

Electronic Supplementary Information for

Controlling Gate Dielectric Properties of Vinyl-Addition Polynorbornene Copolymer via Thiol-Ene Click Chemistry for Organic Field-Effect Transistors

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Experimental Section

Materials. Lithium tetrakis(pentafluorophenyl)borate ethyl etherate (LiFABA, $\geq 97\%$, AdipoGen), tris(dibenzylideneacetone)dipalladium(0) ($\text{Pd}_2(\text{dba})_3$, 97%, Sigma-Aldrich), Norbornene (NB, 98%, Sigma Aldrich), 5-vinyl-2-norbornene (VNB, 95%, Sigma-Aldrich), tricyclohexylphosphine (PCy_3 , Sigma-Aldrich), pentaerythritol tetrakis(3-mercaptopropionate) (PETMP, $>95\%$, Sigma-Aldrich), bis(diethylamino)benzophenone (DEAB, $\geq 99\%$, Sigma-Aldrich), toluene (anhydrous, 99.8%, Sigma-Aldrich), were purchased and used as received. All other reagents and solvents were used as received from standard vendors.

Copolymerization of NB and VNB. The copolymerization was performed under a nitrogen atmosphere. First, the activated catalyst solution was prepared by addition of toluene (10 mL) to $\text{Pd}_2(\text{dba})_3$ 0.045 g (0.0491 mmol), PCy_3 0.055 g (0.196 mmol), LiFABA 0.172 g (0.197 mmol) in 20 mL vials with magnetic stirring bar, and then stirred at room temperature for 1 h. Subsequently, the filtered solution activated catalyst (9.5 mL) was injected into the toluene solution containing NB 0.879 g (9.34 mmol) and VNB 1.12 g (9.32 mmol). The polymerization was carried out at room temperature for 12 hours. After 12 hours, the vial was moved outside the glove box, and the polymer solution was precipitated in an excess of acidified methanol and filtered. The filtered polymer was dissolved in toluene, and then activated charcoal was added into polymer solution. After stirring for 12 hours, this solution was filtered through aluminum powder, and then precipitated in acetone. Finally, the resulting copolymer was dried in a vacuum oven at 60 °C for 12 hours, yielding a white solid (1.82 g, 90.8%). ^1H NMR (400 MHz, CDCl_3 , δ/ppm , tetramethylsilane (TMS)) (Fig. S2): 5.90-5.74 (br, $-\text{CH}=\text{C}-$), 5.27-4.87 (br, $-\text{C}=\text{CH}_2$), 2.46–1.05 (br, NB). GPC-RI analysis: number-average molecular weight (M_n) = 53.6 kDa, molecular weight dispersity (D) = 3.04.

Preparation of the cross-linked P(NB/VNB) polymeric film. The cross-linked P(NB/VNB) films are named as cP(NB/VNB)-#, where # indicates the weight percent of PETMP to P(NB/VNB), and varied as 1, 3, 6, 12 wt % to find the optimized dielectric and surface properties of cP(NB/VNB)s. DEAB was used as a photoinitiator at 1 wt % to the P(NB/VNB). To fabricate cP(NB/VNB) films, appropriate amounts of P(NB/VNB), PETMP, and DEAB were dissolved in toluene, leading to the 4-5 wt% solution. The mixture was spin-coated at 2000 rpm for 60s onto the substrate, which was then annealed at 90 °C for 1 min. Subsequently, the coated samples were irradiated with ultraviolet (UV, $\lambda = 365$ nm, 16 W lamp) at room temperature in an air environment to activate the cross-linking reaction between thiol group and C=C bond. The resultant films were put on a hot-plate and annealed at 90 °C for 20 min. The pristine P(NB/VNB) film without PETMP and DEAB was also prepared for the comparative experiment. To fabricate a photo-patterned cP(NB/VNB) film, 25 μ m-line patterned shadow mask was employed during UV exposure processing. After thermal treatment at 90 °C for 20 min, the cP(NB/VNB) film was immersed in toluene solvent for 5 min to develop the patterns and dried under N₂ flow.

