Electronic Supplementary Information

Janus Ultrathin Film from Multi-Level Self-Assembly at Air-Water Interface

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Synthesis of p-(dodecyloxy)pridylazobenzene (DPAB)

The azopyridine derivative DPAB was synthesized through chemical reactions with two steps, which are shown in Figure S1.

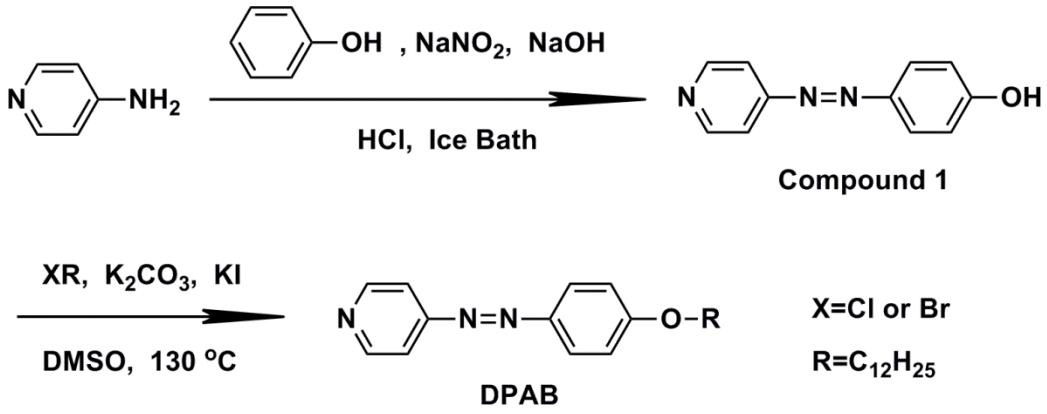

Fig. S1 Synthesis of the p-(dodecyloxy)pridylazobenzene

Step 1: synthesis of compound 1

A 10 wt% NaOH aqueous solution (20 mL) including sodium nitrate (4.00 g, 58 mmol) and phenol (5.00 g, 53 mmol) were prepared and cooled to 0 ^{o}C. Subsequently, it was added dropwise to another aqueous solution with HCl 45 mL (25 mL 11N HCl and 20 mL water) and 4-aminopyridine (6.00 g, 64 mmol). The reaction mixture was stirred under an ice bath (0 ^{o}C) for 0.5 h. Then, the pH of the reaction mixture was adjusted to pH=6-7 by addition of a 10 wt% NaOH aqueous solution. A yellow precipitate was collected by filtration. The crude product was washed with water and recrystallized from acetone. After drying over a vacuum for 24 hours, the resulting bright yellow solid was obtained: yield 2.96 g (32.6 %).

Step 2: synthesis of DPAB

1-Chlorododecane (2.05 g, 10 mmol) was dissolved in dimethyl sulfoxide (20 mL), which was added dropwise to a DMSO (20 mL) solution of K_2CO_3 (6.90 g, 5 mmol), KI (0.01g, 0.1mmol) and 4-(4-hydroxyphenylazo)pyridine (2.00 g, 10 mmol) at 130 ^{o}C. After 5 hours, the mixture was poured into water (200 mL) and then extracted with ethyl acetate (50 mL×3). A rotary evaporator was used to remove all of the solvent. The crude product was purified by silica gel column chromatography with ethyl acetate as eluent; 2.24 g of the pure product was obtained as an orange powder. The NMR spectrum of DPAB was recorded in 5 wt% $CDCl_3$ solution, as shown in Figure S2. Yield: 61 %. Mp: 74.2 ^{o}C. ^{1}H NMR ($CDCl_3$) δ 8.77 (2H, d, Ar-H), δ 7.95 (2H, d, Ar-H), δ 7.71 (2H, d, Ar-H), δ 7.03 (2H, d, Ar-H), δ 4.06 (2H, t, -O-CH_2-), δ 1.85 (2H, m, -CH_2-), δ 1.46 (2H, m, -CH_2-), δ 1.27 (16H, m, -C_8H_{16}-), δ 0.90 (3H, t, -CH_3).

