

## Supporting Information

### Self-Assembling Hole-Transport Material Incorporating Biphosphonic Acid for Dual-Defect Passivation in NiO<sub>x</sub>-Based Perovskite Solar Cells

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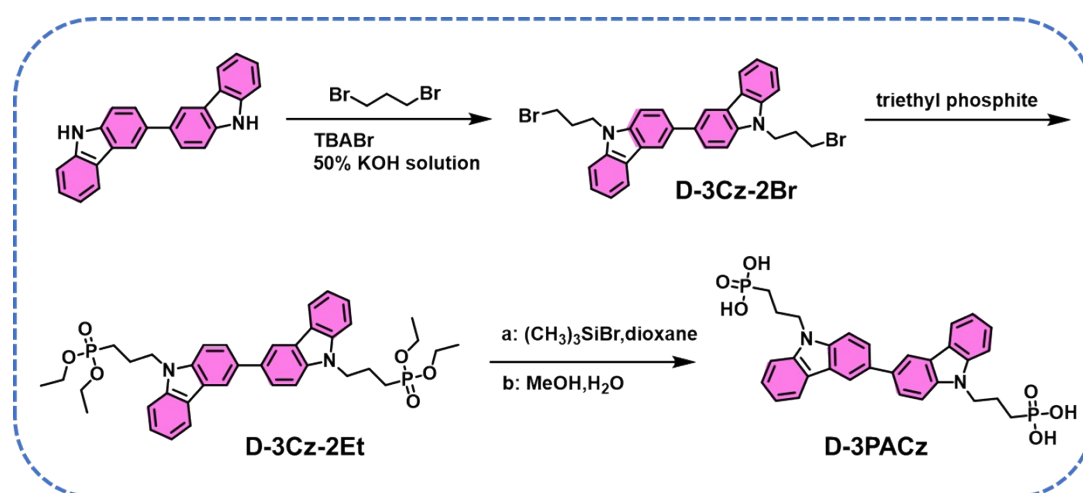
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## 1. Material Synthesis

D-3Cz-2Br, D-3Cz-2Et and D-3PACz were synthesized in this work. All other chemicals or solvents were used directly without further purification, unless otherwise stated. 3-Chlorocarbazole (1Cl-Cz), tetrabutylammonium bromide (TBABr), 1,2-dibromomethane, triethyl phosphite, trimethylsilyl bromide ((CH<sub>3</sub>)<sub>3</sub>SiBr), dioxane, were purchased from Energy Chemical, Adamas or TCL.



**Figure S1.** Synthetic route of self-assembled molecule D-3PACz

### *Synthesis of D-3Cz-2Br*

3,3'-bicarbazole (1.00g, 3.01 mmol) was dissolved in 1,3-dibromopropane (18 ml), and tetrabutylammonium bromide (0.98 g, 3.01 mmol) with 50% KOH aqueous solution (2.70 ml, 48.13 mmol) were added subsequently. Reaction was stirred at 75°C overnight. After completion of the reaction, extraction was done with dichloromethane. The organic layer was dried over anhydrous MgSO<sub>4</sub> and the solvent was distilled off under reduced pressure. The crude product was purified by column chromatography (PE:DCM=3:1, volume ratio) to give 1.31 g (yield 76 %) of white solid. <sup>1</sup>H NMR (400

MHz, CDCl<sub>3</sub>)  $\delta$  8.43 (s, 2H), 8.21 (d,  $J = 7.7$  Hz, 2H), 7.85 (d,  $J = 8.4$  Hz, 2H), 7.58 (d,  $J = 8.4$  Hz, 2H), 7.52 (d,  $J = 3.9$  Hz, 4H), 7.30 (dt,  $J = 7.8, 3.9$  Hz, 2H), 4.55 (t,  $J = 6.4$  Hz, 4H), 3.43 (t,  $J = 6.0$  Hz, 4H), 2.62-2.33 (m, 4H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  141.00, 139.67, 133.81, 126.15, 125.93, 123.77, 123.39, 120.74, 119.42, 119.20, 109.06, 108.94, 41.21, 32.22, 31.10, 29.91.

### *Synthesis of D-3Cz-2Et*

D-3Cz-Br (1.00 g, 1.74 mmol) was dissolved in triethyl phosphite (10 ml) and was heated at reflux for 18 h. After reaction completion, the solvent was distilled off under reduced pressure. The crude product was purified by column chromatography (EA as eluent) to give 0.96 g (yield 80%) of pale-yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.41 (s, 2H), 8.20 (d,  $J = 7.7$  Hz, 2H), 7.84 (dd,  $J = 8.5, 1.5$  Hz, 2H), 7.55 (d,  $J = 8.5$  Hz, 2H), 7.52-7.44 (m, 4H), 7.28 (dd,  $J = 9.6, 3.3$  Hz, 2H), 4.48 (t,  $J = 6.9$  Hz, 4H), 4.21-3.94 (m, 8H), 2.39 -2.14 (m, 4H), 1.92-1.68 (m, 4H), 1.30 (t,  $J = 7.1$  Hz, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  140.97, 139.63, 133.75, 126.08, 125.88, 123.72, 123.33, 120.71, 119.28, 119.19, 109.06, 108.94, 61.93, 43.18, 24.02, 22.61, 22.42, 16.67.

### *Synthesis of D-3PACz*

D-3Cz-2Et (0.93 g, 1.35 mmol) was dissolved in anhydrous 1,4-dioxane (20 ml) under nitrogen. Then, bromotrimethylsilane (2.09 g, 13.67 mmol) was added dropwise. Reaction was kept for 24h at room temperature. Afterwards solvent was distilled off under reduced pressure, solid residue was dissolved in MeOH (10 ml) and distilled water was added dropwise (50 ml). Product was filtered off and washed with water to give 0.51 g (yield 65 %) of white powder. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  8.56 (s,

2H), 8.27 (d,  $J = 7.6$  Hz, 2H), 7.84 (d,  $J = 8.0$  Hz, 2H), 7.67 (dd,  $J = 14.1, 8.4$  Hz, 4H), 7.46 (t,  $J = 7.5$  Hz, 2H), 7.21 (t,  $J = 7.4$  Hz, 2H), 4.48 (m, 4H), 2.00 (m, 4H), 1.69-1.36 (m, 4H).  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  140.51, 139.12, 132.40, 125.86, 125.16, 122.77, 122.36, 120.61, 118.79, 118.41, 109.69, 109.50, 25.94, 24.57, 22.88.

