

Supporting Information for

Highly Emissive Excimers by 2D Compression of Conjugated Polymers

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Experimental

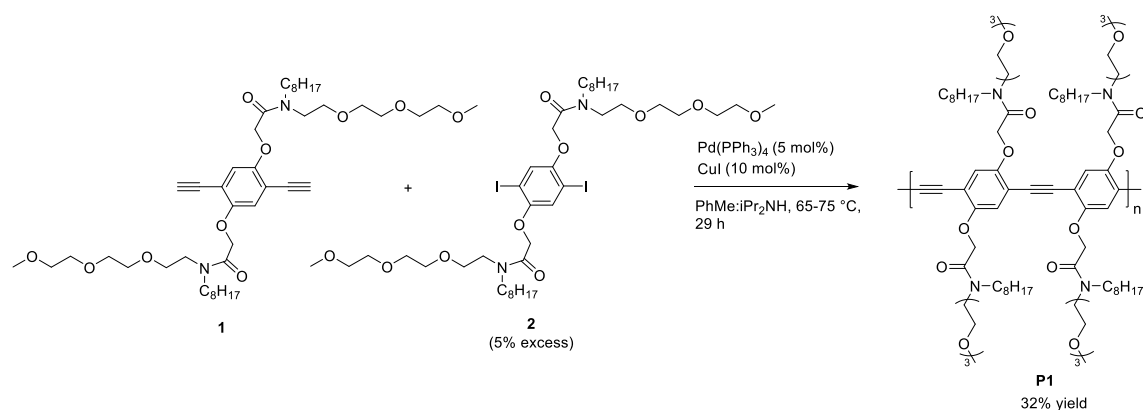
General. Chemicals were purchased from Aldrich, Alfa Aesar, and TCI America without further purification unless noted otherwise. All reactions were carried out under argon with standard Schlenk techniques. Compound **1**, **2**, and **P2** were synthesized by following the literature procedures.¹ All ¹H NMR spectra are reported in ppm on a Bruker Avance-400. ¹H NMR is referenced to a chloroform peak ($\delta = 7.26$ ppm). The multiplicity is reported as follows: s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad. ¹³C NMR is referenced to a 1,1,2,2-tetrachloroethane peak ($\delta = 73.78$ ppm). Coupling constants J are reported in Hz. Elemental analyses were carried out by Robertson Microlit Laboratories, Ledgewood, NJ (USA).

THF Gel Permeation Chromatography (GPC) was performed with a concentration of 0.5 mg/ml on an Agilent 1260 Infinity system, calibrated with monodisperse polystyrene standards. UV-vis spectra were recorded on Agilent Cary 4000 or Cary 5000 spectrometer at room temperature. Fluorescence measurements were performed at room temperature with a Horiba Jobin Yvon SPEX Fluorolog- τ 3 fluorimeter (model FL-321, 450 W Xenon lamp) using right-angle conformation for solution and Langmuir monolayers and front-face conformation for thin films. Lifetime measurements were carried out on a Horiba Jobin Yvon MF2 lifetime spectrometer equipped with a 365 nm laser diode via frequency modulation. POPOP in ethanol was used as a reference lifetime sample ($\tau = 1.35$ ns). For sample preparations of photophysics measurements, the solutions were prepared in chloroform with 10^{-5} M – 10^{-6} M. The solid-state films were prepared on glass by spin-coating 1000 rpm for 60 seconds from the solution in chloroform (5 mg/ml) and annealed at 70 °C for 15 min in ambient atmosphere.

The *in situ* UV/PL measurements on Langmuir monolayers were carried out with fiber optic cables that are connected with the Agilent spectrometer and the Horiba fluorimeter. The Langmuir monolayers were prepared from the polymer in chloroform solution (1 mg/mL) on 102 M trough from NIMA Technology equipped with a fused quartz window, using purified water with > 18 M Ω ·cm as subphase. After drying the chloroform for ca. 15 min, the monolayers were mechanically annealed with 3 compression-expansion cycles and photophysics data were recorded. For the transfer of the monolayers to glass substrates, NIMA 602 M equipped with a vertical dipper was used where the Langmuir monolayers were deposited in the same way as NIMA 102 M. 18×18 mm glass microscope cover slides were sonicated using a detergent solution for 20 min, rinsed with the purified water (> 18 M Ω ·cm) three times, and sonicated with the purified water for 20 min, followed by vacuum drying. For hydrophilic surfaces, the washed glass slides were sonicated with concentrated nitric acid for 20 min, rinsed with the purified water three times, sonicated with 10% sodium hydroxide solution for 20 min, and finally rinsed with the purified water three times, followed by vacuum drying.