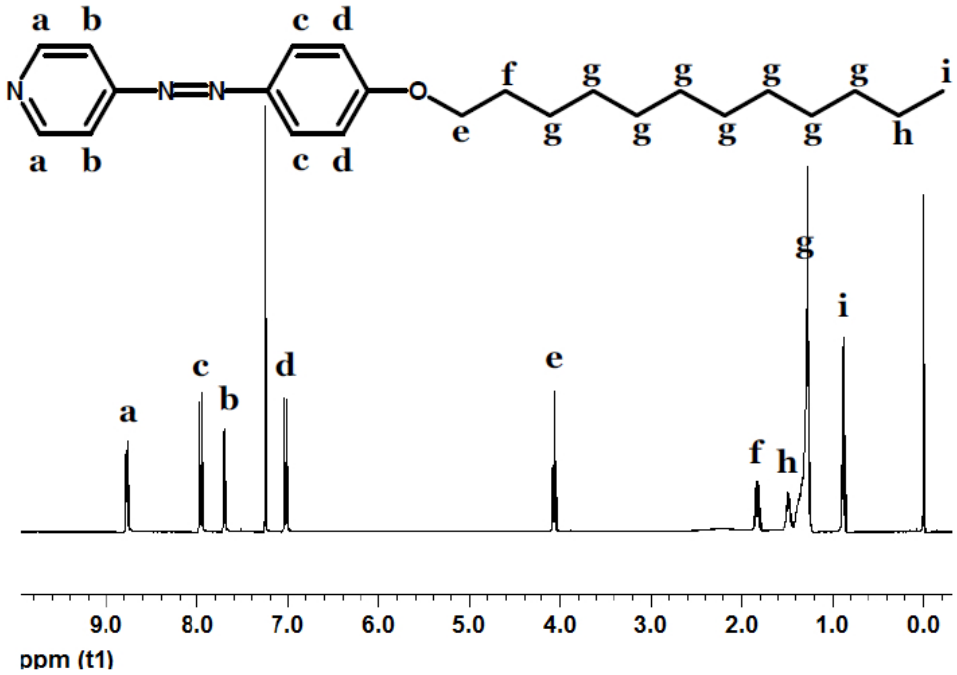

Fig. S2 ^{1}H NMR spectrum of DPAB

Surface morphology of the Janus film

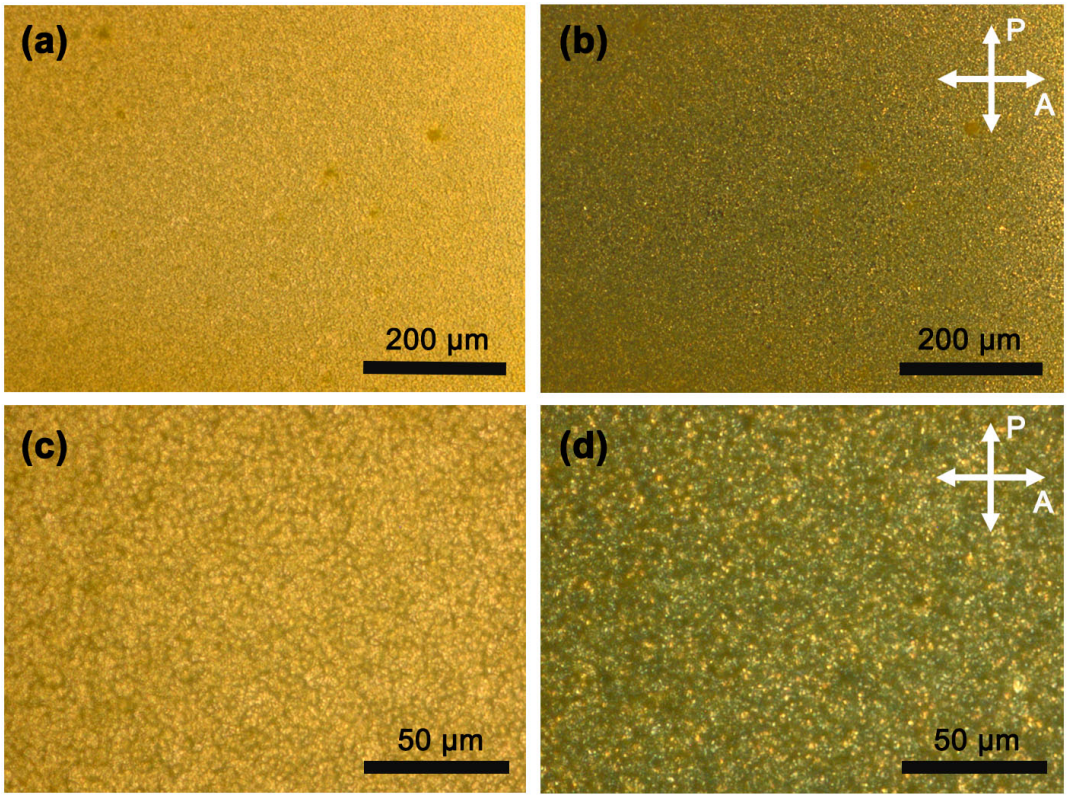

Fig. S3 Morphology of the Janus film surface observed by (a)&(c) optical microscopy and (b)&(D) polarizing optical microscopy.

Section view SEM images of the Janus film

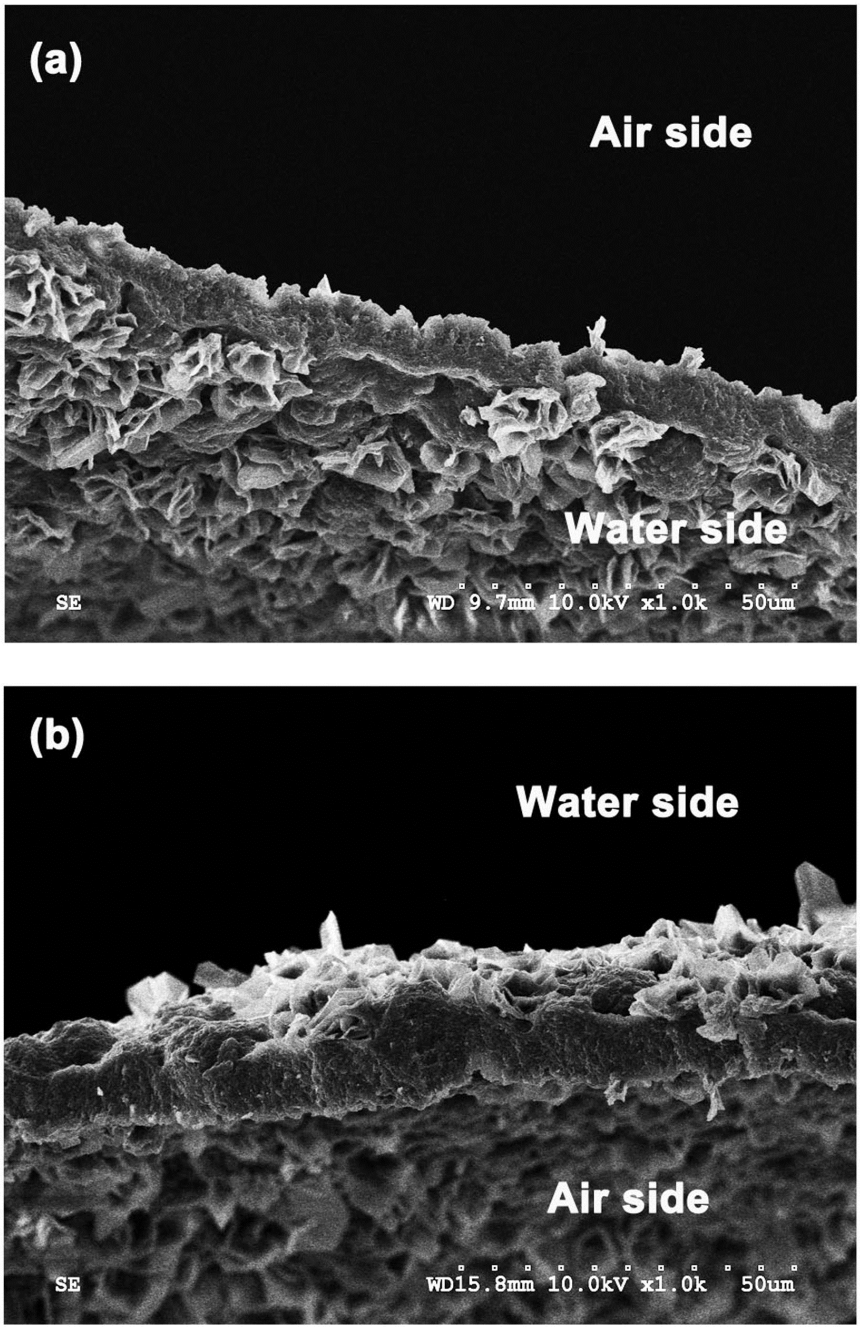

Fig. S4 SEM images of the Janus film surfaces (Section view)

