], Ying Wang[a], Mingyuan Han[a], Rahim Ghadari[b], Yahan Wu[c*], Yong Ding[a], Molang Cai[a], Songyuan Dai[a*]

[a] *Beijing Key Laboratory of Novel Thin-Film Solar Cells, North China Electric Power University, Beijing 102206, China E-mail: liuxuepeng@ncepu.edu.cn sydai@ncepu.edu.cn*
[b] *Computational Chemistry Laboratory, Department of Organic and Biochemistry, Faculty of Chemistry, University of Tabriz, Tabriz 51666164*
[c] *College of Energy and Power Engineering, Inner Mongolia University of Technology, Huhhot, 010051, PR China E-mail: 460253698@qq.com*

Nan Wu and Xianfu Zhang contributed equally to this work.

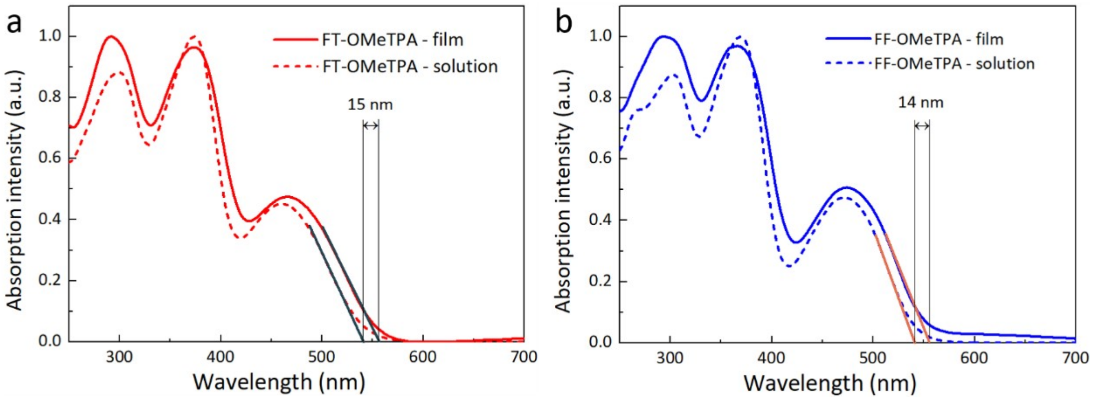


Figure S1. (a) Normalized UV-Vis absorption of film on the FTO substrate or in DCM solution of FT-OMeTPA, and (b) FF-OMeTPA.

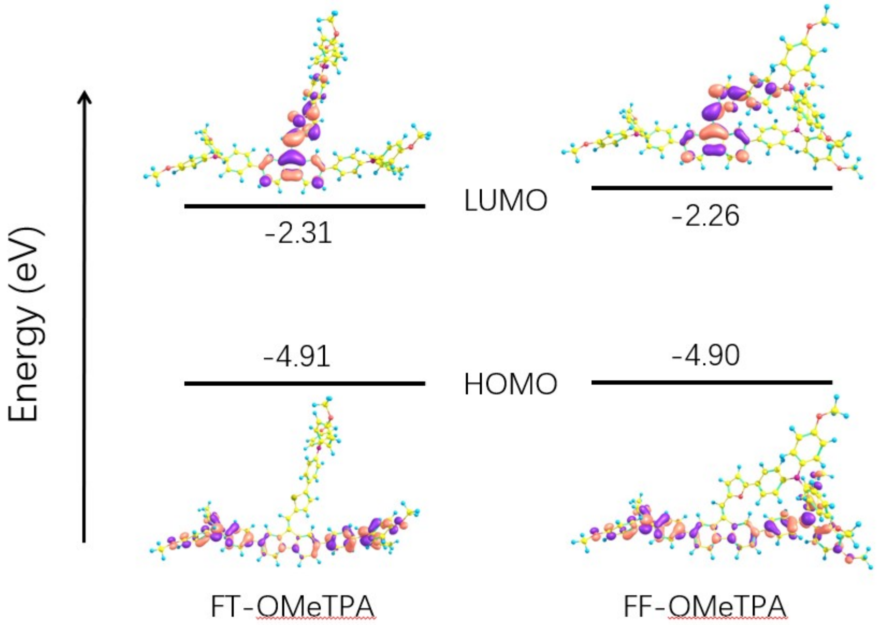


Figure S2. The electronic density distributions of the frontier molecular orbitals, as well as calculated HOMO and LUMO level of FT-OMeTPA and FF-OMeTPA.

