Electronic Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

Solution Processable Hydrogen-Bonded Perylene Bisimide Assemblies Organizing into Lamellar Architectures

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Contents

1. Experimental Procedures:

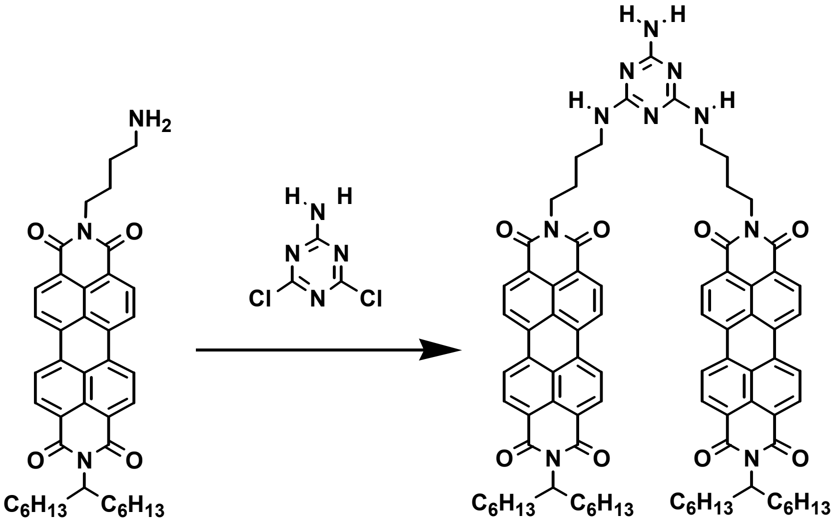
General: Column chromatography was performed on 63–210 μm silica gel. The solvents used for the spectroscopic and microscopic measurements and the gelation experiments are all spectral grade and were used without further purification. All other commercially available reagents and solvents are of reagent grade and were used without further purification. ^{1}H NMR spectra were recorded on JEOL LA500 spectrometer and chemical shifts are reported in ppm with the signals of the residual $CHCl_3$ as internal standard. ESI-MS spectra were measured on an Exactive (Thermo Scientific). UV/Vis spectra were recorded on a JASCO V570 spectrophotometer with Peltier device temperature-control unit. Molecular modeling calculations were performed on MacroModel version 9.0 (MMFF force field). Polarized optical microscopic observation was carried out using an Olympus BX51 optical microscopy system. Powder X-ray diffraction analysis of the dried film samples was performed with a Rigaku Rint-2200 X-ray diffractometer with monochromated $Cu_{K\alpha}$ radiation. AFM images of the OFET devices were acquired under ambient conditions using SPI4000/SPA400 (SII Nanotechnology Inc) in dynamic force (tapping) mode. Silicon micro cantilevers (SI-DF20) with a spring constant of 15 N/m and frequency of 110-150 kHz (nominal value, SII Nanotechnology Inc) were used. The scan rate was varied from 1 to 2 Hz.

Solubility Tests: The solubility of **1** and its hydrogen-bonded complexes with dCA and Bar were estimated in three different solvents, chloroform, toluene and methylcyclohexane. To weighed amount of sample solids were added appropriate amount of solvent and the resulting suspensions were refluxed for a few minutes and then cooled to room temperature. After the solutions were kept at room temperature for 1 h, the solubility was checked whether homogeneous solutions were obtained or not. For the coassembled system (**1**·dCA and **1**·Bar), their 1:1 solid mixture were first dissolved in $CHCl_3$/MeOH mixture and then evaporated to obtain hydrogen-bonded coassemblies. The experiments were performed with concentrations ranging from 1.0×10^{-5} to 2.0×10^{-2} M.

