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Supporting Information

Molecular Tailoring of 2PACz SAMs via Substituent Design Enables Long-Term Stable and Efficient Inverted p-i-n Perovskite Solar Cells

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Materials

All the chemical materials and solvents used for device preparation were purchased and used directly without further purification. PbI_2, FAI, $PC_{61}BM$, BCP and were purchased from Xi'an Yuri Solar Co., Ltd. Patterned indium tin oxide (ITO) glass, Fused quartz were purchased from Advanced Election Technology Co., Ltd. DMSO, DMF, ethanol, chlorobenzene and isopropanol were purchased from Sigma-Aldrich (Merck).

Device Fabrication

The device with a structure of ITO/NiO_x/SAM/perovskite/PCBM/BCP/Ag was fabricated through the following sequential processes:

1) ITO Substrate Preparation: ITO-coated glass substrates were subjected to sequential ultrasonic cleaning in deionized water, acetone, and ethanol (15 min each solvent). The cleaned substrates were dried under nitrogen flow and subsequently treated with UV-ozone for 15 min to enhance surface wettability.

2) Hole Transport Layer (HTL) Deposition: A 15 mg mL^{-1} aqueous dispersion of

NiO_x nanoparticles was spin-coated onto the pre-cleaned ITO substrates at 3000 rpm for 30 s. The films were then thermally annealed at 120°C for 10 min in ambient atmosphere to form compact hole transport layers.

3) Self-Assembled Monolayer (SAM) Modification: Carbazole-based phosphonic acid derivatives (X-2PACz series: NO_2-2PACz, Br-2PACz, Cl-2PACz, 2PACz, MeO-2PACz, and MeS-2PACz) were employed as interfacial modifiers. Ethanol solutions (0.5 mg mL^{-1}) of different SAM molecules were spin-coated onto NiO_x layers at 3000 rpm for 30 s, followed by thermal treatment at 100°C for 10 min to facilitate molecular self-assembly.

4) Perovskite Film Formation: The perovskite precursor solution was prepared by dissolving 461 mg PbI_2 and 169.0 mg MAI in a mixed solvent of DMF:DMSO (636 μL:70.9 μL, v/v) under continuous stirring at 60°C. The fully dissolved solution was processed using a two-step spin-coating protocol: initial acceleration to 1200 rpm (5 s) followed by 4000 rpm (20 s) with antisolvent dripping (400 μL ethyl acetate:diethyl ether = 1:4 v/v) during the final 10 s. Post-deposition thermal annealing was performed at 60°C (1 min) and 100°C (10 min) to induce crystallization.

5) Electron Transport Layer (ETL): PCBM Layer: A 20 mg mL^{-1} solution of [6,6]-phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$) in chlorobenzene was spin-coated at 2500 rpm for 30 s.

6) Cathode Interlayer: Bathocuproine (BCP) is used as the cathode interface material. A saturated solution of BCP in isopropanol is prepared and spin-coated at 4000 rpm for 20 s.

7) Cathode: Finally, 100 nm-thick silver cathodes were thermally evaporated through a shadow mask under high vacuum ($<10^{-6}$ Torr).

Characterization and Measurement Methods

^1H NMR, ^{13}C NMR and ^{31}P NMR spectra were carried out by the Bruker AM 400 spectrometer. Liquid chromatography-mass spectrometry (LC-MS) was performed on Waters micro mass ZQ spectrometer. High resolution mass spectrometry (HRMS) was conducted using a Thermo Fisher Scientific Q Exactive Focus spectrometer equipped with an electrospray ionization (ESI) source, achieving a maximum resolution up to 70,000 at m/z = 200.

UV-vis absorption spectra were carried out with a PerkinElmer Lambda 750 spectrophotometer. X-ray diffraction (XRD) measurements were obtained by Thermo Fisher Scientific EQUINOX 3000 X-ray diffractometer in the 2θ range of 5° to 90°. Current-voltage (*J-V*) characteristics of perovskite solar cells were measured using a Zolix Solar IV photovoltaic characterization system under AM 1.5G simulated sunlight at 1500 W m^{-2}(Oriel Solar 3A), calibrated using a standard silicon reference cell. External quantum efficiency (EQE) was measured using a QE-R30 solar cell quantum efficiency measurement system from ENLITECH.

Electrochemical impedance spectroscopy (EIS) were carried out with a 1260A Impedance/Gain-Phase Analyzer (AMETEK Trading, Shanghai). A 5 V perturbation was applied over a frequency range of 0.1 to 100,000 Hz. High- and mid-frequency data were interpreted using the Randles equivalent circuit model and fitted with ZView software.

Atomic force microscopy (AFM) images were obtained using a Bruker Dimension Icon microscope with SCANASYST-AIR probes. Ultraviolet photoelectron spectroscopy (UPS) was performed using a Thermo Fisher Scientific ESCALAB 250Xi system with a He I source (21.22 eV photon energy). The pass energy was 1 eV, the bias was −10 eV, energy resolution was 0.01 eV, and sensitivity reached 1,000,000 cps. UPS provided the secondary electron cut-off and Fermi edge for different X-2PACz molecules and perovskite films. Work function and HOMO energy levels were calculated using the Einstein photoelectric equation.

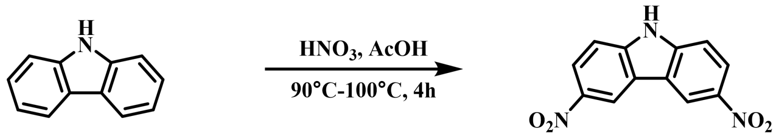
Theoretical Methods

Theoretical calculations of X-2PACz molecules were carried out using the Gaussian software package. The B3LYP-D3 functional combined with the 6-31G(d,p) basis set was employed to optimize the molecular structures and compute their electronic properties. The calculations focused on obtaining the frontier molecular orbitals—HOMO and LUMO—with subsequent visualization of their corresponding electron density distributions to analyze the effects of various substituents.

Synthesis of X-2PACz SAMs

1. Synthesis of NO_2-2PACz

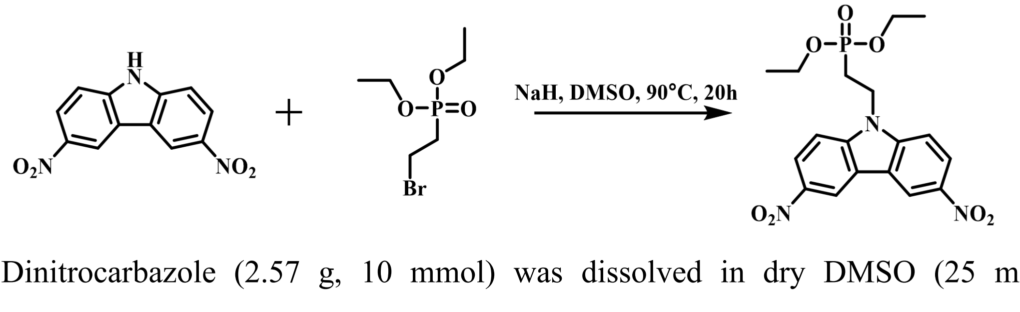
1.1 Synthesis of 3,6-Dinitrocarbazole:



Carbazole (2.51 g, 15 mmol) was dissolved in glacial acetic acid (20 g) in a 100 mL two-neck round-bottom flask equipped with a condenser and an addition funnel under N_2 atmosphere. The mixture was stirred at 40 °C for 1 h. A mixed solution of nitric acid and acetic acid (1:1, w/w, 22.05 g) was added dropwise, and the reaction was heated to 90-100 °C for 4 h. The resulting precipitate was filtered and washed with AcOH (50 mL) and water. The crude solid was treated with saturated ethanolic KOH at 50 °C for 1 h, then filtered and acidified with 10% HCl at 100 °C for 2 h. The final product was purified by dissolving in THF and reprecipitating with distilled water, followed by vacuum drying at 60 °C to yield a yellow solid (3.28 g, 85%).

^{1}H NMR (500 MHz, DMSO-d_6) $\delta = 11.10$ (s, 1H), 9.47 (d, 2H), 8.36 (dd, $J_1 = 9.3$ Hz, $J_2 = 2.7$ Hz, 2H), 7.74 (d, $J = 9.0$ Hz, 2H) ppm.

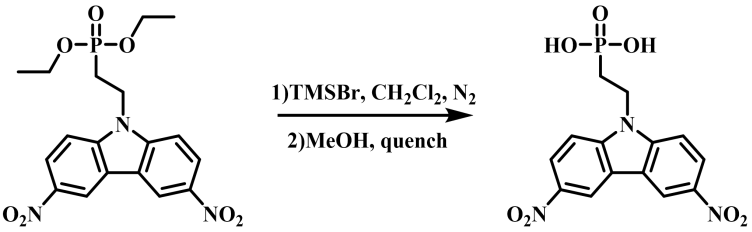
1.2 Synthesis of Diethyl (2-(3,6-dinitro-9H-carbazol-9-yl)ethyl)phosphonate:



3,6-Dinitrocarbazole (2.57 g, 10 mmol) was dissolved in dry DMSO (25 mL), followed by the addition of NaH (0.36 g, 15 mmol) under N_2 atmosphere. The mixture was stirred at room temperature for 30 min. 2-Bromoethyl diethylphosphonate (4.90 g, 20 mmol) was added, and the reaction was stirred at 90 °C for 20 h. After cooling, the mixture was quenched with water (20 mL) and extracted with ethyl acetate (three times, 100 mL each time). The combined organic phases were dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified via silica gel column chromatography (cyclohexane/ethyl acetate = 3:1) to yield a yellow solid (1.26 g, 30%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.06 (d, J = 2.1 Hz, 2H), 8.49 (dd, J = 9.1, 2.2 Hz, 2H), 7.60 (d, J = 9.1 Hz, 2H), 4.74 (dt, J = 13.1, 7.4 Hz, 2H), 4.41 – 3.83 (m, 4H), 2.74 – 2.12 (m, 2H), 1.56 – 1.02 (m, 6H) ppm.