Instrumentation and Characterization. ¹H NMR spectra were recorded on a Bruker Ascend 400 MHz in CDCl₃ solution. The FT-IR spectra were recorded on a Bruker VERTEX 80v FT-IR spectrometer. The number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity index (D) of P(NB/VNB) were measured using gel permeation chromatography (GPC) in THF using Waters 515 Isocratic HPLC pump and Shodex columns (KF-800 series) at 40 °C. The signals were detected using a Waters 2414 refractive index detector. The molecular weights and polydispersity were calculated by a standard procedure relative to monodispersed polystyrene standards. The film thickness was measured with an alpha-step surface profiler (α -step DC50, KLA-Tencor). The contact angles of DI water and diiodomethane were

measured using PHOENIX450 contact angle analyzer and the surface energy was calculated using the following equation:

$$(1 + \cos\theta)\gamma_{pl} = 2(\gamma_s^d\gamma_{pl}^d)^{0.5} + 2(\gamma_s^p\gamma_{pl}^p)^{0.5}$$

, where γ_{pl} is the surface energy of the test liquid and the d and p superscripts represent the dispersive and polar components, respectively. Atomic force microscopy (AFM) images were recorded with a tapping mode microscope (Nanoscope IV, Digital Instrument). The capacitance and DF of MIM capacitors were measured using Agilent E4980A. The electrical characteristics were measured using Keithley 4200A-SCS under the ambient conditions inside a dark box. toluene solvent for 5 min to develop the patterns and dried under N₂ flow.

Device fabrication. An OFET in bottom-gate top-contact structure was fabricated on a glass substrate (Eagle XG, Corning). A gate electrode was formed by depositing 30-nm thick aluminum using thermal evaporator. For gate dielectric layers, COC solutions with various content ratios of PETMP were deposited by spin-coating (2000 rpm for 60 s) on the substrate. In order to crosslinking reaction, deposited COC thin films were treated thermal annealing on a hot plate (100 °C for 1 min) and UV irradiation ($\lambda = 365$ nm) was conducted for 1 J·cm⁻². Pentacene was deposited an evaporation rate of 0.3 Å·s⁻¹ using thermal evaporator with substrate temperature at 80 °C. Finally, a 40 nm-thick gold was deposited to form contact electrodes through a shadow mask, which channel width and length were 1000 μm and 50 μm, respectively, using thermal evaporator. Thermal evaporation was performed under base pressure below 3×10^{-6} Torr.

Synthesis and Characterization of P(NB/VNB)

Table S1. Material properties of P(NB/VNB) using Pd₂(dba)₃/LiFABA /PCy₃^a

entry	[M1]/[M2] in the feed ^b	$M_{n,obsd}$ (kDa) ^d	$M_{w,obsd}$ (kDa) ^d	\bar{D} ^d	yield (%) ^e	Content of M2 (mol%) ^f
1	5:5	25.9	74.9	2.88	92.3	47.9
2	5:5	32.2	113.9	3.54	94.2	42.6
3	5:5	53.6	163.3	3.04	90.8	51.6

^aConditions: 5 wt % of monomer in toluene; [Pd]₀ = 0.01 M; [LiFABA]/[PCy₃]/[Pd] = 2/2/1.

^b[M]₀/[Pd]₀ = 200. ^cDetermined by GPC using differential refractive index (RI) detector, calibrated with narrow distribution polystyrene standards (THF). ^eInsoluble powder. ^fDetermined by ¹H NMR.

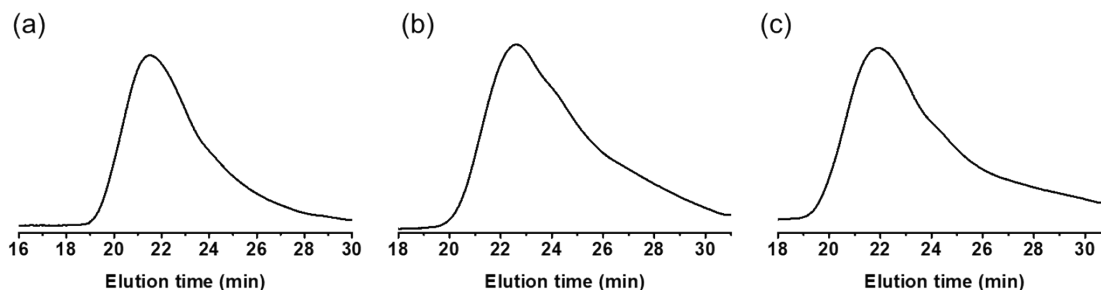


Fig S1. GPC-RI traces of P(NB/VNB): (a) entry 1 (Table S1), (b) entry 2 (Table S1), and (c) entry 3 (Table S1).

