Supporting Information.

Organic Transistor Memory with Charge Storage Molecular Double-Floating-Gate Monolayer

Chiao-Wei Tseng,[1,*] *Ding-Chi Huang,*[2] *and Yu-Tai Tao,*[1,2,*]

[1] Institute of Chemistry, Academia Sinica, Taipei, Taiwan, 11529

[2] Department of Chemistry, National Tsing-Hua University, Hsin-chu, Taiwan, 30013

Email: alextseng@gate.sinica.edu.tw, ytt@gate.sinica.edu.tw,

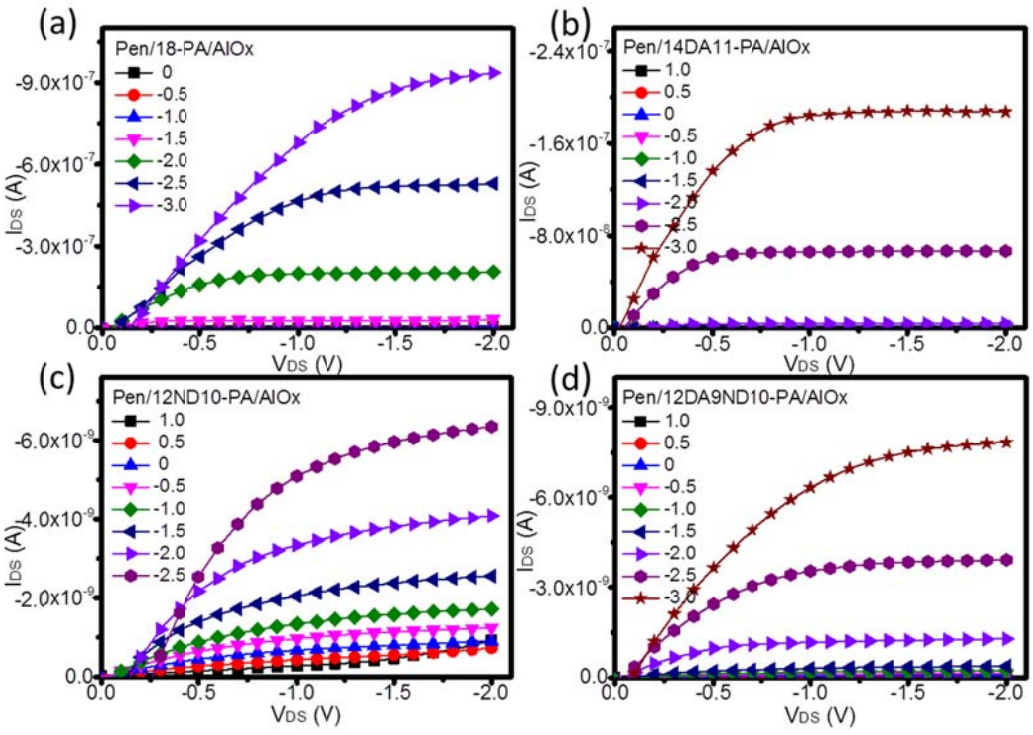
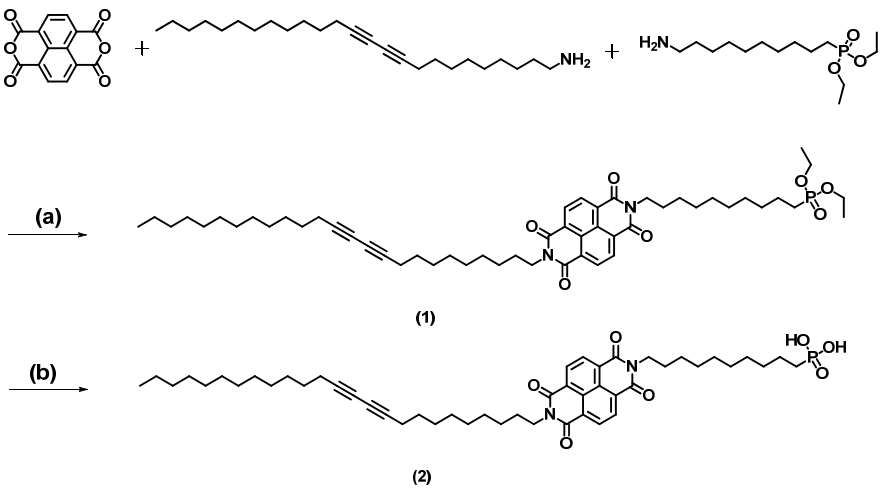


Figure S1. Output characteristics of the devices with the monolayer of (a) 18-PA, (b) 14DA11-PA, (c) 12ND10-PA and (d) 12DA9ND10-PA, respectively.