1.3 Synthesis of (2-(3,6-dinitro-9H-carbazol-9-yl)ethyl)phosphonic acid:



Diethyl (2-(3,6-dinitro-9H-carbazol-9-yl)ethyl)phosphonate (0.42 g, 1 mmol) was dissolved in dry DCM (20 mL), and TMSBr (0.36 g, 3 mmol) was added under N_2. The mixture was stirred at room temperature for 22 h. The solvent was removed under reduced pressure, and methanol (20 mL) was added. After stirring for 30 min, water (60 mL) was introduced, and methanol was again evaporated. The precipitate was collected by filtration, washed with water, and further purified by DCM recrystallization to yield a yellow solid (0.33 g, 90%).

^{1}H NMR (400 MHz, DMSO-d_6) δ = 9.49 (d, J = 2.0 Hz, 2H), 8.45 (dd, J = 9.1, 2.0 Hz, 2H), 7.85 (d, J = 9.1 Hz, 2H), 4.70 (dd, J = 16.7, 8.8 Hz, 2H), 2.22 – 2.06 (m, 2H) ppm.

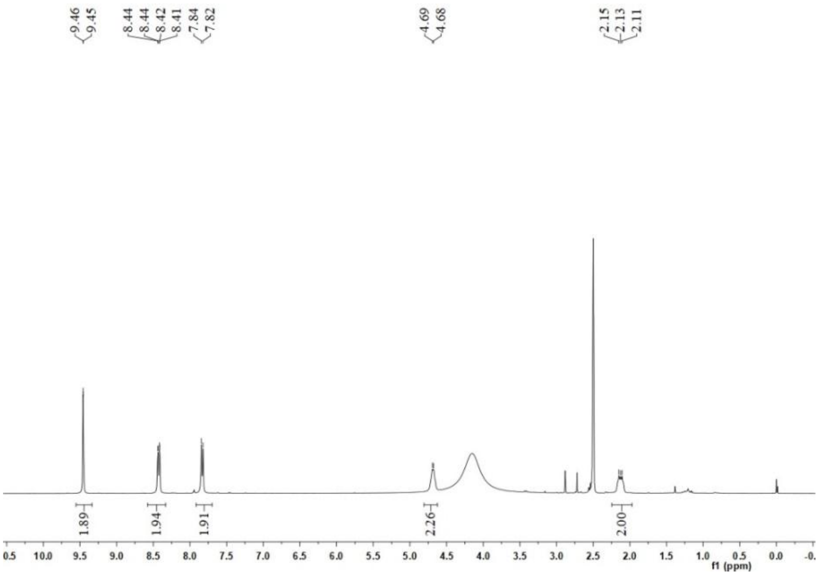


Fig. S1 The ^{1}H NMR (DMSO-d_6) spectrum of NO_2-2PACz.

^{13}C NMR (101 MHz, DMSO-d_6) δ = 144.38, 141.44, 122.80, 122.33, 118.79, 110.94, 38.79, 26.48 ppm.

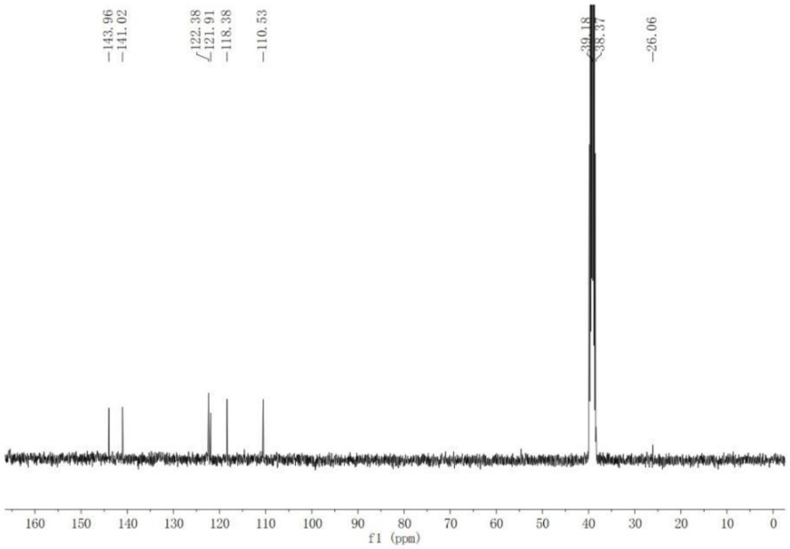


Fig. S2 The ^{13}C NMR (DMSO-d_6) spectrum of NO_2-2PACz.

^{31}P NMR (162 MHz, DMSO-d6) δ = 20.91 ppm.

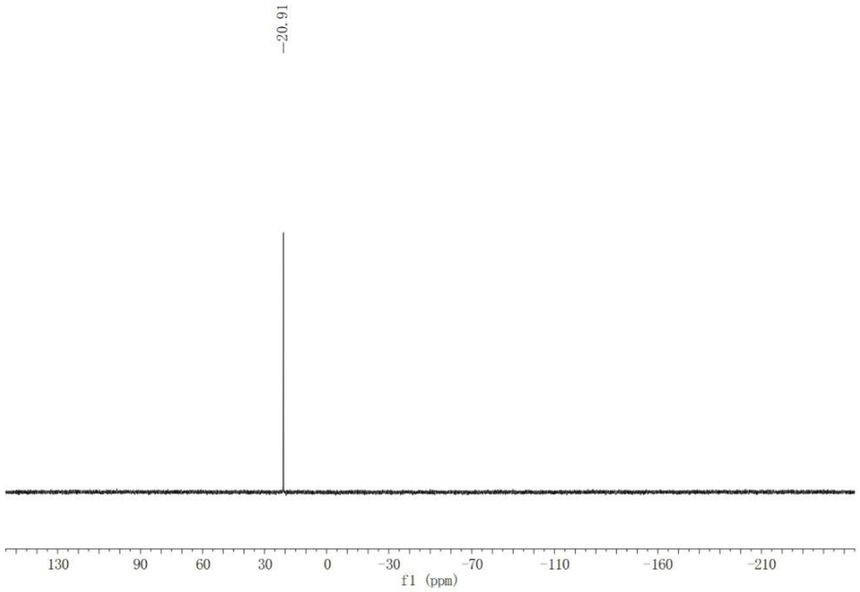


Fig. S3 The ^{31}P NMR (DMSO-d$_6$) spectrum of NO$_2$-2PACz.

LC-MS-ES-API(m/z): [M]$^+$ Calcd. for ($C_{14}H_{12}N_3O_7P$): 365.2, found: 365.0.

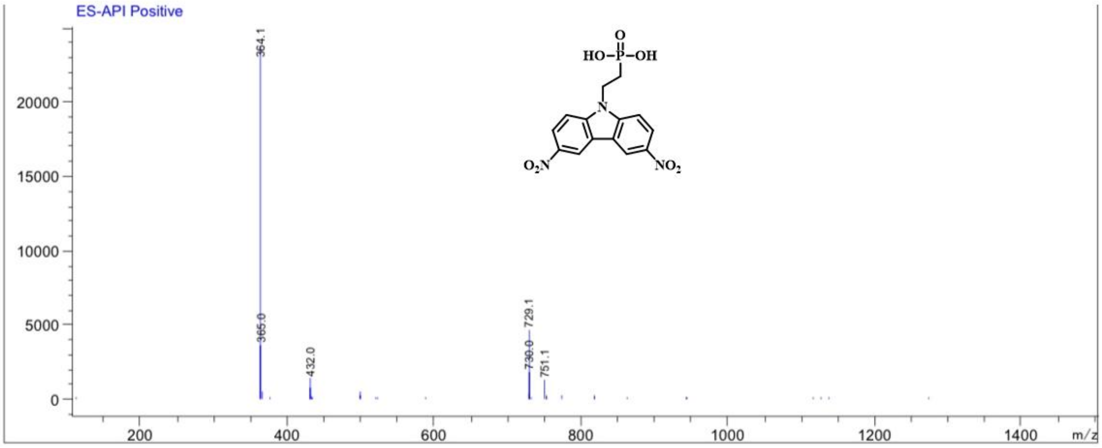
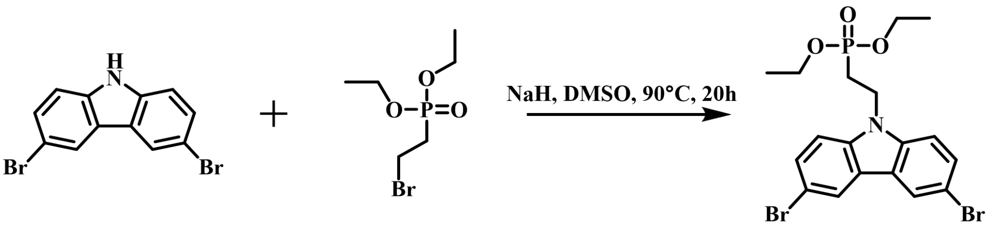


Fig. S4 The Liquid Chromatograph Mass spectrum of NO$_2$-2PACz.