## 2. Material Characterization

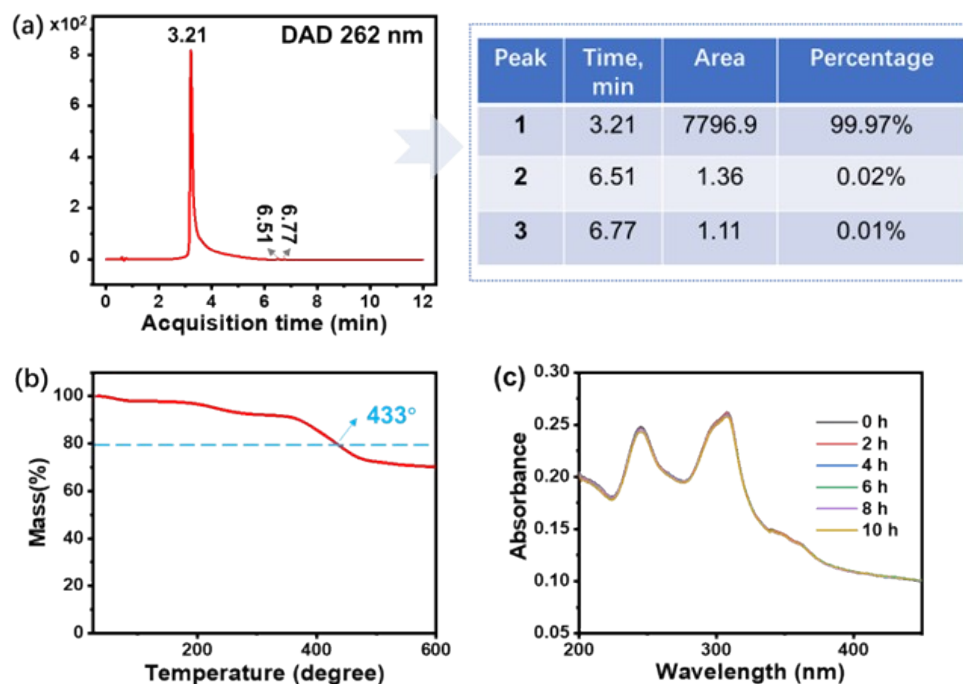
### Computational Methods

Density functional theory (DFT) calculations were performed using the projector-augmented wave (PAW) method as implemented in the Vienna Ab initio Simulation Package (VASP) code. The generalized gradient approximation (GGA) together with Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional was used. The van der Waals (vdW) interactions were also included in the calculations using zero damping DFT-D3 method of Grimme. A uniform grid of  $6 \times 6 \times 6$   $k$ -mesh in the Brillouin zone was employed to optimize the crystal structures of both cubic-phase  $\text{NiO}_x$  and  $\text{FAPbI}_3$  bulk,  $4 \times 4 \times 1$   $k$ -mesh for  $\text{NiO}_x$  and  $\text{PbI}_2$ -rich  $\text{FAPbI}_3$  slabs, and  $2 \times 2 \times 1$   $k$ -mesh for 2PACz/ $\text{NiO}_x$ , D-3PACz/ $\text{NiO}_x$ , and 2PACz/ $\text{FAPbI}_3$ , and D-3PACz/ $\text{FAPbI}_3$  interfaces.  $\text{NiO}_x$  slab model had a  $(3 \times 3)$  lateral periodicity with exposed (100) surface, and  $\text{FAPbI}_3$  slab model had a  $(3 \times 3)$  lateral periodicity with exposed (100) surface and  $\text{PbI}_2$ -rich termination (all slab replicas were separated by  $\sim 20$  Å of vacuum). The energy cutoffs of wave functions were set at 500 eV for the bulk and 400 eV for slabs and interfaces. The atomic positions of all structures were fully relaxed until the Hellman-Feynman forces on each atom is less than 0.015 eV/Å.

The binding energies were calculated using the equation of  $E_{\text{binding}} = E(\text{total}) - E(\text{NiO}) - E(\text{molecule})$  and  $E_{\text{binding}} = E(\text{total}) - E(\text{FAPbI}_3) - E(\text{molecule})$ , where  $E(\text{total})$  are the total energies of molecule/ $\text{NiO}_x$  or molecule/ $\text{FAPbI}_3$  interfaces,  $E(\text{NiO}_x)$  and  $E(\text{FAPbI}_3)$  are the energies of  $\text{NiO}$  ( $100_x$ ) slab and  $\text{FAPbI}_3$  ( $100_x$ ) slab, respectively, and  $E(\text{molecule})$  is the energy of 2PACz or D-3PACz. For the molecular calculations, the geometries of 2PACz and D-3PACz were optimized using B3LYP functional with 6-31+G(d,p) basis set as implemented in Gaussian16 program. The electrostatic

potential mappings were calculated at the same theoretical level.

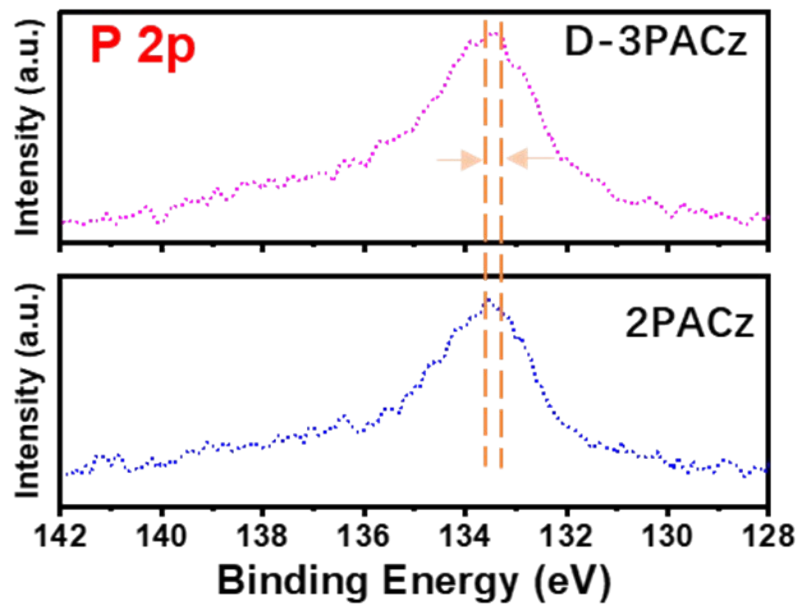
### Purity, thermal/photo stability of D-3PACz



