Supporting Information

Dual-Asymmetric Backbone Constructed Polymerized Small Molecule Acceptors for Efficient All-Polymer Solar Cells

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1. Materials and Methods.

PBQx-TF and PDINN were purchased from Derthon Optoelectronics Material Science Technology Co., Ltd. PNDIT-F3N-Br was purchased from VOLT-AMP Optoelectronics TECH Co., Ltd. MoO_3 was purchased from J&K Scientific. Poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT: PSS, Clevios AI 4083) was purchased from Xi'an Polyper Light Technology Corp. All the other reagents and chemicals were purchased from commercial suppliers and used directly without further purification unless otherwise noted. The pre-patterned high transmittance ITO glass substrate (resistance: ~15 Ω sq^{-1}, maximum transmittance: ~86% at ~550 nm, and size: $14.9 \times 14.9 \times 0.7$ mm^3) was purchased from South China Xiangcheng Technology Co., Ltd.

Thermal gravimetric analysis (TGA). The measurements were performed on TGA Q50 V20.8 Build 34 at a heating rate of 10 °C min^{-1}.

UV-Vis absorption. UV-Vis absorption spectra were performed on Lambda 25 spectrophotometer. All film samples were spin-cast on ITO substrates.

Electrochemical characterizations. Cyclic voltammetry (CV) measurements were performed using a CHI660D electrochemical workstation. The CV experiments were carried out at room temperature with a conventional three-electrode system using a glassy carbon electrode as the working electrode, Pt wire as the counter electrode, and a saturated calomel electrode as the reference electrode. Tetrabutylammonium phosphorus hexafluoride (Bu_4NPF_6, 0.1 M) in acetonitrile solution was used as the supporting electrolyte, and the scan rate was 100 mV/s. Ferrocene/Ferrocenium (Fc/Fc^+) was used as the internal standard, and their energy levels are assumed at -4.8 eV relative to vacuum. Materials were dropped and cast onto the glassy carbon electrode from chloroform solutions (1 mg/mL) to form thin films.

Atomic force microscopy (AFM). The surface morphology of the films was characterized using AFM (Advanced Scanning Probe Microscope, XE-100, PSIA) in tapping mode. The film samples were prepared under the same conditions as those used for device fabrication. The thickness of the active layer was measured by a surface profile measuring system (Dektak XT, Bruker Co., Ltd.).

Grazing incidence wide angle X-ray scattering (GIWAXS). GIWAXS measurements were performed at the 9A (U-SAXS) beamline at the Pohang Accelerator

Laboratory, Korea. The film samples on the Si substrate were prepared under the same conditions as those used for device fabrication.

Device fabrication and measurement. The all-PSCs were fabricated using an inverted structure of ITO/ZnO/PNDIT-F3N-Br/active layer/MoO_3/Ag. The indium tin oxide (ITO)-coated glass substrates were cleaned by ultrasonic treatment in detergent, deionized water, and isopropyl alcohol under ultrasonication for 15 min each and subsequently dried by a nitrogen blow. Then, the ITO glass was treated with a plasma Cleaner for 10 min. Subsequently, ZnO film was deposited by spin coating a ZnO precursor solution on the top of the ITO glass substrates at 4000 rpm for 60 s. The ZnO precursor was prepared by dissolving zinc acetate dihydrate (Aldrich, 99.9%, 1 g) and ethanolamine (Aldrich, 99.5%, 0.28 g) in 2-methoxyethanol (Aldrich, 99.8%, 10 mL) under vigorous stirring for 12 h for the hydrolysis reaction in air. After being baked at 200 °C in air for 1 h, the ZnO coated substrates were transferred into a nitrogen-filled glove box. The PNDIT-F3N-Br was deposited on ZnO film at 3000 rpm without annealing. The PBQx-TF:PSMA (1:1.2, w/w) was dissolved in chlorobenzene at a total blend concentration of 13 mg/mL. The active layers PBQx-TF:PSMA were spin-coated onto ZnO film at 3000 rpm for 40 s. And then the films were treated with thermal annealing at 80 °C for 10 min. Then, MoO_3 (~8 nm) and Ag (~100 nm) were successively evaporated onto the active layer through a shadow mask (pressure ca. 10^{-4} Pa). The effective area for the devices is 4 mm^2.