Fabrication of Organic Field Effect Transistor and charge transporting property Measurements: OFET devices were fabricated on SiO_2/Si substrates which were pretreated by PVA or HMDS. For PVA treatment, PVA solution of toluene with 2 mg/mL was spin-coated on a Si/SiO_2 substrate. For HMDS treatment, the substrate was soaked with HMDS solution for 18 hours, and ultrasonically cleaned with toluene, acetone and 2-propanol for 10 minutes, respectively. Thin films of each PBI hydrogen-bonded assembly were prepared by spin-coating (1000 rpm) from the $CHCl_3$ solutions at a concentration of 5.0×10^{-3} M. These thin films were dried at 200

˚C under vacuum for 2 h. Subsequently, top-contact gold electrodes were deposited through shadow masks under vacuum to define channels with width and length of 5.5 mm and 50 µm, respectively. The OFET device measurements were performed using a semiconductor parameter analyzer (Agilent 4155C) at room temperature in a nitrogen glove box where the concentration of H_2O and O_2 was less than 1 ppm. The electron mobilities were calculated in the saturation regime of transfer characteristics.

2. Synthesis and Characterization of 1

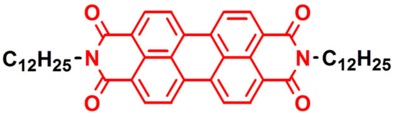
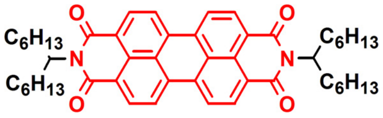


2 **1**

A mixture of **2**[S1] (202 mg, 0.314 mmol), 1-amino-3,5-dichloro-*s*-triazine (20 mg, 0.122 mmol) and *N*,*N*-diisopropylethylamine (1 ml) in dry 1,4-dioxane was heated under nitrogen atmosphere for 22 h. After the solution was cooled to room temperature, the resulting solid was dissolved in chloroform and the mixture was washed with 2M HCl, saturated aqueous $NaHCO_3$ and water, and dried over Na_2SO_4. After the solvent was removed under vacuum, purification by silica gel column chromatography (4% MeOH in chloroform as eluent) and reprecipitation from chloroform-hexane gave pure **1** (51 mg, 30.5 % yield); ^{1}H NMR (500 MHz, $CDCl_3$, 60 °C): δ = 8.40 (m, 8H), 8.19 (m, 8H), 5.13 (m, 2H), 4.61 (m, 2H), 4.21 (m, 4H), 3.53 (m, 4H), 2.25 (m, 4H), 1.90 (m, 8H), 1.78 (m, 4H), 1.42-1.22 (m, 32H), 0.85 (t, 12H, *J* = 7.3 Hz). HRMS (ESI-TOF, positive mode): *m/z* calcd for $C_{85}H_{91}N_{10}O_8$ [MH^+]: 1379.7016; found: 1379.7028.

3. **Supporting Figures**

Table S1. Solubilities of **1** and its 1:1 mixtures with dCA and Bar, and reference compounds *N*,*N*'-didodecyl PBIs and *N*,*N*'-di(2-hexylheptyl) in various solvents at room temperature.

Entries	chloroform	toluene	methylcyclohexane
1	1.4 mg/mL (1.0 × 10^{-3} M)	0.69 mg/mL (5.0 × 10^{-4} M)	0.021 mg/mL (1.5 × 10^{-5} M)
1·dCA	> 34 mg/mL (> 2.0 × 10^{-2} M)	> 34 mg/mL (> 2.0 × 10^{-2} M)	0.85 mg/mL (5.0 × 10^{-4} M)
1·Bar	> 31 mg/mL (> 2.0 × 10^{-2} M)	1.2 mg/mL[a] (8.0 × 10^{-4} M)[a]	0.023 mg/mL (1.5 × 10^{-5} M)
N,*N*'-didodecyl PBI 	0.15 mg/mL (2.0 × 10^{-4} M)	0.073 mg/mL (1.0 × 10^{-4} M)	< 0.0073 mg/mL (< 1.0 × 10^{-5} M)
N,*N*'-di(2-hexylheptyl) PBI 	> 15 mg/mL (> 2.0 × 10^{-2} M)	> 15 mg/mL (> 2.0 × 10^{-2} M)	> 15 mg/mL (> 2.0 × 10^{-2} M)

The experiments were performed with concentrations ranging from 1.0 × 10^{-5} to 2.0 × 10^{-2} M. [a]: Transparent organogels were obtained above this concentration.

