Electronic Supplementary Information (ESI)

Molecular-Switch-Embedded Organic Schottky Barrier Transistors for High Switching Ratio

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Experimental Section

Materials

DPP-DTT was sourced from Ossila. Chlorobenzene (CB) and toluene were purchased from Sigma-Aldrich. ODTS was purchased from Alfa Aesar. The AgNW solution in isopropyl alcohol (IPA) was acquired from Sg Flexio, featuring a concentration of 0.5 wt%, a length of 25 µm, and a diameter of 25 nm. This solution was subsequently diluted to achieve an optimized concentration of 0.25 mg mL^{-1} in IPA.[1] All materials were used without further purification. The synthetic method for DAE-316 can be found in our previously published paper.[5]

Device Fabrication

For the OSBTs, highly doped silicon wafers (Si++) with a thermally grown SiO_2 layer of 100 nm thickness used as substrates. These SiO_2/Si++ substrates were cut into 2 cm × 2 cm squares and cleaned using a piranha solution, followed by treatment in a mixture of sulfuric acid (H_2SO_4) and 30% hydrogen peroxide (H_2O_2) at a ratio of 7:3. The substrates underwent O_2 plasma exposure for 10 min. After cleaning, they were immersed in a 10 µM ODTS-based self-assembled monolayer (SAM) solution, using toluene as the solvent. To eliminate any residual solvent, all substrates were annealed at 150 ˚C for 30 min. Subsequently, the AgNW film was deposited onto the SAM-treated substrates by spin coating the diluted AgNW solution at 2000 rpm for 30 s. This was followed by annealing at 120 ˚C for 5 min to remove the residual solvent. For the active layer, solutions of DPP-DTT and DAE mixed at various concentrations were dissolved in CB for more than 3 days, with a DPP-DTT concentration of 9 mg mL^{-1}. The DPP-DTT/DAE films were deposited onto the AgNWs by spin coating at 1000 rpm for 60 s in a nitrogen glove box. All semiconductor films were not subjected to annealing treatment. To ensure that the source contact was deposited only on the AgNW and not directly on the semiconductor, the sample was immersed in CB solvent for patterning the semiconductor. Finally, a drain electrode consisting of a DMD configuration (MoO_3 5 nm / Ag 10 nm / MoO_3 40 nm) was deposited onto the active layer, and a silver source contact electrode was deposited onto the areas of the AgNWs where the semiconductor had been removed using thermal evaporation under high vacuum. The active area of the fabricated OSBT was 500 µm × 500 µm.

Device Characterization

The electrical characteristics were measured using a semiconductor parameter analyzer (Keysight B1500A) within a nitrogen glove box. AFM (Jupiter XR) and OM (Zeiss Axioplan) were utilized to analyze the surface morphology. 2D-GIXD was conducted at the 3C and 9A beamlines of the Pohang Accelerator Laboratory (PAL) in Korea. A Thermo Scientific Evolution 220 UV-vis spectrophotometer was used to obtain the UV-vis absorption spectra. UV irradiation was provided by a 312 nm handy lamp (6 W, Vilber Lourmat), and visible irradiation was applied using a 520 nm continuous-wave laser (500 mW max, Shanghai Laser & Optics Century Co., Ltd.).

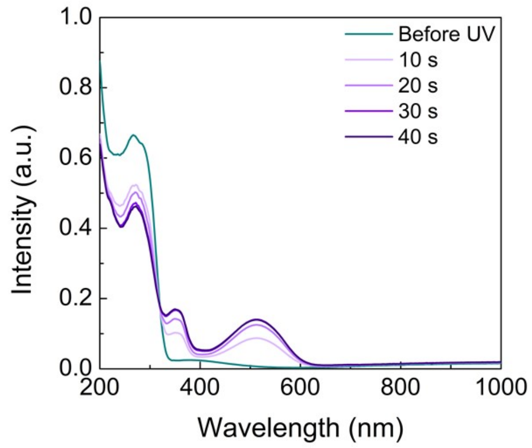

Fig. S1. UV-vis absorption spectra of the DAE-316 film under continuous UV light exposure over time.