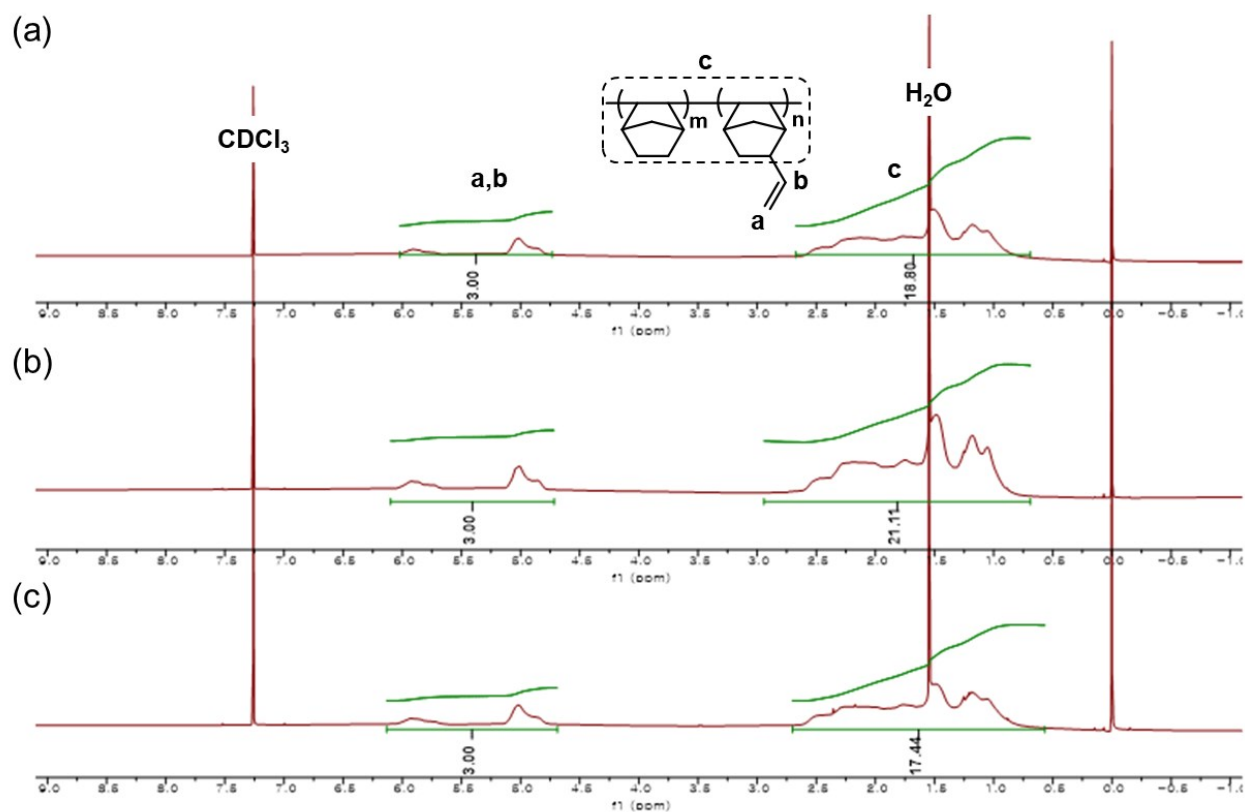


Fig S2. ^1H NMR spectra of P(NB/VNB) (400 MHz, CDCl_3) : (a) entry 1 in Table S1 (47.9 mol % VNB content), (b) entry 2 in Table S1 (42.6 mol % VNB content), and (c) entry 3 in Table S1 (51.6 mol % VNB content).

It is noted that the ratio of aliphatic to vinyl signals is 9:3 in poly(5-vinyl-2-norbornene) (PVNB).

