**Supporting Information**

# Self-assembled molecules for hole extraction in efficient inverted PbS quantum dot solar cells

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## Equipment used and procedures

### X-ray diffraction (XRD)

The crystal structure from the QDs was evaluated by XRD measurements conducted in ambient conditions using a Bruker Advance D8 diffractometer equipped with a 1.6 kW Cu-Anode ($\lambda$ = 1.54060 Å) and a LYNXEYE_XE_T 1D-detector. The scans (step size of 0.02° and resting time of 0.1 s/step) were measured with a height limiting slit of 1.2 mm in 2theta–Omega mode (1D mode) in parallel beam geometry. The measured data was background corrected and the contribution of K$\alpha$2 was stripped using the Diffrac.Eva V4.3 software.

### Ultraviolet–visible spectroscopy

The absorbance spectra were recorded on a Jasco V-770 spectrometer in combination with 1 cm wide quartz cuvettes to collect the absorbance spectra in the UV-vis and the near infrared regions. A highly diluted solution of PbS:OA was prepared in octane, while the reference and the background measurements were pure octane. The same equipment was used for measuring the SAMs films on ITO to obtain Tauc plots for calculating the band gap.

### Transmission electron microscopy (TEM)

Quantum dots were visualized using a Jeol JEM F200 with an acceleration voltage of 200 kV at the Dresden Center for Nanoanalysis (DCN). Carbon grids were used as substrates for drop-casting heavily diluted PbS:OA QDs solution in toluene.

### X-ray and ultraviolet photoemission spectroscopies (XPS and UPS)

The binding energies, work functions and valence band offset of the samples deposited on ITO-covered glass substrates were acquired inside an ultrahigh vacuum chamber (ESCALAB

250Xi, Thermo Scientific) with a base pressure of $2\times10^{-10}$ mbar. For the XPS measurements, an X-ray beam is generated by an XR6 monochromated Al Kα source (hν = 1486.6 eV) with a pass energy of 20 eV. As for the UPS, a double differentially pumped He gas discharge lamp emitting He I radiation (hν = 21.22 eV) with a pass energy of 2 eV and a bias of −5 V was used to ensure secondary electron onset detection.

**Wettability analysis**

The wetting behavior of the QD ink was obtained by measuring the surface contact angle (SCA) between a sessile drop and the different hole transport layers on ITO. Measurements were carried out three times per combination using a drop shape analyzer (Krüss, DSA 100, Germany) with 2 μL droplets of the PbS:$PbX_2$ fabricated ink highly diluted, under ambient conditions and employing a 1.8 mm stainless steel needle to place the drop. The SCA values were calculated using an elliptical fit and the error was described by the standard deviation of the measured values. Additionally, the surface free energy was obtained by using the Owens, Wendt, Rabel and Kaelble (OWRK) method and employing DI water and diiodomethane 99% (Alfa Aesar) as polar and non-polar liquids.

**Scanning electron microscopy (SEM)**

The SEM cross-sectional images were collected using a Gemini 500 instrument (ZEISS) and an acceleration voltage of 1.5 kV under ≈5 × 10−4 mbar using in-lens mode.

**J-V analysis and external quantum efficiency (EQE)**

To evaluate the solar performance, the current-density as a function of the voltage was measured under the solar simulator Abet Sun 3000 Class AAA with AM 1.5 conditions, at room temperature

and in ambient air with the aid of a computer-controlled Keithley 2450 source meter. EQE spectra of the devices were recorded using a monochromatized light of a halogen lamp from 400 to 1100 nm, and the reference spectra were calibrated using a National Institute of Standards and Technology (NIST)-traceable Si diode (Thorlabs). This data was also used to correct the incident light mismatch for the J-V measurements by comparing the real solar spectrum, the spectral response of the reference cell and the spectral response of the devices. All devices were scanned from short circuit to forward bias and reversed with a rate of 0.025 V $s^{-1}$. No treatment was applied before measurements and no mask was used. The light intensity dependence was checked by using optical filters from Thorlabs with defined optical densities.

**Plasma cleaning**

The ITO substrates were treated in a Diener Zepto-QLS plasma cleaner with a pressure of 0.4mbar, power of 100W and during 10 minutes.