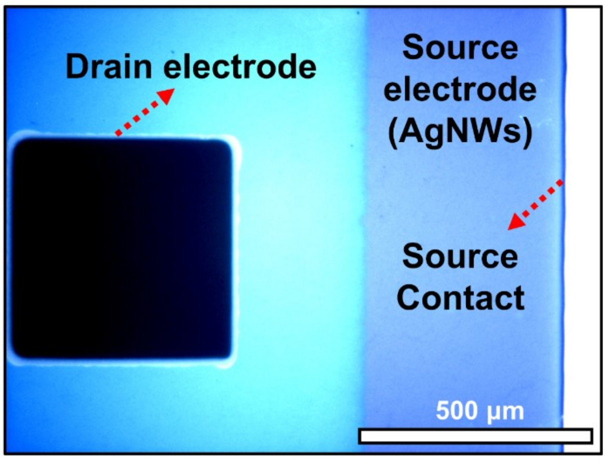

Fig. S2. Optical microscope image of photoprogrammable OSBT.

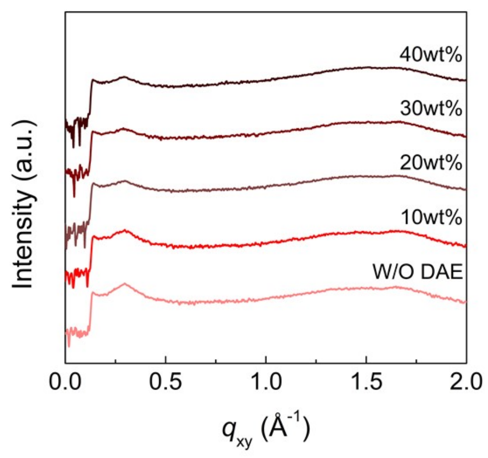

Fig. S3. In-plane direction line-cut profiles of the DPP-DTT film with DAE as a function of DAE concentration.