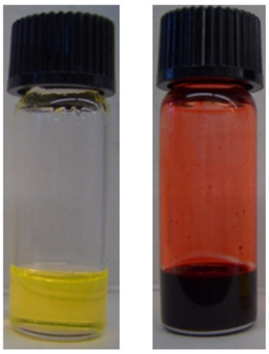


Fig. S1. Photographs of homogeneous chloroform solutions of (left) *N,N'*-didodecyl PBI (0.15 mg/mL, 2.0 × 10^{-4} M) and (right) *N,N'*-di(2-hexylheptyl) PBI (760 mg/mL, 1.0 M). The concentrations are close to the maximum solubilities of these PBIs in chloroform.

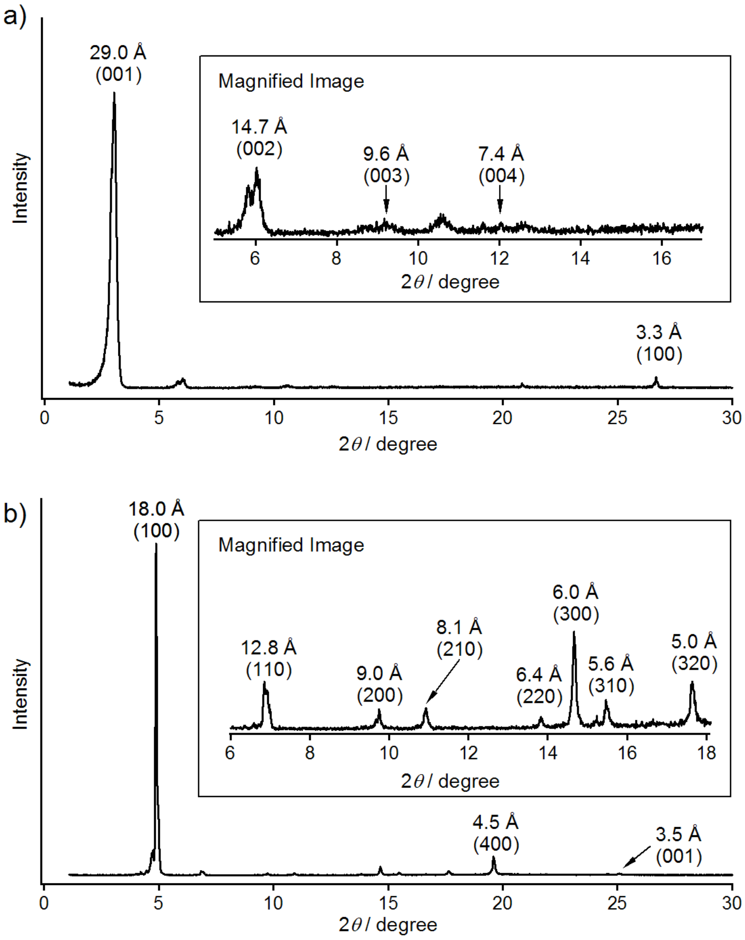


Fig. S2 PXRD patterns of a) *N*,*N*′-didodecyl PBI (0.15 mg/mL, 2.0×10^{-4} M) at 140 °C and b) *N*,*N*′-di(2-hexylheptyl) PBI (760 mg/mL, 1.0 M) at 200 °C. The measurement samples were prepared by depositing solute samples on glass substrate.

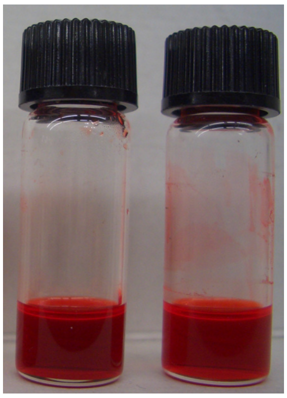


Fig. S3 a) Photographs of homogeneous chloroform solutions of **1**·dCA and **1**·Bar ($c = 5.0 \times 10^{-3}$ M).