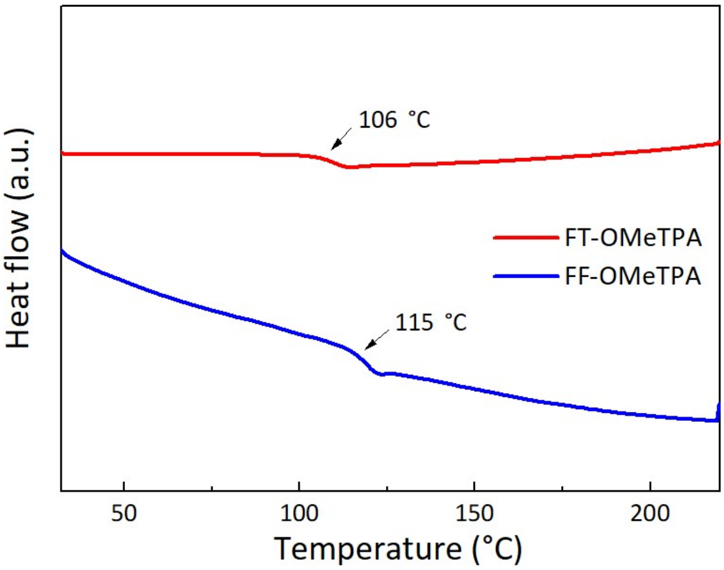


Figure S3. DSC curves of FT-OMeTPA and FF-OMeTPA.

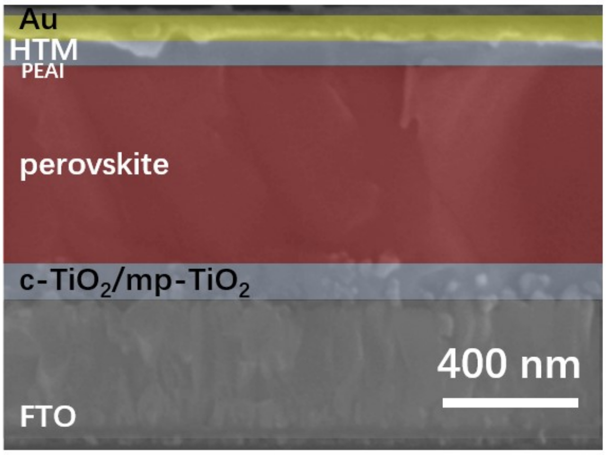


Figure S4. Cross-sectional SEM image of a typical PSC (the concentration of HTM is 40 mg mL^{-1}).

Table S1. Summary of the influence of material concentration and whether there are additives on PCE of device.

FT-OMeTPA	Concentration (mg mL^{-1})	60	40	20
	PCE (%)	3.59	17.81	17.72
FF-OMeTPA	Concentration (mg mL^{-1})	60	40	20
	PCE (%)	20.16	21.64	19.61

Table S2. Mean values with standard deviation (STDEV) of photovoltaic parameters (reverse scan direction) of the PSCs with different HTMs (40 mg mL^{-1}).

HTM	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)

FT-OMeTPA	1.12±0.02	23.89±0.24	65±2.19	17.29±0.37
FF-OMeTPA	1.14±0.01	24.48±0.26	74±1.07	20.76±0.53

Notes: The devices with different HTMs contain 16 independent samples.

