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

Inspired from Spiro-OMeTAD: Developing Ambipolar Spirobifluorene Derivatives as Effective Passivation Molecules of Perovskite Solar Cells

Teng Zhang,[a#] Baohua Zhao, [b#] Zhi Li,[c] Shanshan Liu,[b] Chengben Liu,[b] Xinmei Li,[a] Heyuan Liu,[a] Yanli Chen,[a] Zhaobin Liu[c] and Xiyou Li[a*]*

[a.] School of Materials Science and Engineering, China University of Petroleum (East China), Qingdao, 266580 P. R. China. E-mail: xiyouli@upc.edu.cn; tzhangae@connect.ust.hk

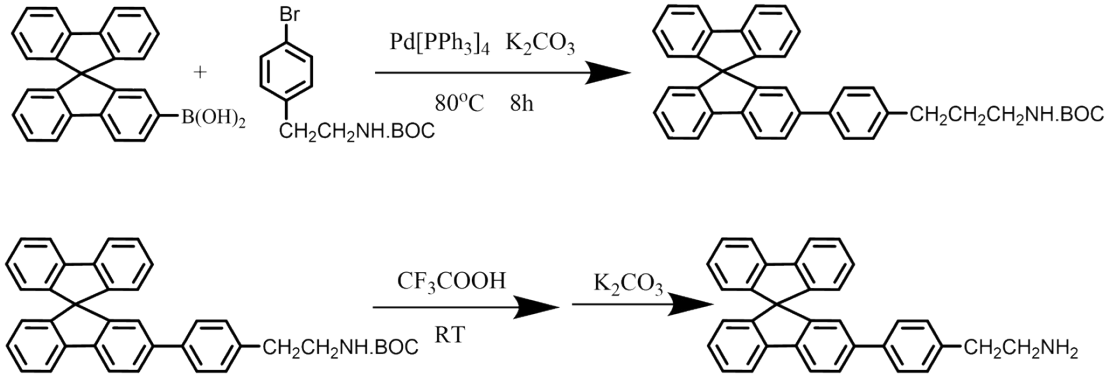
[b.] College of Science, China University of Petroleum (East China), Qingdao, 266580 P. R. China.

[c.] Shandong Energy Group Co., Ltd., 19/F, high salary Wanda J3 office building, 57-1, Gongye South Road, High tech Zone, Jinan City, Shandong Province, China.

