Supporting Information

Printable Crosslinked Polymer Blend Dielectrics. Design Strategies, Synthesis, Microstructures, and Electrical Properties, with Organic Field-Effect Transistors as Testbeds.

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Experimental Section

Reagents and Methods. Poly(4-vinylphenol) (**PVP**, M_n = 20 kg/mol), 1,6-bis(trichlorosilyl)hexane (**C_6Cl**), dimethylhexylchlorosilane (**C_6SiMe_2Cl**), and 4-isopropylphenol (**PhOH**) were purchased from Aldrich. The crosslinker 1,6-bis(trimethoxysilyl)hexane (**C_6OMe**) was purchased from Gelest. All the reagents were used without further purification. ^{1}H and ^{29}Si NMR were performed using an Inova 400 NMR spectrometer. Elemental analyses were performed by Midwest microlab, LLC. Laser desorption mass spectra were obtained with a Perspective BioSystems time-of-flight MALDI mass spectrometer using a dithranol matrix.

Synthesis of 1,6-bis(triacetoxysilyl)hexane (**C_6OAc**). Exactly 10.0 g (0.0283 mol) of 1,6-bis(trichlorosilyl)hexane and 34.7 mL (0.34 mol) of acetic anhydride were slowly added to a 100 mL air-free flask. The reaction solution was then heated to 80 °C for 5 h. Acetyl chloride was periodically distilled out during the reaction period. Finally, after all the volatile fractions were distilled at 120 °C/5 mTorr, 13.8 g (0.0279 mol) of 1,6-bis(triacetoxysilyl)hexane was obtained in a yield of 98.6%. ^{1}H NMR (400MHz, $CDCl_3$): δ 1.1 (t, 4H), 1.3 (m, 4H), 1.4 (s, 4H), 2.1 (s, 18H. ^{29}Si NMR (79.6MHz, $CDCl_3$): -44.8 (s). Anal. Calcd for $C_{18}H_{30}O_{12}Si_2$: C 43.70, H 6.07. Found: C 43.50. H 5.87.

Synthesis of bis(3-triacetoxysilylpropyl)ethylene ether (**EGOAc**). Sodium hydride (5.00 g, 0.208 mol) was slowly added to stirring solution of 2-allyloxyethanol (20 mL, 0.187 mol) in 20 mL THF. Next, 32 mL (0.370 mol) of allyl bromide was added to the suspension and the mixture was heated at 60 °C for 10 h. After cooling to room temperature and filtration, 22 g of di(allyloxy)ethane (yield, 83% based on 2-

allyloxyethanol) was obtained by fractional distillation at 50 °C/100 mTorr from the filtrate. ^{1}H NMR (400MHz, $CDCl_3$): δ 3.6 (t, 2H), 4.0 (d, 2H), 5.1 (d 1H), 5.3 (d 1H), 5.9 (q, 1H).

Next, 20.0 g (0.141 mol) of the distilled diallyl ethylene ether and 40 mg of hydrogen hexachloroplatinate (IV) hydrate were added to a 250 mL air-free reaction flask with a condenser. Trichlorosilane (40 mL, 0.396 mol) was added dropwise to the stirring solution which was then heated to 80 °C in an oil bath. After refluxing for 4 h, the reaction mixture was distilled in vacuo. The fraction boiling at 90 °C/20 mTorr, (bis(3-trichlorosilylpropyl)ethyleneether, 39.0 g (0.0944 mol)) was collected in a yield of 70%, based on diallyl ethylene ether. ^{1}H NMR (400MHz, $CDCl_3$): δ 1.5 (t, 2H), 1.8 (m, 2H), 3.4 (t, 2H), 3.6 (t, 2H). ^{29}Si NMR (79.6MHz, $CDCl_3$): 13.4 (s). Next, 10.0 g (0.0242 mol) of 1,1,1,12,12,12-hexachloro-5,8-dioxa-1,12-disiladodecane and 27 mL (0.048 mol) of acetic anhydride were slowly added to a 100 mL air-free flask. The reaction mixture was then heated to 80 °C with stirring for 5 h, with acetyl chloride periodically distilled out during the reaction period. After the remainder of the volatile fraction was removed by distillation at 120 °C/5 mTorr, 13.4 g (0.0241 mol) of di(3-triacetoxysilyl)propyl ethylene ether was obtained in a yield of 99.6%. ^{1}H NMR (400MHz, $CDCl_3$): δ 1.1 (t, 2H), 1.7 (m, 2H), 2.0 (s, 9H), 3.3 (t, 2H), 3.5 (t, 2H). ^{29}Si NMR (79.6MHz, $CDCl_3$): -44.9 (s). Anal. Calcd for $C_{20}H_{34}O_{14}Si_2$: C 43.31, H 6.18. Found: C 42.79. H 6.16.