**Figure S2.** (a) HPLC analysis of D-3PACz; (b) TG curve of D-3PACz; (c) UV-Vis spectrum of D-3PACz under continuous light exposure

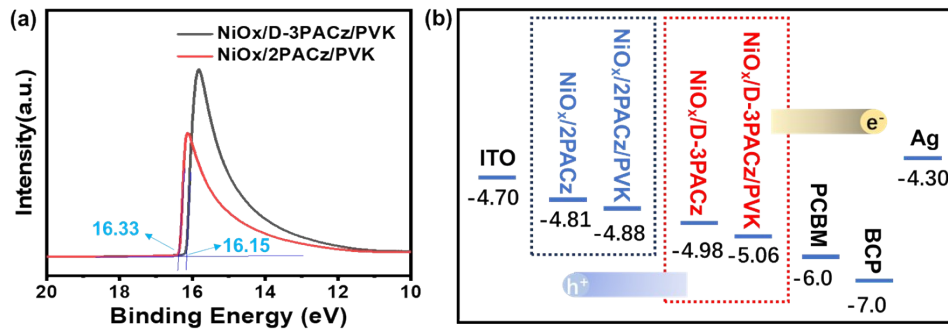
### XPS analysis

For the high-resolution X-ray photoelectron spectroscopy (XPS) measurements, the SAM films were prepared using the same method as for the AFM measurements. The samples were then loaded into the XPS instrument (Thermo Fisher ESCALAB Xi+) and an Al K $\alpha$  (1486.6 eV) X-ray was used as the excitation source. The ultraviolet photoelectron spectroscopy measurements were performed using the same samples of SAM films as XPS. A helium discharge lamp, emitting ultraviolet energy at 21.22 eV, was used for excitation. All ultraviolet photoelectron spectroscopy measurements were performed using standard procedures with a  $-10$ -V bias applied between the samples and detectors. Clean gold was used as a reference.



**Figure S3.** XPS spectra of NiO<sub>x</sub>/2PACz and NiO<sub>x</sub>/D-3PACz for P 2p

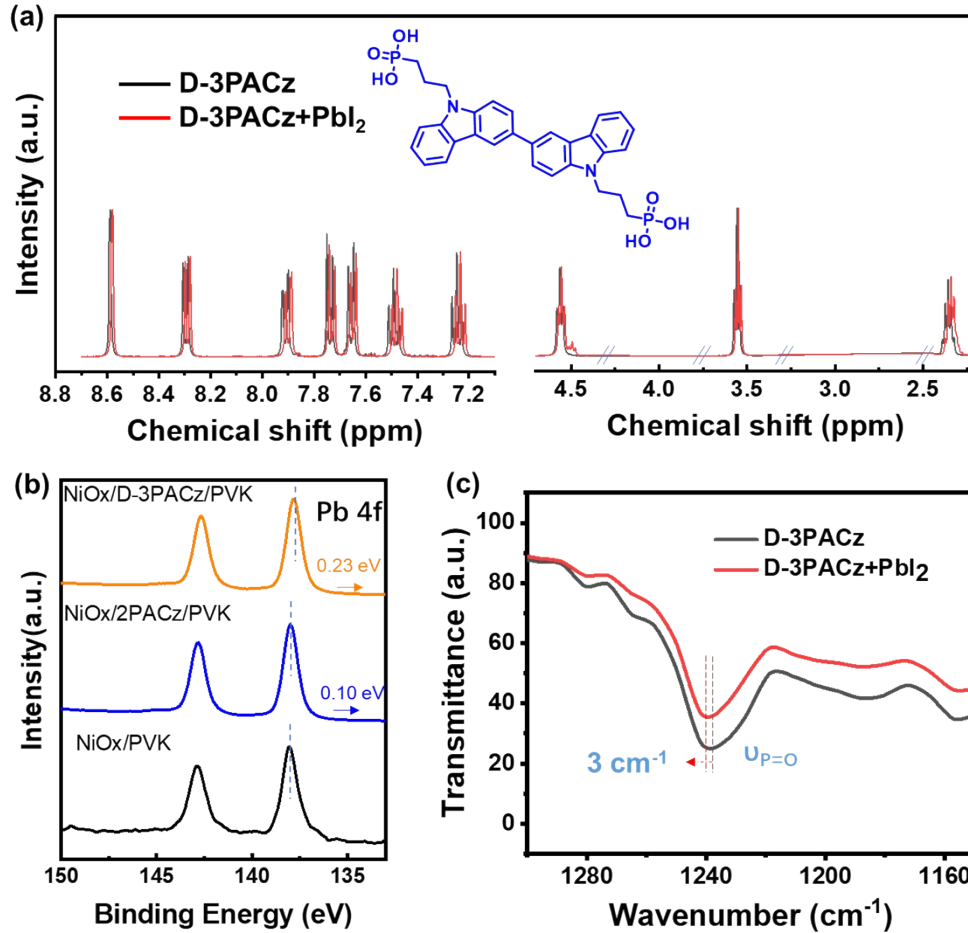
### UPS analysis



**Figure S4.** (a) UPS of NiO<sub>x</sub>/D-3PACz/PVK and NiO<sub>x</sub>/2PACz/PVK; (b) Energy level alignment of the PSC devices

### Interactions between D-3PACz and perovskites

To further examine the interactions between D-3PACz and the perovskite films, NMR, XPS and FTIR measurements were performed. The <sup>1</sup>H NMR spectra of D-3PACz, both with and without PbI<sub>2</sub>, were recorded using dimethyl sulfoxide-d<sub>6</sub> (DMSO-d<sub>6</sub>) as the solvent.



**Figure S5.** (a) NMR spectra for D-3PACz with/without  $\text{PbI}_2$ ; (b) XPS plots of  $\text{NiO}_x/\text{SAMs}/\text{PVK}$ ; (c) FTIR spectra of D-3PACz with and without  $\text{PbI}_2$

### XRD spectra

For the XRD measurements, to assess the perovskite films deposited on top of the molecular layers, the perovskite layers were prepared following the method described above, and the measurements were performed on sealed-tube copper X-ray source, equipped with a 1D LynxEye detector. For the measurements of the molecular films.