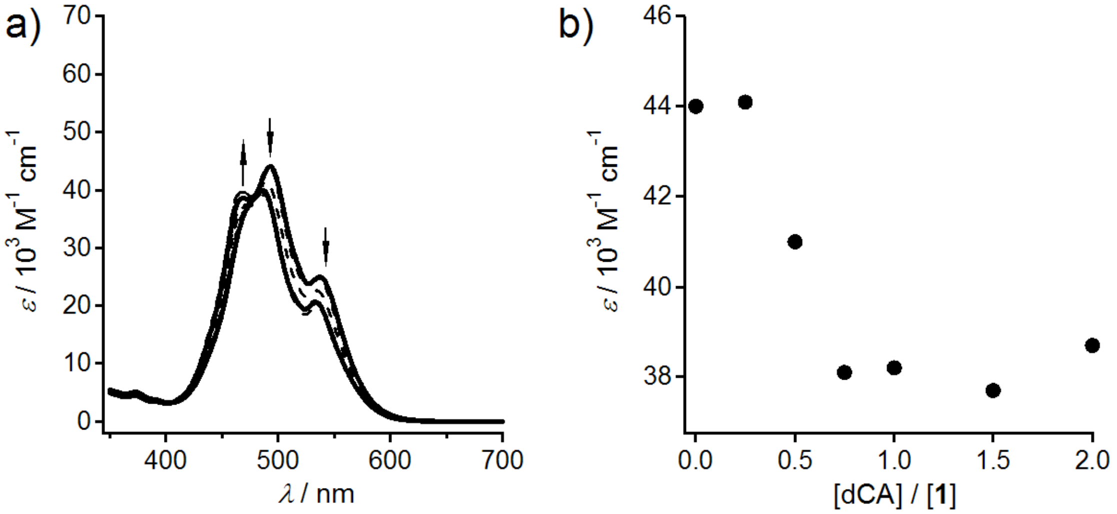


Fig. S4 UV/vis spectra of methylcyclohexane solutions containing constant amount of **1** (= 1.4 × 10^{-5} M) and various amounts of dCA (= 0 to 2.8 × 10^{-5} M) at 25 ˚C. Arrows indicate that spectral changes with increasing amount of dCA molecules. b) Plot of ε at 492 nm versus [dCA] / [**1**].

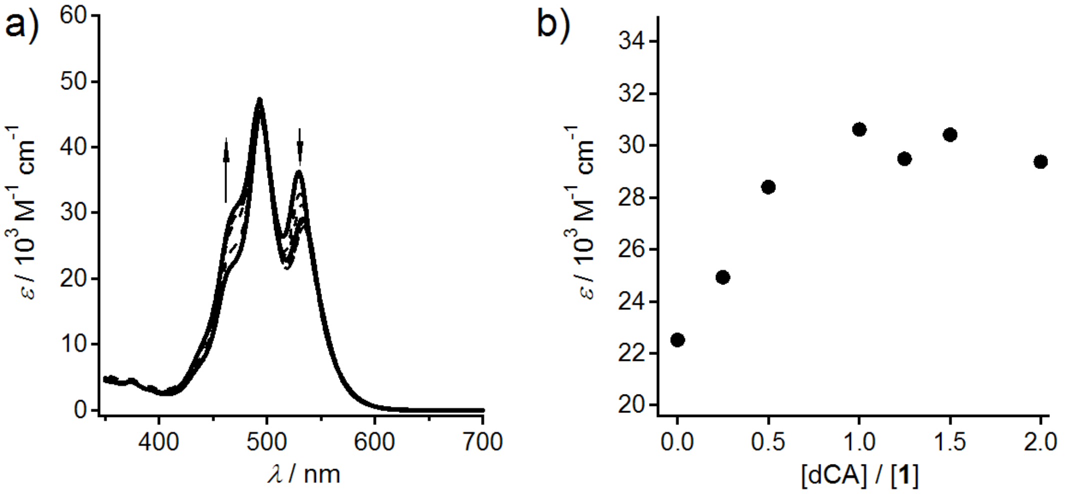


Fig. S5 UV/vis spectra of toluene solutions containing constant amount of **1** (= 1.4 × 10^{-5} M) and various amounts of dCA (= 0 to 2.8 × 10^{-5} M) at 25 ˚C. Arrows indicate that spectral changes with increasing amount of dCA molecules. b) Plot of ε at 470 nm versus [dCA] / [**1**].

