

# Supporting information

## Push-Pull $\pi$ -Electron Phosphonic Acid-Based Self-Assembled Multilayer Nanodielectrics Fabricated in Ambient for Organic Transistors

Young-geun Ha, Antonio Facchetti\*, and Tobin J. Marks\*

Northwestern University, Department of Chemistry, 2145 Sheridan Rd., Evanston, IL 60208

Email: [a-facchetti@northwestern.edu](mailto:a-facchetti@northwestern.edu), [t-marks@northwestern.edu](mailto:t-marks@northwestern.edu).

### SI 1. Synthesis of phosphonic acid-based $\pi$ -electron precursor (PAE)

#### Synthesis of diethyl *p*-tolylphosphonate

A solution of 1-bromo-4-methylbenzene (3.42 g, 20 mmol) in 140 mL of anhydrous THF was stirred at  $-78^{\circ}\text{C}$  under nitrogen and one equivalent of *n*-BuLi in hexane (1.6 M) was added. After 10 min, diethylchlorophosphate (3.45 g, 20 mmol) was added. Then, after stirring for 1 h at  $-78^{\circ}\text{C}$ , the reaction mixture was extracted with ethyl ether (100 mL), then washed with aqueous  $\text{NaHCO}_3$  (~1 g in 100 mL of  $\text{H}_2\text{O}$ ). After reaching room temperature, organic layer was separated and concentrated.

$^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{Cl}$ ):  $\delta$  7.70-7.74 (m, 2H), 7.28-7.30 (m, 2H), 4.06-4.15 (m, 4H), 2.42 (s, 3H), 1.31-1.34 (t, 6H).

#### Synthesis of diethyl 4-(bromomethyl)phenylphosphonate

A small amount of azobisisobutyronitrile (0.016 g, 0.1 mmol) was added in portions to the suspension of diethyl *p*-tolylphosphonate (0.73 g, 3.2 mmol) and N-bromosuccinimide (0.57 g, 3.2 mmol) in anhydrous  $\text{CCl}_4$  (30 mL). The mixture was refluxed for 4 h, then cooled to  $10^{\circ}\text{C}$  and filtered to remove succinimide. The filtrate was washed with water (30 mL) and brine (30 mL) and then dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After filtration, the residue was obtained via evaporation of solvent and purified by chromatography on silica gel (hexene/ethyl acetate: 2/1 as eluent) to provide diethyl 4-(bromomethyl)phenylphosphonate as a colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{Cl}$ ):  $\delta$  7.79-7.83 (m, 2H), 7.50-7.52 (m, 2H), 4.51 (s, 2H), 4.09-4.18 (m, 4H), 1.33-1.36 (t, 6H).

#### Synthesis of 4-[[4-[bis(2-hydroxyethyl)amino]phenyl]diazenyl]-1-[4-(diethoxyphosphoryl)benzyl]pyridinium bromide

A mixture of 4-[[4-[*N,N*-bis(hydroxyethyl)amino]phenyl]azo]pyridine<sup>1</sup>(1) (0.286 g, 1.00 mmol) and 4-(bromomethyl)phenylphosphonate (0.317 g, 1.00 mmol) was dissolved in  $\text{CH}_2\text{Cl}_2$  (10 mL). The

red mixture was heated under a nitrogen atmosphere at 60 °C for 4 h. The solvent was then removed under high vacuum and the residue was dried under high vacuum overnight. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ 9.07 (d, 2H, *J*<sub>H-H</sub> = 6 Hz), 8.14 (d, 2H, *J*<sub>H-H</sub> = 7 Hz), 7.90 (d, 2H, *J*<sub>H-H</sub> = 9.5 Hz), 7.76-7.80 (m, 2H), 7.62-7.64 (m, 2H), 7.07 (d, 2H, *J*<sub>H-H</sub> = 9.5 Hz), 5.88 (s, 2H), 4.95-4.97 (m, 2H), 3.99-4.03 (m, 4H), 3.99-4.03 (m, 4H), 3.66-3.72 (m, 8H), 1.22 (t, 3H). <sup>31</sup>P NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ -18.07 (s, 1P). High resolution EIMS Calcd for C<sub>26</sub>H<sub>34</sub>N<sub>4</sub>O<sub>5</sub>P<sup>+</sup>, 513.22744. Found, 513.22668.