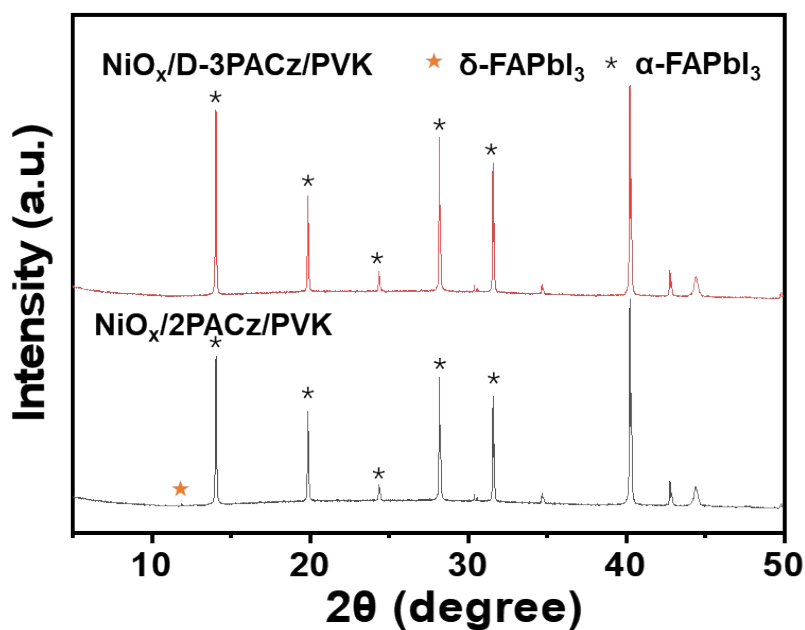


Figure S6. XRD patterns for 2PACz and D-3PACz

### Contact angle measurements

The surface free energy of D-3PACz and 2PACz were investigated using contact angle tests (the details were summarized in Table S1). As observed in Figure 2a, the water contact angles for 2PACz and D-3PACz were measured as  $65.5^\circ$  and  $63.1^\circ$ , respectively, indicating that both materials have good hydrophobic properties. For organic drops, the angles for D-3PACz were decreased to  $6.7^\circ$ , compared to 2PACz ( $23.7^\circ$ ). Consequently, D-3PACz exhibited a higher surface free energy of  $53.1 \text{ mN m}^{-1}$ , while 2PACz displayed the free energy at  $49.4 \text{ mN m}^{-1}$ .

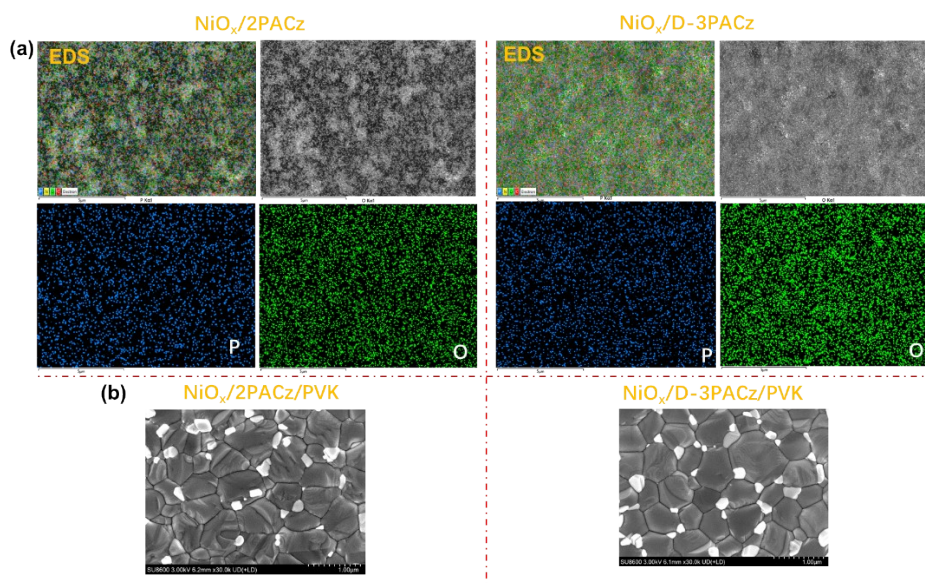


**Table S1** Contact angle details for ITO/2PACz and ITO/D-3PACz

<b>SAMs</b>	<b>Water</b>	<b>Diiodo-methane</b>	<b>Surface Energy</b>
<b>2PACz</b>	<b>65.5°</b>	<b>23.7°</b>	<b>49.4 mN m<sup>-1</sup></b>
<b>D-3PACz</b>	<b>63.1°</b>	<b>6.7°</b>	<b>53.1 mN m<sup>-1</sup></b>

### AFM and TEM Characterization

For the AFM/TEM measurements, the SAM films were prepared in a nitrogen glovebox by spin-coating the SAM precursor solutions (0.1 mg mL<sup>-1</sup> in mixed solvent of ethanol and DMF at a volume ratio of 3:1) at 1,000 rpm for 10 s and subsequently 3000 rpm for 40 s, followed by annealing at 130 °C for 20 min. The samples were then transferred into a container filled with nitrogen after cooling to room temperature. The as-prepared NiO<sub>x</sub>/SAMs samples were subsequently sent out for the AFM/TEM measurements. The filtered perovskite precursor was then spin-coated on substrate at 1,000 rpm for 10 s and 5,000 rpm for 40 s in a nitrogen glovebox. During the second spinning step, 250 μL of ethyl acetate anti-solvent was dropped quickly at 25 s. Afterwards, the film was annealed at 110 °C for 20 min. The as-prepared NiO<sub>x</sub>/SAMs/PVK samples were sent out for the AFM/TEM measurements.