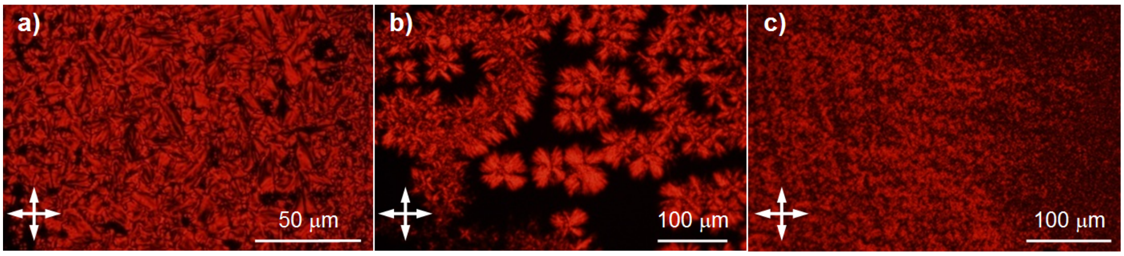


Fig. S6 Polarized optical microscopic images of solvent-free films of a) **1**, b) **1**·dCA and c) **1**·Bar at room temperature upon slow cooling (ca. 1 °C min^{-1}) from the isotropic state.

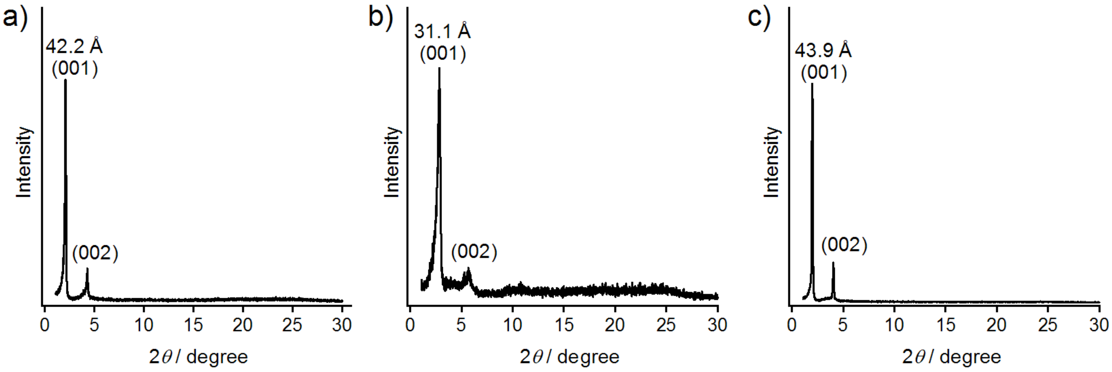


Fig. S7 PXRD patterns of dried films of a) **1**, b) **1**·dCA and c) **1**·Bar at room temperature after annealing at 240 °C. The dried film samples were prepared on glass substrate by drop cast from chloroform solutions of these assemblies.

