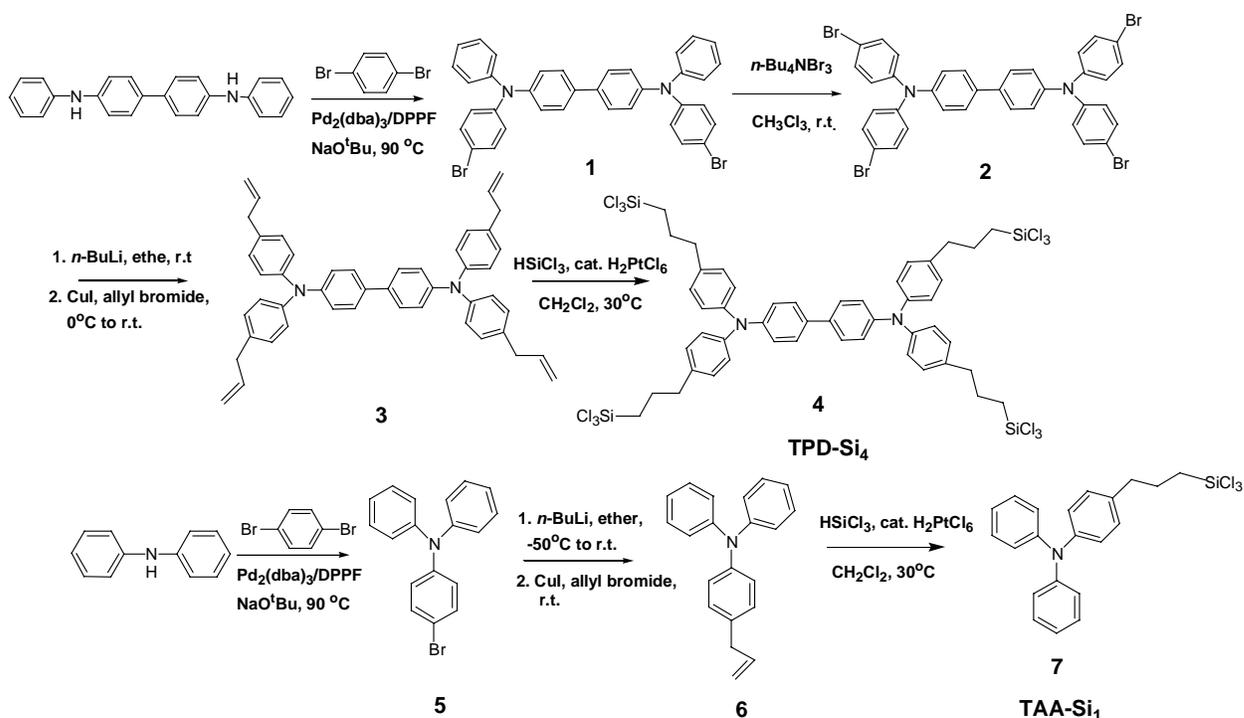


Supporting Information

Systematic Investigation of Nanoscale Adsorbate Effects at Organic Light-Emitting Diode Interfaces. Interfacial Structure-Charge Injection-Luminance Relationships.

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Scheme 1. Synthesis of interfacial modification precursors TPD-Si₄ and TAA-Si₁.



Synthesis of 4,4'-bis[(p-bromophenyl)phenylamino]biphenyl (1). To a solution of tris(dibenzylideneacetone)dipalladium (0.55 g, 0.60 mmol) and bis-(diphenylphosphino)ferrocene (0.50 g, 0.90 mmol) in 50 mL toluene, was added 1,4-dibromobenzene (18.9 g, 0.0800 mol) at 25 °C, and the solution stirred under N₂ for 10 min. Subsequently, sodium *tert*-butoxide (4.8 g, 0.050 mol) and N,N'-diphenylbenzidine

(6.8 g, 0.020 mol) were added, and the reaction mixture stirred at 90 °C for 12h. The reaction mixture was subsequently cooled to 25 °C and poured into water. The organic layer was separated, and the aqueous layer was extracted with toluene (3 x100 mL). The extracts were combined with the original organic layer, and the solvent was removed under vacuum to afford the crude product. The crude product was purified by chromatography on silica gel using hexane: ethylene chloride (6:1) as the eluant.