**Figure S7.** (a) EDS mapping of NiO<sub>x</sub>/2PACz and NiO<sub>x</sub>/D-3PACz; (b) SEM images for NiO<sub>x</sub>/2PACz/PVK and NiO<sub>x</sub>/D-3PACz/PVK at a scale of 1 μm

## Device Performance

### Materials

The perovskite raw materials, including lead iodide (PbI<sub>2</sub>, purity 99.999%), formamidinium iodide (FAI, purity 99.99%), caesium iodide (CsI, purity 99.999%), PCBM (purity 99.9%) and Bathocuproine (purity 99%) were all purchased from Advanced Election Technology. The required solvents, including DMF (extra dry, purity 99.8%), isopropanol (IPA, extra dry, purity 99.8%), ethanol (extra dry, purity 99.8%) and ethyl acetate (extra dry, purity 99.5%) were purchased from J&K Scientific. Dimethyl sulfoxide (DMSO, anhydrous, ≥99.9%) and silver (purity 99.99%) was purchased from Sigma-Aldrich. All chemical reagents were used as received without further purification unless otherwise specified.

### Preparation of perovskite films

For the preparation of perovskite films with a composition of  $\text{Cs}_{0.07}\text{FA}_{0.93}\text{PbI}_3$ . 1.65-M perovskite precursor solution was prepared by dissolving CsI, FAI, and PbI<sub>2</sub> in 1 mL mixed solvent of DMF and DMSO at a volume ratio of 4:1. and the solution was stirred overnight. The filtered perovskite precursor was then spin-coated on substrate at 1,000 rpm for 10 s and 5,000 rpm for 40 s in a nitrogen glovebox. During the second spinning step, 250  $\mu\text{L}$  of ethyl acetate anti-solvent was dropped quickly at 25 s. Afterwards, the film was annealed at 110 °C for 20 min.

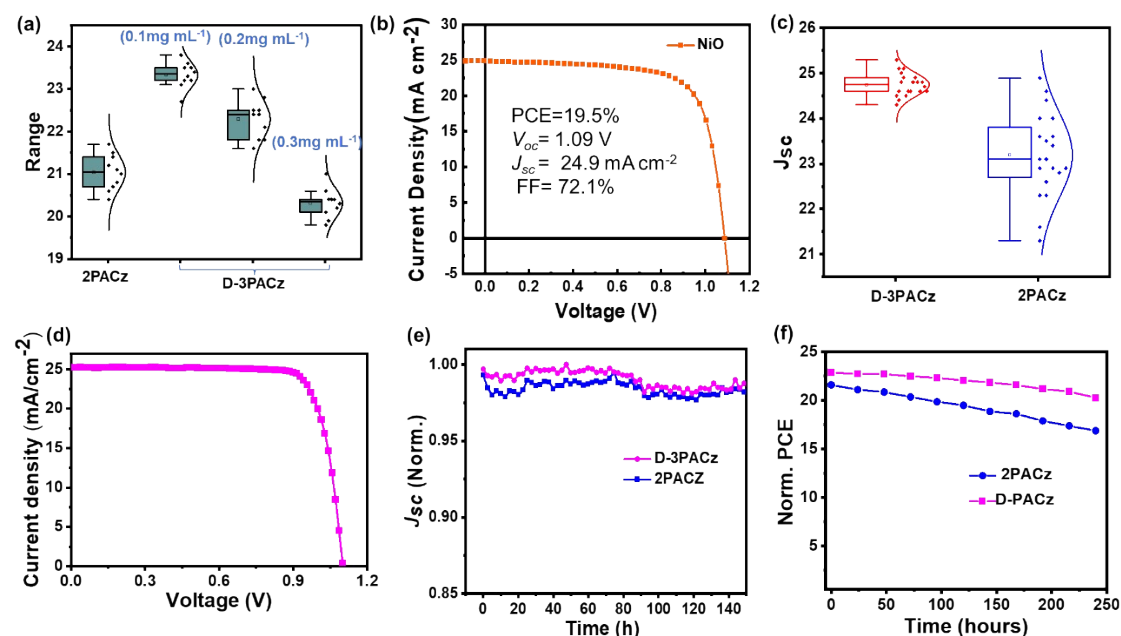
#### *Fabrication of inverted PSC devices*

First, the ITO glass (15 mm  $\times$  15 mm) was washed with detergent solution, acetone and absolute ethanol under sonication for 30 min each, followed by drying with a pure nitrogen flow. The cleaned and dry ITO substrates were then treated with ultraviolet ozone for 25 min, and then transferred into a glovebox filled with nitrogen. To deposit the 2PACz or D-3PACz layer on the ITO glass, the molecule solution with 0.1 mg mL<sup>-1</sup> in mixed solvent of ethanol and DMF at a volume ratio of 3:1 was spin-coated at 1,000 rpm for 10 s and 3,000 rpm for 40 s in a nitrogen glovebox. The role of adding DMF as a co-solvent is to improve the dispersion of the molecules in the solvent. Afterwards, the film was annealed at 130 °C for 20 min. After cooling to room temperature, the perovskite films were coated following the abovementioned method. Then PCBM (CB solvent, 20 mg/ml) and BCP (IPA solvent, 0.5 mg/ml) were subsequently deposited on top of perovskite film. After cooling to room temperature, the whole device was transferred to a vacuum chamber under a base pressure of  $<5.0 \times 10^{-4}$  Pa. Finally, 120-nm-thick silver electrode at a rate of 1.5  $\text{\AA s}^{-1}$  was

deposited to complete the devices for  $J$ - $V$  measurements or stability tests.

### Device characterization

The  $J$ - $V$  characteristics of photovoltaic cells were measured using a Keithley 2400 source measure unit under a simulated AM 1.5G spectrum, with an Oriel 9600 solar simulator. The illumination light was calibrated to  $100 \text{ mW cm}^{-2}$  AM 1.5G using a silicon reference cell. Typically, the devices were measured in reverse scan ( $1.20 \text{ V} \rightarrow 0 \text{ V}$ , step  $0.02 \text{ V}$ ). All the devices were measured without pre-conditioning such as light soaking and applied a bias voltage. Steady-state PCE was calculated by measuring stabilized photocurrent density under a constant bias voltage.