**Silver contact evaporation**

For the silver evaporation, a Mantis deposition system was used with base pressure 1E-6 mbar and rate of 0.1 Å/s for the first 10 nm and then 0.6 Å/s until an 80 nm thick layer was achieved.

**Solar cell prototype conditions**

The useful solar cell area is determined by the intersection between the masked area that received the silver deposition and the ITO patterned area, resulting in a value of 4.5 $mm^2$. The devices were not legged nor encapsulated, and were measured right after the evaporation.

## Figures

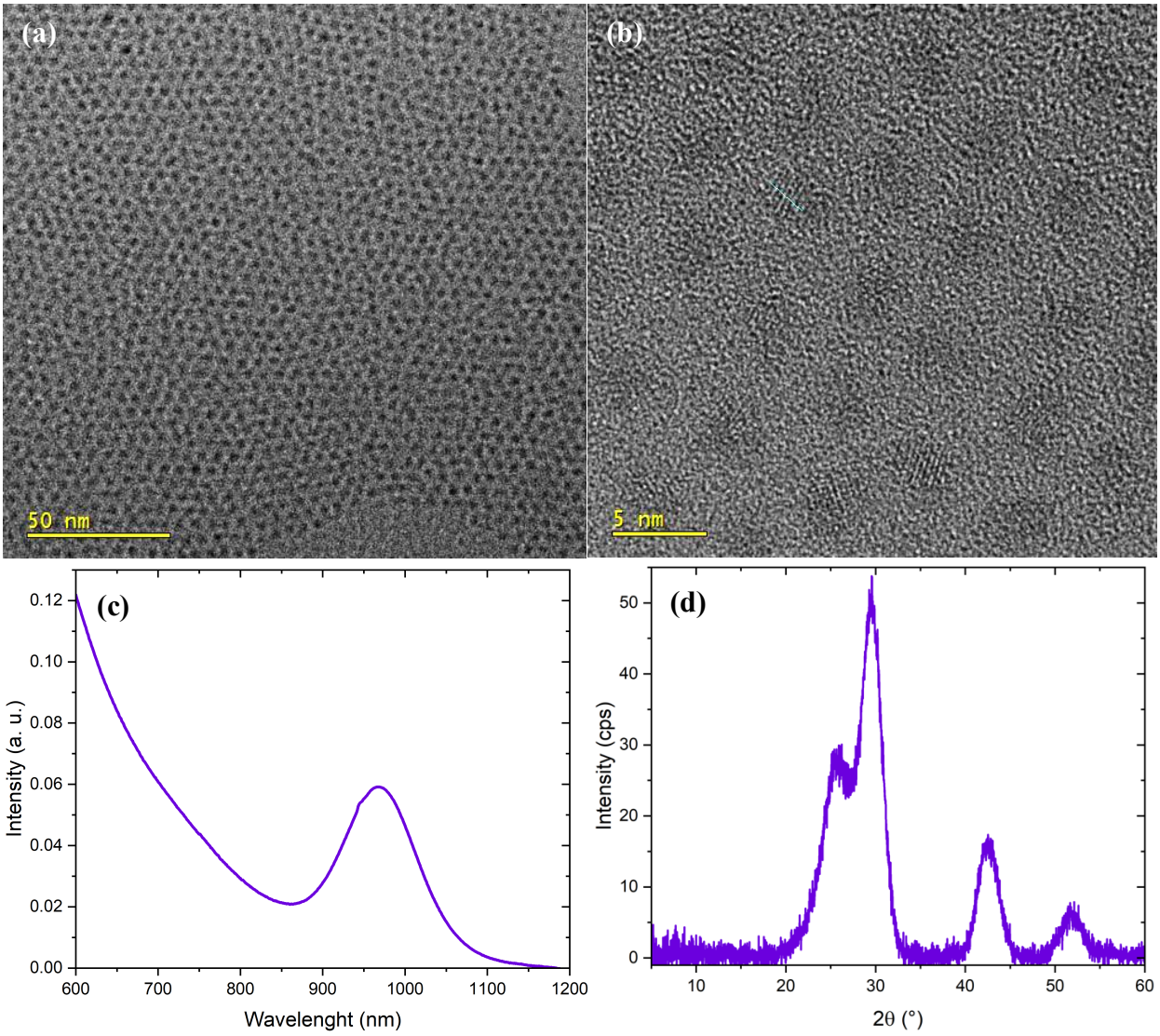


Figure S1. TEM images (a, b) from the PbS:OA quantum dots, (c) UV-Vis spectra for the PbS:OA solution and (d) XRD pattern from the PbS:$PbX_2$ film.