2. Synthesis of Br-2PACz

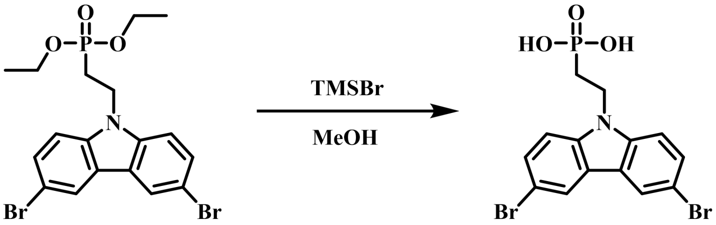
2.1 Synthesis of diethyl (2-(3,6-dibromo-9H-carbazol-9-yl)ethyl)phosphonate:



3,6-Dibromocarbazole (3.25 g, 10 mmol) was dissolved in dry DMSO (30 mL), and NaH (0.36 g, 15 mmol) was added under N$_2$ atmosphere. The mixture was stirred at room temperature for 30 min. 2-Bromoethyl diethylphosphonate (4.90 g, 20 mmol) was added, and the reaction was stirred at 90 °C for 20 h. Upon completion, the reaction was quenched with water (20 mL) and extracted with ethyl acetate (3 times 100 mL each time). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by silica gel chromatography (cyclohexane/ethyl acetate = 3:1) to afford a white solid (4.01 g, 82%).

^1H NMR (400 MHz, $CDCl_3$) $\delta = 8.15$ (d, J = 1.6 Hz, 2H), 7.60 (dd, $J_1 = 6.8$ Hz, $J_2 = 1.6$ Hz, 2H), 7.42 (d, J = 6.8 Hz, 2H), 4.58 (m, 2H), 4.06 (m, 4H), 2.24 (m, 2H), 1.26 (t, J = 5.6 Hz, 6H) ppm.

2.2 Synthesis of (2-(3,6-dibromo-9H-carbazol-9-yl)ethyl)phosphonic acid:



Diethyl (2-(3,6-dibromo-9H-carbazol-9-yl)ethyl)phosphonate (0.49 g, 1 mmol) was dissolved in dry DCM (20 mL), and TMSBr (0.36 g, 3 mmol) was added under N_2 atmosphere. The mixture was stirred at room temperature for 22 h. After solvent removal under reduced pressure, methanol (15 mL) was added and stirred for 50 min. Water (70 mL) was then added, and the methanol was partially evaporated under reduced pressure. The resulting precipitate was filtered, washed with water, and dried. The solid was further recrystallized by stirring in DCM (25 mL) overnight, then filtered and dried under vacuum to yield a white solid (0.41 g, 95%).

^1H NMR (400 MHz, DMSO-d_6) $\delta = 8.47$ (d, J = 1.9 Hz, 2H), 7.63 (dd, J = 8.7, 2.0 Hz, 2H), 7.54 (d, J = 8.7 Hz, 2H), 5.31 (br, 2H), 4.53 (dd, J = 16.0, 8.6 Hz, 2H), 2.11 – 1.91 (m, 2H) ppm.

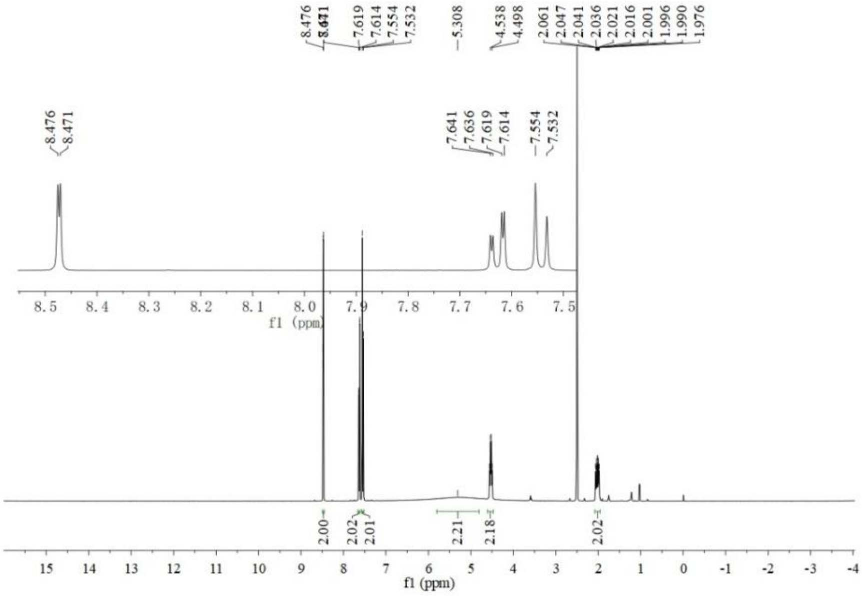


Fig. S5 The ^{1}H NMR (DMSO-d$_6$) spectrum of Br-2PACz.

^{13}C NMR (101 MHz, DMSO-d$_6$) δ = 138.67, 129.06, 123.64, 123.26, 111.60, 111.56, 37.86, 27.24 (d, $J_{C\text{-}P}$ = 131.6 Hz) ppm.

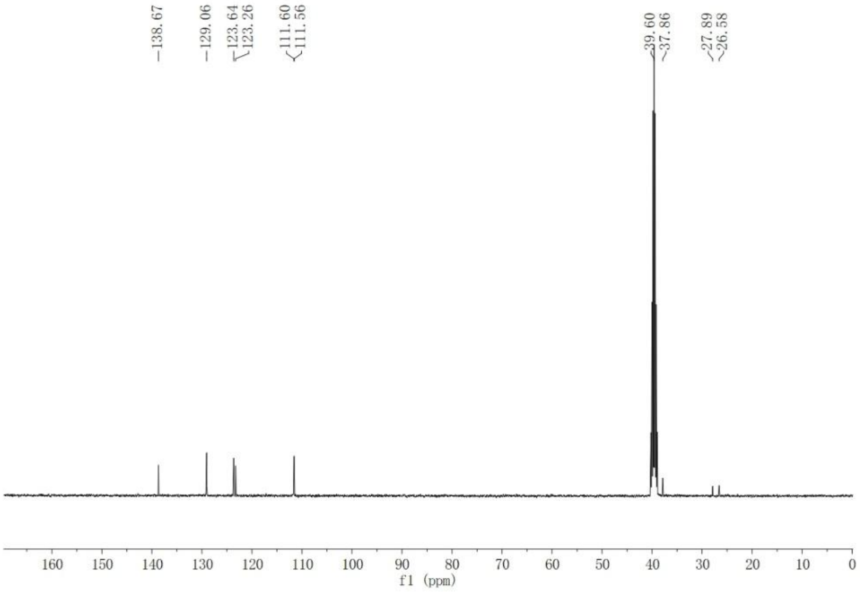


Fig. S6 The ^{13}C NMR (DMSO-d$_6$) spectrum of Br-2PACz.

^{31}P NMR (162 MHz, DMSO-d$_6$) δ = 21.35 ppm.

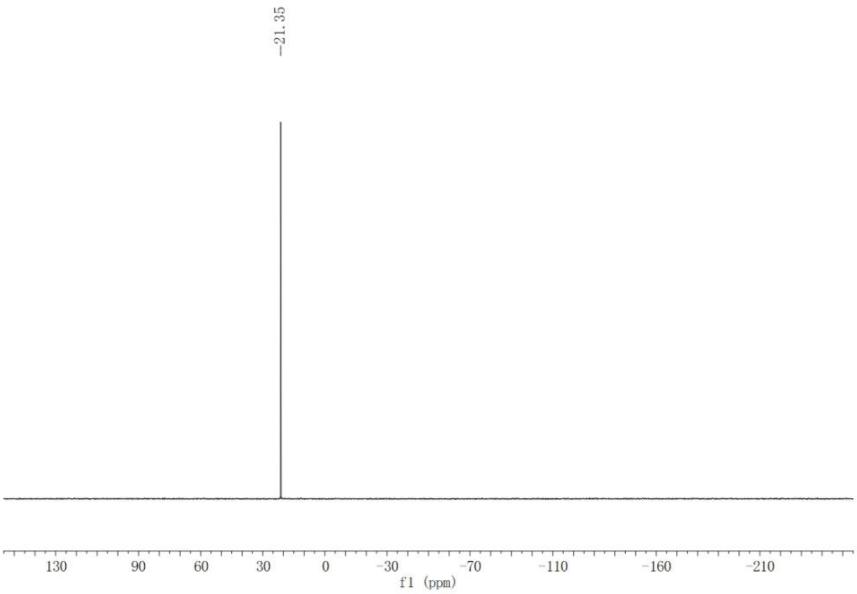
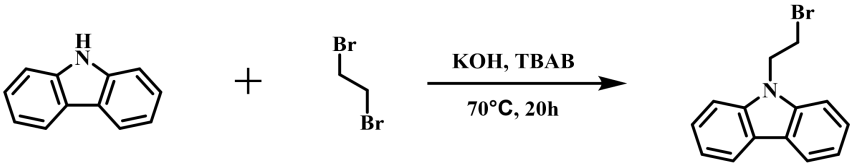


Fig. S7 The ^{31}P NMR (DMSO-d_6) spectrum of Br-2PACz.

3. Synthesis of 2PACz

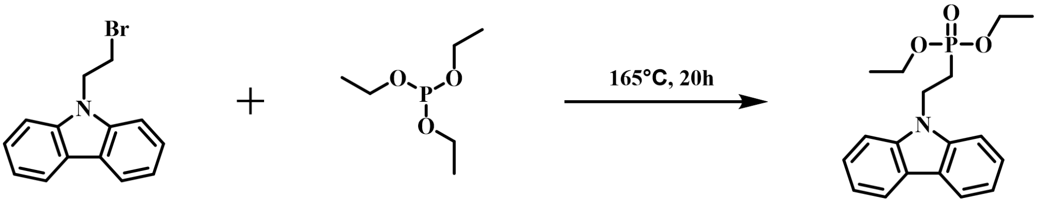
3.1 Synthesis of 9-(2-Bromoethyl)carbazole:



9H-Carbazole (4.01 g, 24 mmol) was dissolved in 1,2-dibromoethane (40 mL), followed by the addition of tetrabutylammonium bromide (0.16 g, 0.5 mmol) and 50% KOH aqueous solution (14.4 mL). The reaction mixture was stirred at 70 °C for 6 h and monitored by TLC (acetone/hexane = 3:22, v/v). Upon completion, the reaction mixture was extracted with ethyl acetate (3 times, 50 mL each time). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel chromatography (cyclohexane/ethyl acetate = 15:1) to yield a white crystalline solid (4.93 g, 75%).