For sensing experiments, a solvent of interest is contained in a scintillation vial with a cap being closed so that the inside of the vial is saturated with the solvent vapor. The cap is open and the LB film is placed on top of the vial under a hand-held UV lamp with 365 nm.

Polymerization procedure for P1. **1** (1.00 eq, 0.100 mmol, 79.0 mg), **2** (1.05 eq, 0.105 mmol, 104.4 mg), Pd(PPh₃)₄ (5 mol%, 5.8 mg), and CuI (10 mol%, 1.9 mg) are added into a flame-dried flask equipped with a magnetic stirrer bar. Then the flask containing reagents was evacuated and back-filled with argon for 5 times. The mixture of dry toluene:diisopropylamine (3:1 v/v) was degassed with nitrogen for 30 min. 4 mL of the mixture was added to the flask. The reaction mixture was stirred for 30 min at room temperature to completely dissolve all the materials. Temperature was increased into 65 °C and stirred for 7 h, followed by increasing the temperature into 75 °C and stirring for additional 22 h. After cooling down



Scheme S1. Polymerization for **P1**.

to room temperature, the solvents in the reaction mixture was evaporated under reduced pressure, and the contents are dissolved in dichloromethane (DCM). The mixture was filtered through a short plug of silica gel and eluted with excess amount of DCM. The filtrate was evaporated under reduced pressure, precipitation was obtained from DCM/hexane and subsequent centrifugation was carried out at 12,000 rcf for 10 min. Preparative GPC in THF was used to separate high molecular weight fraction of the solid product. The resulting fraction in THF was evaporated under reduced pressure, and further precipitation in DCM/hexane was carried out with the subsequent centrifugation at 12,000 rcf for 10 min. The product was dried in vacuo, affording a dark yellow rubbery solid (49 mg, 32 %). ^1H NMR (400 MHz, CDCl_3): δ = 7.13 (br, 2H), 4.88-4.84 (br, 4H), 3.60-3.33 (br, 34H), 1.55 (br, 4H), 1.25 (br, 20H), 0.86 (br, 6H). A complete ^{13}C NMR cannot be obtained as a result of insufficient solubility in solvents that would not obscure key signals such as chloroform or at high temperature (70–80 °C) 1,1,2,2-tetrachloroethane. We were also to detect the side chain resonances, which are ^{13}C NMR (101 MHz, $\text{CDCl}_2\text{CDCl}_2$, 70 °C): δ = 71.8, 70.3, 70.2, 58.5, 31.6, 29.1, 29.0, 22.4, 13.8. GPC (THF): M_n = 33 kDa (DP = 22), Đ = 1.40. The relatively short polymerization time could lead to the incompleteness of the reaction and thus smaller degree of polymerization than the theoretical value (DP = 41). Anal. Calcd for $\text{C}_{84}\text{H}_{140}\text{N}_4\text{O}_{20}$ (repeat unit): C, 66.11; H, 9.25; N, 3.67; O, 20.97. Found: C, 62.73; H, 8.79; N, 3.44.