[#] T. Zhang and B. Zhao contributed equally to the work

Synthesis section

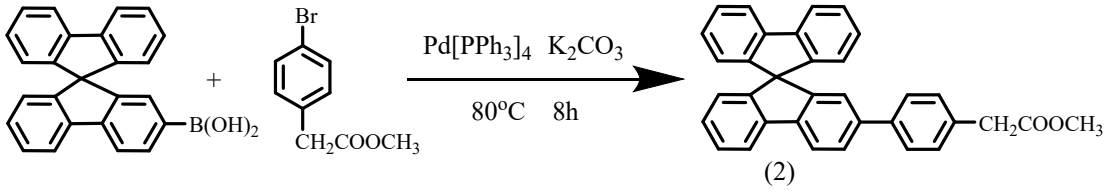
Synthesis of BSBF-NH_2



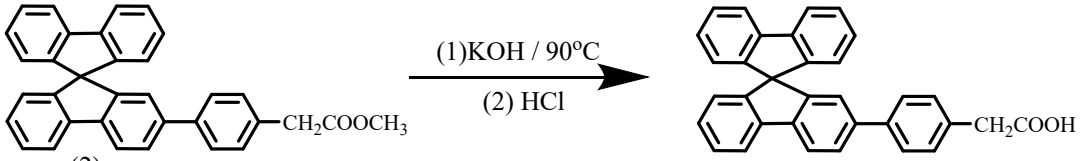
2-ylboronicacid-9,9'-spirobifluorene(144.08 mg, 0.4 mmol), tert-Butyl(4-bromophenyl)carbamate (100 mg, 0.33 mmol), $Pd(PPh_3)_4$ (15.430 mg, 0.013 mmol) and K_2CO_3 (110.6 mg, 0.803 mmol) were dissolved in the tetrahydrofuran (15mL). The mixture was sealed in a vial tube under N_2 and stirred at 80°C for 8 h in a microwave reactor. After the reaction, the mixture was poured into 50 mL CH_2Cl_2 and washed with water (100 mL×3). The organic layer was collected and dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude product was purified using silica gel column chromatography (CH_2Cl_2). After removing CH_2Cl_2 under reduced pressure, the colorless solid (1) was obtained. Under N_2 atmosphere, trifluoroacetic acid (TFA, 1.2 mL) was added to the solution of (1) (185.11 mg, 0.320 mmol) in CH_2Cl_2 (8 mL). The mixture was stirred at RT for 4 h. After the reaction, the solvents were removed under reduced pressure. 5% Na_2CO_3 aqueous solution (8 mL) and CH_2Cl_2 (6.5 mL) were added to the crude product, and the reaction waskept at RT for 6 h. The organic layer was collected and dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The precipitate was collected and washed with

$CHCl_2$ and ethanol. The pale yellow solid was dried under reduced pressure at 60°C. Yield: 262 mg, 73%. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ = 2.82 (t, 2H), 2.99(s, 2H), 7.15(t, 3H), 7.23(d, 2H), 7.40-7.44(m, 5H), 7.72(d, 3H), 8.05-8.07(m, 2H),8.12(d,1H).

Synthesis of BSBF-COOH



(2)



(2)

3-ylboronicacid-9,9'-spirobifluorene (144.08 mg, 0.4 mmol), methyl 2-(4-bromophenyl)acetate (75.57 mg, 0.33 mmol), $Pd(PPh_3)_4$ (15.430 mg, 0.013 mmol) and K_2CO_3 (110.6 mg, 0.803 mmol) were dissolved in the tetrahydrofuran (15mL). The mixture was sealed in a vial tube under N_2 and stirred at 80°C for 8 h in a microwave reactor. After the reaction, the mixture was poured into 50 mL CH_2Cl_2 and washed with water (100 mL×3). The organic layer was collected and dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude product was purified using silica gel column chromatography (CH_2Cl_2). After removing CH_2Cl_2 under reduced pressure, the colorless solid (2) was obtained. Add product (2) to methanol dioxane mixed solvent(V/V=1/4), stir at 90 degrees Celsius. Then KOH(2mol/L) solution was added to it and stirred until the solution was clear. After acidification treatment with HCl, a light yellow powder is obtained. Yield: 112 mg,

65%. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 6.59 (d, 1H), 6.61(d, 2H), 6.88(s, 1H), 7.15(d, 3H), 2.20-7.22(d, 2H), 7.35-7.38(q, 4H), 7.75(d, 1H),8.16(t, 3H), 8.27(d, 1H), 12.28(s, 1H).

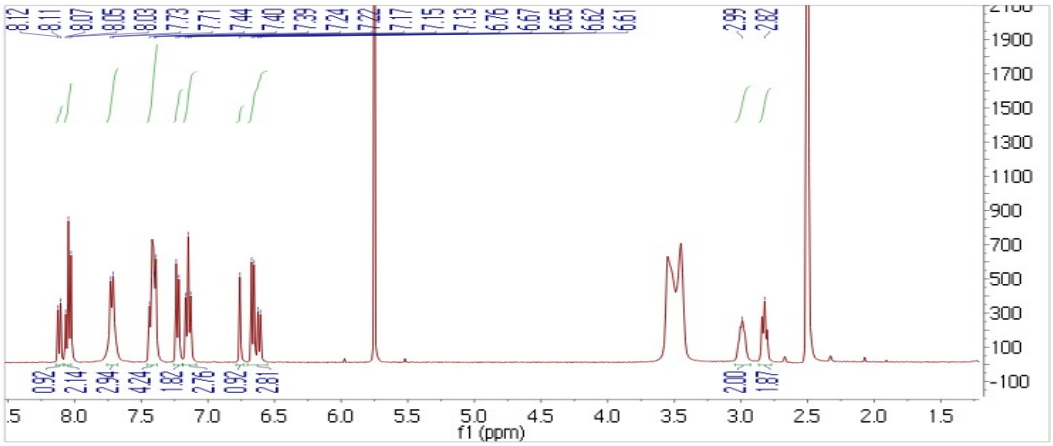


Fig. S1 The 1H NMR spectrum of the synthesized BSBF-NH_2 molecule.