^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.08 (d, J = 7.7 Hz, 2H), 7.51-7.36 (m, 4H), 7.29-7.20 (m, 2H), 4.66 (t, J = 7.5 Hz, 2H), 3.64 (t, J = 7.5 Hz, 2H) ppm.

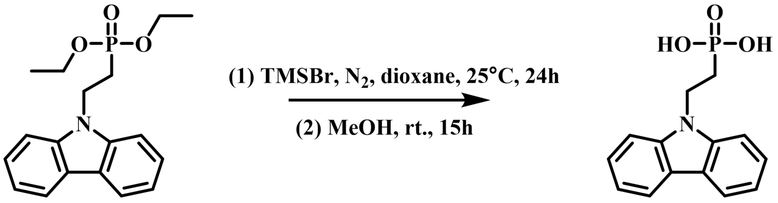
3.2 Synthesis of diethyl (2-(9H-carbazol-9-yl)ethyl)phosphonate:



9-(2-Bromoethyl)carbazole (1.14 g, 4.16 mmol) was dissolved in triethyl phosphite (14 mL) and refluxed for 20 h. The reaction progress was monitored by TLC (acetone/hexane = 7:18, v/v). After completion, the solvent was removed under reduced pressure. The crude product was purified by silica gel chromatography, starting with hexane and gradually transitioning to acetone/hexane = 1:4 (v/v), yielding a clear liquid (1.25 g, 91%).

^{1}H NMR (400 MHz, DMSO-d_6) δ= 8.15 (dd, J = 7.9, 1.9 Hz, 2H), 7.58 (d, J = 8.2 Hz, 2H), 7.52 – 7.43 (m, 2H), 7.26 – 7.17 (m, 2H), 4.65 – 4.54 (m, 2H), 3.94 – 3.85 (m, 4H), 2.35 – 2.21 (m, 2H), 1.23 (t, J = 7.0 Hz, 6H) ppm.

3.3 Synthesis of (2-(9H-carbazol-9-yl)ethyl)phosphonic acid:



Diethyl (2-(9H-carbazol-9-yl)ethyl)phosphonate (1.00 g, 3.02 mmol) was dissolved in dry 1,4-dioxane (30 mL), and TMSBr (4 mL) was added dropwise under a nitrogen atmosphere. The mixture was stirred at 25 °C for 24 h. The solvent was removed under reduced pressure. The residue was dissolved in methanol (30 mL), followed by the dropwise addition of distilled water (150 mL) until turbidity was observed. The mixture was stirred for 24 h and then concentrated under reduced pressure. The resulting solid was filtered, washed with water, and dried to yield a white solid (0.510 g, 61%).

^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.15 (d, J = 7.7 Hz, 2H), 7.54 (d, J = 8.1 Hz, 2H), 7.46 (t, J = 7.6 Hz, 2H), 7.21 (t, J = 7.4 Hz, 2H), 4.85 – 4.32 (m, 2H), 2.09 – 1.96 (m, 2H) ppm.

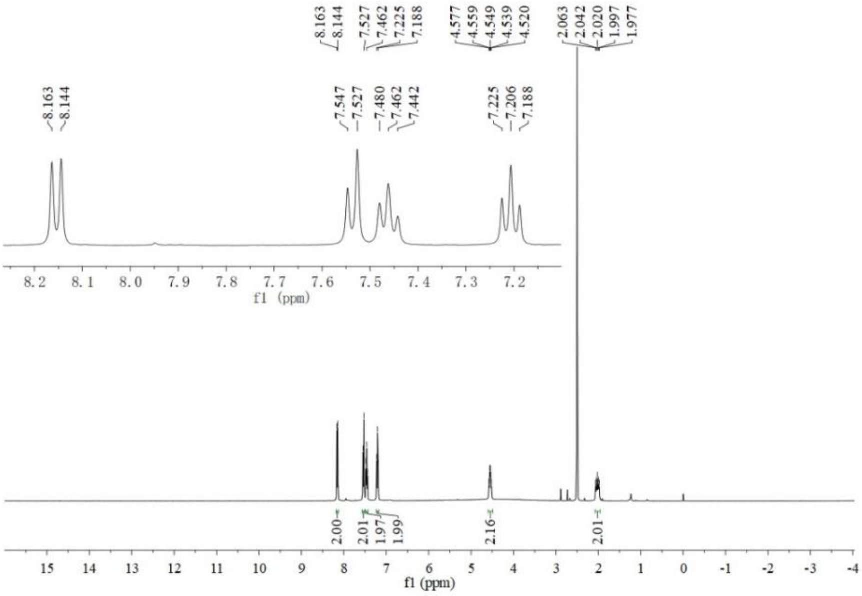


Fig. S8 The ^{1}H NMR (DMSO-d_6) spectrum of 2PACz.

^{13}C NMR (101 MHz, DMSO-d_6) δ = 139.49, 125.94, 122.35, 120.51, 119.03, 109.01, 37.53, 27.47 (d, J_{C-P} = 130.6 Hz) ppm.

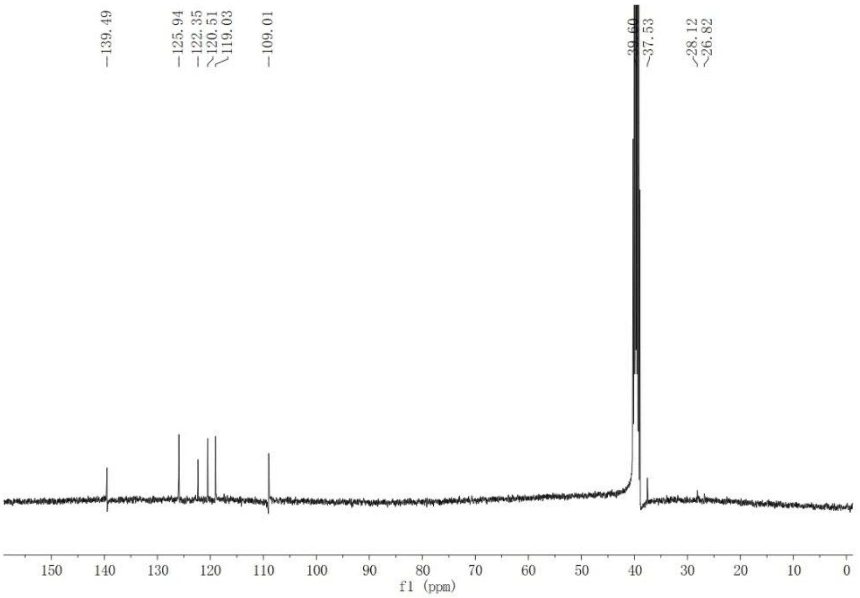


Fig. S9 The ^{13}C NMR (DMSO-d_6) spectrum of 2PACz.

^{31}P NMR (162 MHz, DMSO-d_6) δ = 21.30 ppm.

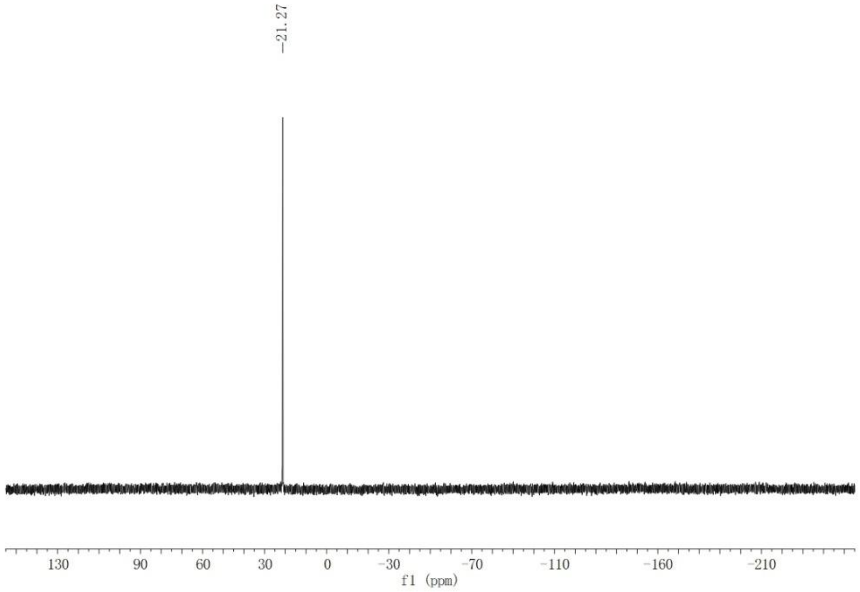


Fig. S10 The ^{31}P NMR (DMSO-d_6) spectrum of 2PACz.

HRMS-ESI (m/z): $[M+H]^+$ Calcd. for ($C_{14}H_{14}NO_3P$): 276.24, found: 276.08.