Therefore, the VNB content ratio in the copolymers is calculated using the following equation:

$$\text{VNB content} = \frac{9}{\text{integration of aliphatic signal}} \times 100$$

Structural Characterization of Cross-Linked P(NB/VNB) (c-P(NB/VNB)) Thin Films

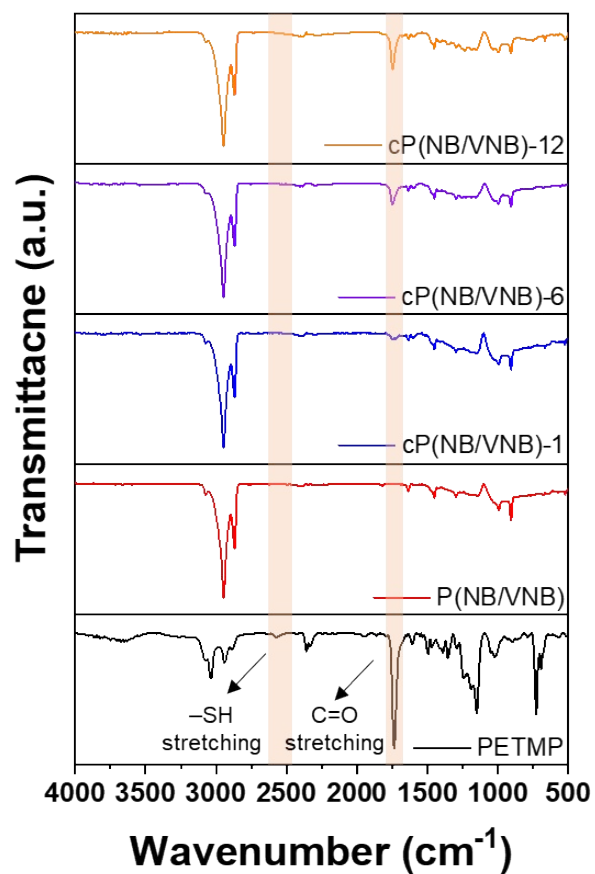


Fig S3. FT-IR spectra of PETMP, P(NB/VNB), cP(NB/VNB)-1, cP(NB/VNB)-6, and cP(NB/VNB)-12 thin films.