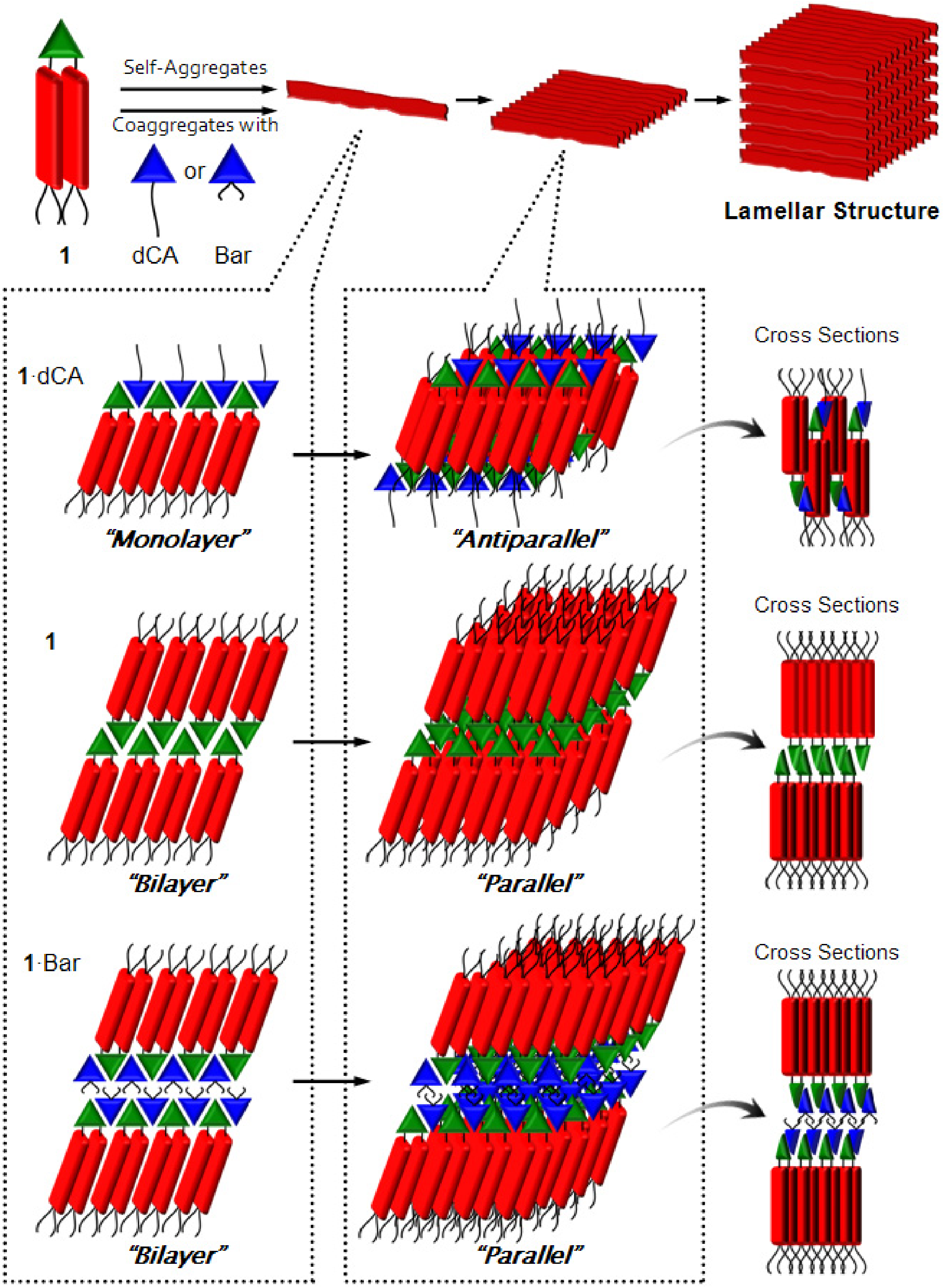


Fig. S8 Schematic representations of self-aggregation of **1** and its coassemblies with dCA and Bar into lamellar structures through the formation of hydrogen-bonded tapes.

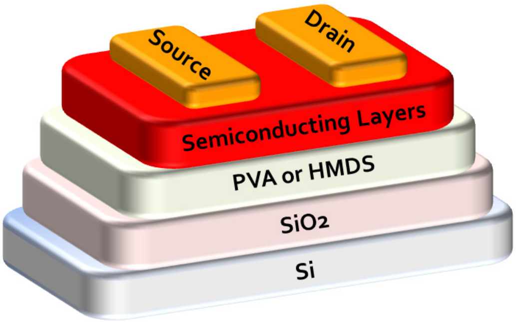


Fig. S9 Top-contact, bottom-gate OFET device structure used in this study.