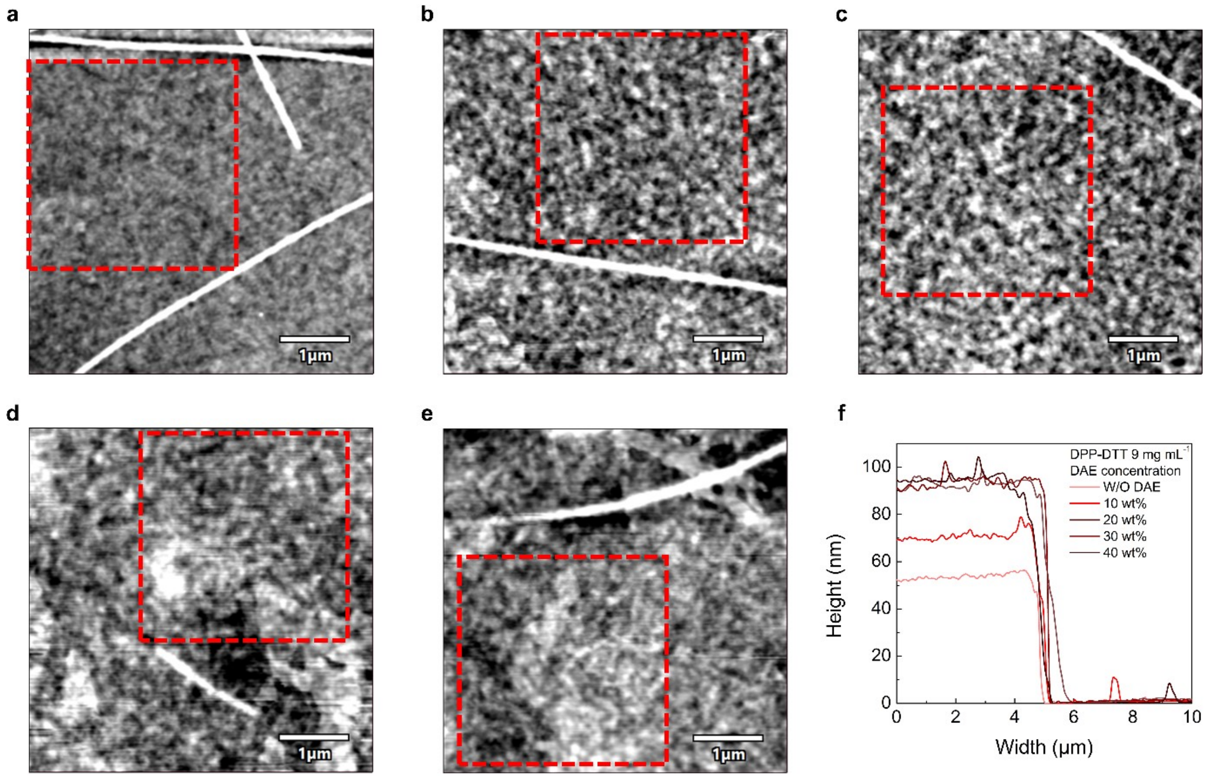

Fig. S4. Atomic force microscopy (AFM) images of the DPP-DTT film: (a) without DAE, (b) 10 wt% DAE, (c) 20 wt% DAE, (d) 30 wt% DAE, (e) 40 wt% DAE. Roughness was assessed in the dashed region. (f) Height profiles of DPP-DTT films without DAE and at varying concentration DAE, extracted from AFM images.

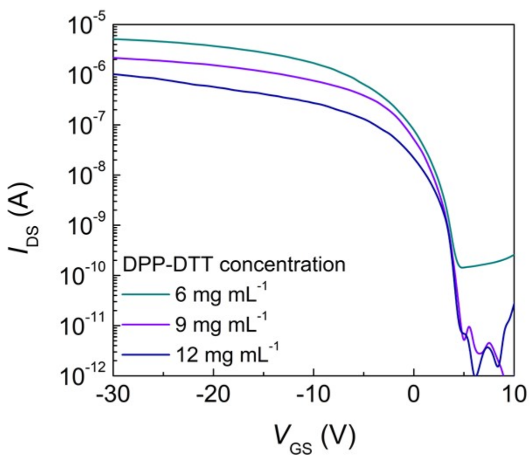

Fig. S5. Transfer characteristics of OSBTs utilizing DPP-DTT with varying concentrations of the DPP-DTT solution.