Compound **1** was obtained as a colorless solid (6.9 g) in 50% yield. ¹H NMR (CDCl₃): δ 6.99(d, J = 8.8 Hz, 4H), 7.02-7.16(m, 10H), 7.28(t, J = 7.6Hz, 4H), 7.34(d, J = 8.8Hz, 4H), 7.45(d, J = 8.4Hz, 4H).

Synthesis of N,N,N',N'-tetrakis-(p-bromophenyl)-biphenyl-4,4'-diamine (2).

To a stirring chloroform solution (20 mL) of **1** (0.5 g, 0.77 mmol), tetrabutylammonium tribromide (0.74 g, 1.54 mmol) was added in one portion at 25 °C. The reaction was monitored by TLC (elution hexane: ether = 7:1) and was found to be complete after 0.5 h. The reaction mixture was then washed with aqueous sodium thiosulfate and water until pH = 7, followed by removing solvent under vacuum to afford a pale-yellow solid. Next, 500 mL ether was added and the solution was washed with water (3 x100 mL) and brine (2 x100 mL), and dried over anhydrous Na₂SO₄. Following filtration, solvent was removed in vacuum to yield a colorless solid. Recrystallization from chloroform: hexane (1:10) afforded 0.49 g of **2** as a colorless solid. Yield, 79%. ¹H NMR (CDCl₃): δ 6.99(d, J = 9Hz, 8H), 7.11(d, J = 9Hz 4H), 7.38(d, J = 9Hz, 8H), 7.47(d, J = 9Hz, 4H), MS(*m/z*): 804.8 [M,100]

Synthesis of N,N,N',N'-tetrakis-(p-allylphenyl)-biphenyl-4,4'-diamine (3). To a stirring, anhydrous ether solution (8 mL) of **2** (0.050 g, 0.062 mmol) under inert

atmosphere, was added dropwise at 25 °C, *n*-butyl lithium(1.6 M in hexanes, 0.31 mL, 0.50 mmol), and the mixture stirred for 2 h. The reaction mixture was then cooled to 0 °C, followed by addition of cuprous iodide (0.10 g, 0.50 mmol). After stirring for 5 min., allyl bromide (0.070 g, 0.60 mmol) was added in one portion. The solution was gradually warmed to 25 °C and stirred for 12 h, after which time it was quenched with 100 mL saturated aqueous NH₄⁺Cl⁻ solution, followed by extraction with ether (3 x100 mL). The combined ether extracts were washed with water (2 x100 mL) and brine (2 x100 mL), and dried over anhydrous Na₂SO₄. Following filtration, solvent was removed in vacuum to yield an oil. Chromatography on silica gel with hexane: methylene chloride (10:1) afforded 0.027 g of **3** as a colorless solid. Yield, 68%. ¹H NMR (CDCl₃): δ 3.37(brs, J = 10Hz, 8H), 5.06- 5.12(m, 8H), 5.95- 6.03(m, 4H), 7.08(brs, 20H), 7.41(brs, 4H). Anal. Calcd for C₄₈H₄₄N₂: C 88.83, H 6.85, N 4.32; Found, C 88.89, H 6.91, N 4.28.