Synthesis of 1,6-bis[tri(dimethylamino)silyl]hexane (**C_6NMe_2**). A 25 mL THF solution of 1,6-bis(trichlorosilyl)hexane (2.0 mL, 7.518 mmol) was placed in a 100 mL air-free flask under a nitrogen atmosphere. The solution was then cooled in an ice bath and 50 mL of a THF solution of dimethylamine (2.0 M, 90.2 mmol) was added dropwise while stirring. During this time, a colorless solid precipitated from the solution. After the addition of dimethylamine, the mixture was slowly warmed to 50 °C, and maintained at this temperature overnight, then filtered through an air-free frit. The solvent was removed from the filtrate under vacuum, and 3.0 g of 1,6-bis[tri(dimethylamino)silyl]hexane was obtained in a yield of 98%. ^1H NMR (400MHz, $CDCl_3$): δ 0.65 (t, 4H), 1.35 (m, 8H), 2.42 (s, 36H). ^{29}Si NMR (79.6MHz, $CDCl_3$): -16.6 (s). Anal. Calcd for $C_{18}H_{48}N_6Si_2$: C 53.41, H 11.95, N 20.76. Found: C 51.07. H 11.39, N 18.11.

Synthesis of dimethylhexylacetoxysilane (**C_6SiMe_2OAc**). Acetic anhydride (5.5 mL, 0.0578 mol) was added to a 25 mL flask containing 5.0 g (0.028 mol) of chlorodimethylhexylsilane. The mixture was then heated with stirring to 80^{o}C for 5 h. Acetyl chloride was periodically removed by distillation during the reaction period. Dimethylhexylacetoxysilane (5.1 g, 0.025 mol) was obtained in 91% yield after distillation at 55 °C/50 mTorr. ^1H NMR (400 MHz, $CDCl_3$): δ 2.03 (s, 6H), 1.45-1.18 (m, 8H), 0.86 (t, 3H), 0.72 (t, 2H), 0.22 (s, 6H). ^{29}Si NMR (79.6 MHz, $CDCl_3$): 23.7 (s).

Synthesis of dimethylhexyl(dimethylamino)silane (**$C_6SiMe_2NMe_2$**). Chlorodimethylhexylsilane (4.00 g, 0.0224 mol) in 10 mL of THF was placed in a 100 mL air-free flask under nitrogen. The solution was then cooled in an ice bath and 30 mL of a THF solution of dimethylamine (2.0 M, 60 mmol) was added dropwise while stirring. This resulted in formation of a while precipitate. After the addition of the dimethylamine, the mixture was allowed to slowly warm up to 50^{o}C, kept at this temperature for overnight, and then filtered under nitrogen. The solvent was then distilled from the filtrate to yield 4.0 g (93% yield) of dimethylhexyl(dimethylamino)silane. ^1H

NMR (400 MHz, $CDCl_3$): δ 2.42 (s, 6H), 1.32 (m, 8H), 0.88 (t, 3H), 0.58 (t, 2H), 0.08 (s, 6H). ^{29}Si NMR (79.6 MHz, $CDCl_3$): 8.7 (s).

Synthesis of dimethylhexylmethoxylsilane ($\mathbf{C_6SiMe_2OMe}$**).** Chlorodimethylhexylsilane (3.0 g, 0.0168 mol) in 8 mL of THF was placed in a 50 mL air-free flask under a nitrogen atmosphere. Next, 0.80 mL anhydrous methanol (0.0198 mol) was added to the solution and the mixture was refluxed overnight. Dimethylhexylmethoxylsilane (2.9g, 99% yield) was obtained after distillation at 50 °C/50 mTorr. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.55 (s, 3H), 1.32 (m, 8H), 0.90 (t, 3H), 0.52 (t, 2H), 0.05 (s, 6H). ^{29}Si NMR (79.6 MHz, $CDCl_3$): 7.5 (s).