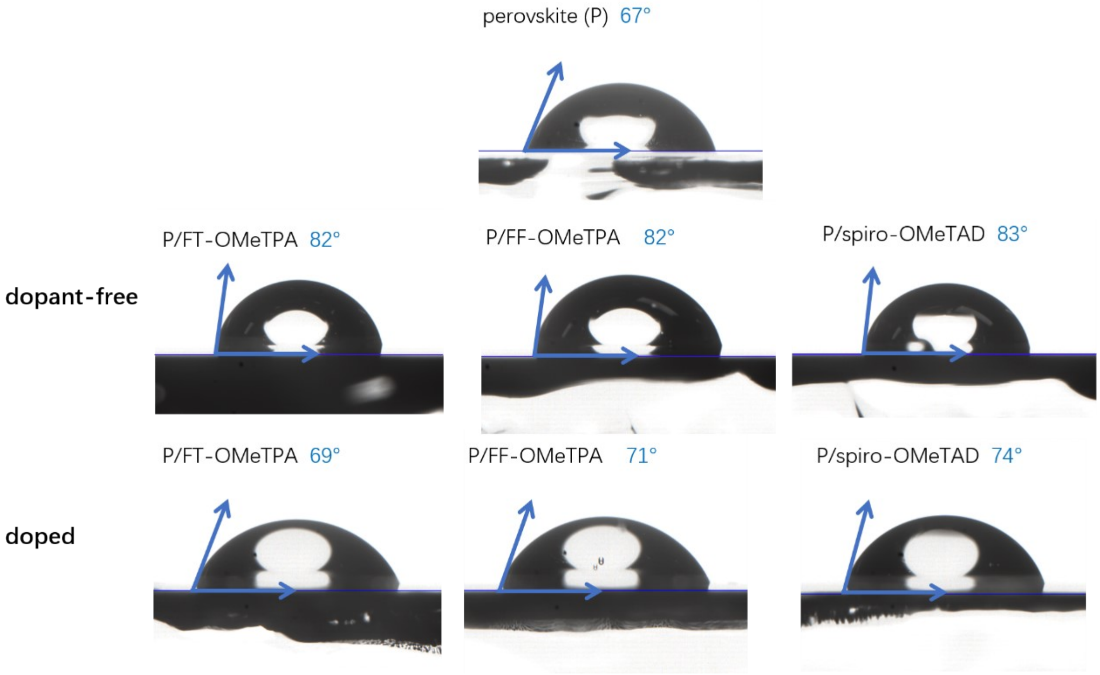


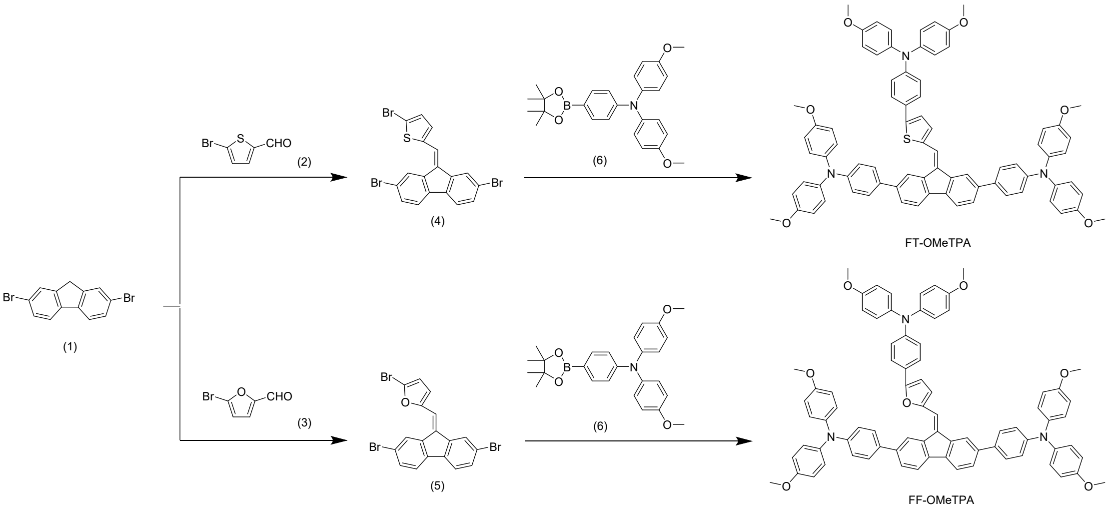
Figure S5. Water contact angles of perovskite, and perovskite coated with dopant-free or doped HTMs.

Experimental section

Materials and Synthesis

All chemicals and reagents were purchased from TCI, Alpha, Sigma-Aldrich and Sinopharm, etc., and all chemicals were directly used without further processing. The synthetic routes of FT-OMeTPA[1] and FF-OMeTPA are shown in Scheme S1. These HTMs were synthesized through two-step reactions, namely Knoevenagel condensation reaction and Suzuki coupling reaction. Compound 6 was synthesized in our lab according to our previous report.[2] Detailed synthesis details are shown below.