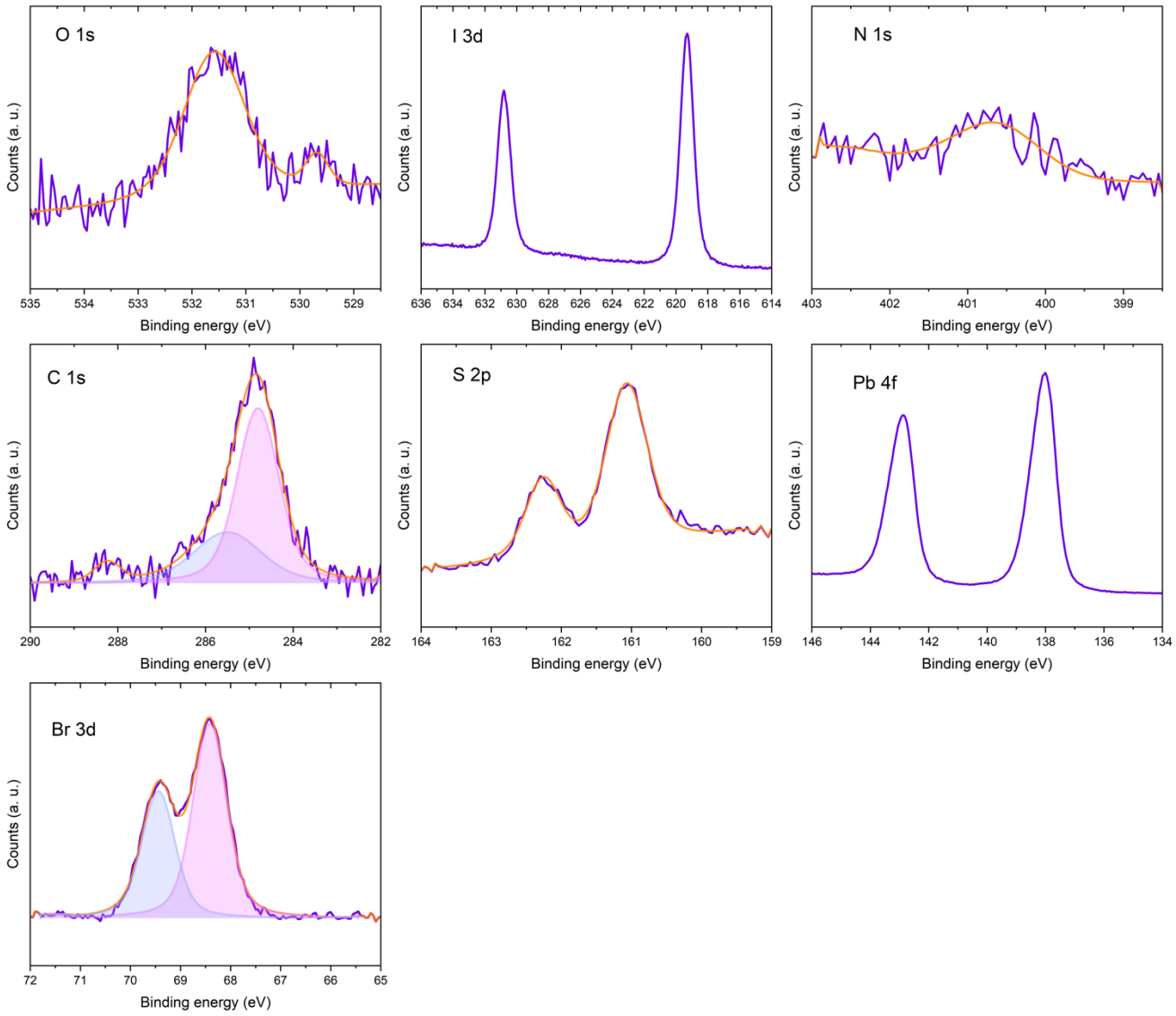


Figure S2. XPS data for the PbS:$PbX_2$ film.