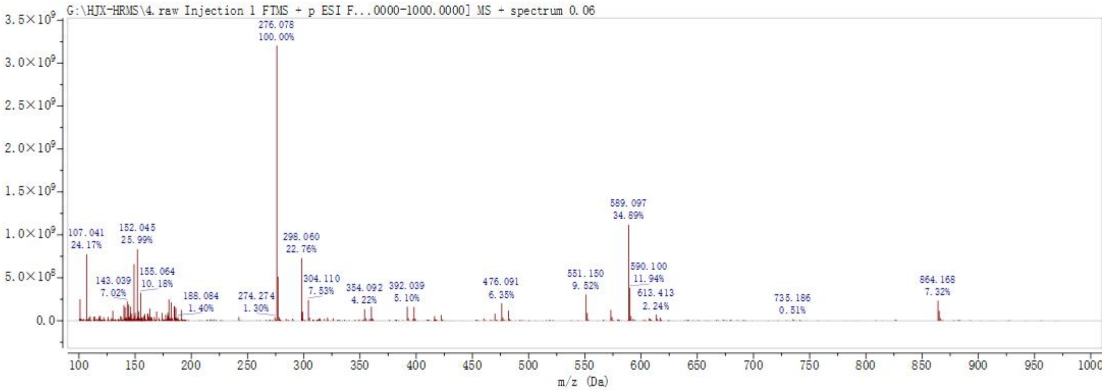
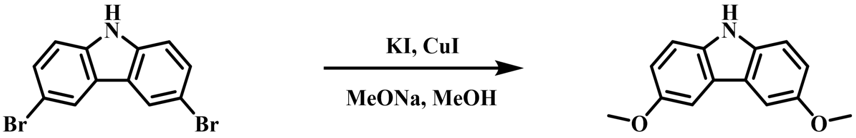


Fig. S11 The high-resolution mass spectrum of 2PACz.

4. Synthesis of MeO-2PACz

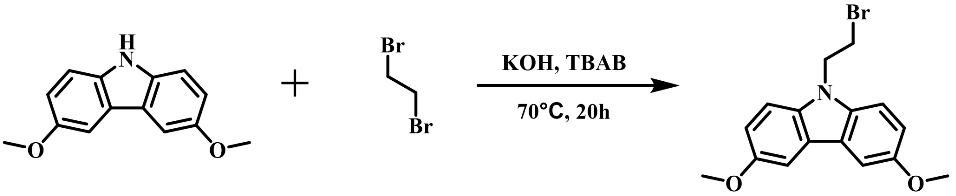
4.1 Synthesis of 3,6-Dimethoxycarbazole:



In a 100 mL two-neck round-bottom flask under a nitrogen atmosphere, 3,6-dibromocarbazole (1.20 g, 3.69 mmol), CuI (2.96 g, 15.5 mmol), KI (2.57 g, 15.5 mmol), sodium methoxide solution (3.4 mol L^{-1} in MeOH, 10 mL), and dry methanol (40 mL) were combined. The mixture was refluxed for 3 h. Upon completion, ethyl acetate (160 mL) was added, and the mixture was filtered through diatomaceous earth. The filtrate was washed with saturated brine (3 times, 75 mL each time), dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by column chromatography (CH_2Cl_2/petroleum ether = 1:1) to yield a white solid (0.746 g, 89%).

^1H NMR (400 MHz, $CDCl_3$) δ= 9.89 (s, 1H); 7.64 (d, J = 2.4 Hz; 2H); 7.37 (m, 2H); 7.00 (dd, J_1 = 8.7 Hz, J_2 = 2.5 Hz, 2H), 3.87 (s, 6H) ppm.

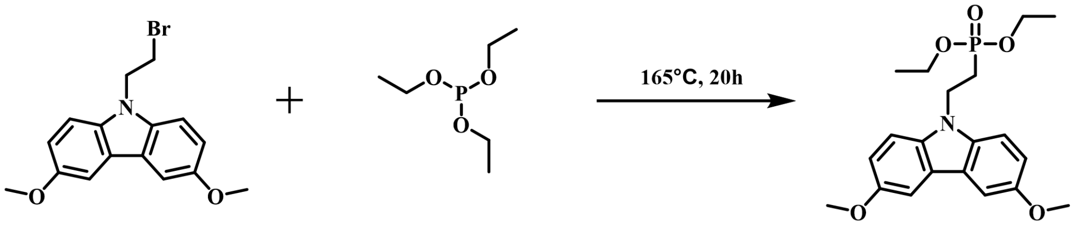
4.2 Synthesis of 9-(2-bromoethyl)-3,6-dimethoxy-9H-carbazole:



3,6-Dimethoxycarbazole (0.534 g, 2.35 mmol) was dissolved in 1,2-dibromoethane (8 mL) in a 50 mL round-bottom flask. Tetrabutylammonium bromide (0.08 g, 0.25 mmol) and 50% aqueous KOH (6.9 mL) were added. The reaction mixture was stirred at 70 °C for 20 h (TLC monitored; acetone/hexane = 3:22, v/v). After completion, the mixture was extracted with ethyl acetate, and the organic layer was dried over Na_2SO_4 and concentrated. The crude product was purified by silica gel chromatography (acetone/hexane = 1:49), yielding a white crystalline solid (0.352 g, 60%).

^1H NMR (400 MHz, $CDCl_3$) δ= 7.51 (d, J = 2.5 Hz, 2H), 7.29 (d, J = 8.8 Hz, 2H), 7.10 (dd, J = 8.8, 2.5 Hz, 2H), 4.62 (t, J = 7.5 Hz, 2H), 3.93 (s, 6H), 3.62 (t, J = 7.5 Hz, 2H) ppm.

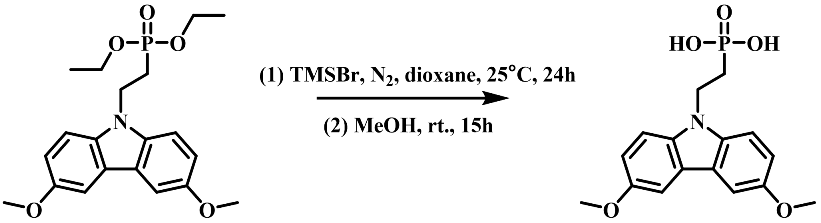
4.3 Synthesis of diethyl (2-(3,6-dimethoxy-9H-carbazol-9-yl)ethyl)phosphonate:



9-(2-Bromoethyl)-3,6-dimethoxycarbazole (0.316 g, 0.95 mmol) was dissolved in triethyl phosphite (2.7 mL) in a 50 mL round-bottom flask and heated under reflux for 18 h. Reaction progress was monitored by TLC (acetone/hexane = 1:4, v/v). After completion, the solvent was removed under reduced pressure. The crude product was purified by column chromatography (acetone/hexane = 1:1), yielding a clear liquid (0.353 g, 95%).

^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.52 (d, J = 2.5 Hz, 2H), 7.30 (d, J = 8.8 Hz, 2H), 7.10 (dd, J = 8.8, 2.5 Hz, 2H), 4.60-4.49 (m, 2H), 4.09-4.03 (m, 4H), 3.93 (s, 6H), 2.29-2.15 (m, 2H), 1.28 (t, J = 7.1 Hz, 6H) ppm.

4.4 Synthesis of (2-(3,6-dimethoxy-9H-carbazol-9-yl)ethyl)phosphonic acid:



Diethyl (2-(3,6-dimethoxy-9H-carbazol-9-yl)ethyl)phosphonate (0.335 g, 0.86 mmol) was dissolved in dry 1,4-dioxane (25 mL) under nitrogen, and TMSBr (1.12 mL) was added dropwise. The mixture was stirred at 25 °C for 24 h. After solvent removal under reduced pressure, the residue was dissolved in methanol (15 mL), followed by slow addition of distilled water (30 mL) until turbidity appeared. The suspension was stirred for an additional 15 h. The mixture was concentrated, and the resulting solid was filtered and washed with water to yield a yellow solid (0.230 g, 80%).

^{1}H NMR (400 MHz, DMSO-d_6) δ= 7.72 (d, J = 2.5 Hz, 2H), 7.39 (d, J = 8.9 Hz, 2H), 7.07 (dd, J = 8.8, 2.5 Hz, 2H), 4.54-4.39 (m, 2H), 3.85 (s, 6H), 3.34 (s, 2H), 2.04-1.87 (m, 2H) ppm.

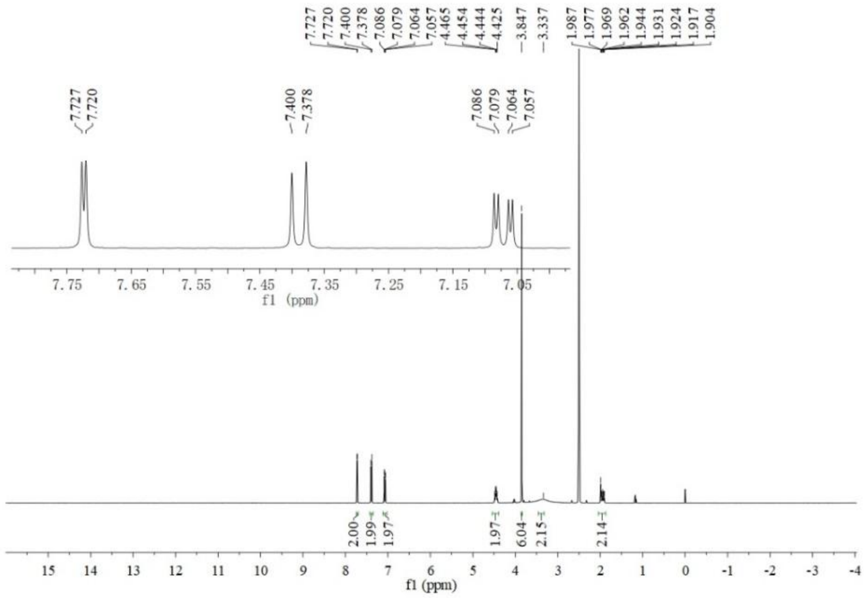


Fig. S12 The ^{1}H NMR (DMSO-d_6) spectrum of MeO-2PACz.