Synthetic procedures and characterization of the intermediates

All starting materials were purchased from Acros, Aldrich and TCI respectively. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AV500 spectrometer. The proton and carbon chemical shifts (δ) are reported in ppm relative to the residual signals for $CDCl_3$ (^{1}H- 7.24; ^{13}C-77.00). Molecular weight was determined by EI mass spectrometry on JMS-700 double focusing mass spectrometer (JEOL, Tokyo, Japan), MALDI mass spectrometry with Applied Biosystems 4800 Proteomics Analyzer (Applied Biosystem, Foster City) and HR ESI (Electrospray) with dual ionization ESCi® (ESI/APCi) source options, and Waters LCT Premier XE (Waters Corp., Manchester, UK) respectively. The general synthetic routes of these ND- and DA-carrying phosphonic acid derivatives were presented in scheme S1-2.



Scheme S1. Synthetic route of 12DA9ND10PA[a]

[a] Reagents and conditions: (a) DMF, 65 ℃; (b) BrTMS, CH_2Cl_2.

(1)

Diethyl(10-(1,3,6,8-tetraoxo-7-(pentacosa-10,12-diyn-1-yl)-3,6,7,8-tetrahydro-benzo[lmn][3,8]phenanthrolin-2(1H)-yl)decyl)phosphonate (12DA9ND10PE)

Naphthalene-1,4,5,8-tetracarboxylic acid dianhydride (1.24 g, 4.6 mmol), diethyl (10-aminodecyl)phosphonate (2.0 g, 5.6 mmol), and 1-amino-10, 12-pentacosadiyne (1.63 g, 5.6 mmol) in dry DMF (100 mL) were stirred in the dark at 60 ℃ under nitrogen for 18 h. After cooled down to room temperature, the solution was poured into ice water. The product was extracted with dichloromethane, dried by anhydrous magnesium sulfate. The crude compound were purified by column chromatography (silica gel, using CH_2Cl_2: EA= 6: 1) to give the compound as light pink solid. The yield was 42 %.^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.74 (s, 4H), 4.18 -4.04 (m, 8 H), 2.22 (t, *J* = 7.0 Hz, 4H), 1.72 -1.32 (m, 62H), 0.86 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$, δ): 162.79, 161.02, 130.88, 126.68, 126.63, 77.54, 77.43, 67.40, 65.25, 65.20, 63.30, 61.36, 61.30, 43.21, 40.92, 39.80, 38.16, 33.07, 31.86, 30.76, 30.60, 30.52, 30.47, 30.16, 29.88, 29.57, 29.42, 29.37, 29.28, 29.25, 29.20, 29.17, 29.04, 28.94, 28.81, 28.74, 28.47, 28.31, 28.27, 28.13, 28.02, 27.21, 27.01, 26.97, 26.84, 26.73, 26.51, 26.24, 25.84, 25.12, 22.98, 22.62, 22.44, 22.38, 22.34, 19.67, 19.15, 17.67, 16.45, 16.40, 14.94, 14.04.; HRMS (MALDI) m/z: $[M+H]^+$ calcd for $C_{53}H_{78}N_2O_7P$, 885.5541; found, 885.5505.

(2)

(10-(1,3,6,8-tetraoxo-7-(pentacosa-10,12-diyn-1-yl)-3,6,7,8-tetrahydrobenzo-[lmn][3,8]phenanthrolin-2(1H)-yl)decyl)phosphonic acid (12DA9ND10PA)

12DA9ND10PE (1 g, 1.1 mmol) and dry dichloromethane (50 mL) were stirred in a flask cooled with an ice-bath. Trimethylsilyl bromide (1.7 g, 11.3 mmol) was added drop-wise. After the addition was completed, the solution was warmed to room temperature and stirred overnight.

The solvent was removed by rota-vap, and the residue was hydrolyzed with methanol. The crude compound was recrystallized from THF containing several drops of trifluoroacetic acid and was washed by MeOH, THF, diethyl ether, acetone to give pure product as light pink powder. The yield was 76 %.^{1}H NMR (500 MHz, $CDCl_3$/trifluoroacetic acid, δ): 8.82 (s, 4 H), 4.20 (t, *J* = 7.8 Hz, 4 H), 2.22 (t, *J* = 7.0 Hz, 4 H), 1.95 -1.89 (m, 2 H), 1.72 -1.24 (m, 50 H), 0.87 (t, *J* = 7.0 Hz, 3 H),^{13}C NMR (126 MHz, $CDCl_3$/trifluoroacetic acid, δ): 163.77, 163.66, 131.82, 126.56, 126.48, 126.34, 77.64, 77.51, 65.18, 41.62, 31.82, 29.98, 29.84, 29.54, 29.38, 29.25, 29.16, 29.00, 28.86, 28.80, 28.69, 28.57, 28.26, 28.21, 27.82, 27.72, 26.84, 26.70, 22.57, 21.48, 19.07, 13.90; HRMS (MALDI) m/z: $[M+Na]^+$ calcd for $C_{49}H_{69}N_2O_7P$ Na, 851.4734; found, 851.4730.