The current density-voltage (*J-V*) characteristics of solar cells were performed in a glove box filled with nitrogen at room temperature, using a programmable Keithley

2400 source measurement unit under simulated solar light of AM 1.5 G (XES-40S3, SAN-EI ELECTRIC CO., LTD.). The light intensity was determined by a monocrystal silicon cell (VLSI Standards Inc.) at 100 mW cm^{-2}. The *J-V* curves were tested by forward scan with the scan step of 0.02 V and the delay time of 1 ms. EQE measurement spectra were measured by a system of QE-R3011 (Enli Technology Co., Ltd).

Space-charge-limited current (SCLC) measurement. The hole and electron mobilities of devices were obtained by using the SCLC method. The structures of electron-only and hole-only devices are ITO/ZnO/active layer/PNDIT-F3N-Br/Ag and ITO/PEDOT:PSS/active layer/MoO_3/Ag, respectively. Mobilities were obtained by fitting the current-voltage curves in the space charge limited range, where the SCLC is described following the equation below:

$$J = \frac{9\varepsilon_r\varepsilon_0\mu_0(V - V_{bi})^2}{8L^3}$$

Here ε_0 is the permittivity of free space, ε_r is the relative permittivity of the material, μ_0 is the hole or electron mobility, V is the applied voltage, V_{bi} is the built-in voltage, respectively.

Photoluminescence (PL). The PL spectra were taken on an Edinburgh Instrument FLS 980.

2. Synthesis of PY1S1Se-C9, PY1S1Se-C11, and PY1S1Se-BO.

Materials: Compounds of BPT-C9, BPT-C11, BPT-BO, monomer Y1S1Se-C11, and polymer PY1S1Se-C11 were synthesized according to the previous reports.[1-2] Dual-asymmetric PY1S1Se-C9 and PY1S1Se-BO were developed according to the following procedures:

Y1S1Se-C9: In a dry 50 mL flask, compounds BPT-C9 (0.23 g, 0.154 mmol), 2-(5-bromo-3-oxo-2,3-dihydroinden-1-ylidene)malononitrile (IC-Br, 0.15 g, 0.538 mmol), and pyridine (0.15 mL) were added to 15 mL of degassed chloroform under argon and stirred vigorously at 65 °C for 18 h. Then the mixture was poured into methanol (150 mL) followed by precipitation, and the sediments were collected. The resulting crude compound was purified by column chromatography on silica gel with PE/CH_2Cl_2 (3:1, *v/v*) as eluent to give Y1S1Se-C9 as a black solid (0.26 g, 84%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS), (ppm): δ 9.27 (s, 1H), 9.17 (s, 1H), 8.59-8.50 (m, 2H), 8.03 (dd, *J* = 4.0, 1.7 Hz, 2H), 7.85 (ddd, *J* = 8.4, 3.4, 1.9 Hz, 2H), 4.75 (dd, *J* = 21.9, 7.0 Hz, 4H), 3.22 (s, 4H), 2.24-2.08 (m, 2H), 1.87 (d, *J* = 5.5 Hz, 4H), 1.64-1.47 (m, 4H), 1.32-1.15 (m, 92H), 0.89-0.76 (m, 30H). ^{13}C NMR (600 MHz, $CDCl_3$, TMS), (ppm): δ 186.66, 185.93, 158.87, 158.72, 155.59, 152.59, 146.51, 146.46, 146.31, 144.14, 140.69, 137.48, 137.36, 137.28, 137.19, 137.01, 136.91, 136.81, 136.77, 136.63, 134.84, 134.50, 133.41, 133.29, 133.07, 132.46, 129.71, 129.00, 128.43, 128.30, 125.68, 125.66, 125.38, 125.37, 125.35, 119.10, 118.22, 114.23, 113.86, 112.68, 112.30, 67.31, 67.14, 54.65, 54.62, 38.11, 37.92, 30.93, 30.91, 30.86, 30.59, 30.58, 30.30, 30.28, 30.23, 29.58, 29.56, 29.40, 29.36, 28.98, 28.93, 28.87, 28.82, 28.80, 28.75, 28.69, 28.62, 28.60, 28.55, 28.52, 28.48, 28.46, 28.41, 28.39, 28.34, 28.32, 24.63, 24.59, 24.50, 24.44, 21.69, 13.11.