Characterization Data

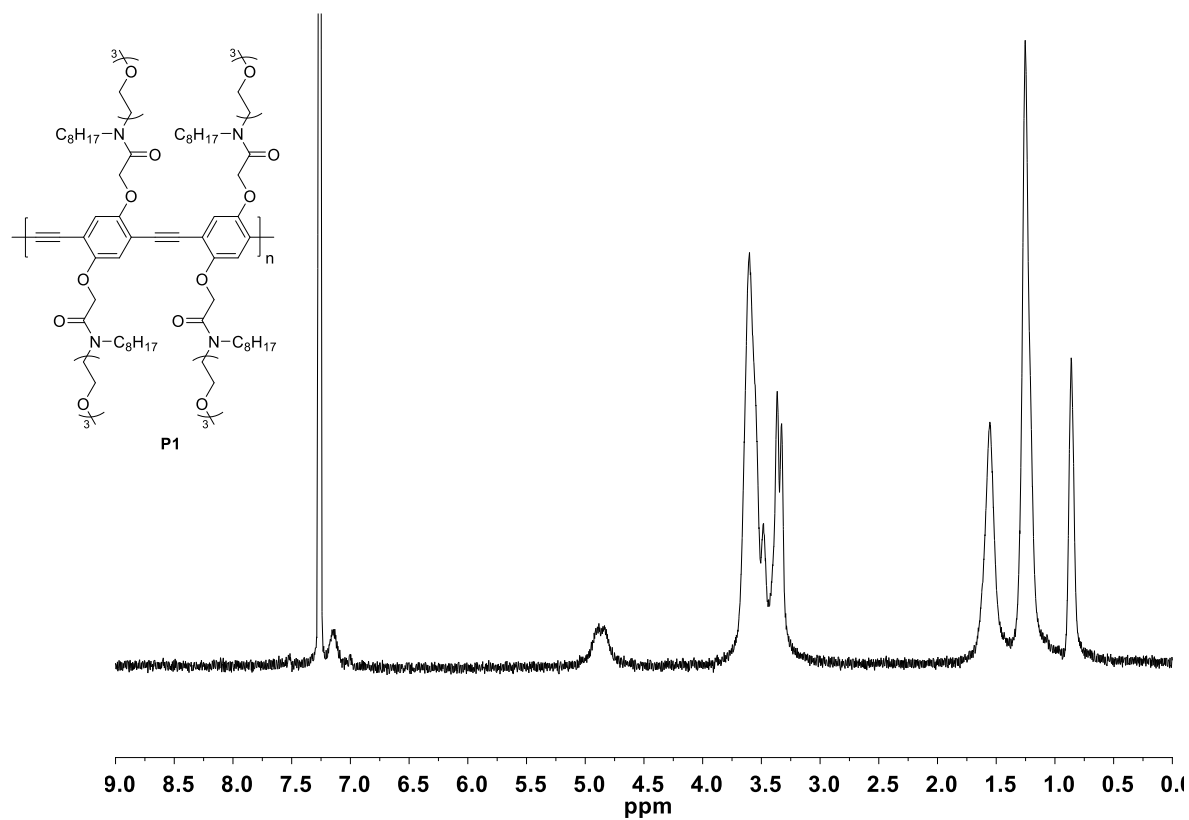


Figure S1a. ^1H NMR of **P1** in CDCl_3 .