(3)

Diethyl(10-(7-dodecyl-1,3,6,8-tetraoxo-3,6,7,8-tetrahydrobenzo[lmn][3,8]-phenanthrolin-2(1H)-yl)decyl)phosphonate (12ND10PE)

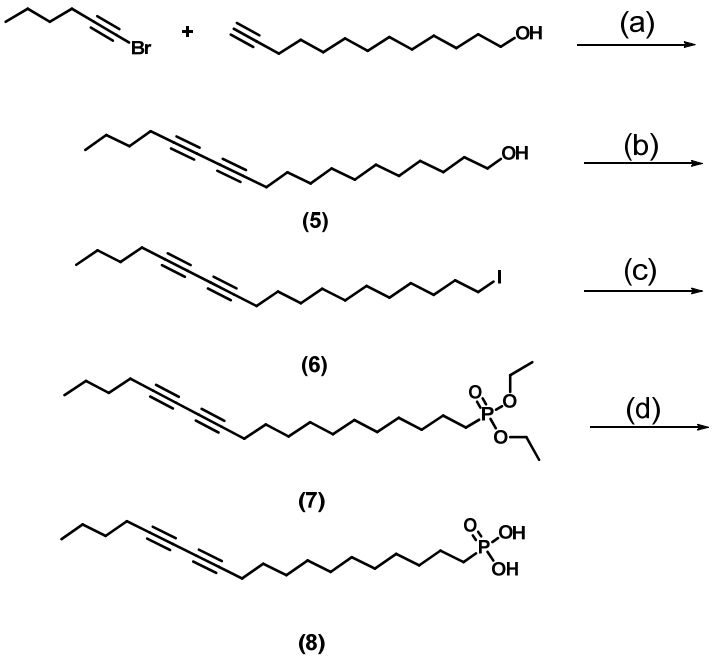
Compound 12ND10PE (3) and compound 12ND10PA (4) were prepared by similar method, using 1-dodecylamine as the starting material.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.73 (s, 4 H), 4.18 -4.02 (m, 8 H), 1.72 -1.32 (m, 44 H), 0.86 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$, δ): 162.79, 161.12, 130.87, 126.67, 126.64, 61.36, 61.31, 40.95, 38.22, 31.85, 30.60, 30.46, 29.56, 29.46, 29.37, 29.27, 29.20, 29.00, 28.03, 27.03, 26.79, 26.23, 25.11, 22.62, 22.37, 22.33, 16.44, 16.40, 14.03; HRMS (MALDI) m/z: $[M+H]^+$ calcd for $C_{40}H_{59}N_2O_7P$, 711.4132; found, 711.4118.

(4)

(10-(7-Dodecyl-1,3,6,8-tetraoxo-3,6,7,8-tetrahydrobenzo[lmn][3,8]phenanthrolin-2(1H)-yl)decyl)phosphonic acid (12ND10PA)

^{1}H NMR (500 MHz, $CDCl_3$/trifluoroacetic acid, δ): 8.83 (s, 4 H), 4.20 (t, *J* = 7.8 Hz, 4 H), 1.93 - 1.89 (m, 2 H), 1.72 -1.24 (m, 36 H), 0.87 (t, *J* = 7.0 Hz, 3 H), ^{13}C NMR (126 MHz, $CDCl_3$/trifluoroacetic acid, δ): 163.78, 163.71, 131.84, 126.56, 126.48, 126.35, 41.68, 31.82, 30.00, 29.87, 29.52, 29.45, 29.38, 29.24, 29.14, 29.02, 28.87, 28.83, 28.59, 27.85, 27.73, 26.89, 26.71, 26.60, 25.50, 22.57, 21.50, 13.89; HRMS (MALDI) m/z: $[M+H]^+$ calcd for $C_{36}H_{52}N_2O_7P$, 655.3506; found, 655.3516.