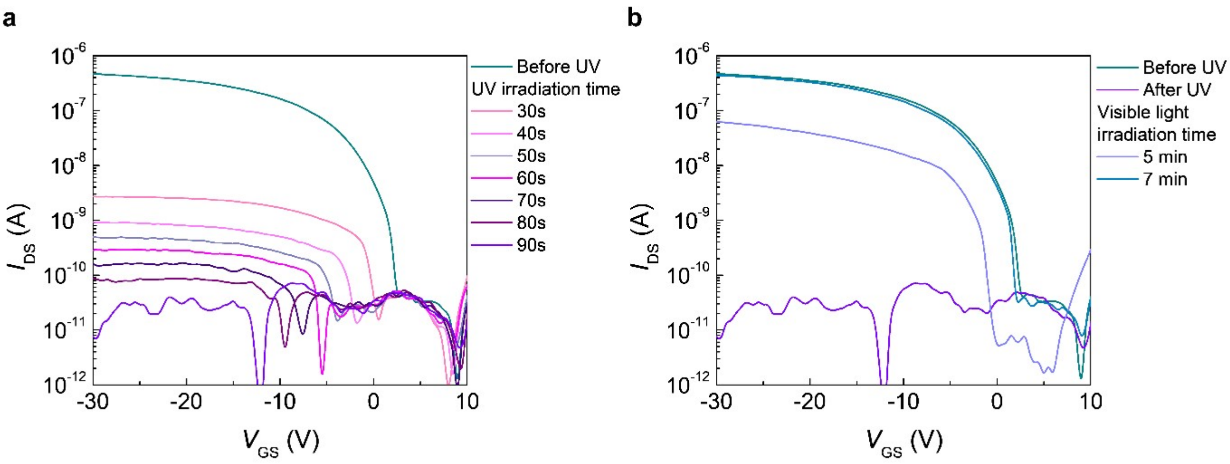

Fig. S6. Transfer characteristics of the OSBT with DAE 30 wt% under continuous UV and visible light exposure over time.

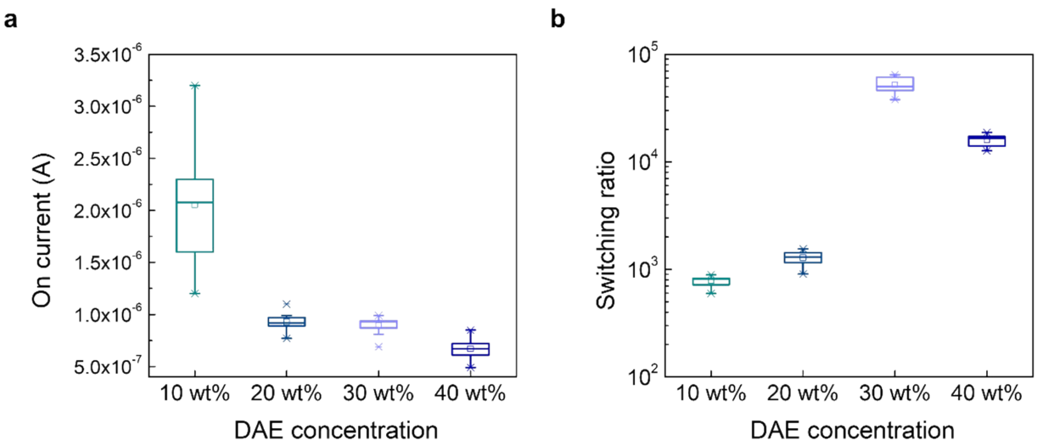

Fig. S7. Measurements of on-current and switching ratio for 10 devices at each DAE concentration, displayed as box plots.