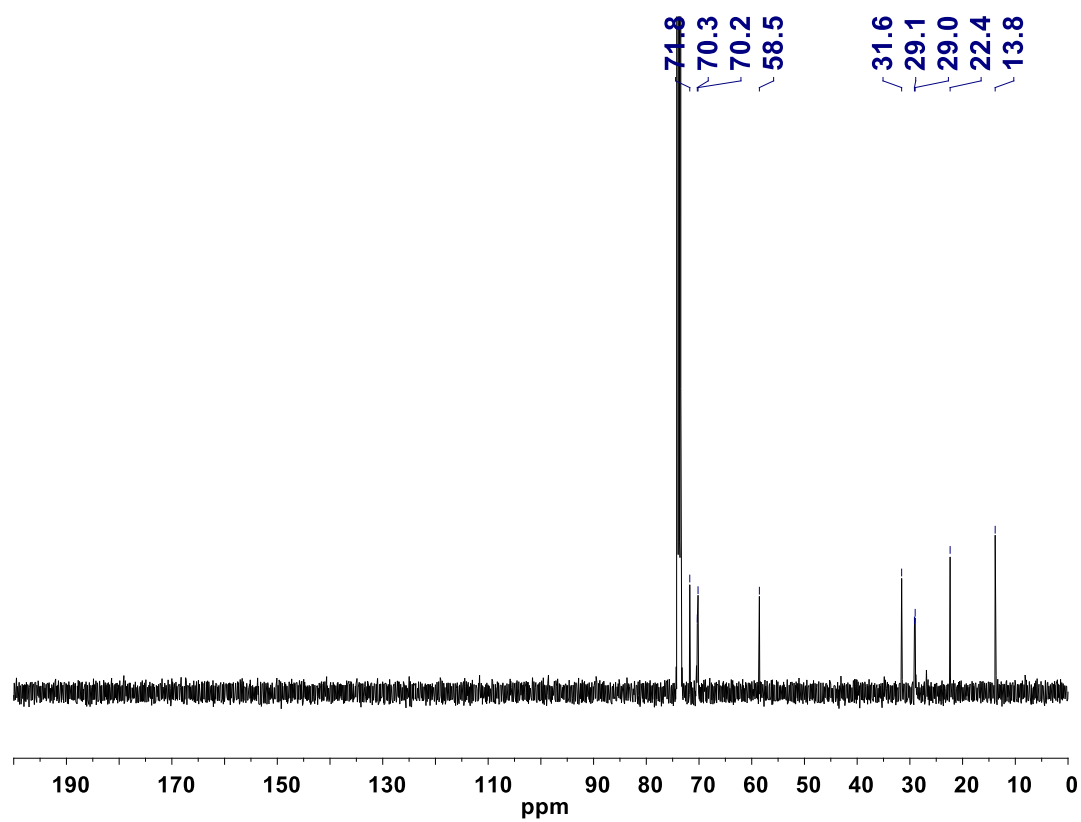


Figure S1b. ¹³C NMR of **P1** in 1,1,2,2-tetrachloroethane-d₂ at 70 °C.

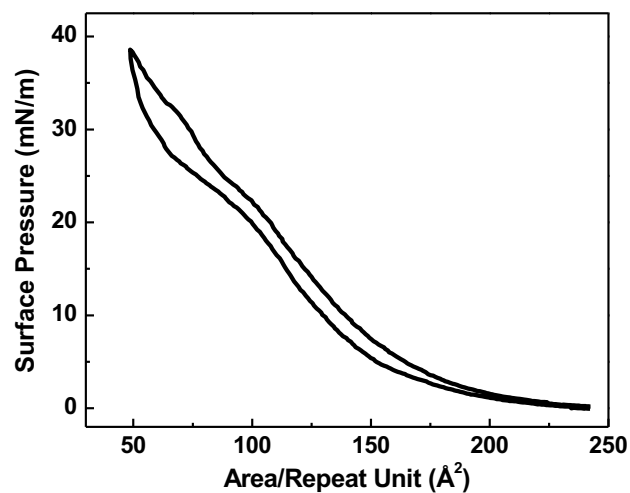


Figure S2. Pressure-area isotherm of **P1** with the small amount of sample loading to observe the onset point.

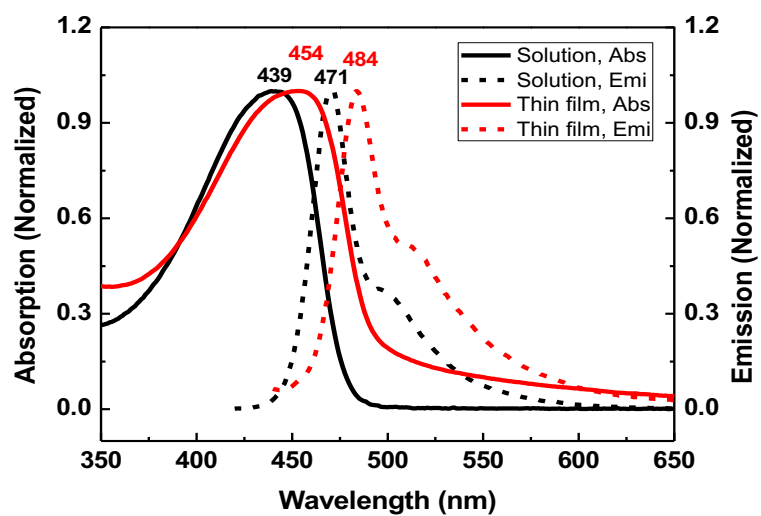


Figure S3. Spectra of solution and thin films of **P1** that do not display emissive excimers. Absorption (solid) and emission (dotted) spectra in solution (black) and thin films (red) are obtained. Thin films show no excimeric emission.