Synthesis of N,N,N',N'-tetrakis[(*p*-trichlorosilylpropyl)-phenyl]-biphenyl-4,4'-diamine (TPD-Si₄; **4).** To a solution of **3** (0.040 g, 0.062 mmol) in 25 mL dry CH₂Cl₂ at 25 °C. under inert atmosphere was added H₂PtCl₆·xH₂O (0.001 g), followed by trichlorosilane (0.042 g, 0.31 mmol). The reaction solution was warmed to 30 °C and monitored by NMR until the completion of reaction after 6 h. Removal of the solvent in vacuum yielded an oil. Next, 20 mL dry toluene was added to the residue and the resulting solution filtered into a Schlenk flask by cannula. The filtrate was concentrated under vacuum to give **4** as an air-sensitive pale-yellow oil. Yield, 98%. ¹H NMR (benzene-d₆): δ0.91(brs, 4H), 1.56(brs, 8H), 2.21(brs, 8H), 6.81-7.39(m, 24H). Anal. Calcd for C₅₂H₆₄Cl₁₂N₂Si₄: C 49.77, H 5.14, N 2.23; Found, C 50.69, H 5.20, N 2.12.

Synthesis of 4-bromo-phenyl-diphenyl-amine (5). To a solution of tris(dibenzylideneacetone)dipalladium (0.41 g, 0.44 mmol), and bis-(diphenylphosphino)ferrocene (0.37 g, 0.67 mmol) in 50 mL dry toluene under inert atmosphere, was added sodium *tert*-butoxide (4.2 g, 0.04 mol) at 25 °C. The mixture was stirred for 15 min, followed by addition of 1,4-dibromobenzene (27.9 g, 0.12 mol), and then stirred for another 15 min. Diphenylamine (5.0 g, 0.029 mmol) was next added, and the reaction mixture was heated at 90 °C for 15 h. The reaction mixture was subsequently cooled to 25 °C and poured into water. The organic layer was separated, and the aqueous layer was extracted with toluene (3 x100 mL). The extracts were combined with the original organic layer, and the solvent was removed under vacuum to give the resultant crude product. The crude product was purified by chromatography on silica gel using hexane: ethylene chloride (6:1) as the eluant. Compound **5** was obtained as a colorless solid (5.6 g) in 59% yield. ¹H NMR (CDCl₃): δ 6.94(d, J = 8 Hz, 2H), 7.01-7.08(m, 6H), 7.23- 7.27(m, 4H), 7.32(d, J = 8Hz, 2H). MS (*m/z*): 323.2 [M,100]

Synthesis of 4-allyl-phenyl-diphenyl-amine (6). To a stirring, anhydrous ether solution (20 mL) of **5** (0.58 g, 1.8 mmol) under inert atmosphere, *n*-butyl lithium(1.6 M in hexanes, 1.20 mL, 1.92 mmol) was added slowly at -50°C, and the mixture was stirred at -50°C for 15 min, and gradually warmed up to 25 °C. After 3 h, cuprous iodide (0.51 g, 2.7 mmol) was added, followed by dropwise addition of allyl bromide (0.32 g, 2.7 mmol). The solution was stirred for 12 h, followed by quenching with 100mL saturated aqueous NH₄⁺Cl⁻ solution and extraction with ether (3 x100 mL). The combined ether extracts were washed with water (2 x100 mL) and brine (2 x100 mL), and dried over anhydrous Na₂SO₄. Following filtration, solvent was removed in vacuum to yield an oil.

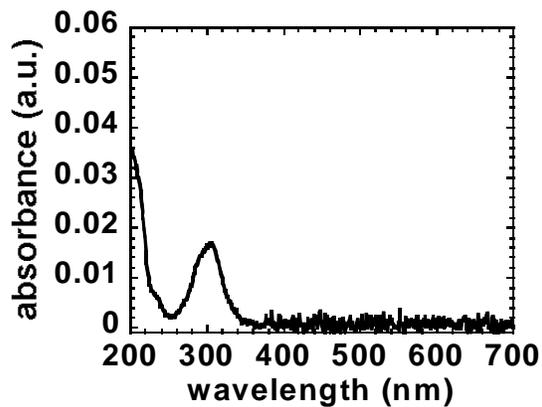
Chromatography on silica gel with hexane: methylene chloride (4:1) afforded 0.18 g of **6** as a colorless oil. Yield, 35%. ^1H NMR (CDCl_3): δ 3.40(d, $J = 7.5\text{Hz}$, 2H), 5.11- 5.32(m, 2H), 5.98- 6.07(m, 1H), 6.98-7.15(m, 8H), 7.22-7.37(m, 6H). Anal. Calcd for $\text{C}_{21}\text{H}_{19}\text{N}$: C 88.36, H 6.72, N 4.91; Found, C 88.34, H 6.10, N 4.24.