**Figure S8** (a) Optimization process for the optimal amount of SAM molecules; (b)  $J$ - $V$  curves of the cells without SAMs; (c) The statistics of  $J_{sc}$  values of the devices based on 2PACz and D-3PACz; (d)  $J$ - $V$  curves of the devices with co-deposition of D-3PACz with perovskites; (e) Normalized  $J_{sc}$  curved against time under illumination; (f) Device

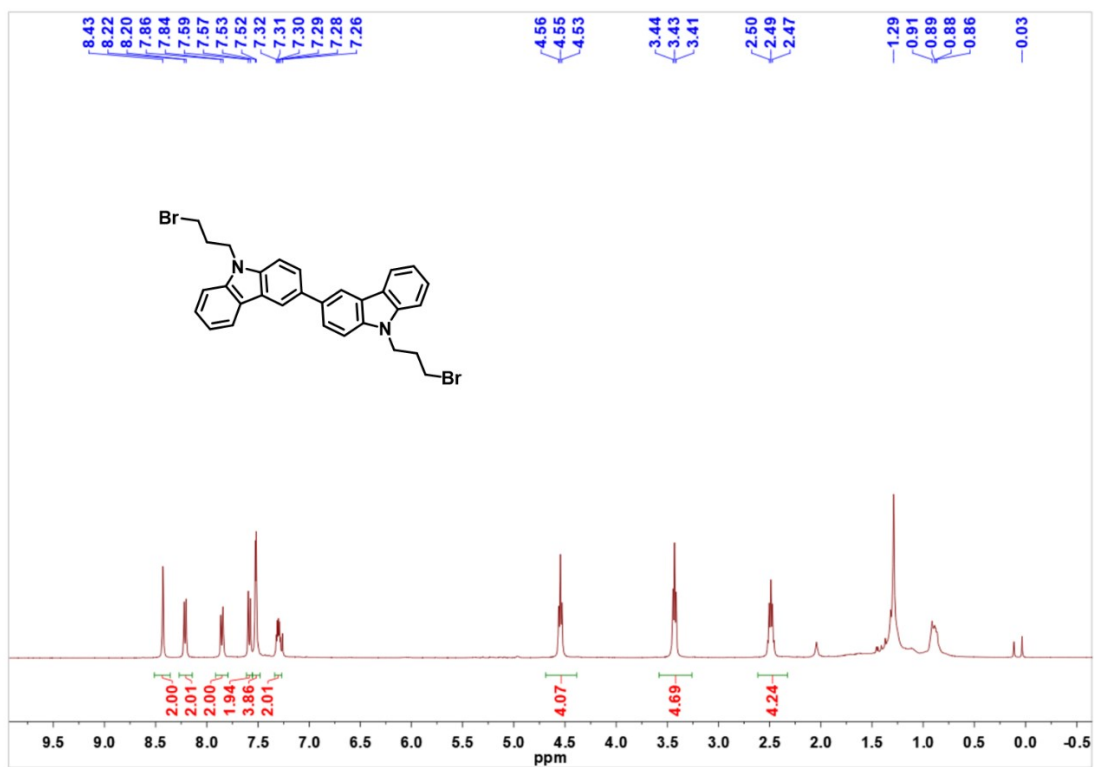
stability with the high temperature of 65°C.

### TRPL spectroscopy

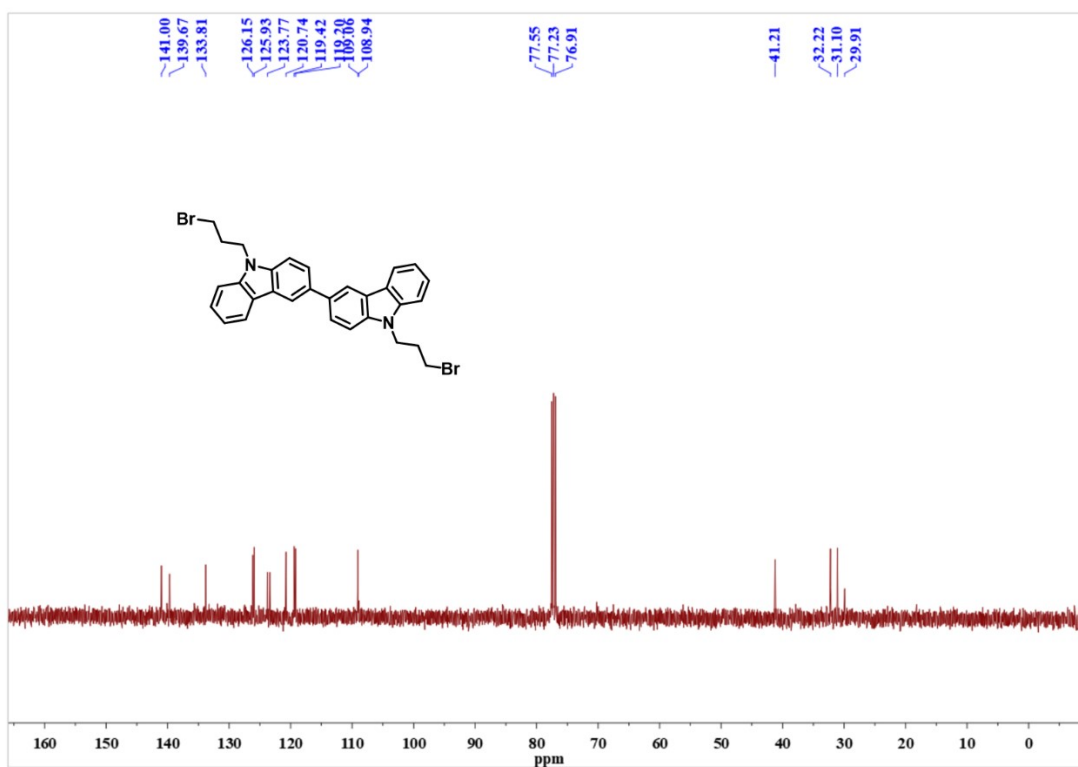
For the time-resolved photoluminescence (TRPL) spectroscopy measurements, the sample was excited with a picosecond pulsed diode laser (Pico-quant LDH 450), with a 70-ps pulse width and 20-MHz repetition rate, focused on sample with a  $\times 100$  objective (numerical aperture 0.90). The photoluminescence signal was acquired through the TCSPC strobelock system. The energy density of laser for TRPL measurements was set to be  $2.6 \text{ nJ cm}^{-2}$  and  $26.2 \text{ nJ cm}^{-2}$ , respectively.

### 3. NMR and Mass Spectrum\

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker Ascend 400 instrument with sample solutions in  $\text{CDCl}_3$  or  $\text{DMSO-d}_6$  using tetramethyl silane (TMS) as internal standard.