Y1S1Se-BO: In a dry 50 mL flask, compounds BPT-BO (0.16 g, 0.104 mmol), IC-Br (0.10 g, 0.364 mmol), and pyridine (0.1 mL) were added to 10 mL of degassed chloroform under argon and stirred vigorously at 65 °C for 18 h. Then the mixture was poured into methanol (100 mL) followed by precipitation, and the sediments were collected. The resulting crude compound was purified by column chromatography on silica gel with PE/CH_2Cl_2 (3:1, *v/v*) as eluent to give Y1S1Se-BO as a black solid (0.19 g, 89%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS), (ppm): δ 9.27 (s, 1H), 9.16 (s, 1H), 8.54 (t, *J* = 8.2 Hz, 2H), 8.02 (s, 2H), 7.84 (d, *J* = 8.4 Hz, 2H), 4.75 (dd, *J* = 24.5, 7.4 Hz, 4H), 3.30-3.10 (m, 4H), 2.23-2.01 (m, 2H), 1.93-1.80 (m, 4H), 1.53 (d, *J* = 22.0 Hz, 4H), 1.46-1.08 (m, 98H), 0.99-0.86 (m, 30H). ^{13}C NMR (600 MHz, $CDCl_3$, TMS), (ppm): δ 186.66, 185.81, 159.11, 158.72, 155.60, 152.21, 146.53, 146.50, 146.29, 144.33, 140.70, 137.45, 137.36, 137.29, 137.18, 136.91, 136.80, 136.71, 136.62, 136.60, 134.92, 134.59, 133.42, 133.30, 133.28, 133.04, 129.77, 128.99, 128.42, 128.30, 125.66, 125.34, 119.24, 118.21, 114.39, 114.24, 113.88, 112.66, 112.29, 67.36, 67.13, 54.68, 39.01, 38.14, 37.91, 33.68, 32.55, 32.29, 30.93, 30.91, 30.84, 30.58, 30.30, 29.60, 29.40, 28.98, 28.75, 28.69, 28.66, 28.65, 28.63, 28.59, 28.55, 28.52, 28.48, 28.46, 28.39, 28.33, 27.82, 25.55, 24.64, 24.51, 22.00, 21.68, 21.64, 13.11, 13.08, 13.06.

PY1S1Se-C9: In a dry 50 mL flask, $Pd_2(dba)_3$ (1.4 mg) and P(*o*-tol)$_3$ (3.7 mg) were added to a solution of 2,5-bis(trimethylstannyl)thiophene (20.43 mg, 0.0499 mmol) and

Y1S1Se-C9 (100 mg, 0.0499 mmol) in 6 mL degassed toluene under argon and stirred vigorously at 110 °C for 17 hours until the reaction mixture became viscous. Then the mixture was poured into methanol (100 mL) and precipitation occurred. The obtained crude polymer was dissolved in warm chloroform and then the solution was quickly filtered through a pre-prepared wet silica gel column with chloroform (100-200 mesh). The collected chloroform solution was concentrated and precipitated in methanol to get PY1S1Se-C9 as a dark solid (61 mg, 63%). M_n = 6.04 kDa, Đ = 1.65.

PY1S1Se-BO: In a dry 50 mL flask, $Pd_2(dba)_3$ (2.4 mg) and $P(o\text{-tol})_3$ (3.8 mg) were added to a solution of 2,5-bis(trimethylstannyl)thiophene (20.01 mg, 0.0488 mmol) and Y1S1Se-BO (100 mg, 0.0488 mmol) in 6 mL degassed toluene under argon and stirred vigorously at 110 °C for 16 hours until the reaction mixture became viscous. Then the mixture was poured into methanol (100 mL) and precipitation occurred. The obtained crude polymer was dissolved in warm chloroform and then the solution was quickly filtered through a pre-prepared wet silica gel column with chloroform (100-200 mesh). The collected chloroform solution was concentrated and precipitated in methanol to get PY1S1Se-BO as a dark solid (63 mg, 66%). M_n = 10.9 kDa, Đ = 1.55.