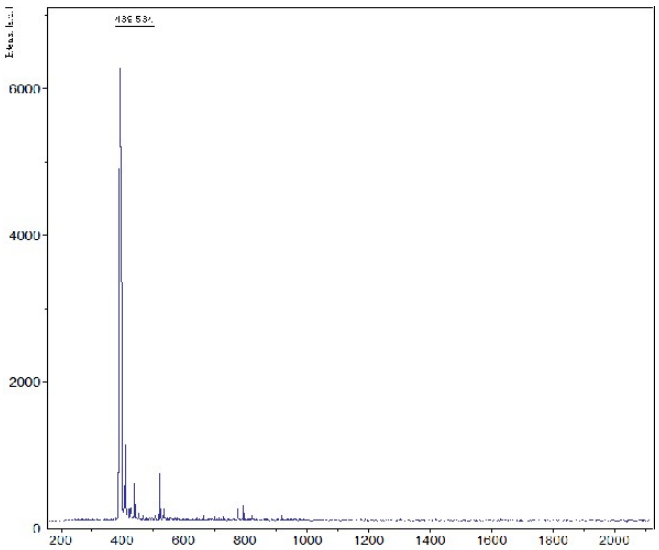


Fig. S2 The MALDI-TOF mass spectrum of synthesized BSBF-NH_2 molecule.