**Figure S9.** <sup>1</sup>H NMR spectrum of D-3Cz-2Br.



**Figure S10.** <sup>13</sup>C NMR spectrum of D-3Cz-2Br.

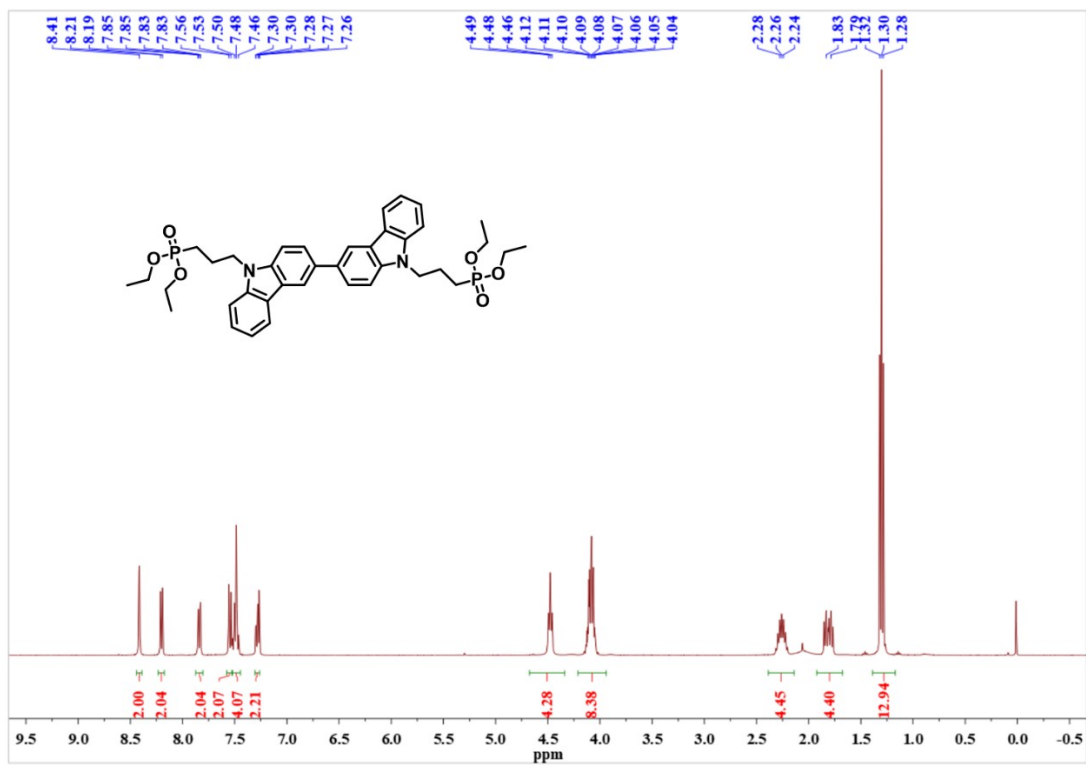


Figure S11. <sup>1</sup>H NMR spectrum of D-3Cz-2Et.

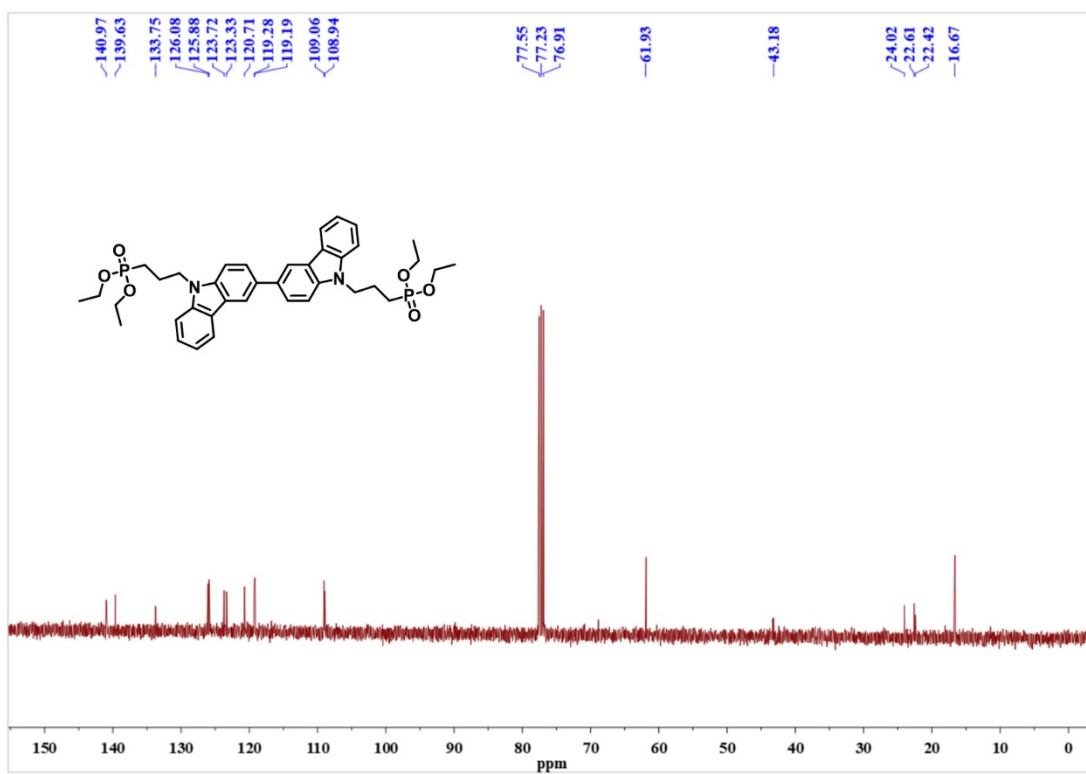


Figure S12. <sup>13</sup>C NMR spectrum of D-3Cz-2Et.