ATR-FTIR characterization of the Janus film

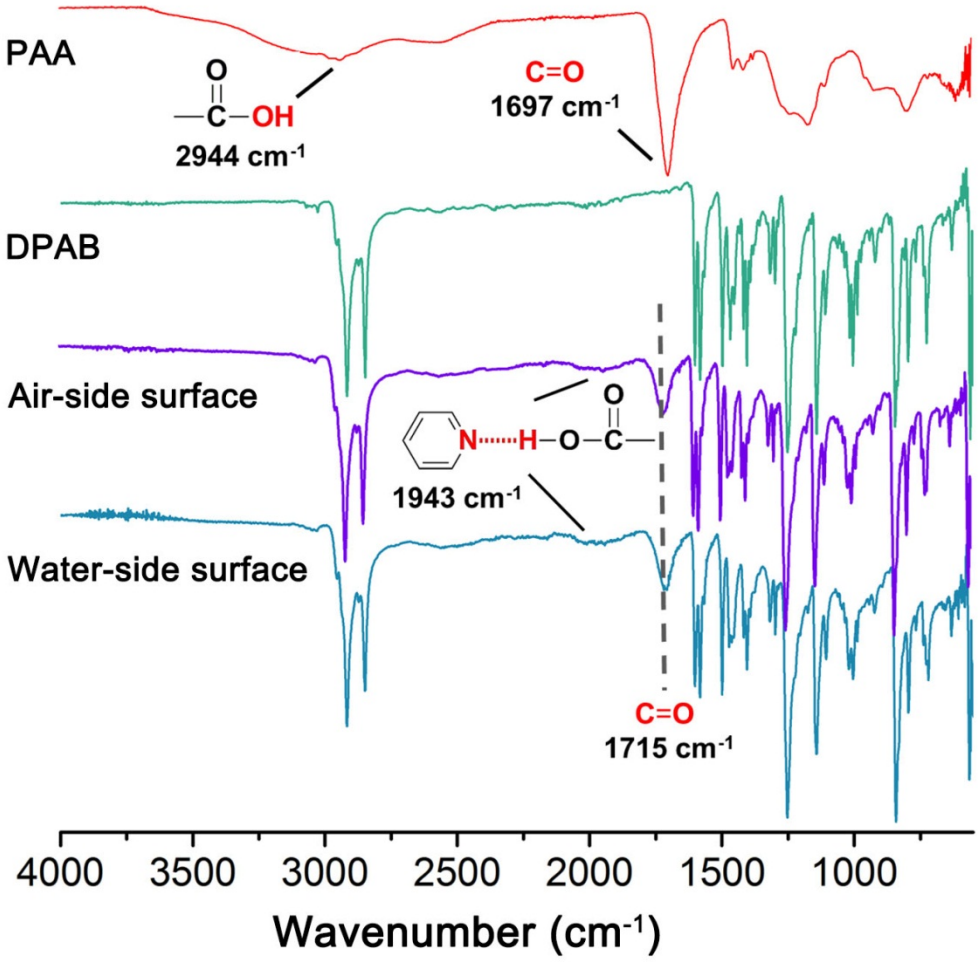

Fig. S5 ATR-FTIR spectra of DPAB, PAA and two surfaces of the Janus film.

Measurements

^{1}H-NMR spectra of the compounds were recorded on a Bruker Avance III 400. Optical and polarizing optical images were obtained using Zeiss Axio Scope A1 Microscope. SEM images were taken using Hitachi S570 SEM. XRD characterization was performed using Rigaku MultiFlex XRD. ATR-FTIR spectra were obtained by ATR-FTIR, Cary 600 Series FTIR Spectrometer. The images of contact angles were taken by stereo microscope (Olympus SZ61) and their values were then quantified using image analysis software ImageJ.