Synthesis of Diphenyl-[4-(3-trichlorosilyl-propyl)-phenyl]-amine (TAA-Si₁;7).

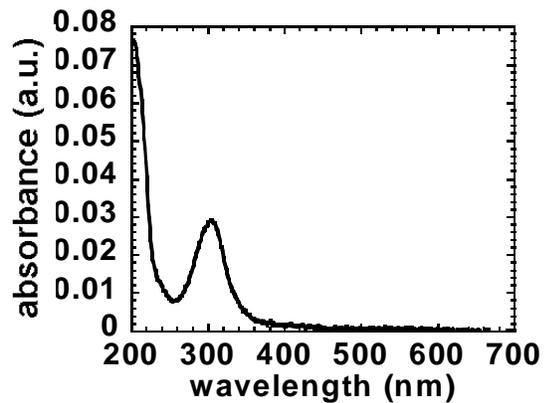
To a solution of **6** (0.18 g, 0.65 mmol) in 25 mL dry CH_2Cl_2 at 25 °C under inert atmosphere was added $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ (0.001 g), followed by trichlorosilane (0.88 g, 6.5 mmol). The reaction solution was warmed to 30 °C and monitored by NMR until the completion of reaction after 4 h. Removal of the solvent in vacuum yielded an oil. Next, 20 mL dry toluene was added to the residue and filtered into a Schlenk flask by cannula. The filtrate was concentrated under vacuum to give **7** as an air-sensitive oil. Yield, 98%. ^1H NMR (benzene- d_6): δ 0.90(t, $J = 8\text{Hz}$, 2H), 1.55(m, 2H), 2.20(t, $J = 8\text{Hz}$, 2H), 6.75- 6.83(m, 4H), 6.98- 7.14(m, 10H). Anal. Calcd for $\text{C}_{21}\text{H}_{20}\text{Cl}_3\text{NSi}$: C 59.93, H 4.79, N 3.33; Found, C 60.21, H 4.80, N 3.14.

Figure 1. UV-vis absorption of self-assembled triarylamine siloxane films on quartz substrates. A) TAA-Si₁; B) TAA-Si₃; C) TPD-Si₂; D) TPD-Si₄.

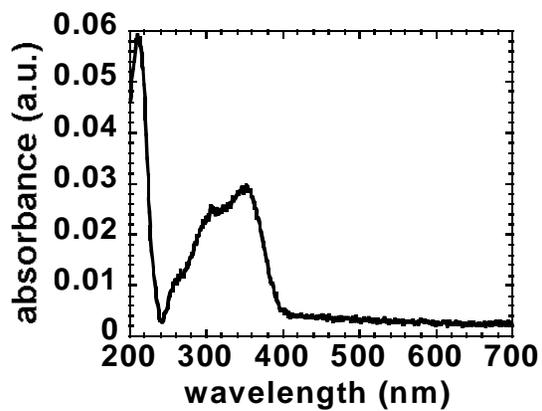
A.



B.



C.



D.