During the Knoevenagel condensation reaction, the active methylene on 2,7-dibromofluorene (1) was condensed with the aldehyde group on p-bromobenzaldehyde and 5-bromothiophene-formaldehyde (2)/p-bromobenzaldehyde and 5-bromofuran-2-formaldehyde (3) under alkaline environment to form complex 4/5. The intermediate 4/5 was also used as the reactant of Suzuki coupling reaction to react with 4-methyloxy-N-(4-methylthiophenyl)-N-(4-(4,4,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl) tannin (6) to generate the target crude product FT-OMeTPA/FF-OMeTPA. The crude products were purified by column chromatography to obtain pure target products. The molecular structure of the product was confirmed with NMR and mass spectroscopy.



Scheme S1. The synthetic routes of FT-OMeTPA and FF-OMeTPA.

Synthesis of 2,7-dibromo-9-[2-(5-bromothiophen-2-yl)-ethanyl]-9H-fluorene (compound 4) [1] 2,7-dibromofluorene (1) (0.8 g, 2.48 mmol), EtOH (15 mL), KOtBu (0.38 g, 3.39 mmol), were mixed in a 100 mL flask. The mixture was degassed and stirring at 70 ℃ for 60 min under N_2 purge. After the yellow precipitate was precipitated, a large amount of yellow precipitate was immediately produced by adding reactant p-bromobenzaldehyde and 5-bromothiophene-formaldehyde (2) (0.48 g, 2.4 mmol), and the reaction was continued stirring at 80 ℃ for 20 min in N_2 atmosphere. After cooling to room temperature, neutralize the reaction mixture with concentrated HCl. The precipitate was filtered, washed with ethanol for several times, and the reagent was completely removed. Finally, the product was yellow solid (compound 4, 1.18 g, 96%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.20 (dd, 2H), 8.02 (s, 1H), 7.85 (dd, 3H), 7.58 (dd, 3H), 7.42 (2H).

Synthesis of 2,7-dibromo-9-[2-(5-bromofuran-2-yl)-ethanyl]-9H-fluorene (compound 5)

2,7-Dibromofluorene (1) (0.8 g, 2.48mmol), EtOH (15 mL), KOtBu (0.38 g, 3.39 mmol), were mixed in a 100 mL flask. The mixture was degassed and stirring at 70 ℃ for 60min under N_2 purge. After the yellow precipitate was precipitated, a large amount of yellow precipitate was immediately produced by adding reactant p-bromobenzaldehyde and 5-bromofuran-2-formaldehyde (3) (0.42 g, 2.4 mmol), and the reaction was continued stirring at 80 ℃ for 20 min in N_2 atmosphere. After cooling to room temperature, neutralize the reaction mixture with concentrated HCl. The precipitate was filtered, washed with ethanol for several times, and the reagent was completely removed. Finally, the product was yellow solid (compound 5, 1.16 g, 97%).

^{1}H NMR (400 MHz, DMSO-d$_6$) δ 8.82 (d, 1H), 8.19 (d, 1H), 7.91 (d, 1H), 7.86 – 7.82 (m, 1H), 7.76 (s, 1H), 7.64 (dd, 1H), 7.55 (dd, 1H), 7.07 (d, 1H), 6.95 (d, 1H).

Synthesis of FT-OMeTPA[1]

Compound 4 (0.20 g, 0.4 mmol), compound 6(0.87 g, 2 mmol), Pd(PPh$_3$)$_4$ (57 mg, 0.05 mmol), DMF (20 mL), 2 M solution of K_2CO_3 (1.1 g, 8 mmol) in H_2O were mixed in a 100 mL flask. The mixture was degassed and stirring at 90 ^{o}C for 20 h under N_2 purge. After cooling to room temperature, pouring mixture into 300 mL cold brine, crude product precipitates out as solids. After drying, the crude product was purified by column chromatography (DCM) to obtain the product as red solid (FT-OMeTPA, 370 mg, 79%). ^{1}H NMR (500 MHz, DMSO-d$_6$) δ 8.58 (s, 1H), 8.22 (s, 1H), 8.07 (s, 1H), 7.89 (d, J = 7.9 Hz, 1H), 7.84 (d, J = 7.9 Hz, 1H), 7.67 – 7.58 (m, 4H), 7.54 – 7.42 (m, 5H), 7.09 – 7.01 (m, 12H), 6.97 – 6.86 (m, 14H), 6.78 (dd, 4H), 6.67 (d, J = 8.6 Hz, 1H), 3.75 (s, 6H), 3.74 (s, 6H), 3.72 (s, 6H). HRMS-ESI m/z: [M-H] calcd, 1168.4438; found, 1168.4353.