^{13}C NMR (101 MHz, DMSO-d_6) δ = 153.07, 134.98, 122.68, 115.06, 109.79, 103.45, 55.74, 37.61 ppm.

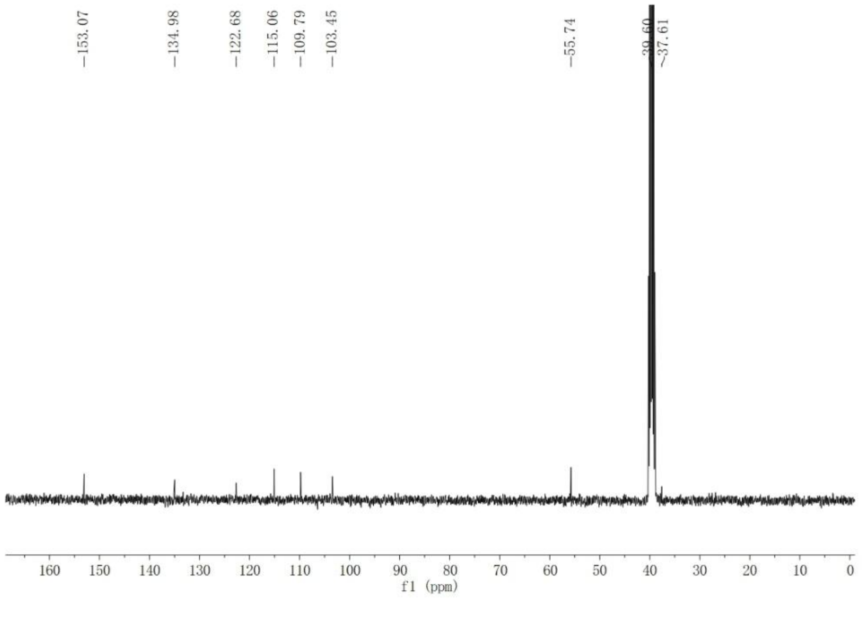


Fig. S13 The ^{13}C NMR (DMSO-d_6) spectrum of MeO-2PACz.

^{31}P NMR (162 MHz, DMSO-d_6) δ = 21.64 ppm.

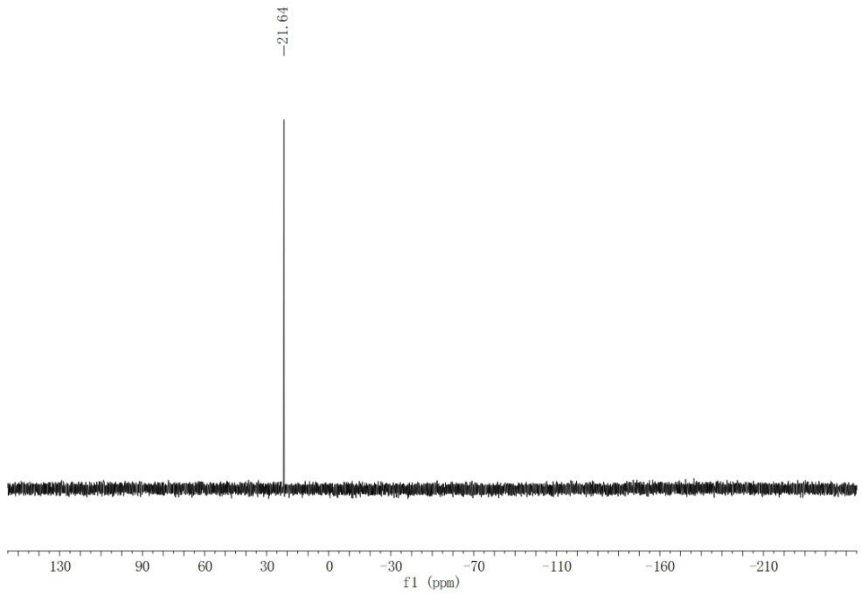


Fig. S14 The ^{31}P NMR (DMSO-d$_6$) spectrum of MeO-2PACz.

HRMS-ESI (m/z): $[M+H]^+$ Calcd. for ($C_{16}H_{18}NO_5P$): 336.30, found: 336.10.

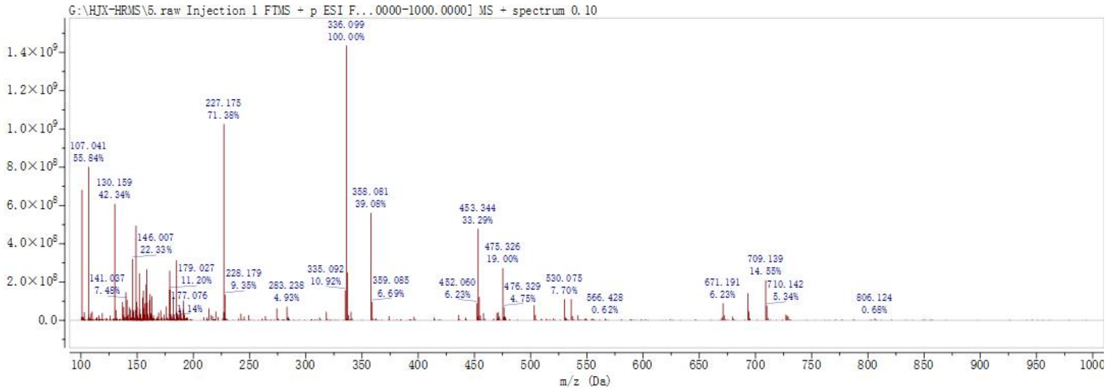
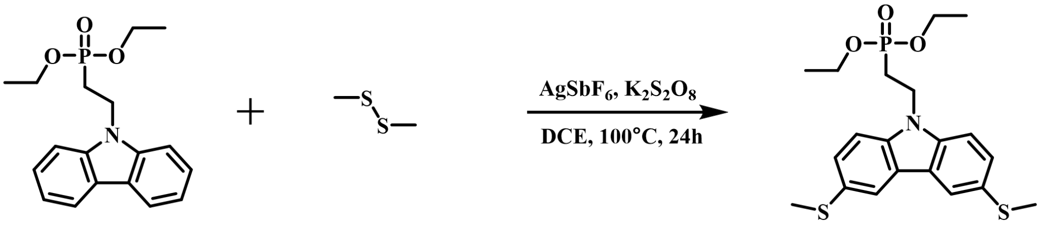


Fig. S15 The high-resolution mass spectrum of MeO-2PACz.

5. Synthesis of MeS-2PACz

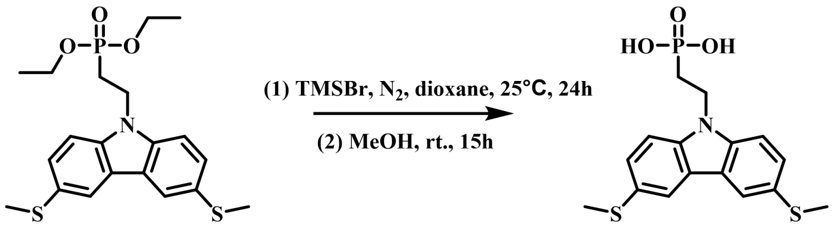
5.1 Synthesis of diethyl (2-(3,6-bis(methylthio)-9H-carbazol-9-yl)ethyl)phosphonate:



In a 50 mL round-bottom flask, [2-(9H-carbazol-9-yl)ethyl]phosphonic acid diethyl ester (0.83 g, 2.5 mmol), dimethyl disulfide (0.35 g, 3.75 mmol), $AgSbF_6$ (0.26 g, 0.75 mmol), $K_2S_2O_8$ (2.03 g, 7.5 mmol), and 1,2-dichloroethane (DCE, 20 mL) were added.

The reaction mixture was stirred at 100 °C for 24 h, then cooled to room temperature. The reaction was quenched with saturated $NaHCO_3$ solution (50 mL), and the organic products were extracted with ethyl acetate (2 times, 100 mL each time). The combined organic layers were washed with brine (60 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude residue was purified by silica gel flash chromatography using a petroleum ether/ethyl acetate gradient, yielding a gray solid (0.85 g, 80%).

5.2 Synthesis of (2-(3,6-bis(methylthio)-9H-carbazol-9-yl)ethyl)phosphonic acid:



Diethyl (2-(3,6-bis(methylthio)-9H-carbazol-9-yl)ethyl)phosphonate (0.42 g, 1.0 mmol) was dissolved in anhydrous 1,4-dioxane (25 mL) under a nitrogen atmosphere. TMSBr (1.12 mL) was added dropwise, and the reaction mixture was stirred at 25 °C for 24 h. After completion, the solvent was evaporated under reduced pressure. The residue was dissolved in methanol (18 mL), followed by slow addition of distilled water (35 mL) until turbidity appeared. The suspension was stirred for an additional 15 h. The resulting solid was filtered and washed with water, affording a gray solid (0.33 g, 90%).

^{1}H NMR (400 MHz, DMSO-d6) δ= 8.21 (d, J = 1.4 Hz, 2H), 7.49 (d, J = 8.6 Hz, 2H), 7.43 (dd, J = 8.6, 1.6 Hz, 2H), 4.50 (d, J = 8.0 Hz, 2H), 2.54 (s, 6H), 2.04 – 1.92 (m, 2H) ppm.