In Situ NMR Kinetic Studies of Model Reactions. In a glove box, 80 mg of 4-isopropylphenol (**PhOH**) (0.587 mmol) and 0.0587 mmol of the appropriate $\mathbf{C_6SiMe_2X}$ reagent [dimethylhexylchlorosilane, dimethylhexylacetoxysilane, dimethylhexylmethoxysilane, or dimethylhexyl(dimethylamino)silane] were charged into a 5 mm J-Young NMR tube equipped with a Teflon valve, and ~ 0.7 mL of deuterated 1,1,2,2-tetrachloroethane was then added to bring the total volume of the solution to 0.95 mL. The tube was closed, quickly removed from the glove box, and maintained at -78 °C until NMR measurements were begun. Quick warming and insertion into the NMR probe that had been previously equilibrated to 110 °C initiated the reaction, and data were then acquired using four scans per time interval and with a long pulse delay to avoid saturation of the signal. The ^{1}H peak at δ 2.85 ppm assigned to the methine resonance of **PhOH** was set as an internal standard. The $\mathbf{C_6SiMe_2X}$ concentration at time *t* was calculated based on the integrals of corresponding resonances using the total concentration of $\mathbf{C_6SiMe_2X}$ and $\mathbf{C_6SiMe_2OPh}$. The sum remains constant and equals the initial concentration of silane (t = 0) during the entire reaction process. All data collected could be fit (R^2 = 0.983-0.994) by least squares to eq. 3, where

$$\ln C = mt + \ln \boldsymbol{C_0}$$

(3)

$\boldsymbol{C_0}$ is the initial concentration of silane, and rate constant k can be calculated from the slope m / [**PhOH**]$_0$.

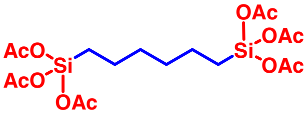
Materials for Thin Film Characterization. Highly n-doped silicon wafers (n^{++}-Si, Montco Silicon Tech), flexible ITO/Mylar, and Al/PEN substrates were cleaned by sonication in absolute ethanol for 3 min and by oxygen plasma treatment for 5 min (1 min for flexible substrates) before use. Pentacene (**P5**) was purchased from Aldrich and purified by vacuum gradient sublimation. α,ω-diperfluorohexylcarbonylquarterthiophene (**DFHCO-4T**) was available in our laboratory and was purified as described previously.[1]

CPB Dielectric Fabrication and Characterization. PVP and various crosslinking reagents were individually dissolved in the appropriate solvent (anhydrous THF, dioxane, cyclopentanone, ethyl alcohol, methyl alcohol, or ethyl acetate) and combined at specific volume ratios. These precursor solutions were then spin-coated onto freshly oxygen plasma-treated Si, Al/PEN, or ITO/Mylar substrates and cured in a vacuum oven at 110 °C for 2 – 3 h. Dielectric coating by printing was performed on freshly oxygen plasma-treated ITO/Mylar or Al/PEN substrates using an IGT Reprotest F1 printing press (IGT, Amsterdam, Netherlands) operating in the gravure mode with the following parameters: Anilox force, 100 N; printing speed, 0.4 m/s; anilox cylinder, 402.206 (copper engraved-chromium plated, stylus 120°, screen angle 45°, volume 7.5 mL/m^2). Film thicknesses were measured by profilometry (Tencor, P10). Atomic force microscopic (AFM) images including RMS roughness were obtained using a JEOL-5200 Scanning Probe Microscope with silicon cantilevers in the tapping mode.

Device Fabrication. For OFETs, organic semiconducting materials were vacuum deposited at ~ 5 × 10^{-6} Torr (500 Å, 0.2 – 0.3 Å/s) while maintaining the substrate temperature at 50 °C. Gold electrodes for OFET/MIS/MIM devices were vacuum-deposited through shadow masks at < 1 × 10^{-6} Torr (700 Å, 0.5 Å/s).