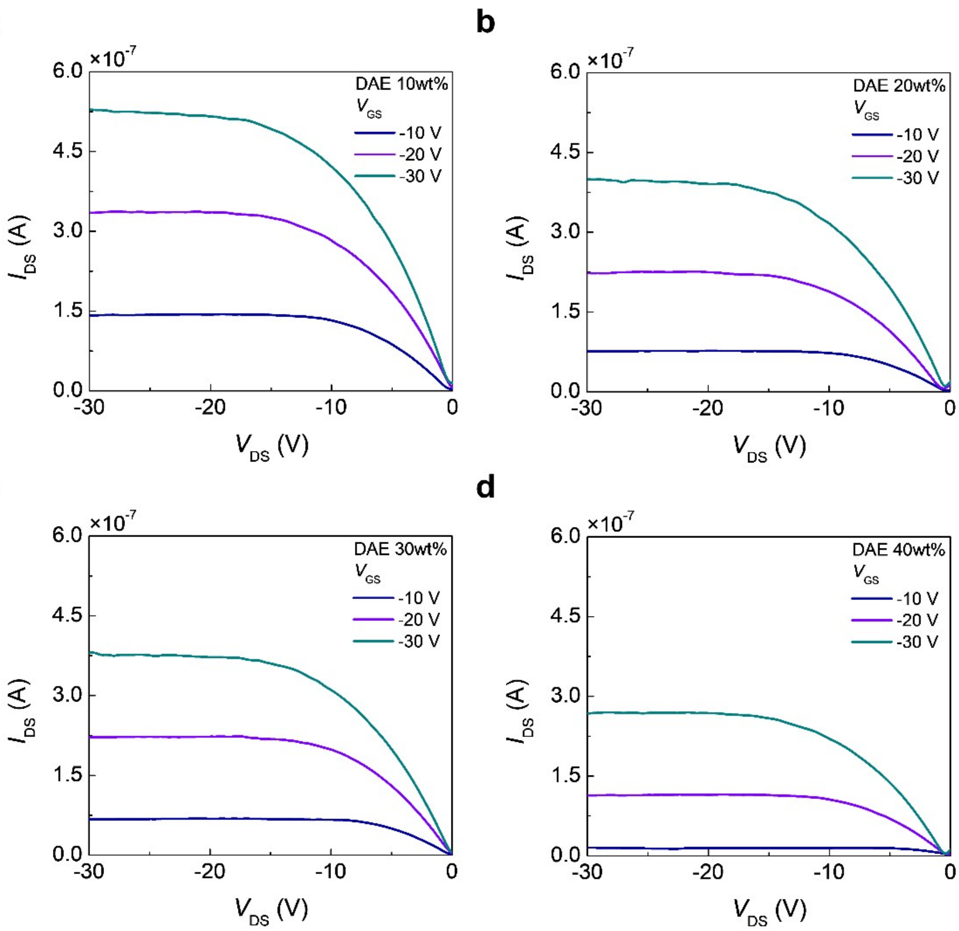

Fig. S8. Output characteristics of the OSBTs with varying concentrations: (a) 10 wt%, (b) 20 wt%, (c) 30 wt%, and (d) 40 wt% DAE-316.

Table S1. Crystallographic information of DPP-DTT films with varying DAE concentrations, extracted from 2D-grazing X-ray diffraction measurements.

sample	q_z (100) Å^{-1}	$d_{lamellar}$ Å	q_{xy} (010) Å^{-1}	$d_{\pi\text{-}\pi}$ Å
DPP-DTT without DAE	0.284	22.13	1.651	3.81
DPP-DTT with DAE 10 wt%	0.278	22.59	1.650	3.81
DPP-DTT with DAE 20 wt%	0.275	22.84	1.649	3.81
DPP-DTT with DAE 30 wt%	0.273	23.01	1.647	3.81
DPP-DTT with DAE 40 wt%	0.270	23.24	1.634	3.85

Table S2. Summary of photoprogrammable OSBT performance with varying DAE concentrations. Each data was extracted from Figure 3.

DAE concentration	I_{on} (DAE_o) A	I_{on} (DAE_c) A	I_{off} (DAE_o) A	Switching ratio	On/off ratio
10 wt%	2.56×10^{-6}	2.89×10^{-9}	1.95×10^{-11}	887	1.32×10^{5}
20 wt%	9.81×10^{-7}	6.34×10^{-10}	2.37×10^{-12}	1,547	4.14×10^{5}
30 wt%	9.35×10^{-7}	1.45×10^{-11}	2.91×10^{-12}	64,576	3.21×10^{5}
40 wt%	6.27×10^{-7}	3.35×10^{-11}	2.62×10^{-12}	18,717	2.40×10^{5}

Table S3. Summary of photoprogrammable performance of DAE-embedded organic transistors.

System	Type	Switching ratio	Number of repeating steps	References
P3HT/DAE-Me	Lateral	approximately 10	4	2
F8T2/DAE-Me	Lateral	approximately 1,000	4	2
F8T2/DL2	Lateral	approximately 1,000	100	3
PCbD-IDTTP/DAE-Me	Lateral	1,026	10	4
PCbD-IDTTP/DAE-316	Lateral	2,588	150	4
DPP-DTT/DAE-Me	Lateral	approximately 100	4	2
DPP-DTT/DAE-^{t}Bu	Lateral	approximately 10	4	2
DPP-DTT/DAE-316	Lateral	4,405	100	5
DPP-DTT/DAE-316	Vertical	64,576	100	This work

References

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