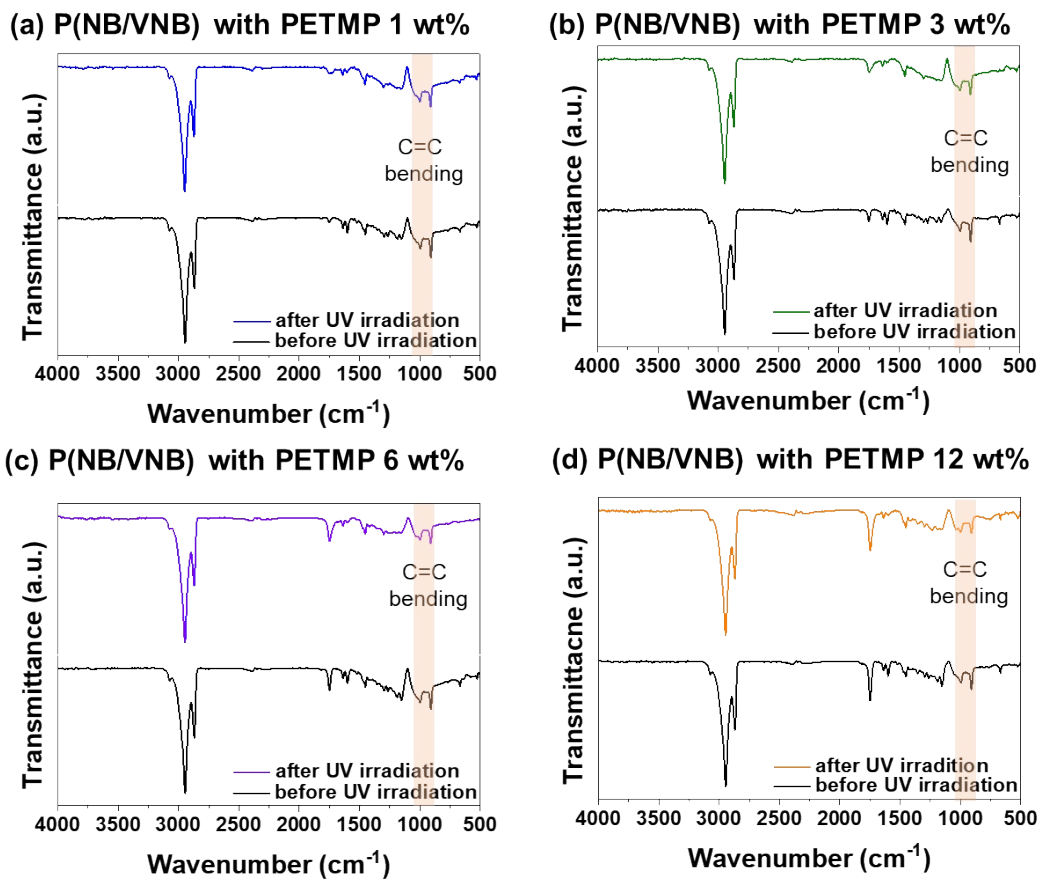


Fig S4. FT-IR spectra of before and after UV irradiation of vinyl-addition polynorborene copolymer thin films containing DEAB 1 wt%.

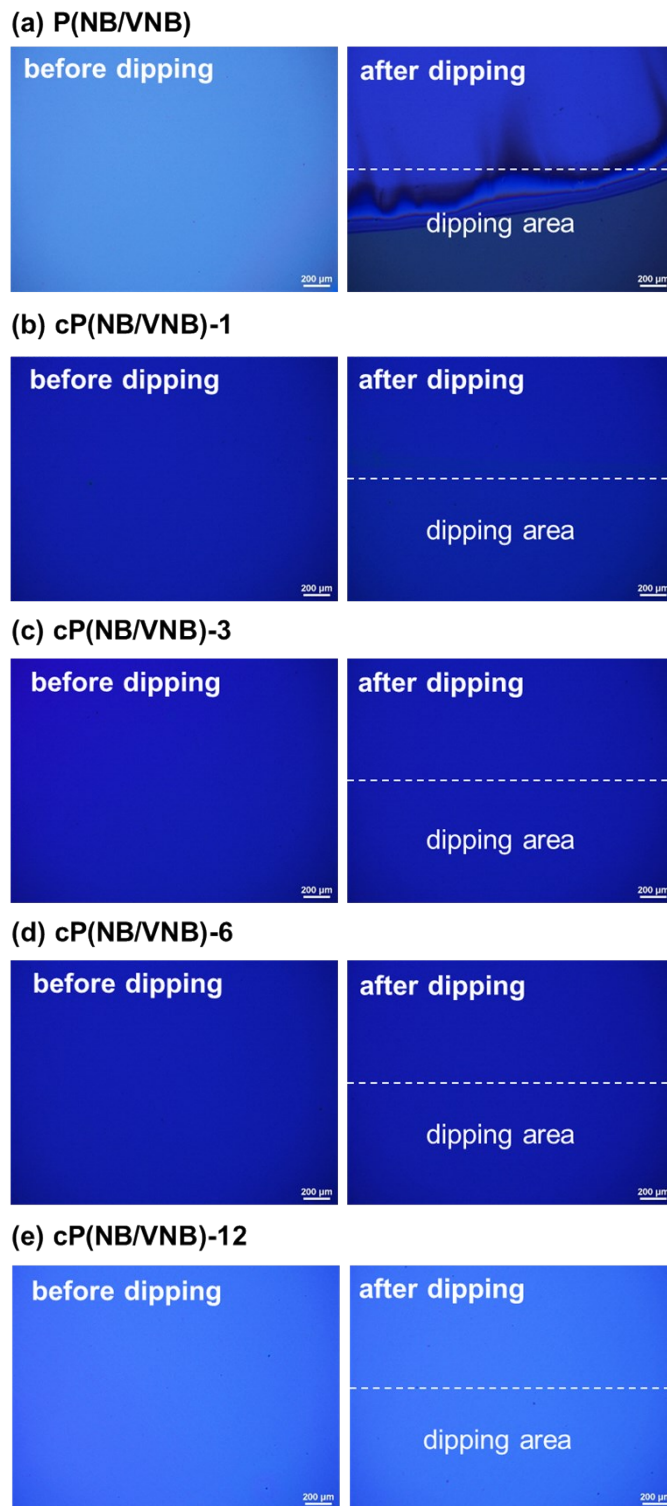


Fig S5. Optical microscope images of vinyl-addition polynorbornene copolymer thin films; before and after dipping in toluene for 5 min.