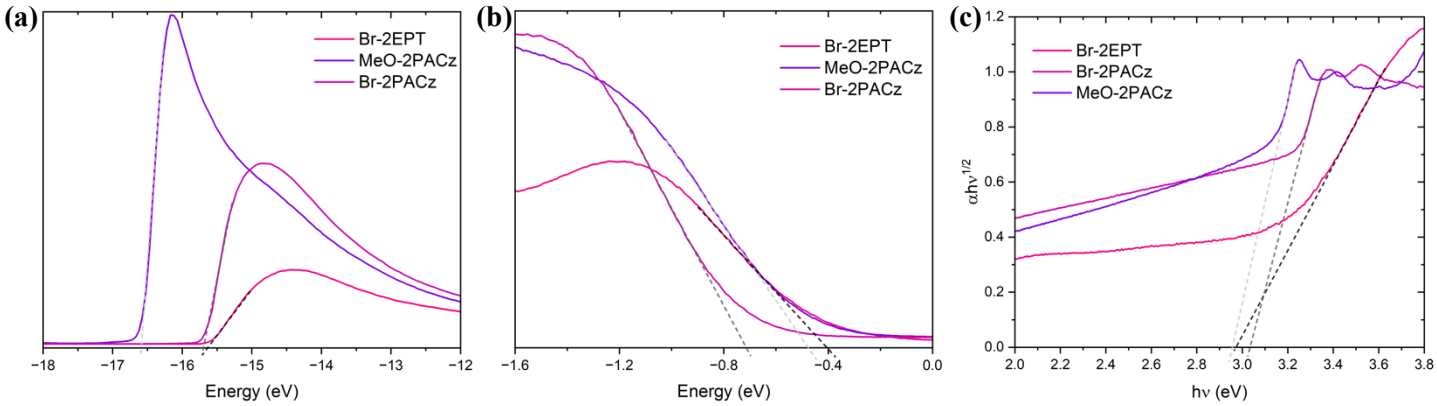


Figure S3. Data used for calculating the energy levels (Fig. 1 of the main text) from the different SAMs: UPS work function (a) and valence band onset (b), and Tauc plots generated from the UV-vis absorption (c).

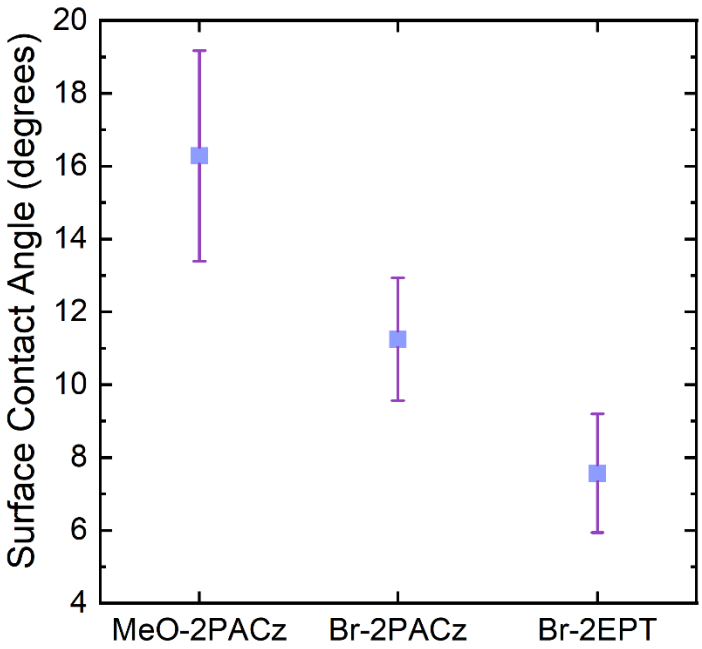


Figure S4. Average contact angle and standard deviation of PbS:PbX2 ink in butylamine on the corresponding interlayer.