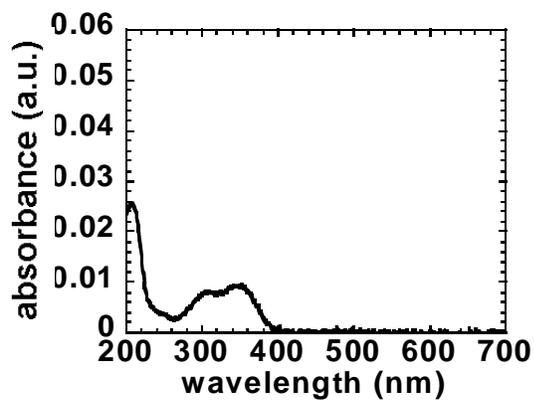


Figure 2. Tapping mode AFM images of self-assembled siloxane films on ITO substrates. A) Bare ITO. RMS roughness = 2.56 nm; B) TAA-Si₁. RMS roughness = 2.81 nm; C) TAA-Si₃. RMS roughness = 2.67 nm; D) TPD-Si₂. RMS roughness = 1.39 nm; E) TPD-Si₄. RMS roughness = 2.01 nm

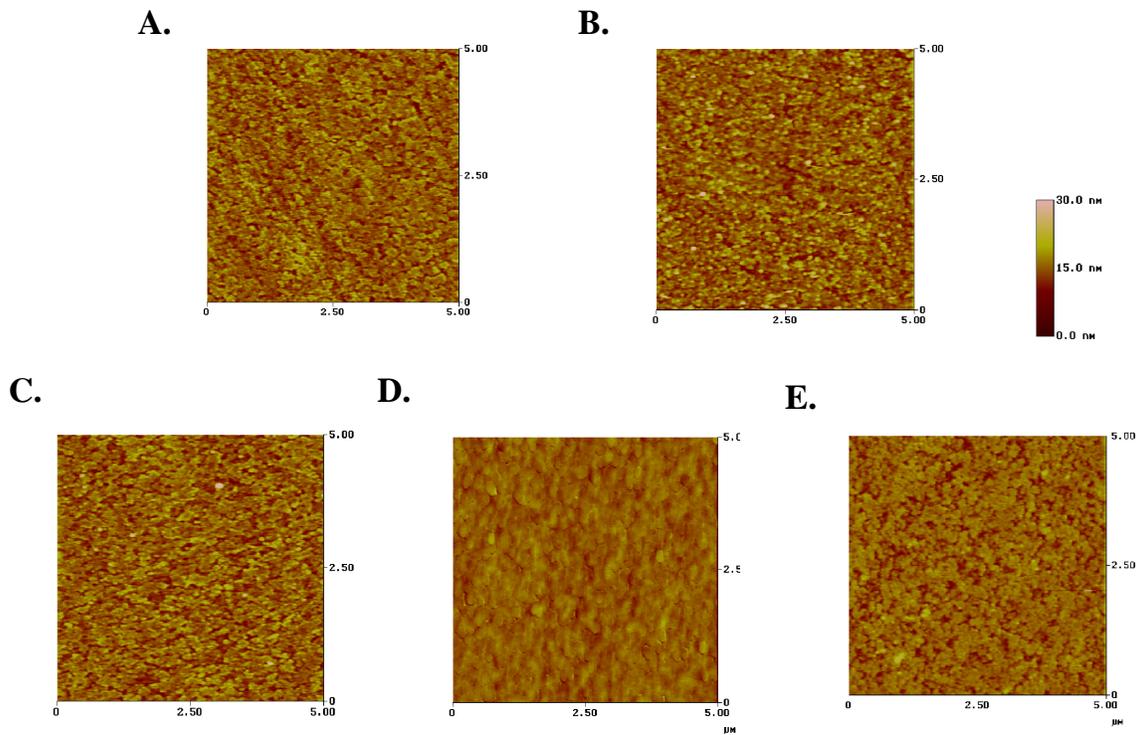
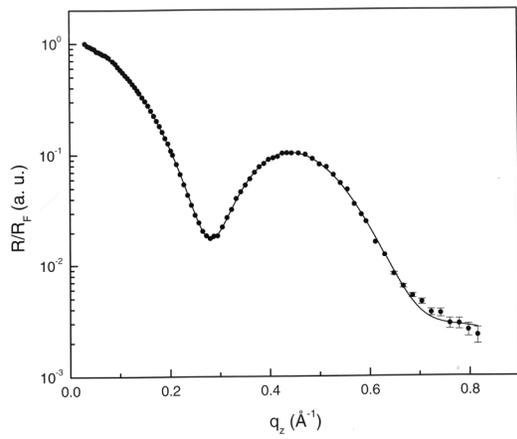
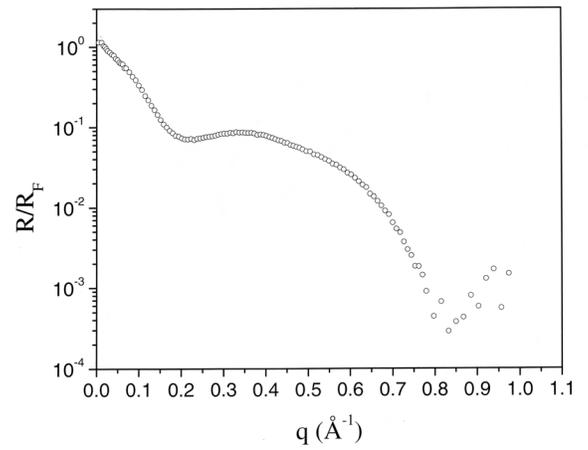