Surface Properties of c-P(NB/VNB) Thin Films

Table S2. Surface properties of vinyl-addition polynorbornene copolymer gate dielectric thin films.

Surface	Contact angle (°)		Energy (mJ/m ²)		
	Water	Diiodomethane	γ_{sp}	γ_{sd}	γ_s
P(NB/VNB)	77.67	29.07	3.89	41.55	45.44
P(NB/VNB)-1	74.41	28.87	5.20	40.99	46.19
cP(NB/VNB)-1	78.12	26.37	3.50	42.80	46.29
P(NB/VNB)-3	77.86	27.31	3.66	42.35	46.02
cP(NB/VNB)-3	76.84	26.86	4.02	42.33	46.35
P(NB/VNB)-6	75.35	22.20	4.24	43.81	48.05
cP(NB/VNB)-6	74.87	25.45	4.69	42.50	47.19
P(NB/VNB)-12	65.36	22.27	8.97	41.81	50.78
cP(NB/VNB)-12	70.11	26.35	6.94	41.19	48.14

Electrical Properties of c-P(NB/VNB) Thin Films

Table S3. Dielectric properties of MIM capacitors with vinyl-addition polynorbornene copolymer gate dielectrics.

	t_d [nm]	ϵ_r @ 100Hz	DF @ 1MHz	EBD [MV·cm ⁻¹]
P(NB/VNB)	355	2.25	0.003	2.54
cP(NB/VNB)-1	427	2.82	0.036	2.46
cP(NB/VNB)-3	470	2.85	0.041	3.10
cP(NB/VNB)-6	512	2.99	0.047	3.21
cP(NB/VNB)-12	592	3.39	0.075	3.27

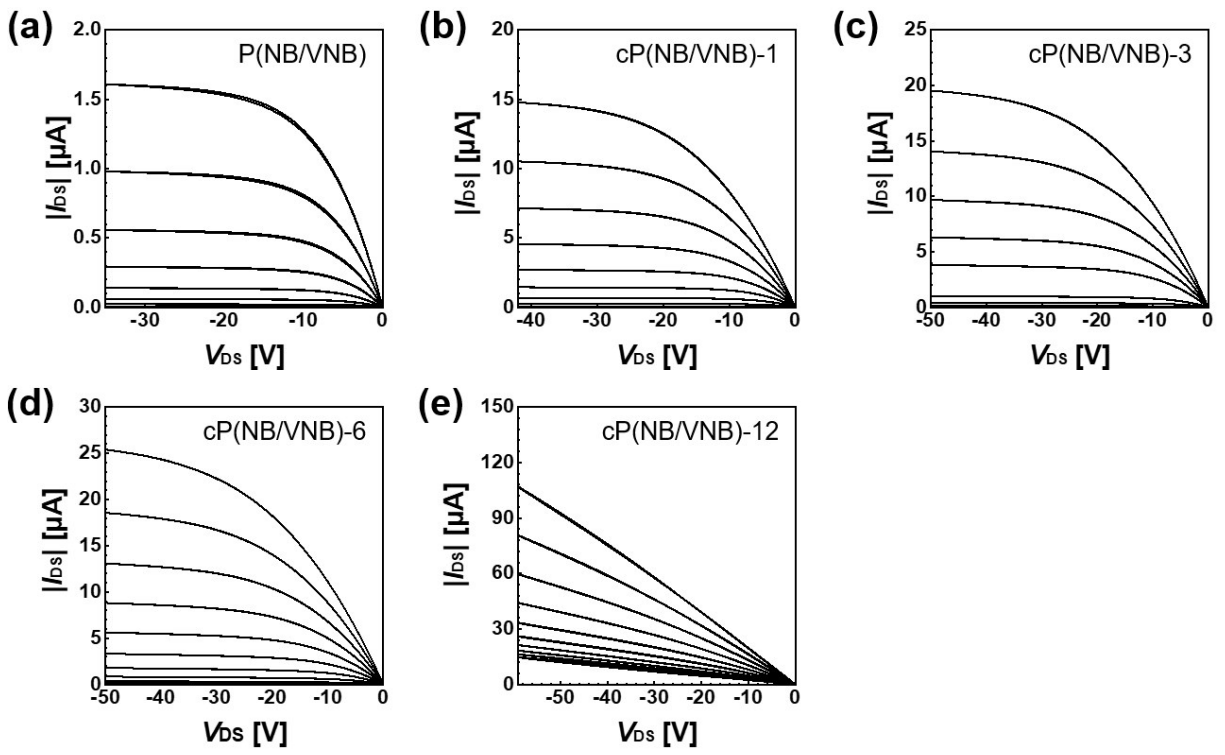


Fig. S6 Typical output characteristics for pentacene-based OFETs with (a) P(NB/VNB), (b) cP(NB/VNB)-1, (c) cP(NB/VNB)-3, (d) cP(NB/VNB)-6, and (e) cP(NB/VNB)-12 gate dielectrics.