Electrical Measurements. Electrical measurements (leakage current and OFET response) were carried out under various relative humidity (RH) levels (under vacuum, RH 8%, 26%, and 36%). RH = 8%, 26%, and 36% measurements were made under house N_2, over a saturated potassium acetate solution, and in laboratory air, respectively. All OFET measurements were performed using a Keithly 6430 subfemtoammeter and a Keithly 2400 source meter, operated by a local Labview program and GPIB communication. Triaxial and/or coaxial shielding was incorporated into Signatone probe stations to minimize the noise level. Capacitance measurements were performed under vacuum using a digital capacitance meter (Model 3000, GLK Instruments) and HP4192A impedance analyzer.

Table S1. Gravure-Printed **CPB** Dielectric Film Fabrication Conditions and Film Properties -- Polymer:Crosslinker Ratio (mg:mg), Solvent, Film Quality, Film Thickness (D, nm), RMS Roughness (ρ, nm), and Areal Capacitance Value (C_i, nF cm^{-2}). Films were fabricated on Al/PEN or ITO/Mylar substrate.

Crosslinker	**Ratio (mg:mg)**	**Solvent (0.4 mL)**	**Quality**[a]	D	ρ	C_i
 **C_6OAc**	100:50	THF	G	500–600	0.3–0.5	5.0–7.0
		Dioxane	P			
		EtOAc	E			
		CP	P			
		EtOH	G			
		MeOH	P			
	100:20	EtOAc	P	500–600	0.3–0.5	5.0–7.0
	100:30		P			
	100:40		G			
	100:50		E			
	100:60		G			
	100:70		G			

[a] Film morphological quality rated as E (Excellent), G (Good), or P (Poor). See text for explanation of terminology.

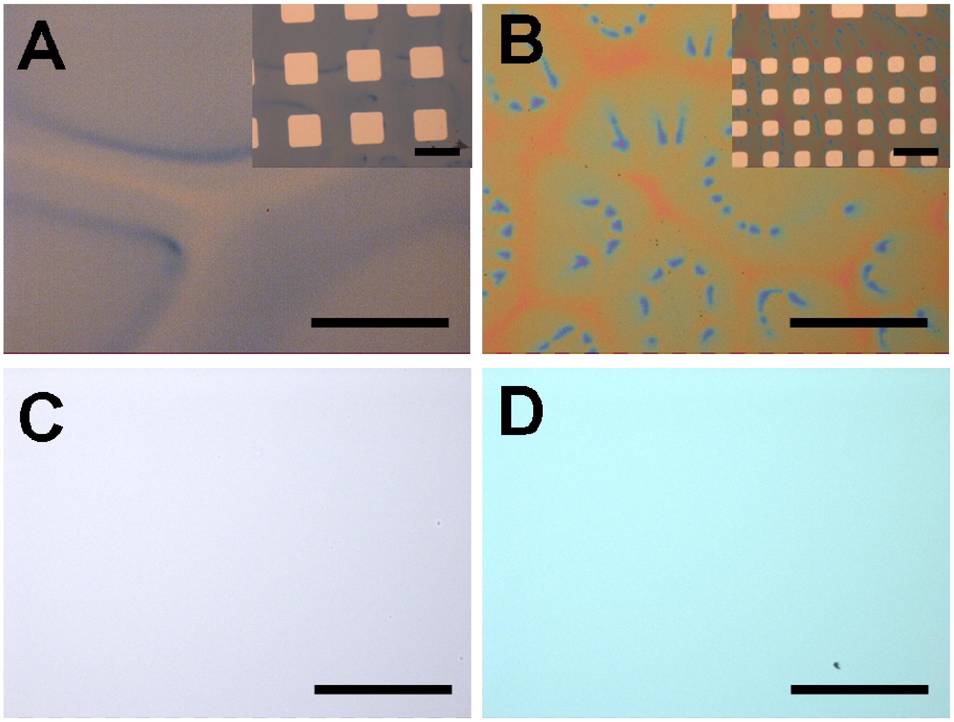


Figure S1. Optical microscope images of spin-coated thick **CPB** films: (A) **PVP-C_6Cl** (40:40), (B) **PVP-C_6Cl** (80:80), (c) **PVP-EGOAc** (40:40), (d) **PVP-EGOAc** (80:80) (**PVP** (mg):crosslinker (mg) in 2 mL THF and dioxane for **C_6Cl** and **EGOAc**, respectively). Scale bars indicate 200 μm.