Scheme S2. Synthetic route of 4DA11PA[a]

[a] Reagents and conditions: (a) CuCl, NH_2OH · HCl, ethylamine (70%), methanol, 0℃; (b) PPh_3, I_2, imidazole, CH_2Cl_2; (c) Diethyl phosphonate, Cs_2CO_3, TBAI, DMF, rt, overnight; (d) TMSBr, CH_2Cl_2.

(5)

Nonadeca-12, 14-diyn-1-ol (4DA11OH)

Copper chloride (2.52 g, 25 mmol) was placed in a flask under nitrogen. Ethylamine (70 % in water, 106 mL) was added into the flask to produce a blue color solution. Hydroxylamine

hydrochloride was added to the solution until the solution turned transparent. The solution was bathed in ice, then tridec-12-yn-1-ol (20 g, 102 mmol) and methanol (30 mL) was added into this flask. After addition, 1-bromohex-1-yne (18 g, 112 mmol) in THF (60 mL) was added drop-wise into this solution. The mixture was warmed to room temperature and stirred overnight. The mixture was poured into ice and 6 N hydrogen chloride (300 mL) was added. The solution was extracted with dichloromethane and the organic layer was dried with anhydrous magnesium sulfate and then concentrated. The crude was purified by column chromatography (silica gel, using hexane: EA= 5: 1) to give the target compound as transparent liquid. (13.3 g, 47%). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 3.62 (t, *J* = 6.5 Hz, 2 H), 2.24 -2.20 (m, 4 H), 1.56 -1.34 (m, 22 H), 0.89 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR (12 6MHz, $CDCl_3$, δ): 77.45, 77.42, 65.23, 63.02, 32.75, 30.34, 29.50, 29.44, 29.37, 29.35, 29.01, 28.77, 28.30, 25.68, 21.85, 19.14, 18.83, 13.44.; HRMS (EI+) m/z: $[M]^+$ calcd for $C_{19}H_{32}O$, 276.2453; found, 276.2455.

(6)

19-Iodononadeca-5, 7-diyne (4DA11I)

Nonadeca-12, 14-diyn-1-ol (7 g, 25.3 mmol), triphenylphosphine (7.3 g, 27.9 mmol), imidazole (2.06 g, 30 mmol) were dissolved in dry dichloromethane (200 mL). The solution was cooled in an ice bath. Iodine (6.74 g, 26.6 mmol) was added in portions. After the addition was completed, the solution was stirred for another two hours and the reaction progress was checked by TLC. Then the solvent was removed, and the crude was purified by column chromatography (silica gel, using hexane as eluent) to give the target compound as transparent liquid (9.27 g, 95%).

^{1}H NMR (500 MHz, $CDCl_3$, δ): 3.17 (t, *J* = 7.0 Hz, 2 H), 2.25-2.21 (m, 4 H), 1.83 -1.77 (m, 2 H) 1.56 -1.34 (m, 22 H), 0.89 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$, δ): 77.45, 65.23,

33.53, 30.45, 30.35, 29.39, 29.33, 29.32, 29.00, 28.76, 28.46, 28.29, 21.86, 19.15, 18.84, 13.45, 7.14; HRMS (MALDI) m/z: $[M+Na]^+$ calcd for $C_{19}H_{31}INa$, 409.1362; found, 409.1377.

(7)

Diethyl nonadeca-12, 14-diyn-1-ylphosphonate (4DA11PE)

The synthetic process was similar to Salvatore's method.[1] Cesium carbonate (6.81 g, 21 mmol), tetrabutylammonium iodide (8.29 g, 21 mmol), and diethyl phosphite (1.92 g, 14 mmol) were stirred in dry DMF (50 mL) for 1 h. 19-Iodononadeca-5,7-diyne (7 g, 18.1 mmol) in dry THF (20 mL) was added by a syringe. After stirring under nitrogen overnight, the reaction was quenched by ice water. The mixture was extracted with diethyl ether, and then the organic layer was dried by anhydrous magnesium sulfate and concentrated. The crude was purified by column chromatography (silica gel, using hexane: EA= 2: 1 as eluent) to give the target compound as transparent liquid. (4.33 g, 78%).^{1}H NMR (500 MHz, $CDCl_3$, δ): 4.11 -4.02 (m, 4 H), 2.24 -2.20 (m, 4H), 1.73 -1.24 (m, 30 H), 0.88 (t, *J* =7.0 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$, δ): 77.43, 65.22, 61.33, 61.28, 30.60, 30.47, 30.34, 29.43, 29.35, 29.28, 29.01, 28.76, 28.29, 26.23, 25.11, 22.36, 22.32, 21.84, 19.14, 18.82, 16.43, 16.38, 13.44; HRMS (MALDI) m/z: $[M+Na]^+$ calcd for $C_{23}H_{41}O_3PNa$, 419.2685; found, 419.2686.