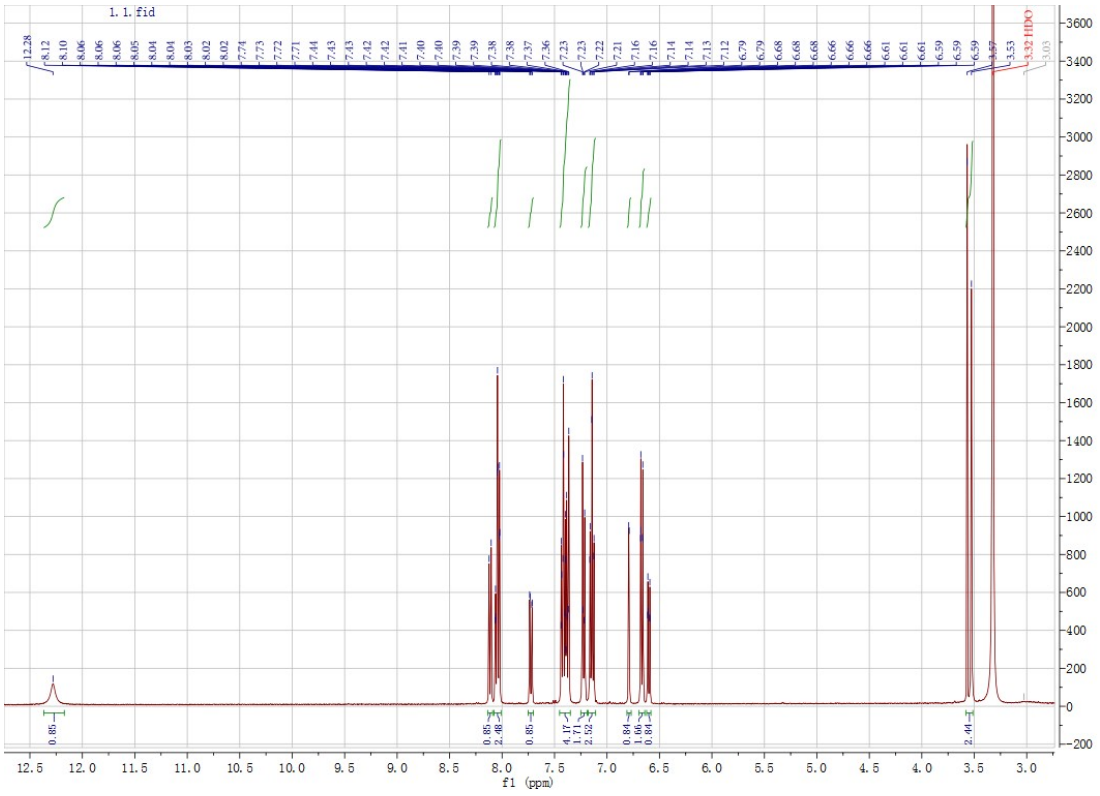


Fig. S3 The 1H NMR spectrum of the synthesized BSBF-COOH molecule.

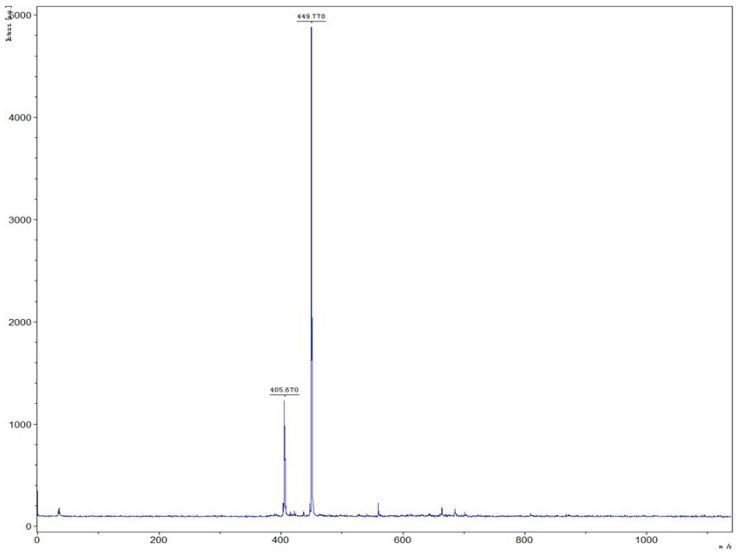


Fig. S4 The MALDI-TOF mass spectrum of synthesized BSBF-COOH molecule.

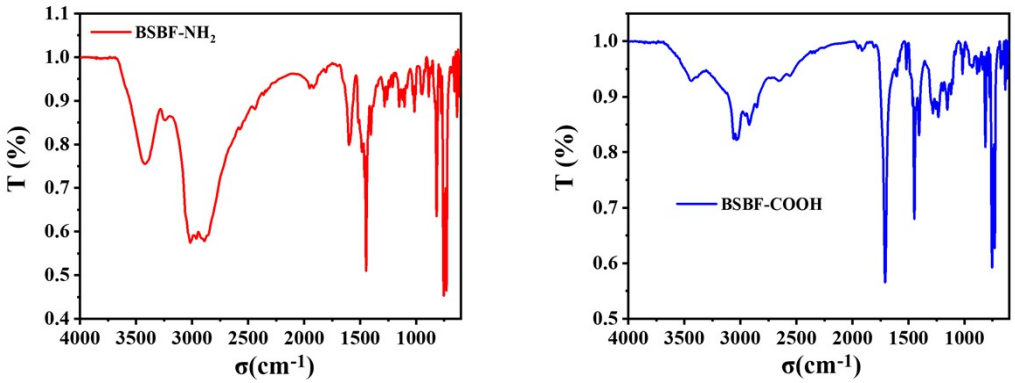


Fig. S5 The Infrared (IR) Spectroscopy of synthesized BSBF-COOH and BSBF-NH_2 molecule.