Synthesis of FF-OMeTPA

Compound 5 (0.19 g, 0.4 mmol), compound 6 (0.87 g, 2 mmol), Pd(PPh$_3$)$_4$ (57 mg, 0.05 mmol), DMF (20 mL), 2 M solution of K_2CO_3 (1.1 g, 8 mmol) in H_2O, were mixed in a 100 mL flask. The mixture was degassed and stirring at 90 ℃ for 20 h under N_2 purge. After cooling to room temperature, pouring mixture into 300 mL cold brine, crude product precipitates out as solids. After drying, the crude product was purified by column chromatography (DCM) to obtain the product as red solid (FF-OMeTPA, 295 mg, 64%). ^{1}H NMR ^{1}H NMR (500 MHz, DMSO-d$_6$) δ 8.91 (s, 1H), 8.20 (s, 1H), 7.89 (dd, J = 24.0, 7.9 Hz, 2H), 7.78 (s, 1H), 7.70 – 7.51 (m, 6H), 7.49 – 7.40 (m, 2H), 7.15 – 6.98 (m, 8H), 6.99 – 6.82 (m, 22H), 6.69 (dd, J = 15.8, 8.7 Hz, 4H), 3.78 – 3.69 (m, 18H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.57, 156.06, 155.89, 155.74, 147.96, 147.61, 141.21, 140.96, 140.45, 139.78, 139.40, 139.00, 137.26, 137.09, 135.83, 133.93, 127.91, 127.57, 127.18, 126.50, 126.23, 125.32, 123.35, 121.07, 120.94, 120.62, 119.78, 118.67, 117.91, 114.73, 83.44, 55.53, 55.46. HRMS-ESI m/z: [M-H] calcd, 1152.4666; found, 1152.4579.

Device fabrication

FTO glass was ultrasonically cleaned in detergent, ethanol and deionized water for 15 minutes and dried. The compact TiO_2 (c-TiO_2) layer (0.6 mL titanium diisopropoxide and 0.4 mL bis(acetylacetonate) dissolved in 15 mL ethanol) deposited on UV/O_3 treated FTO substrate by spray pyrolysis at 500 °C and stored at 500 °C for 30 min. After cooling, the mesoporous titanium dioxide layer was prepared by spin coating the diluted titanium dioxide paste (Dyesol 30NR-T, 1:12 w/w diluted in ethanol) on the prepared substrate at 3000 rpm for 30 s and annealed at 500 C for 30 min. Before coating the perovskite film, the substrate was treated with UV/O_3 for 10 minutes. In order to prepare perovskite solution with component $Cs_{0.05}(FA_{0.85}MA_{0.15})_{0.95}Pb(I_{0.85}Br_{0.15})_3$, PbI_2 (1.35 M), $PbBr_2$ (0.2 M), CsI (0.07 M), MABr

(0.2 M), and FAI (1.2 M), dissolved in a mixed solvent of DMF and DMSO solution (1000 µL, volume ratio 8 : 2). Then, 20 µL filtered solution was uniformly dispersed on the above mp-TiO$_2$ substrate at the speed of 5000 rpm. Within 10 seconds before the end of rotation, 200 µL of chlorobenzene was dropped. The film after spin coating was annealed at on the hotplate. After complete cooling, 20 µL PEAI solution (5 mg 2-phenylethanamine iodide dissolved in 1 mL isopropanol) was spin-coated at a speed of 5000 r to passivate the defects of perovskite layer. During the preparation of the hole transport layer, 73.5 mg spiro-OMeTAD was added to 1 mL chlorobenzene with additives of 17 µL Li-TFSI, 8 µL FK209 and 29 µL tBP. For preliminary optimization, FT-OMeTPA and FF-OMeTPA were prepared different concentrations of chlorobenzene solutions and the concentrations were 60, 40 and 20 mg mL^{-1}, and the additives with the same proportion as spiro-OMeTAD were added. For the second batch of the device, the concentration of FT-OMeTPA and FF-OMeTPA is 40 mg mL^{-1}. Finally, a 70 nm gold counter electrode was deposited by thermal evaporation. The active area of the device was defined by a black mask with a size of 0.1225 cm^2 for all measurements.