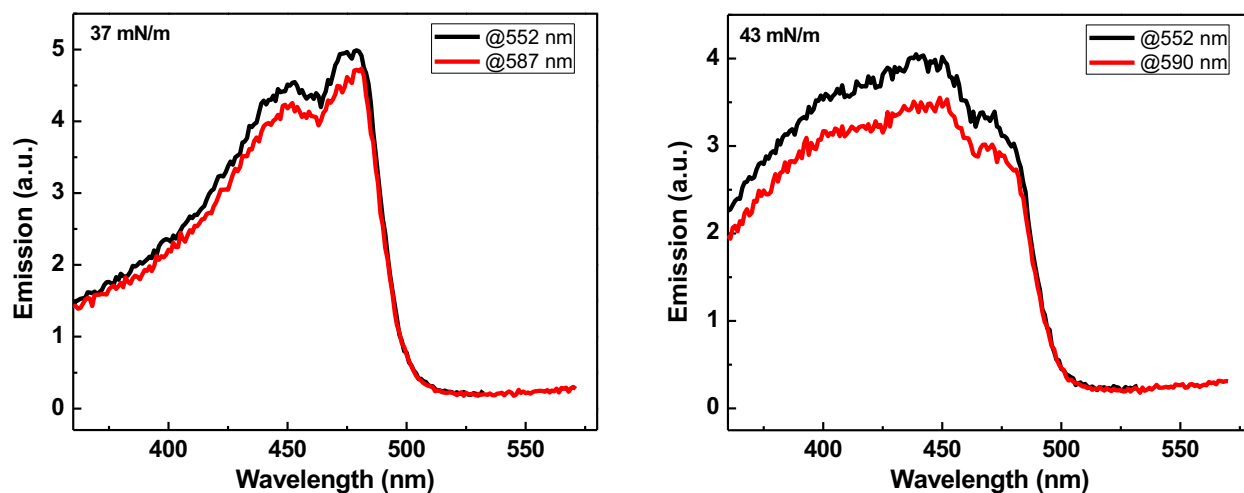


Figure S4. Excitation spectra at 37 mN/m (left) and 43 mN/m (right) of the **P1** monolayer at the air-water interface.

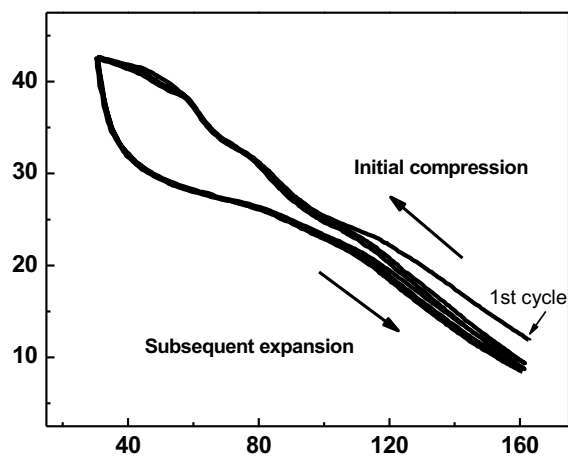


Figure S5. The pressure-area isotherms of the first three cycles for mechanical annealing, supplemental to Figure 3d. The consistent shapes indicate the reversible and reproducible formation of incline-stack conformation. The first cycle is slightly off from the equilibrium, implying that the mechanical annealing indeed helps the polymers pack each other after one compression-expansion cycle.

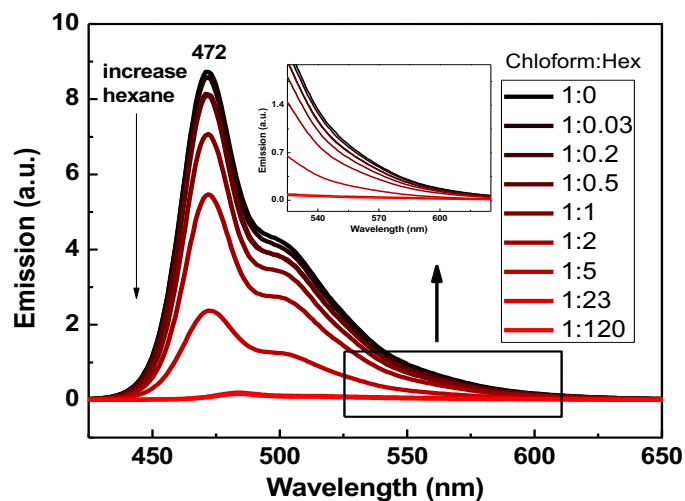


Figure S6. Emission spectra of solution aggregates of **P1** that do not display emissive excimers. Aggregate dispersions by adding a poor solvent (hexane) are generated. The increased amount of hexane triggers the self-quenching as a result of cofacial ground-state aggregates (see Figure S7 for absorption spectra). The enlarged spectra in inset confirm the absence of excimers.