### **Synthesis of 4-[[4-[bis(2-hydroxyethyl)amino]phenyl]diazenyl]-1-(4-phosphonobenzyl)pyridinium bromide**

To a solution of 4-[[4-[bis(2-hydroxyethyl)amino]phenyl]diazenyl]-1-(4-phosphonobenzyl)pyridinium bromide (0.297 g, 0.5 mmol) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (30 mL), trimethylbromosilane (10 eq., 0.66 mL) was added dropwise over 10min. The mixture was then stirred overnight at room temperature under a nitrogen atmosphere. After completion of the reaction, the solvent was then evaporated and residue was dissolved in methanol (5 mL). Filtration and evaporation of solvent afforded 0.29 g of pure product **PAE** as a red powder. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ 9.05 (d, 2H, *J*<sub>H-H</sub> = 7 Hz), 8.12 (d, 2H, *J*<sub>H-H</sub> = 6.5 Hz), 7.90 (d, 2H, *J*<sub>H-H</sub> = 9.5 Hz), 7.70-7.74 (m, 2H), 7.55-7.57 (m, 2H), 7.10 (d, 2H, *J*<sub>H-H</sub> = 9.5 Hz), 5.04 (s, 2H), 3.65-3.74 (m, 8H). <sup>31</sup>P NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ -12.83 (s, 1P). High resolution EIMS: Calcd for C<sub>22</sub>H<sub>26</sub>N<sub>4</sub>O<sub>5</sub>P<sup>+</sup>, 457.16408. Found, 457.16532.

## **SI 2. Fabrication and characterization of Organic Thin-Film Transistors using p-SAND**

### **Film preparation (dielectric layer)**

Heavily doped n<sup>+</sup>- silicon (Montco Silicon Technologies, INC.) substrates were cleaned in MeOH (Aldrich, absolute, 200 proof) with sonication for 2 min and then dried with flowing nitrogen, followed by oxygen plasma treatment for 5 min. The hydroxyl-functionalized Si/SiO<sub>2</sub> substrate was then immersed in an anhydrous CH<sub>3</sub>CN solution of POCl<sub>3</sub> (0.2 M)/ 2,4,6- collidine (0.2 M) at room temperature for 18 h. The substrate was then removed, washed with water, and dried under a nitrogen stream. The deposition of the zirconium phosphate (**ZrP**) primer layer was achieved by immersion of the substrate in a 5.0 mM aqueous ZrOCl<sub>2</sub> solution at room temperature for 12 h, followed by rinsing with water and drying under a nitrogen stream to complete the primer layer. For deposition of the first chromophore layer, the substrate with the primer layer was immersed in a solution of the phosphonic-acid based π-electron precursor (**PAE**; 3.0 mM in methanol) at 60°C for 2

h. After rinsing with MeOH and water, the samples were dried under a nitrogen stream. The hydroxylated surface was next phosphorylated by immersion in solution of  $\text{POCl}_3$ / 2,4,6- collidine at room temperature for 2 h and rinsed with water and dried. The third step of deposition was accomplished by immersion in a 5.0 mM aqueous  $\text{ZrOCl}_2$  solution at room temperature for 2 h, followed by rinsing with DI  $\text{H}_2\text{O}$  and drying. Repetition of these three steps resulted in multilayer formation.

### **Device fabrication**

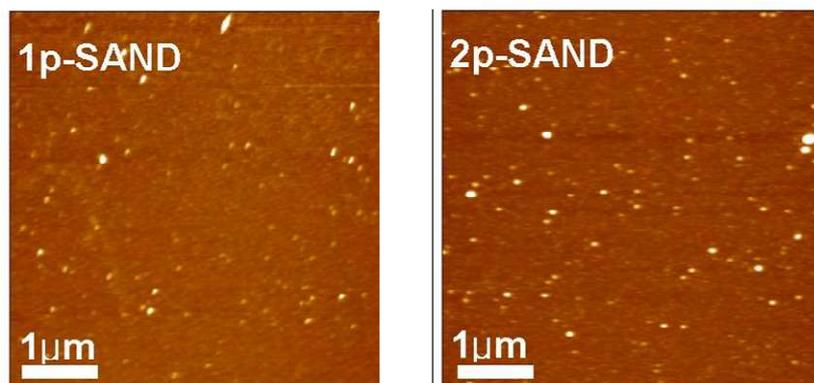
Bottom gate/ top contact OTFTs were fabricated by vacuum deposition of pentacene (50nm,  $5 \times 10^{-6}$  Torr 0.05nm/s) onto each p-SAND hybrid nanodielectric, followed by gold S/D electrode vacuum-deposition (50nm, 0.02nm/s) through a shadow mask (L= 100  $\mu\text{m}$ , W= 2000  $\mu\text{m}$ ). For MIS structures, gold electrodes were directly deposited (200  $\mu\text{m}$  X 200  $\mu\text{m}$ ) onto each p-SAND through a shadow mask.