Characterizations

The instruments used at work refer to our previous report.[3, 4] NMR spectra were recorded on a Brücker spectrometer (400 or 500 MHz). UV-vis spectra of investigated molecules are carried out on a UV-vis spectrophotometer (UV-3600 plus, Shimadzu Co. Ltd, Japan). The PL measurements of HTM were recorded on the fluorescence spectrophotometer (Hitachi F4600, Japan). The PL spectrum of perovskite/HTM films were obtained from a fluorescence spectrometer (FLS980, Edinburgh, UK) with the excitation wavelength of 488 nm. Cyclic voltammetry was tested with a CHI660d electrochemical analyzer (CH Instruments, InC, China). A normal three electrode system was used consisting of a platinum wire counter electrode, a platinum working electrode, as well as a calomel reference electrode. Redox potential of investigated compounds was tested in DCM with 0.1 M tetrabuty-lammonium hexafluorophosphate with a scan rate of 50 mV s^{-1}. Differential scanning calorimetry is carried out with a scan rate of 15 ^{o}C min^{-1} (METTLER-Toledo DSC1). The *J-V* characteristics were carried out using a Keithley 2400 source meter under AM 1.5G and a 3A grade solar simulator (Newport, USA) with an intensity of 100 mW cm^{-2}. The incident photon-to-current conversion efficiency (IPCE) was recorded on QE/IPCE measurement kit (Sofn Instruments Co., LTD, China). The moisture resistance of HTMs was measured on a contact angle tester (METATEST E3-300). HRMS (ESI) were recorded on a XEVO-G2QTOF.

Cost Evaluation for FF-OMeTPA

Table S3. Cost evaluation of 2,7-dibromo-9-[2-(5-bromofuran-2-yl)-ethanyl]-9H-fluorene (compound 5)

Chemical	Weight Reagent or	Price of chemical	Cost of chemical	Total cost ($/g)

	solvent (g/g)	($/g)	($/g product)	
2,7-dibromofluorene	0.69	0.44	0.30	
5-bromofuran-2-formaldehyde	0.36	1.33	0.48	
EtOH	80	0.0085	0.68	
KOtBu	0.33	0.049	0.02	
HCl	0.31	0.062	0.02	
Compound 5				1.50

Table S4. Cost evaluation of FF-OMeTPA.

Chemical	Weight Reagent or solvent (g/g)	Price of chemical ($/g)	Cost of chemical ($/g product)	Total cost ($/g)
Compound 5	0.64	1.50	0.96	
Compound 6	2.94	10	29.4	
$Pd(PPh_3)_4$	0.24	8.16	1.96	
DMF	80	0.004	0.32	
K_2CO_3	4.68	0.006	0.03	
CH_2Cl_2	300	0.006	1.8	
FF-OMeTPA				34.5

Reference

1. F. Meng, Y. Jia, J. Wang, X. Huang, Z. Gui, L. Huang, R. Li, R. Chen, J. Xu, W. Chen, Z. He, H.-Y. Hsu, E. Zhu, G. Che and H.-L. Wang, *Solar RRL*, 2019, **3**, 1900319.
2. M. Li, S. Ma, M. Mateen, X. Liu, Y. Ding, J. Gao, Y. Yang, X. Zhang, Y. Wu and S. Dai, *Solar Energy*, 2020, **195**, 618-625.
3. X. Zhang, X. Liu, N. Wu, R. Ghadari, M. Han, Y. Wang, Y. Ding, M. Cai, Z. Qu and S. Dai, *J. Energy Chem.*, 2022, **67**, 19-26.
4. Y. Liang, J. Chen, X. Zhang, M. Han, R. Ghadari, N. Wu, Y. Wang, Y. Zhou, X. Liu and S. Dai, *J. Mater. Chem. C*, 2022, **10**, 10988-10994.