3. Figures and tables

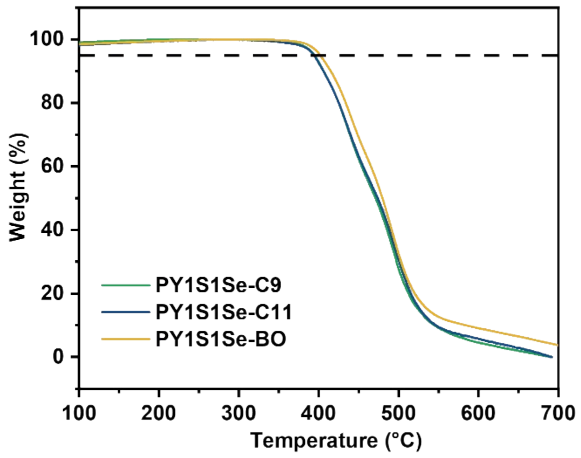

Figure S1. TGA curves of PY1S1Se-C9, PY1S1Se-C11, and PY1S1Se-BO.

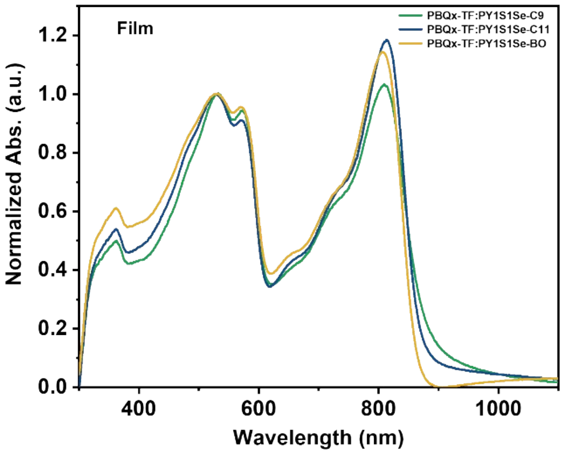

Figure S2. Normalized absorption spectra of the PBQx-TF:PY1SISe-X blends.

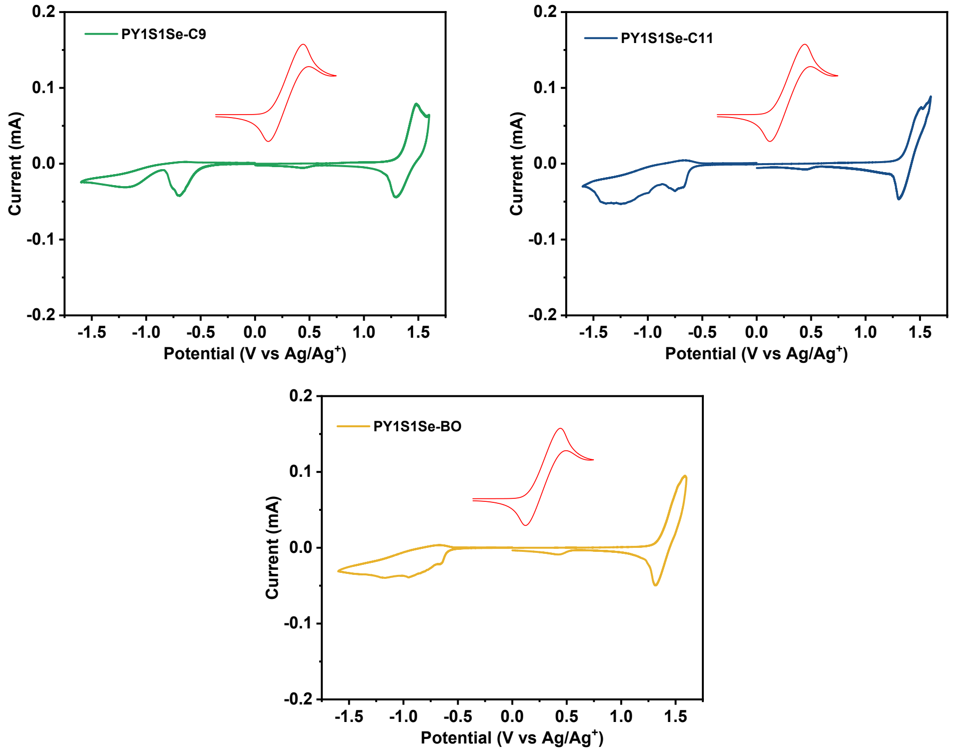

Figure S3. CV curves of PY1S1Se-C9, PY1S1Se-C11, and PY1S1Se-BO neat films, with a scan rate of 0.1 V s^{-1} (calibrated by Fc/Fc$^+$ redox couple).