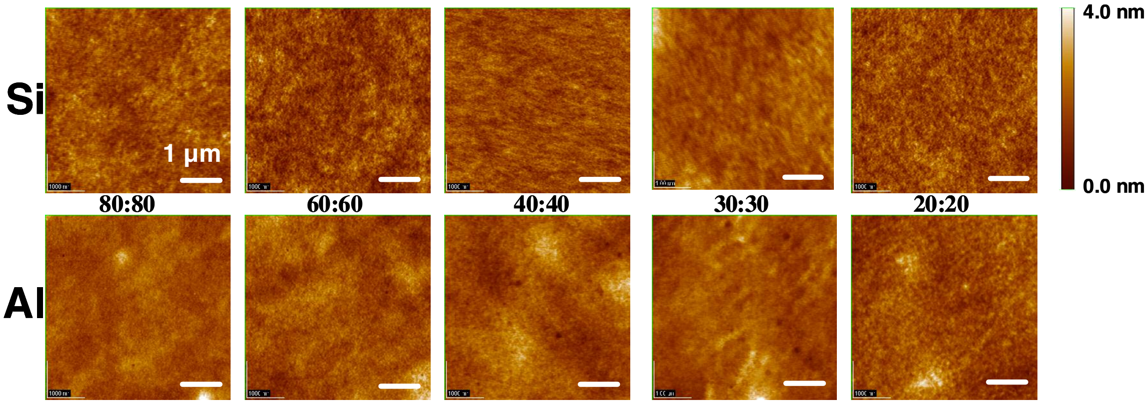


Figure S2. AFM images of spin-coated **CPB** thick films fabricated from **PVP-EGOAc** on Si (top) and Al/PEN (bottom) substrates (**PVP** (mg):**EGOAc** (mg) in 2 mL dioxane). Scale bars indicate 1 μm.

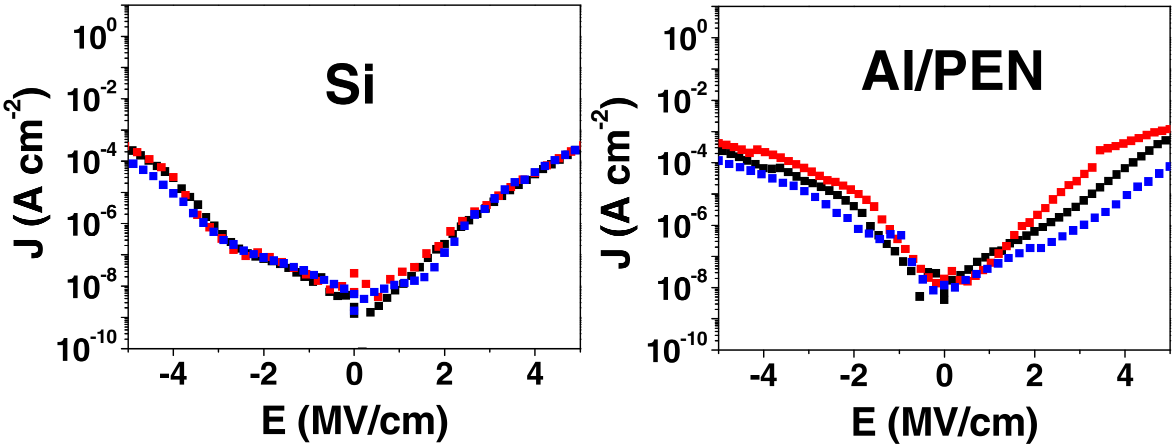


Figure S3. I–V plots for spin-coated **CPB** thick films fabricated from **PVP-EGOAc** on Si and Al/PEN substrates (**PVP** (mg):**EGOAc** (mg) in 2 mL dioxane; black : 80:80, red : 60:60, green : 40:40, blue : 30:30, purple : 20:20).