Table S4. Electrical characteristics of pentacene-based OFETs with vinyl-addition polynorbornene copolymer gate dielectrics.

	μ_{FET} [cm ² ·V ⁻¹ ·s ⁻¹]	V_{th} [V]	E_{th} [MV·cm ⁻¹]	$I_{\text{on}}/I_{\text{off}}$
P(NB/VNB)	0.11	-20.4	-0.58	5.55×10^4
cP(NB/VNB)-1	0.24	-16.6	-0.40	1.06×10^5
cP(NB/VNB)-3	0.23	-19.2	-0.38	3.41×10^5
cP(NB/VNB)-6	0.21	-19.4	-0.38	3.89×10^5
cP(NB/VNB)-12	0.10	N.A.	N.A.	1.98×10

Table S5. Comparison of dielectric properties of polymer gate dielectrics

Polymer gate dielectric	Ref.	d_t (nm) ^a	Dielectric constant (ϵ_r)	J_{leak} (A cm ⁻²) ^b	E_{bd} [MV cm ⁻¹]
PS ^c	S1	400	2.8 (20 Hz)	10 ⁻⁷ (1.5 MVcm ⁻¹)	–
	S2	350	2.36 (10 kHz)	5 × 10 ⁻⁵ (2.0 MVcm ⁻¹)	–
	S3	260	2.9 (10 kHz)	10 ⁻⁶ (bias voltage 20 V)	–
PMMA ^d	S1	410	3.7 (20 Hz)	10 ⁻⁷ (1.5 MVcm ⁻¹)	–
	S3	180	4.0 (10 kHz)	10 ⁻⁶ (bias voltage 20 V)	–
PVP ^e	S4	200	5 (100 Hz)	10 ⁻⁶ (0.8 MVcm ⁻¹)	> 1
	S5	350	5.66 (1 MHz)	10 ⁻⁷ ~ 10 ⁻⁶ (bias voltage 20 V)	< 0.5
PVA ^f	S6	248	6.3 (1 kHz)	10 ⁻⁹ (1 MV/cm ⁻¹)	> 2
	S7	537	6.0 (100 kHz)	10 ⁻¹⁰ (1 MV/cm ⁻¹)	> 1.9
Polyimide	S8	200	3.2 (100 Hz)	10 ⁻⁸ (2.0 MVcm ⁻¹)	< 2.5
	S9	300	3.3 (10 kHz)	10 ⁻¹⁰ (2.0 MVcm ⁻¹)	> 3
ENC ^g	S2	350	2.35	10 ⁻⁷ (2.0 MVcm ⁻¹)	–
	S10	300	2.27 ~ 2.34	10 ⁻¹⁰ ~ 10 ⁻⁷ (2.0 MVcm ⁻¹)	–
P(NB/VNB)	This work	350 ~ 592	2.82 ~ 3.39	10 ⁻¹⁰ ~ 10 ⁻⁷ (2.0 MVcm ⁻¹)	> 2.46

^a Thickness, ^b The leakage current density, ^c Polystyrene, ^d Poly(methyl methacrylate), ^e Poly(4-vinylphenol), ^f Polyvinyl alcohol, ^g Ethylene-norbornene copolymer

Table S6. Measurement conditions for OFETs based on pentacene with COC gate dielectrics.

	Start V_{GS} [V] at 0.5 MV/cm	End V_{GS} [V] at -1.0 MV/cm	Voltage step [V]
P(NB/VNB)	17.5	-35	0.7
cP(NB/VNB)-1	21	-35	0.84
cP(NB/VNB)-3	25	-35	1
cP(NB/VNB)-6	25	-35	1
cP(NB/VNB)-12	29.5	-35	1.18

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