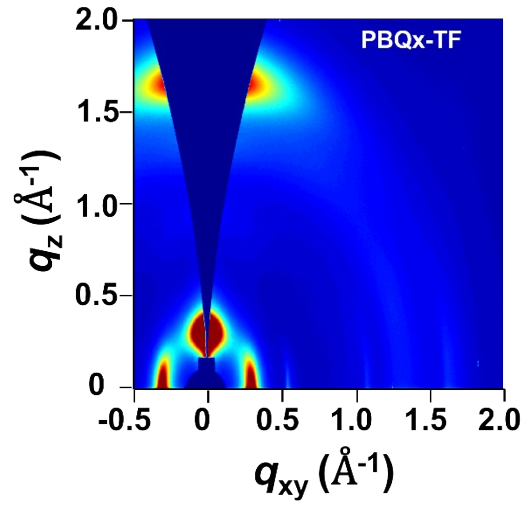

Figure S4. 2D GIWAXS images of PBQx-TF neat film.

Table S1. Detailed GIWAXS data of neat films.

Active Layer	Out-of-plane				In plane			
	q (Å^{-1})	*d*-spacing (Å)	FWHM (Å^{-1})	CCL (Å)	*q* (Å^{-1})	*d*-spacing (Å)	FWHM (Å^{-1})	CCL (Å)
PBQX-TF	1.649	3.8	0.210	27.2	1.074 (100)	5.8	0.075	76.0
					0.543 (200)	11.6	0.049	115.3
PY1S1Se-C9	1.587	4.0	0.279	20.4	0.351	17.9	0.169	33.5
PY1S1Se-C11	1.551	4.0	0.287	19.9	0.353	17.8	0.182	31.0
PY1S1Se-BO	1.561	4.0	0.295	19.3	0.355	17.7	0.187	30.3

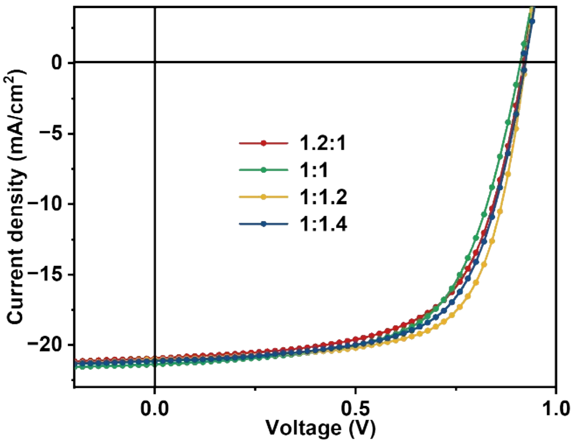

Figure S5. *J*-*V* curves of the all-PSCs based on PBQx-TF:PY1SISe-BO with different D:A weight ratios.

Table S2. Photovoltaic data of the all-PSCs based on PBQx-TF:PY1SISe-BO with different D:A weight ratios under the illumination of AM 1.5G, 100 mW cm^{-2}.

D:A	**V_{OC} (V)**	**J_{SC} (mA/cm^2)**	**FF (%)**	**PCE (%)**
1.2:1	0.919	20.95	62.95	12.07
1:1	0.911	21.37	62.70	12.15
1:1.2	0.923	21.05	68.07	13.18
1:1.4	0.923	21.14	64.83	12.60

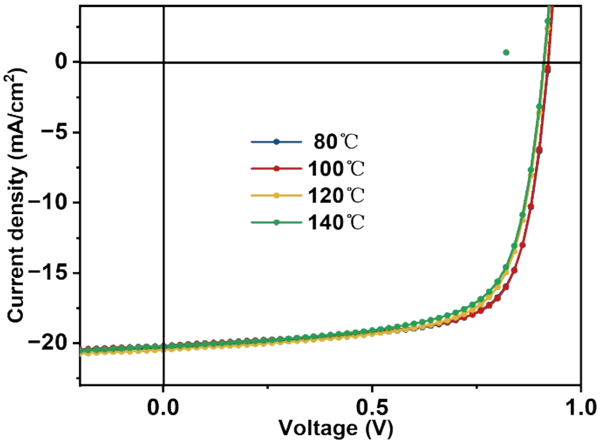

Figure S6. *J-V* curves of the all-PSCs based on PBQx-TF:PY1SISe-BO with different annealing temperatures.