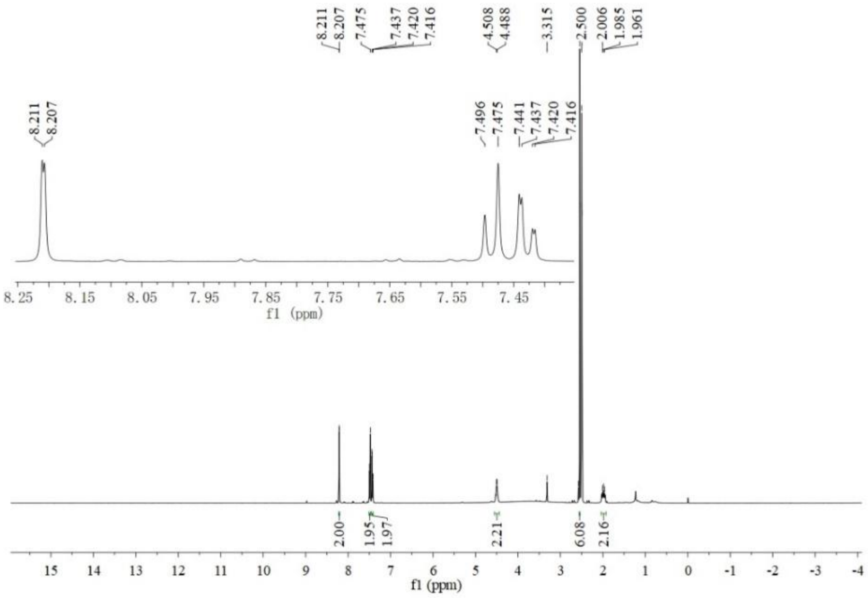


Fig. S16 The ^{1}H NMR (DMSO-d$_6$) spectrum of MeS-2PACz.

^{13}C NMR (101 MHz, DMSO-d6) δ = 138.26, 127.19, 126.89, 122.61, 120.43, 109.88, 37.78, 28.18, 17.43 ppm.

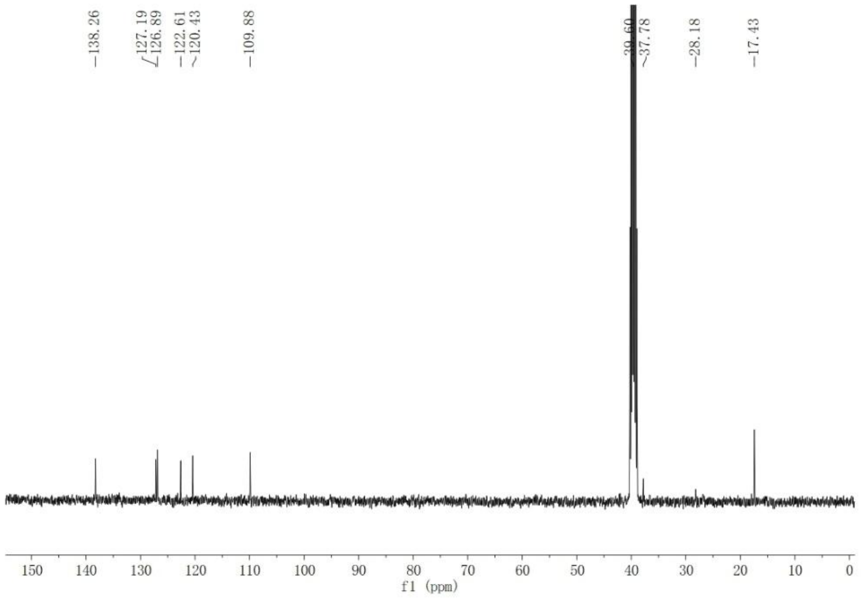


Fig. S17 The ^{13}C NMR (DMSO-d$_6$) spectrum of MeS-2PACz.

^{31}P NMR (162 MHz, DMSO-d6) δ = 21.09 ppm.

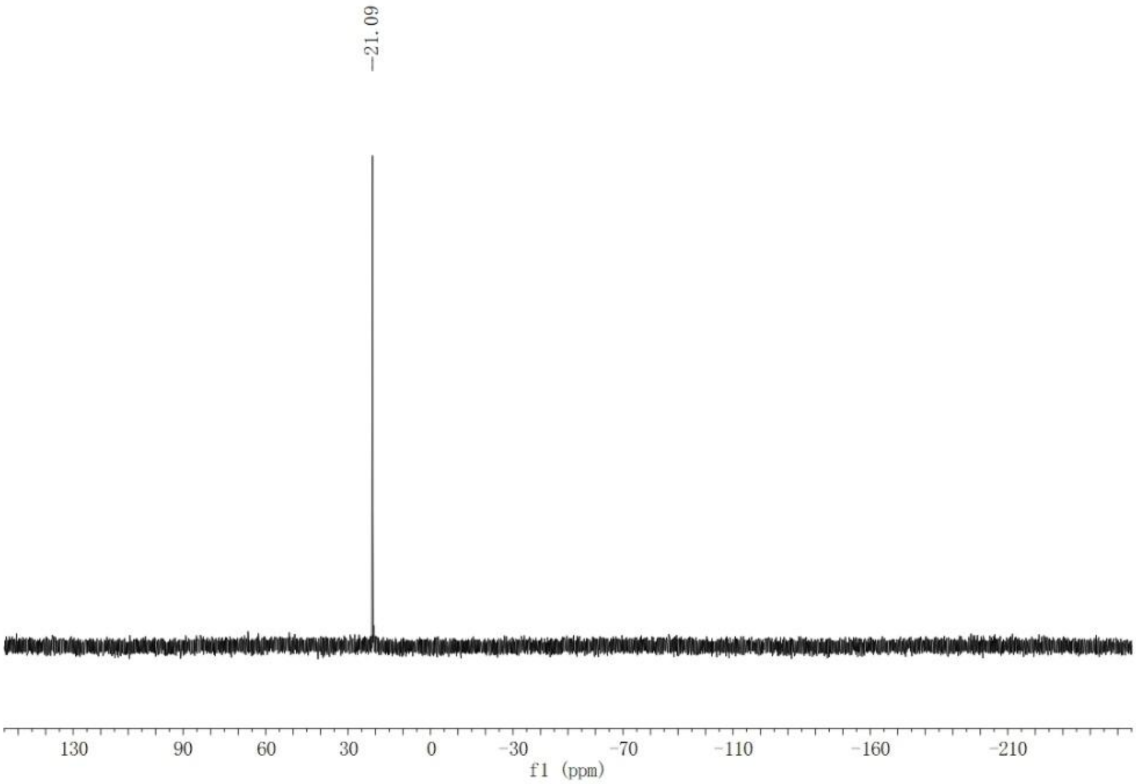


Fig. S18 The ^{31}P NMR (DMSO-d_6) spectrum of MeS-2PACz.

LC-MS-ES-API(m/z): $[M-H]^-$ Calcd. for ($C_{16}H_{18}NO_3PS_2$): 366.4, found: 366.1.

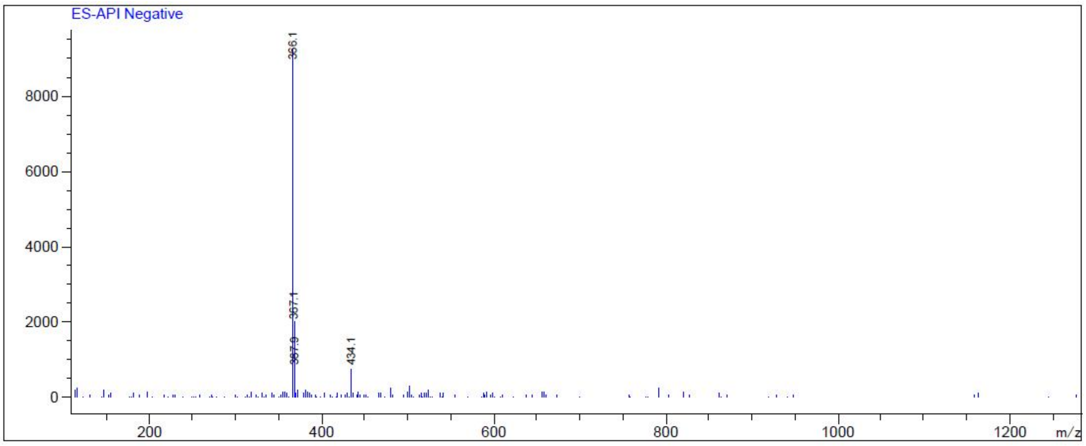


Fig. S19 The Liquid Chromatograph Mass spectrum of MeS-2PACz.