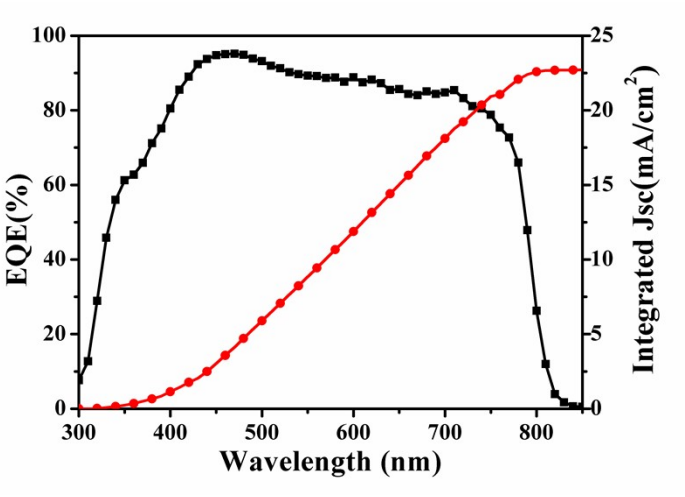


Fig. S6 Incident photon-to-current efficiency (IPCE) of the best performed BSBF-NH_2 passivated PSCs.

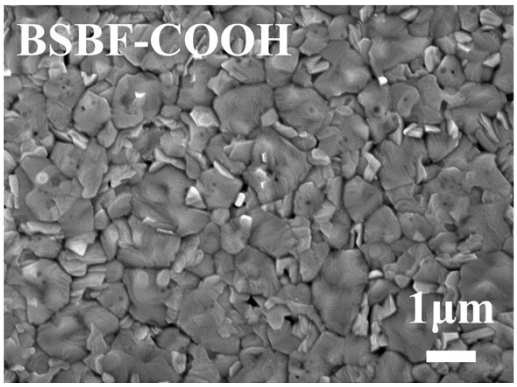


Fig. S7 Top view SEM images of the BSBF-COOH passivated perovskite films.

Table S1. Summary of the characterization for BSBF-NH_2 and BSBF-COOH.

	BSBF-NH_2	BSBF-COOH
Name	2-(4-(9,9'-spirobi[fluoren]-2-yl)phenyl)ethan-1-amine	2-(4-(9,9'-spirobi[fluoren]-2-yl) phenyl)acetic acid
Form	solid	solid
Colour	Pale yellow	Pale yellow
Chemical formula	$C_{33}H_{25}N$	$C_{33}H_{22}O_2$
Molecular weight	435.20	450.54
Melting point	191℃	138℃

Table S2. Summary of the photovoltaic parameters for BSBF-NH_2 passivated PSCs.

	Jsc (mA/cm^2)	Voc (V)	FF	PCE (%)
Control	23.62	1.07	0.73	18.45
1.25 mmol/L	23.46	1.08	0.76	19.25
2.50 mmol/L	23.67	1.10	0.77	20.05
5.00 mmol/L	23.41	1.08	0.74	18.71

Table S3. Summary of the photovoltaic parameters for BSBF-COOH passivated PSCs.

	Jsc (mA/cm^2)	Voc (V)	FF	PCE (%)
Control	23.60	1.06	0.73	18.26
1.25 mmol/L	23.21	1.08	0.76	19.05
2.50 mmol/L	23.12	1.08	0.77	19.23
5.00 mmol/L	23.41	1.08	0.75	18.21

Table S4. PL lifetimes and the corresponding component percentage of the control，BSBF-COOH and BSBF-NH_2 passivated perovskite films obtained by using a biexponential fitting model.

	τ_1 (ns)	A_1 (%)	τ_2 (ns)	A_2 (%)
Control	2.51	32.17	212.37	67.83
BSBF-COOH	2.03	26.23	323.82	73.58
BSBF-NH_2	2.02	24.40	350.61	75.60

Table S5 Summary of the time constants from fits to the transient absorption data in Figure 4f.

	τ_1 (ps)	τ_2 (ps)
Control	302	2792
BSBF-NH_2	139	2060