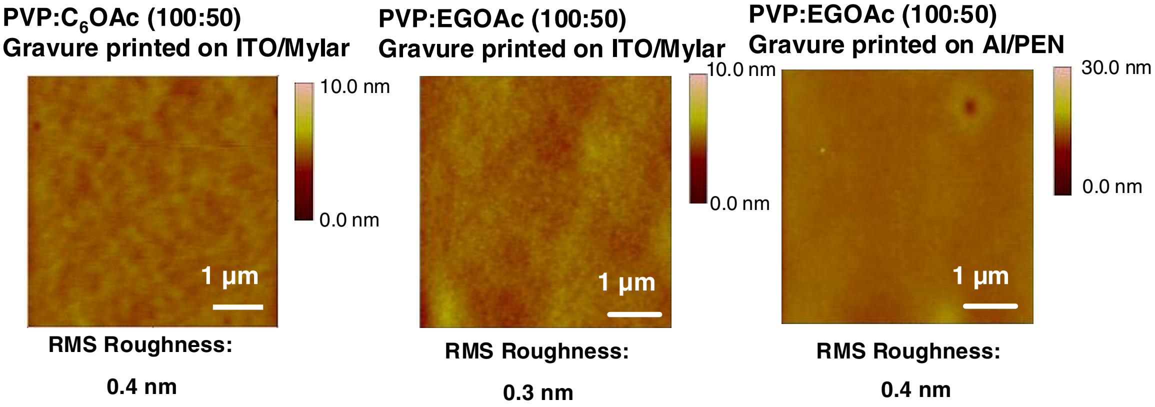


Figure S4. AFM images of different gravure-printed **CPB** films (**PVP** (mg):crosslinker (mg) in 0.4 mL EtOAc).

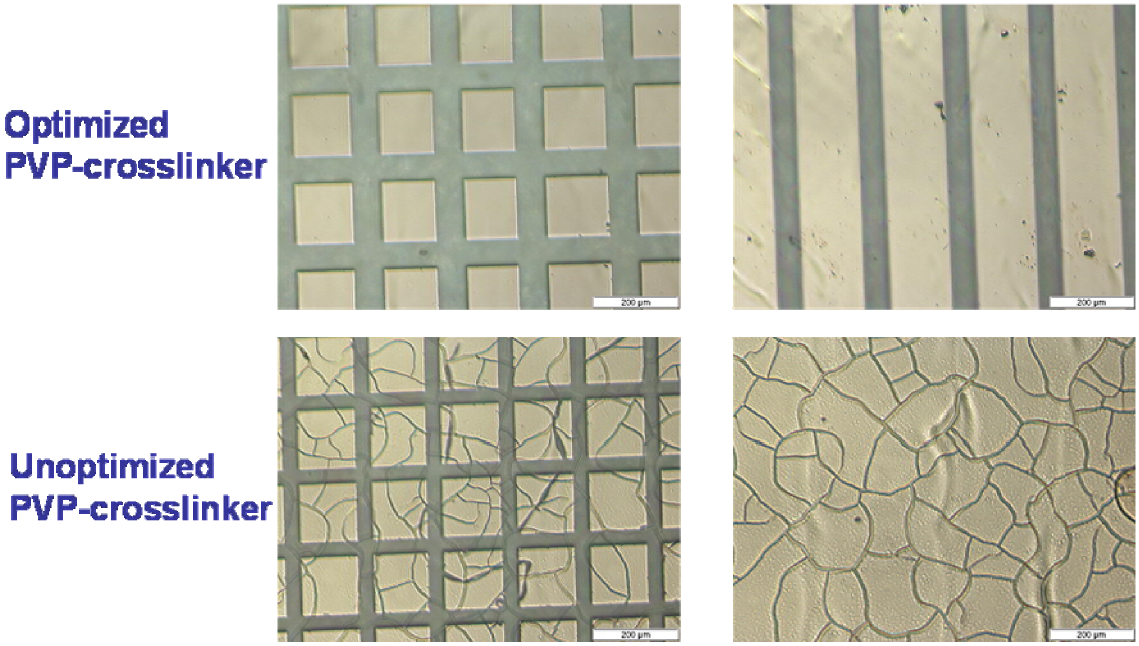


Figure S5. Optical images of gravure-printed **CPB** films with vapor-deposited Au electrodes; Optimized – **PVP-EGOAc** (100:50), Unoptimized – **PVP-C$_6$Cl** (100:50). The scale bars indicate 200 μm.