(8)

Nonadeca-12, 14-diyn-1-ylphosphonic acid (4DA11PA)

Diethyl nonadeca-12, 14-diyn-1-ylphosphonate (2.0 g, 5 mmol) and dichloromethane (50 ml) were stirred in a flask cooled by an ice-bath. Trimethylsilyl bromide (4.63 g, 30 mmol) was added drop-wise. After the addition, the solution was warmed to room temperature and stirred overnight. The solvent was removed by rota-vap and the residue was hydrolyzed with methanol. The crude was purified by recrystallization from hexane to give the target pure compound as

white powder (1.5 g, 87%).^{1}H NMR (500 MHz, $CDCl_3$, δ): 5.35 (br, 2 H), 2.24 -2.21 (m, 4 H), 1.75 -1.24 (m, 24 H), 0.90 (t, *J* =7.0 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$, δ): 77.43, 65.25, 30.44, 30.35, 29.48, 29.40, 29.31, 29.04, 29.02, 28.80, 28.32, 25.87, 24.72, 21.86, 19.16, 18.84, 13.46.HRMS (MALDI) m/z: $[M+Na]^+$ calcd for $C_{19}H_{33}O_3PNa$, 363.2059; found, 363.2070.

(9)

Nonacosa-12, 14-diyn-1-ol (14DA11OH)

Compound 9 to 12 were prepared by similar method.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 3.62 (t, *J* = 6.5 Hz, 2 H), 2.23-2.20 (m, 4 H), 1.56-1.23 (m, 42 H), 0.86 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$, δ): 77.52, 77.48, 65.23, 63.05, 32.78, 31.87, 29.60, 29.55, 29.50, 29.45, 29.42, 29.38, 29.36, 29.30, 29.04, 28.80, 28.31, 25.68, 22.63, 19.16, 14.04; HRMS (EI+) m/z: $[M]^+$ calcd for $C_{29}H_{52}O$, 416.4018; found: 416.4022.

(10)

1-Iodononacosa-12, 14-diyne (14DA11I)

^{1}H NMR (500 MHz, $CDCl_3$, δ): 3.17 (t, *J* = 7.0 Hz, 2H), 2.23 -2.21 (m, 4H), 1.83-1.77 (m, 2H) 1.56-1.34 (m, 40H), 0.86 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$, δ): 77.58, 77.51, 65.30, 65.27, 33.59, 31.92, 30.50, 29.68, 29.67, 29.64, 29.63, 29.60, 29.47, 29.45, 29.39, 29.36, 29.35, 29.33, 29.10, 29.07, 29.05, 28.86, 28.84, 28.82, 28.52, 28.50, 28.37, 28.35, 22.68, 19.22, 14.10, 7.19; HRMS (EI+) m/z: $[M]^+$ calcd for $C_{29}H_{51}I$, 526.3036; found, 526.3028.

(11)

Diethyl nonacosa-12, 14-diyn-1-ylphosphonate (14DA11PE)

^{1}H NMR (500 MHz, $CDCl_3$, δ): 4.12- 4.01 (m, 4 H), 2.23- 2.20 (m, 4 H), 1.71-1.23 (m, 50 H), 0.86 (t, *J* =7.0 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$, δ): HRMS (MALDI) m/z: $[M+H]^+$ calcd for $C_{33}H_{61}O_3P$, 537.4431; found, 537.4421.

(12)

Nonacosa-12, 14-diyn-1-ylphosphonic acid (14DA11PA)

^{1}H NMR (500 MHz, $CDCl_3$, δ): 5.35 (br, 2 H), 2.24 -2.21(m, 4 H), 1.75 -1.24 (m, 24 H), 0.90 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$, δ): 77.56, 77.51, 65.28, 65.26, 61.37, 61.32, 31.92, 30.67, 30.54, 29.70, 29.68, 29.66, 29.64, 29.60, 29.52, 29.50, 29.47, 29.45, 29.41, 29.34, 29.11, 29.07, 29.05, 28.85, 28.84, 28.36, 26.30, 25.18, 22.68, 22.43, 22.39, 19.21, 16.50, 16.45, 14.09; HRMS (EI+) m/z: $[M]^+$ calcd for $C_{29}H_{53}O_3P$, 480.3732; found, 480.3741.

Reference

1. Cohen, R. J.; Fox, D. L.; Eubank, J. F.; Salvatore, R. N. Mild and Efficient Cs_2CO_3-Promoted Synthesis of Phosphonates. *Tetrahedron Lett.* **2003**, *44*, 8617-8621.