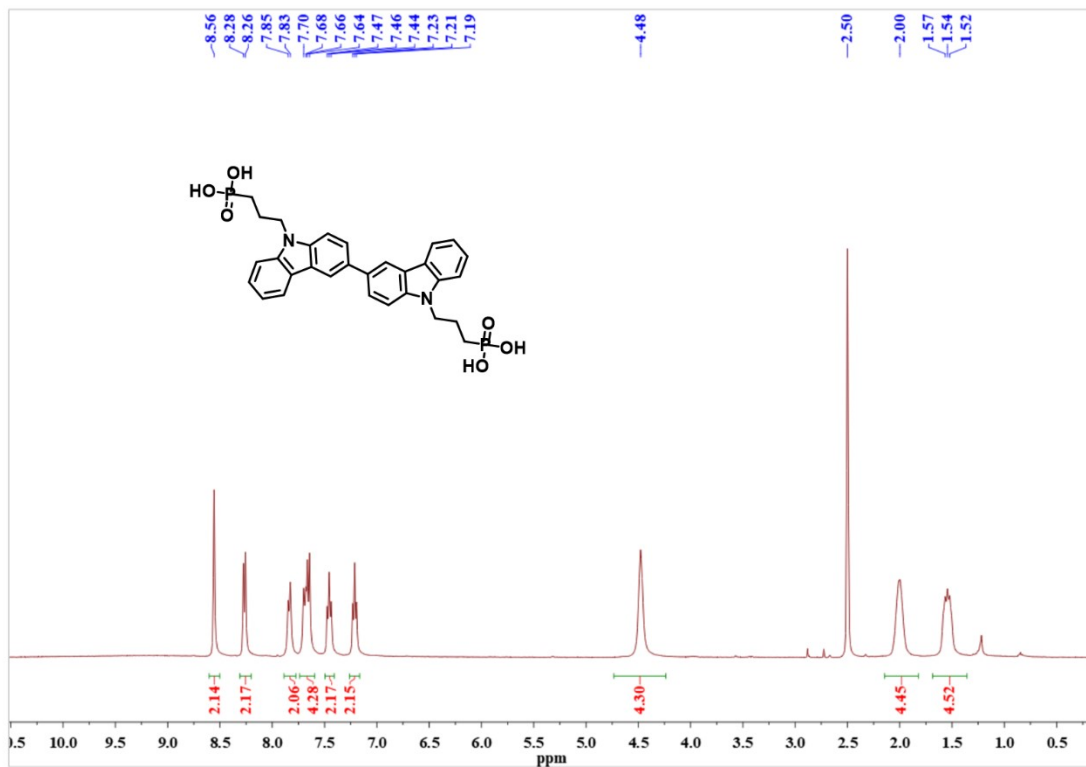


Figure S13.  $^1\text{H}$  NMR spectrum of D-3PACz.

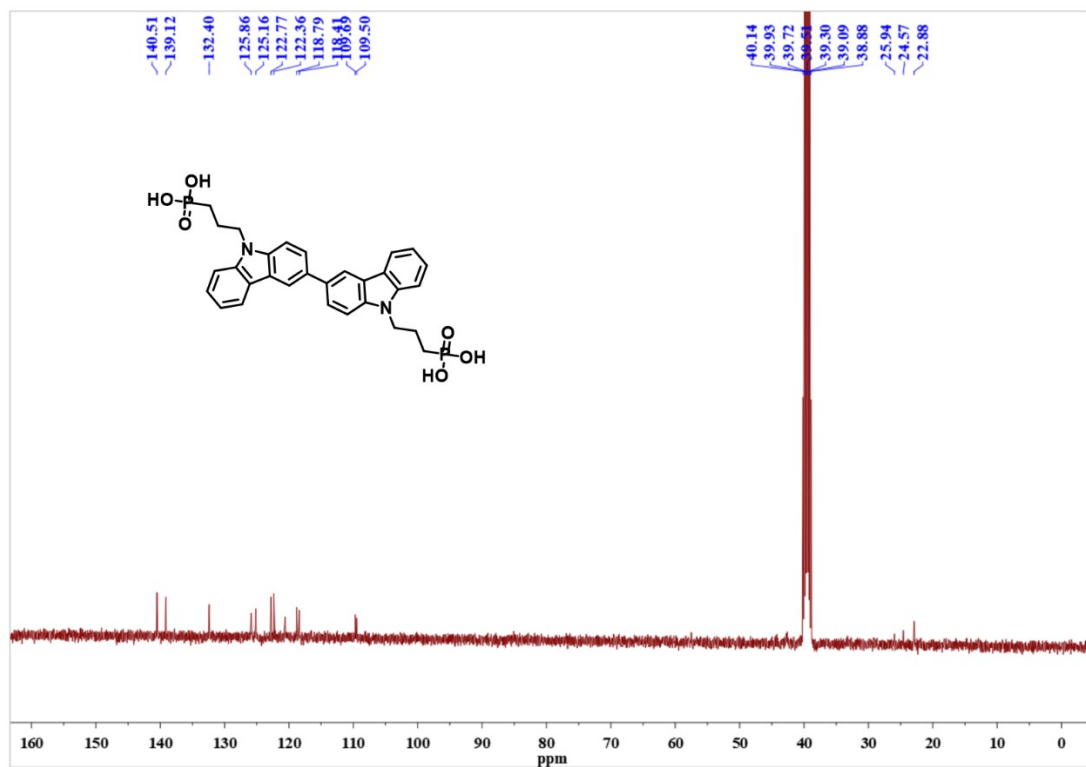
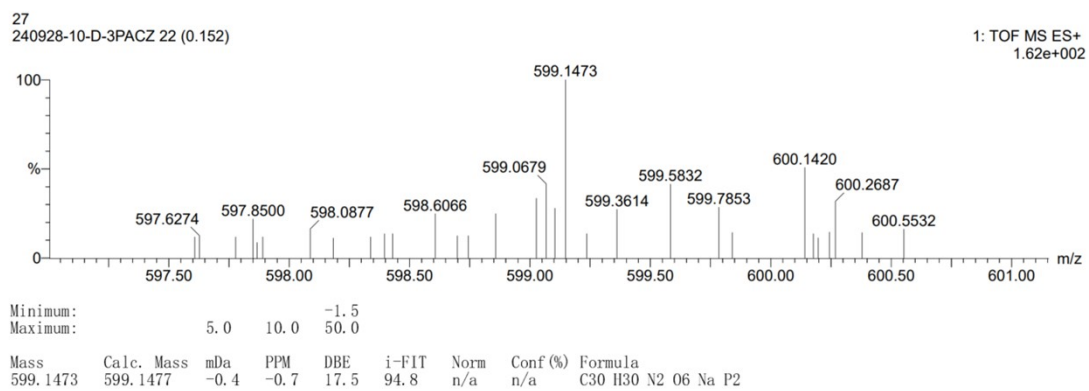


Figure S14.  $^{13}\text{C}$  NMR spectrum of D-3PACz.





**Figure S15.** High resolution mass spectrum of D-3PACz.