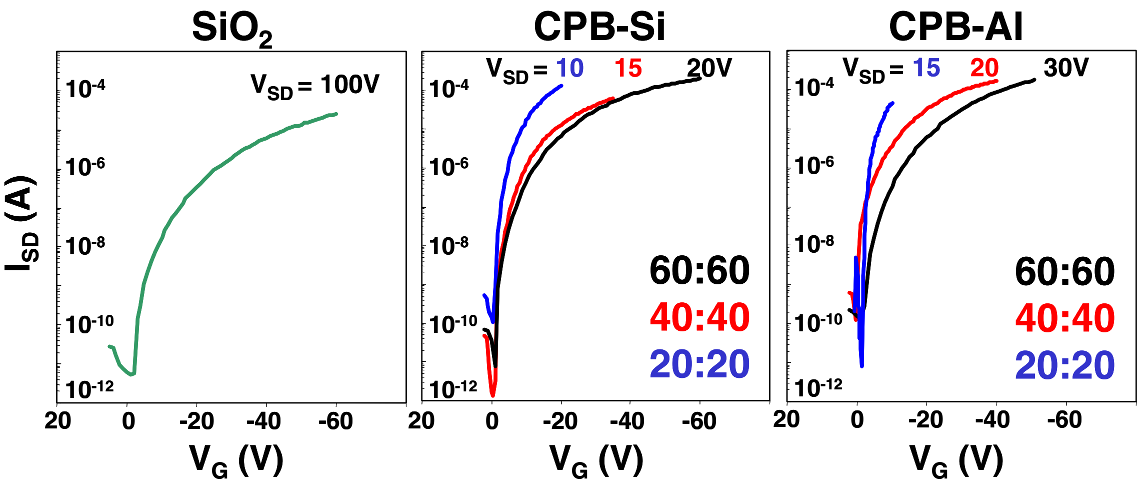


Figure S6. Transfer plots for pentacene OFET devices on Si/SiO$_2$ (300 nm) and for spin-coated **CPB** (**PVP-EGOAc**) dielectrics on Si and Al/PEN substrates. The channel length and width are 100 and 2000 μm, respectively.

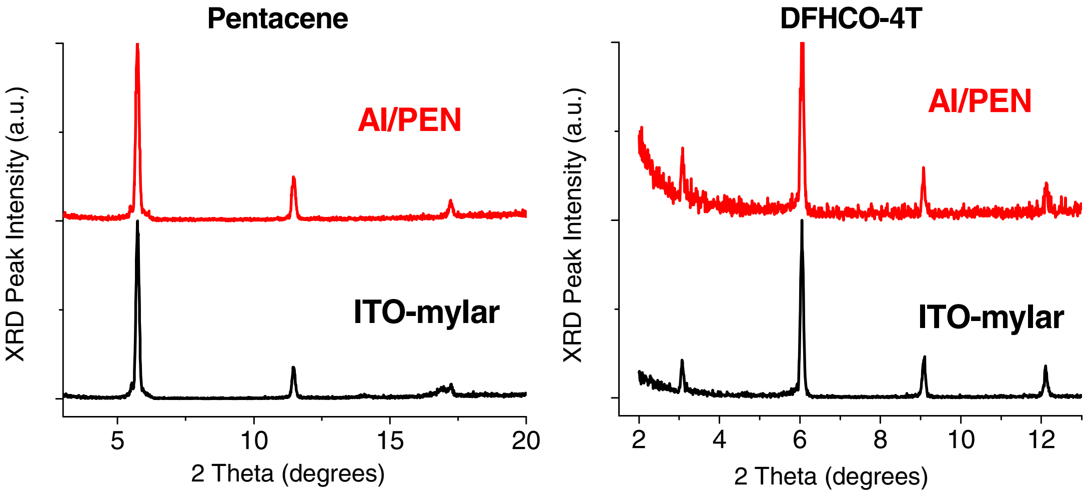


Figure S7. *θ-2θ* XRD scans of 50nm-thick **P5** (left), and **DFHCO-4T** (right) films vapor-deposited on gravure–printed **CPB** (**PVP** 100mg + **EGOAc** 50mg in 0.4ml EtOAc) dielectrics.

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1. Yoon, M.-H.; DiBenedetto, S. A.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2005**, *127*, 1348-1349.