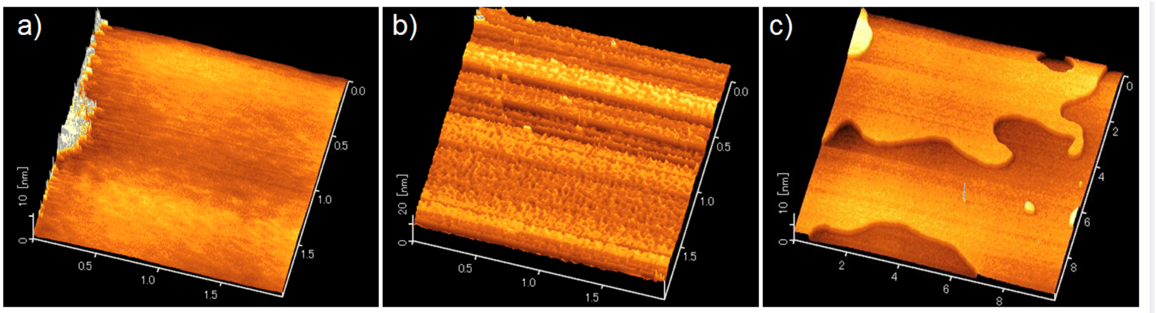


Fig. S10 AFM images of the OFET devices using thin films of a) **1**, b) **1**·dCA and c) **1**·Bar at rt spin-coated from chloroform solutions onto PVA-coated SiO_2/Si substrate. The images are taken at room temperature after annealing the devices at 200 °C for 2 h under vacuum.

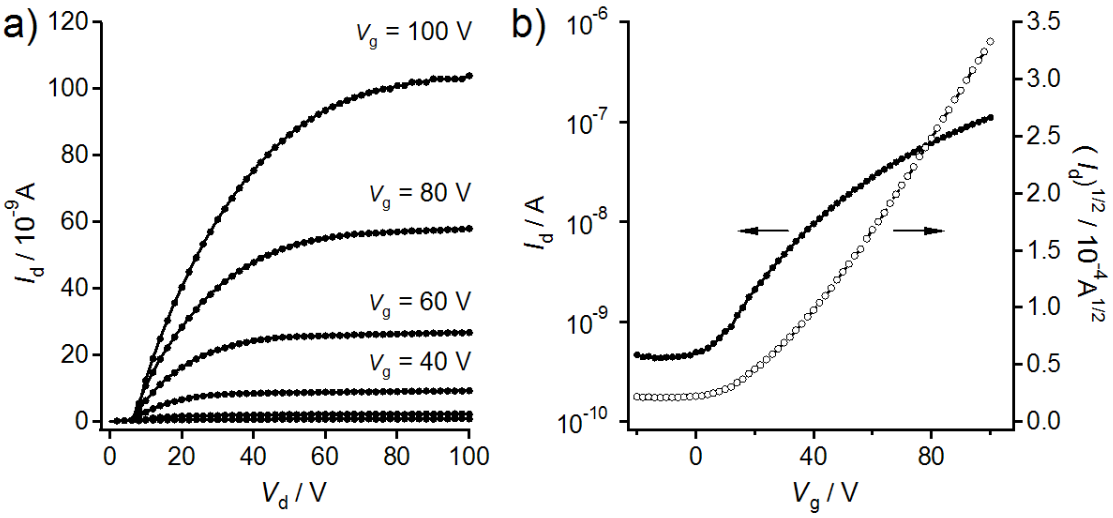


Fig. S11 a) Output and b) transfer characteristics of OFETs using thin films of **1** prepared on PVA-treated SiO_2/Si substrate by spin-coating.