Characterizations of X-2PACz SAMs

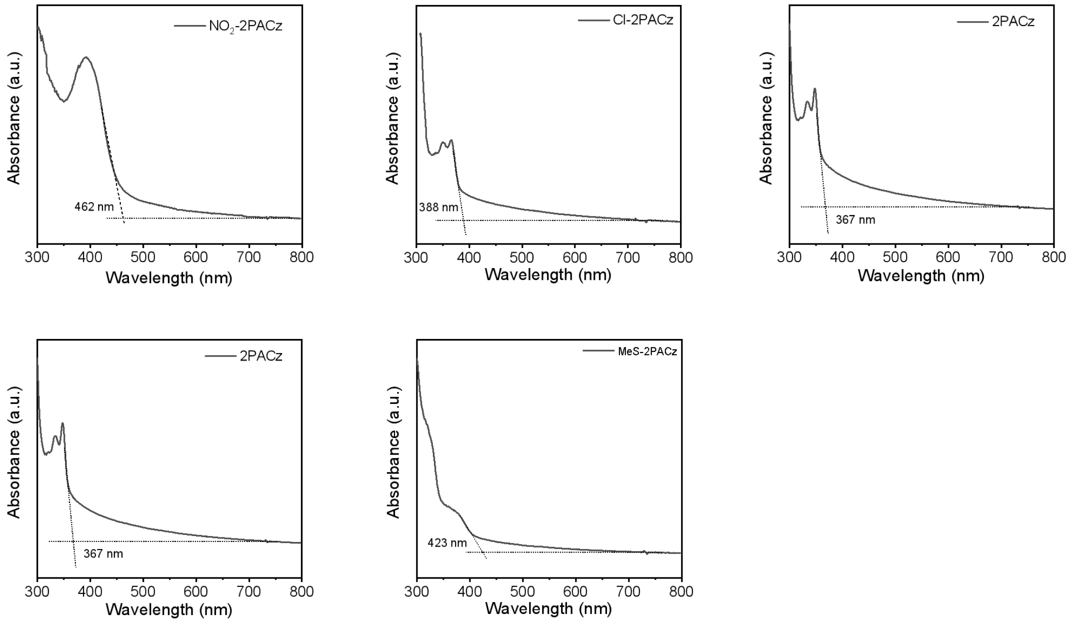


Fig. S20 UV-vis absorption spectra of X-2PACz SAMs films.

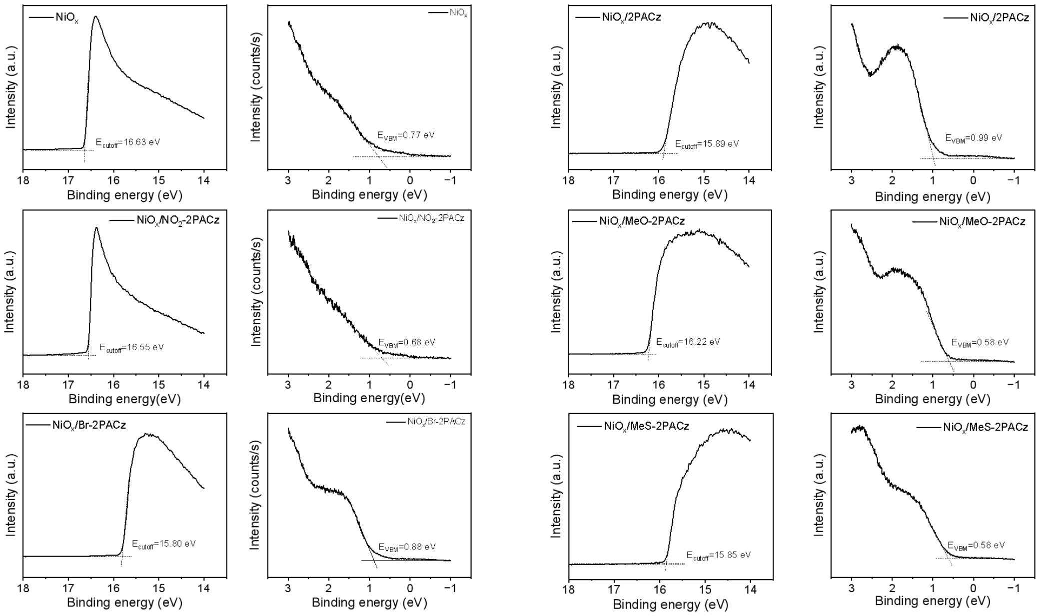


Fig. S21 UPS of X-2PACz SAMs modified NiO$_x$ films, with the secondary cutoff edge on the left and the Fermi edge on the right.

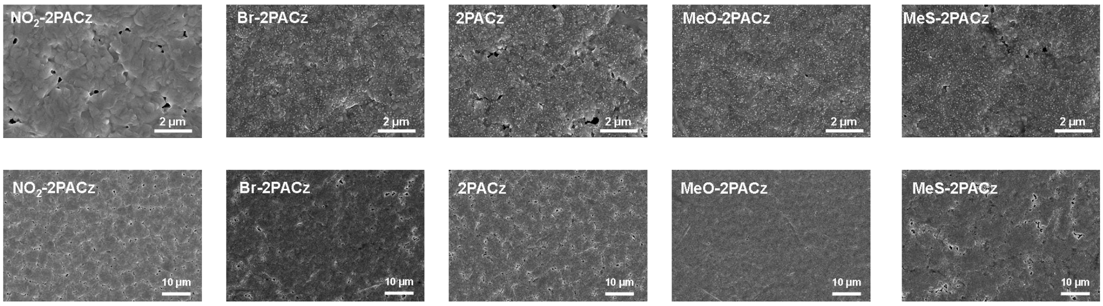


Fig. S22 SEM images of perovskite films on X-2PACz substrates.

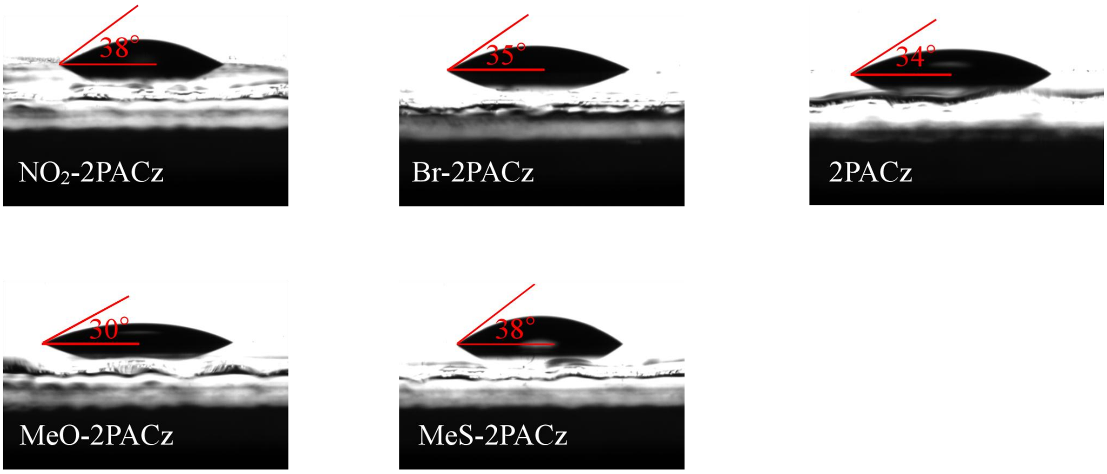


Fig. S23 Contact angles of the perovskite precursor solution on NiO$_x$ substrates modified with X-2PACz.

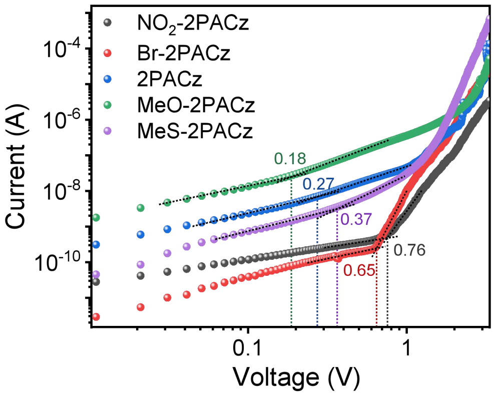


Fig. S24 SCLC measurements were performed on hole-only devices with the structure NiO$_x$/X-2PACz/Perovskite/PTAA/MoO$_x$/Ag.

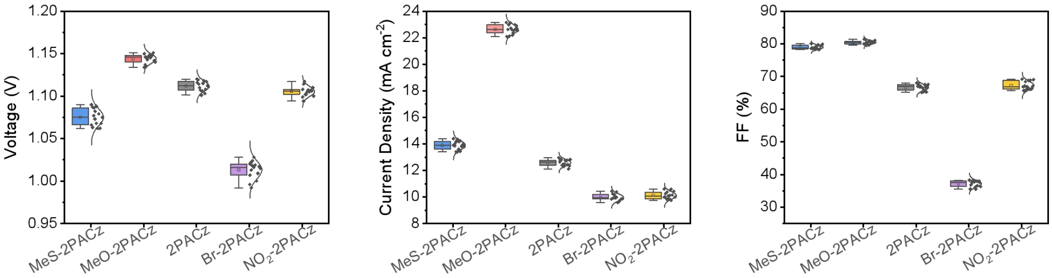


Fig. S25 Photovoltaic performance statistics of devices based on different X-2PACz SAMs with NiO_x. NiO_x serves as the hole transport layer and X-2PACz serves as the SAM layer.

Table S1. Optical properties of X-2PACz SAMs

SAM	λ_{max} (nm)	λ_{onset} (nm)	E_g^{opt} (eV)[a]	W_F (eV)[b]	HOMO (eV)[b]	LUMO (eV)[b]
NO_2-2PACz	393	435	2.85	-4.61	-4.70	-1.85
Br-2PACz	367	369	3.36	-5.21	-6.03	-2.67
2PACz	348	411	3.02	-5.36	-6.14	-3.12
MeO-2PACz	382	399	3.11	-5.05	-5.53	-2.42
MeS-2PACz	374	348	3.56	-5.61	-6.03	-2.47

a Estimated from the absorption edge in solution using the equation $E_g = 1240/\lambda_{onset}$ (eV).

b The W_F and HOMO energy level were extracted from Fig. S21 (excitation energy is 21.22 eV). Additionally, the LUMO energy level was calculated based on the HOMO energy level and the optical band gap (E_g^{opt}).

Table S2 Device performance of X-2PACz based PSCs.

X-2PACz	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
NO_2-2PACz	1.11	10.61	69.2	7.48
Br-2PACz	1.02	10.44	38.3	4.07
2PACz	1.12	12.95	68.0	9.92
MeO-2PACz	1.15	23.15	81.4	21.67
MeS-2PACz	1.09	14.39	80.0	12.50