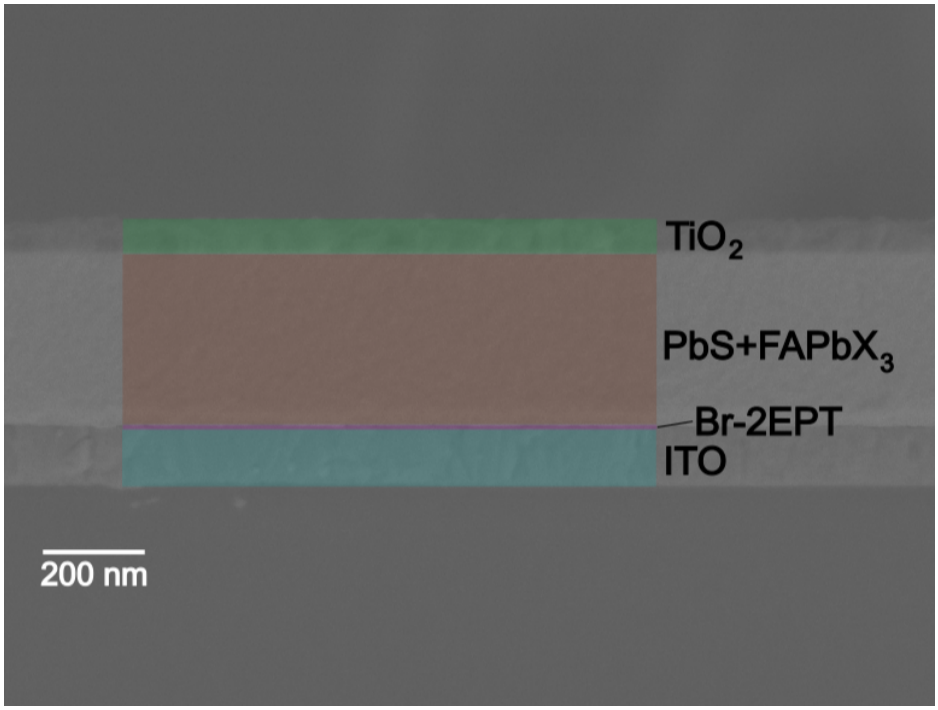


Figure S5. Cross section SEM from the prototype.