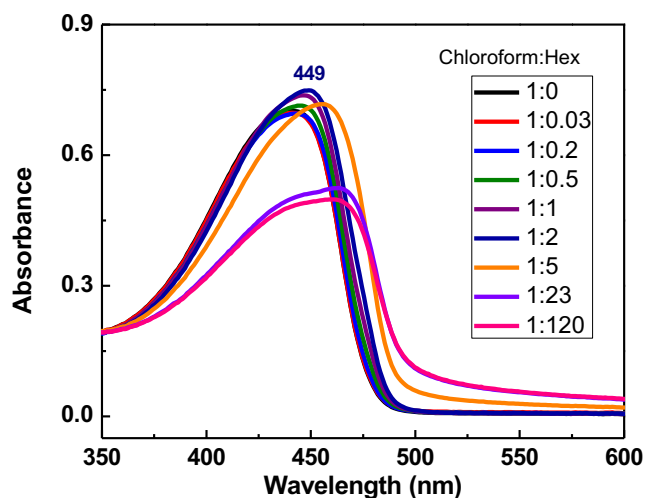


Figure S7. Absorption spectra of solution aggregates of **P1** in varying ratio of hexane to chloroform.

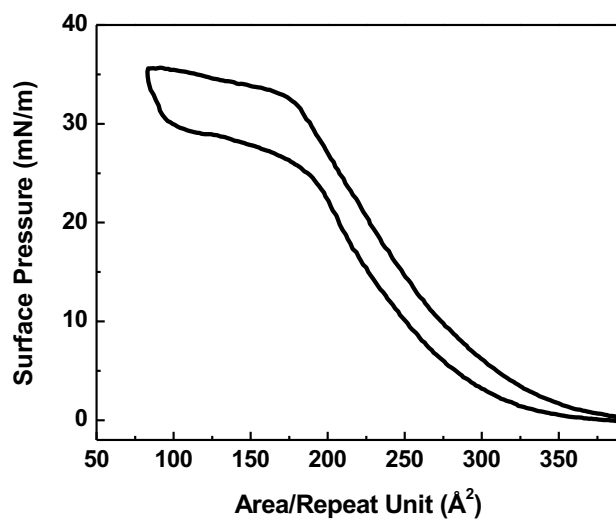
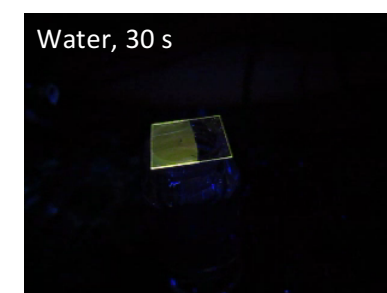
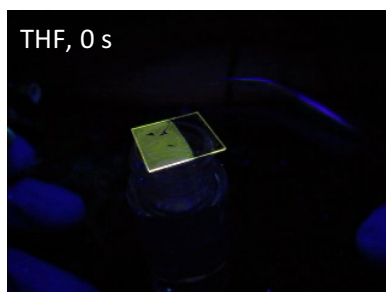
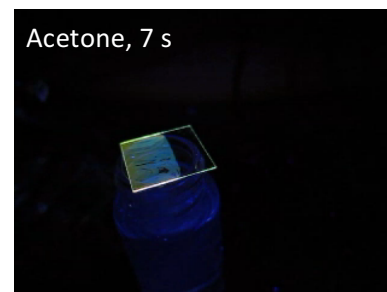
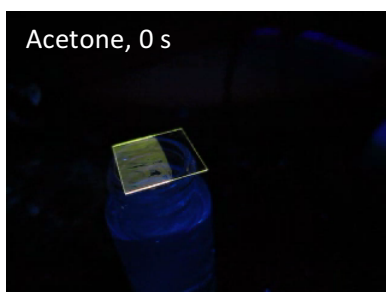
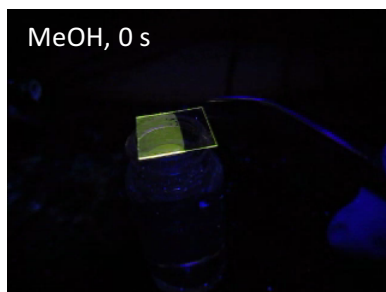


Figure S8. Pressure-area isotherm of hetero-type PPE (**P2**), supplemental to Figure 4. The repeat unit on the x-axis contains two phenylene ethynylenes.

Sensing Pictures



References

1. Bouffard, J.; Swager, T. M. *Chem. Commun.* **2008**, 5387-5389.