### **Electrical measurements**

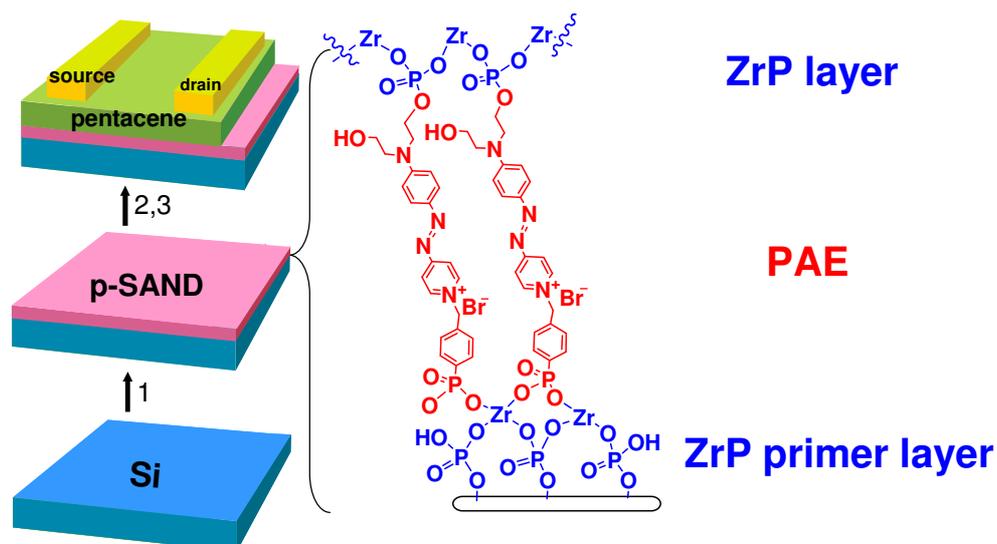
MIS direct current and OTFT measurements were carried out under ambient conditions using a Signatone probestation using Keithley 6430 Sub-Femtoamp Remote Source Meter and a Keithley 2400 source meter with a local LabVIEW program. An impedance analyzer (HP 4192A) was used for capacitance measurements.

### **Film microstructure characterization**

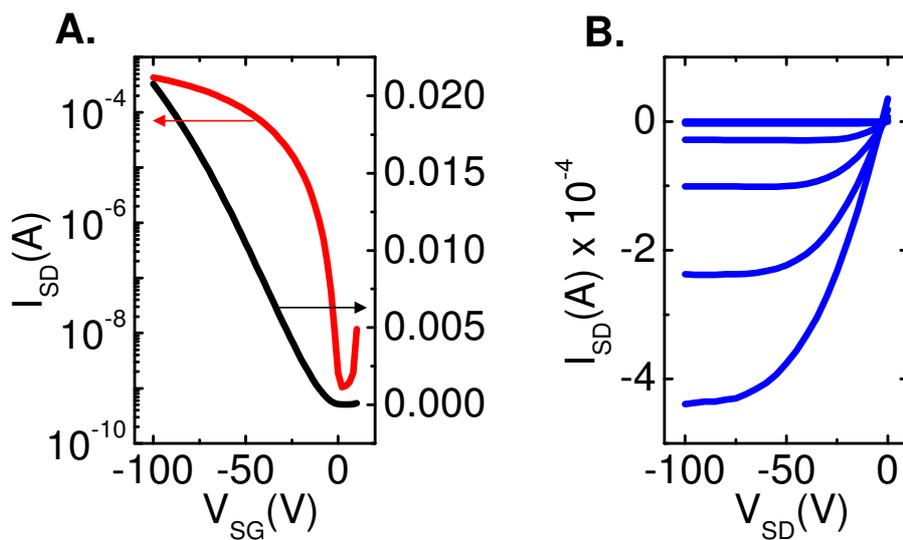
AFM images were obtained using a JEOL-5200 scanning probe microscope with silicon cantilevers in the tapping mode. The film thickness of p-SANDs was analyzed by X-ray reflectivity (XRR) using  $\text{CuK}\alpha$  radiation (Rigaku ATX-G Thin-film Diffraction Workstation). X-ray reflectivity data of each p-SAND on Si substrates. Film thicknesses are estimated from the fringe positions. Further details concerning the refinement procedures are provided in the aforementioned incorporated references and are also reported in the literature. See: Zhu, P.; van der Boom, M. E.; Kang, H.; Evmenenko, G.; Dutta, P.; Marks, T. J. *Chem. Mater.*, **2002**, *14*, 4982.



**Figure S1.** AFM images of films of a) 1p-SAND and b) 2p-SAND. Maximum RMS roughness is 0.6 nm (1p-SAND) and 0.9 nm (2p-SAND), respectively.



**Figure S2.** OTFT device fabrication: 1. Solution deposition of **ZrP** primer layer, phosphonic acid-based  $\pi$ -electron layer (**PAE**), and **ZrP** layer for **1p-SAND** 2. Vapor deposition of pentacene (50 nm), and 3. Vapor deposition of Au (50 nm) S & D contacts through a shadow mask to complete the OTFT device.



**Figure S3.** Transfer (A) and output (B) plots for 50 nm pentacene deposited on 300 nm conventional SiO<sub>2</sub>. (L = 100  $\mu$ m and W = 5000  $\mu$ m).

### Reference

1. Lin, W.; Lin, W.; Wong, G; Marks, T. J., *J. Am. Chem. Soc.*, **1996**, *118*, 8034.