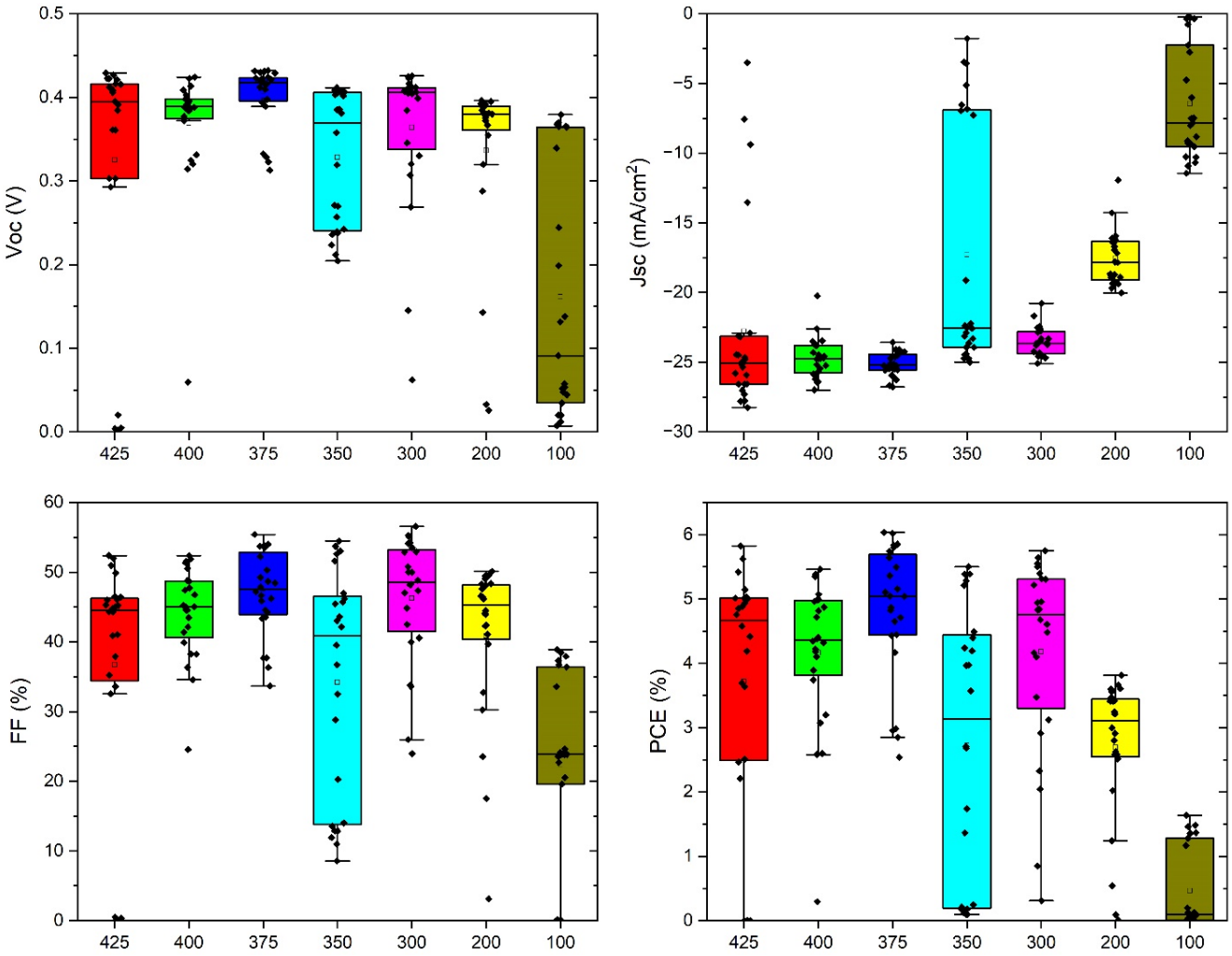


Figure S6. Statistical plots from the parameters extracted from the J-V curves for varying only active layer thicknesses, while keeping Br-2EPT as a SAM.

Table S1. Mean values for the extracted parameters from the J-V-characteristics and record cells in brackets.

| | $V_{OC}$ (V) | $J_{SC}$ (mA/cm²) | FF (%) | PCE (%) | HI (%) |
|---|---|---|---|---|---|
| **MeO-2PACz** | 0.21 (0.26) | 20.1 (21.3) | 32.3 (39.9) | 1.42 (2.21) | (15.0) |
| **Br-2PACz** | 0.15 (0.24) | 3.75 (5.96) | 21.8 (20.6) | 0.14 (0.29) | (82.8) |
| **Br-EPT** | 0.40 (0.43) | 26.4 (26.6) | 47.0 (55.4) | 5.07 (6.36) | (12.4) |

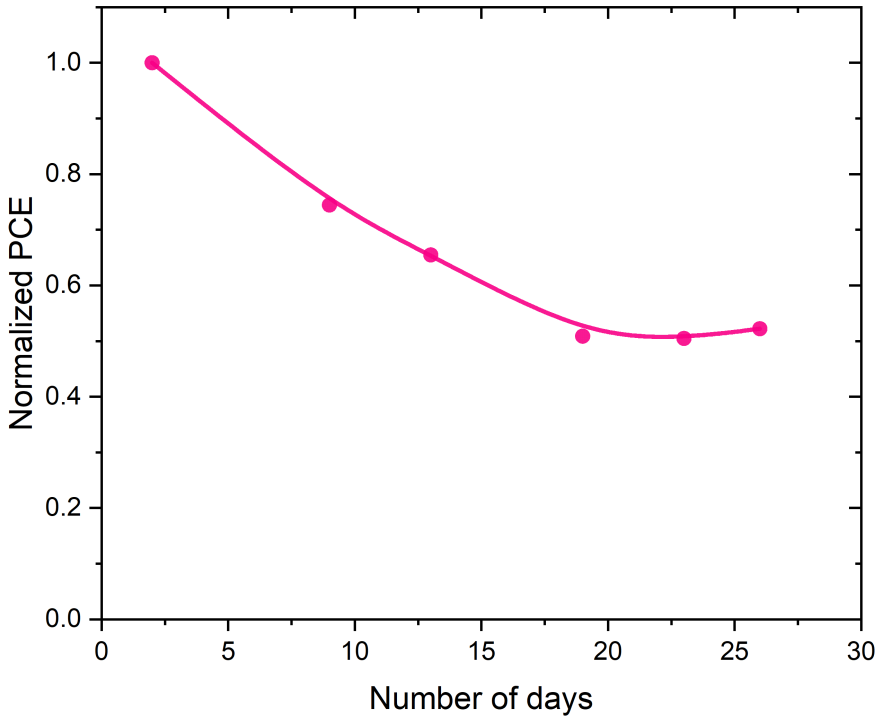


Figure S7. Stability average data from the Br-2EPT prototypes under nitrogen.