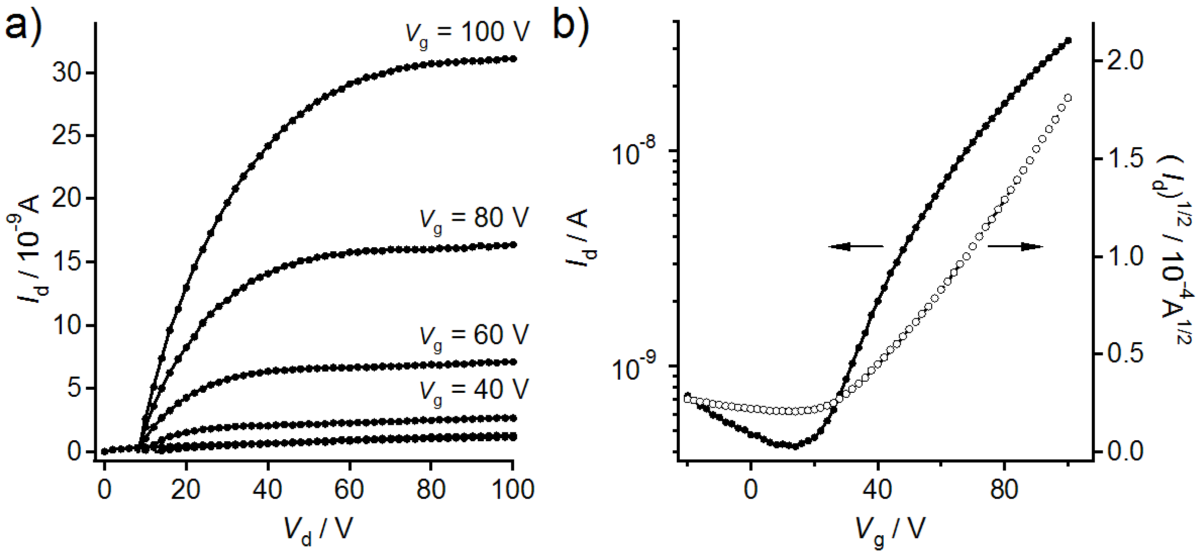


Fig. S12 a) Output and b) transfer characteristics of OFETs using thin films of **1**·dCA prepared on PVA-treated SiO_2/Si substrate by spin-coating.

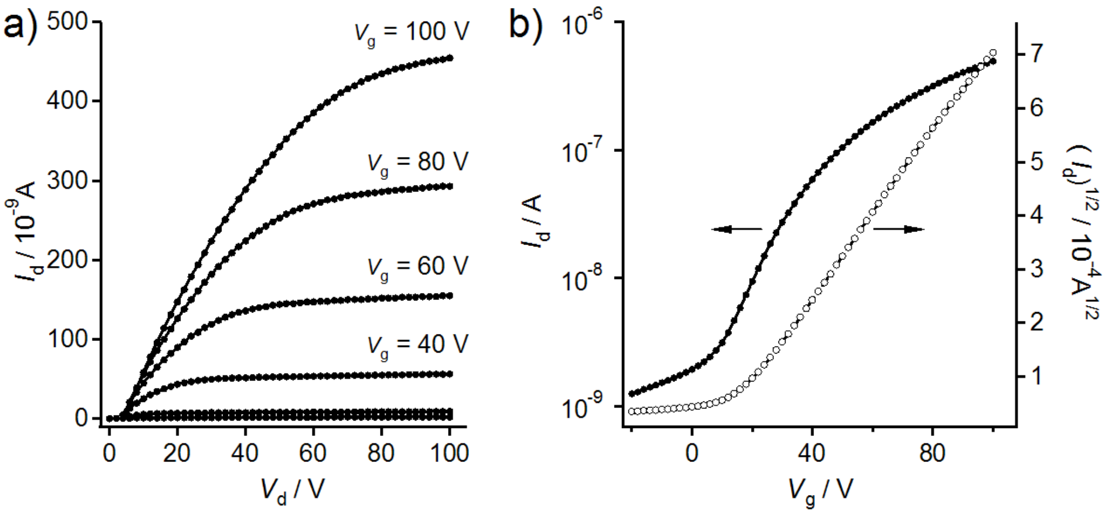


Fig. S13 a) Output and b) transfer characteristics of OFETs using thin films of **1**·Bar prepared on HMDS-treated SiO_2/Si substrate by spin-coating.

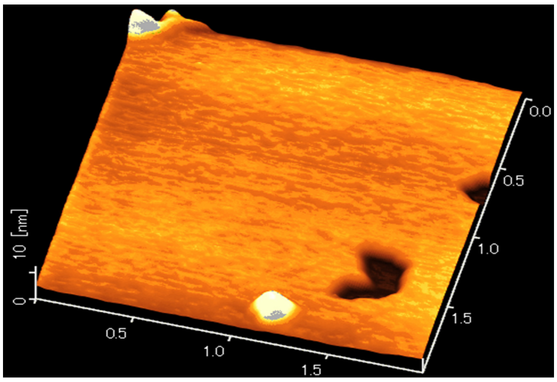


Fig. S14 AFM image of OFETs using thin film of **1**·Bar prepared on HDMS-treated SiO_2/Si substrate by spin-coating. The images are taken at room temperature after annealing the devices at 200 ˚C for 2h under vacuum.

4. Reference:

S1. T. Seki, A. Asano, S. Seki, Y. Kikkawa, H. Murayama, T. Karatsu, A. Kitamura, S. Yagai, *Chem. Eur. J.*, 2011, **17**, 3598–3608.