Table S3. Photovoltaic data of the all-PSCs based on PBQx-TF:PY1SISe-BO with different annealing temperatures under the illumination of AM 1.5G, 100 mW cm^{-2}.

Temperatures	***V*$_{OC}$ (V)**	***J*$_{SC}$ (mA/cm^2)**	**FF (%)**	**PCE (%)**
80 °C	0.921	20.18	72.73	13.52
100 °C	0.912	20.46	70.15	13.09
120 °C	0.910	20.21	69.60	12.81
140 °C	0.922	20.31	71.97	13.47

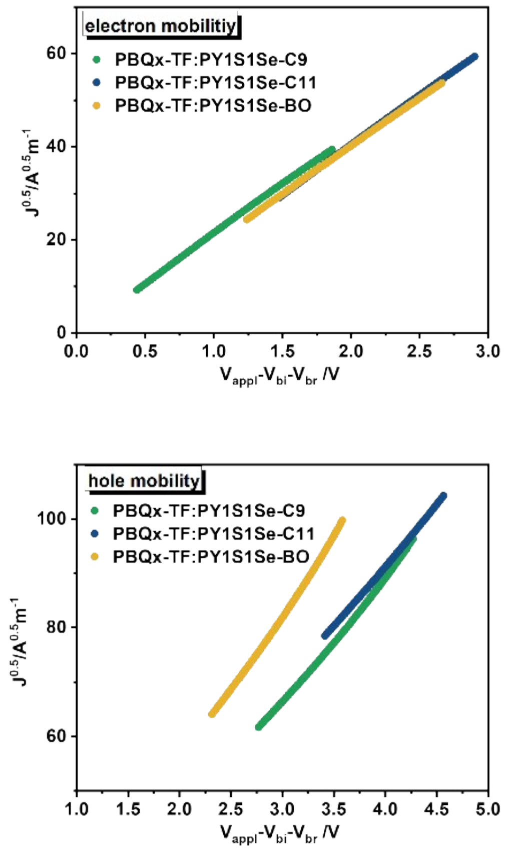

Figure S7. Electron and hole mobilities of the devices based on PBQx-TF:PY1SISe-X.

Table S4. Detailed GIWAXS data of blend films.

Active Layers	Out-of-plane				In plane			
	q (Å^{-1})	*d*-spacing (Å)	FWHM (Å^{-1})	CCL (Å)	*q* (Å^{-1})	*d*-spacing (Å)	FWHM (Å^{-1})	CCL (Å)
PBQx-TF:PY1SISe-C9	1.634	3.8	0.237	24.1	0.302	20.8	0.054	104.8
					0.543	11.6	0.058	98.5
PBQx-TF:PY1SISe-C11	1.649	3.8	0.226	25.3	0.302	20.8	0.052	109.2
					0.543	11.6	0.049	116.6
PBQx-TF:PY1SISe-BO	1.645	3.8	0.217	26.4	0.302	20.8	0.040	141.6
					0.543	11.6	0.048	117.9

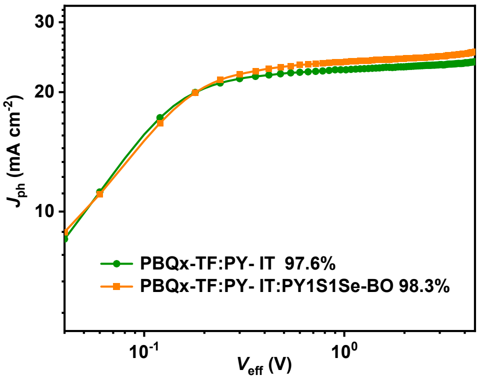

Figure S8. Curves of J_{ph} vs V_{eff} of the all-PSCs based on PBQx-TF:PY-IT and PBQx-TF:PY-IT:PY1SISe-BO.

References

[1] H. Fu, Q. Fan, W. Gao, J. Oh, Y. Li, F. Lin, F. Qi, C. Yang, T. J. Marks and A. K.-Y. Jen, *Sci. China Chem.* 2022, **65**, 309.

[2] Q. Fan, R. Ma, J. Yang, J. Gao, H. Bai, W. Su, Z. Liang, Y. Wu, L. Tang, Y. Li, Q. Wu, K. Wang, L. Yan, R. Zhang, F. Gao, G. Li and W. Ma, *Angew. Chem. Int. Ed.*, 2023, **62**, e202308307.