Figure 3. Representative X-ray reflectivity data showing response from self-assembled siloxane films on the native oxide of a single-crystal Si (100) substrate. A) TAA-Si₁; B) TAA-Si₃; C) TPD-Si₂; D) TPD-Si₄.

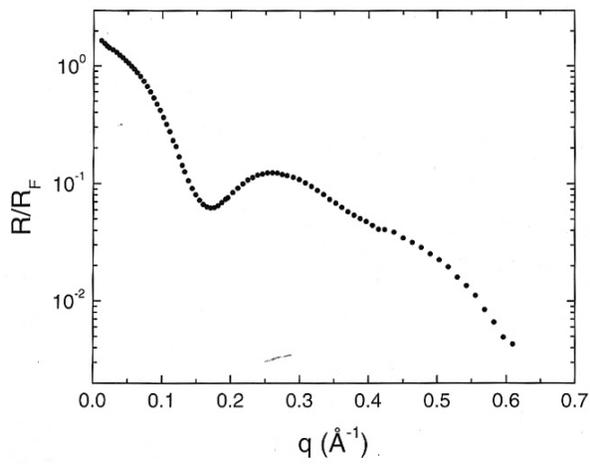
A.



B.



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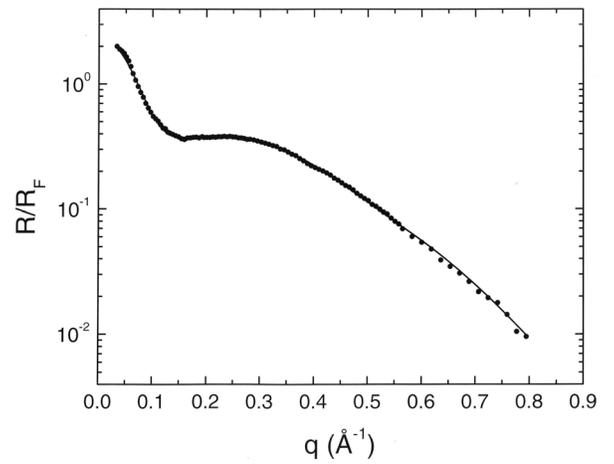


Table 1. Self-assembled siloxane film characterization

	TAA-Si ₁	TAA-Si ₃	TPD-Si ₂	TPD-Si ₄
Aqueous contact angle (°)	90	87	90	90
λ_{\max} (nm)	303	304	352	352
AFM rms roughness (nm)	2.81	2.67	1.39	2.01
HOMO (eV)	-	5.8	6.1	-