Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

High Mobility n-Channel Single-crystal Field Effect Transistors Based on 5,7,12,14-Tetrachloro-6,13-diazapentacene

M. Minarul Islam,[a,b,c] Someshwar Pola,[a] and Yu-Tai Tao[a,c*]

[a]Institute of Chemistry, Academia Sinica, Taipei, 115, Taiwan

[b]Taiwan International Graduate Program, Academia Sinica, Taipei, 115, Taiwan

[c]Department of Chemistry, National Tsing Hua University, Hsinchu 30013, Taiwan

[*]To whom correspondence should be addressed

E-mail: ytt@chem. Sinica.edu.tw

Optical Properties

The optical properties of 5,7,12,14-tetrachloro-6,13-diazapentacene **(TCDAP)** were investigated by HP 845x UV-visible spectrophotometer. Solution was prepared in chloroform and UV-vis spectra were recorded for chemical stability measurement. UV-vis spectra of TCDAP does not show any change even after 60 min under ambient condition (Fig. S1). This result indicates that TCDAP is more chemically stable compound. The onset HOMO-LUMO energy gap of **TCDAP** is found 2.66 eV by using UV-vis spectrophotometer.

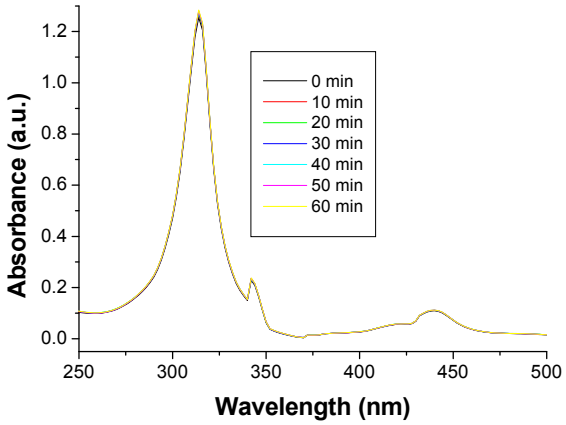


Figure S1. UV-vis spectra of **TCDAP** in chloroform solution.

Electrochemical Properties

The electrochemical properties of **TCDAP** were performed with cyclic voltammetry (CV) using a glassy carbon as working electrode, a platinum wire counter electrode and Ag/AgCl reference electrode. It exhibits two reversible reduction waves (Fig. S2a), whereas within the accessible scanning range in hot dichloromethane/Bu_4NPF_6 no oxidation wave was detected. The choice of the solvent was governed by the solubility of the **TCDAP**. Exemplified cyclic voltammogram for **TCDAP** is shown in Fig. S2. The onset reduction potential is 0.530 V. The measured LUMO and HOMO energies are 3.79 eV and 6.45 eV respectively. Typically n-type organic semiconductors have LUMO level between 3 and 4 eV.

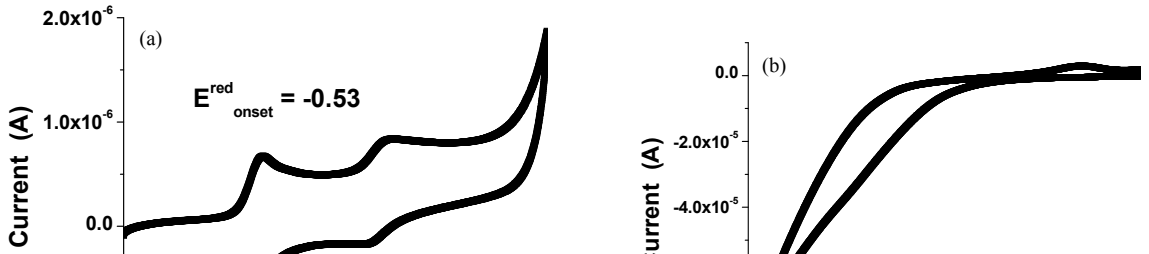


Figure S2. Cyclic Voltammogram of **TCDAP: (a)** reduction and **(b)** oxidation potential.

Growth of Single-crystal and X-ray Analysis

TCDAP was sublimed with three consecutive vacuum sublimation systems by using a temperature gradient furnace for purification. The three temperature zones were set at 340°, 270° and 250°C with vacuum pressure 10^{-6} Torr. In the range of ~ 1.0 - 2.5 cm long and ~ 0.10 - 0.20 mm wide needle-like single-crystals of **TCDAP** were grown by physical vapour transport method in a stream (50 cc/min) of ultra pure argon at 310^{0}C (Fig. S3).

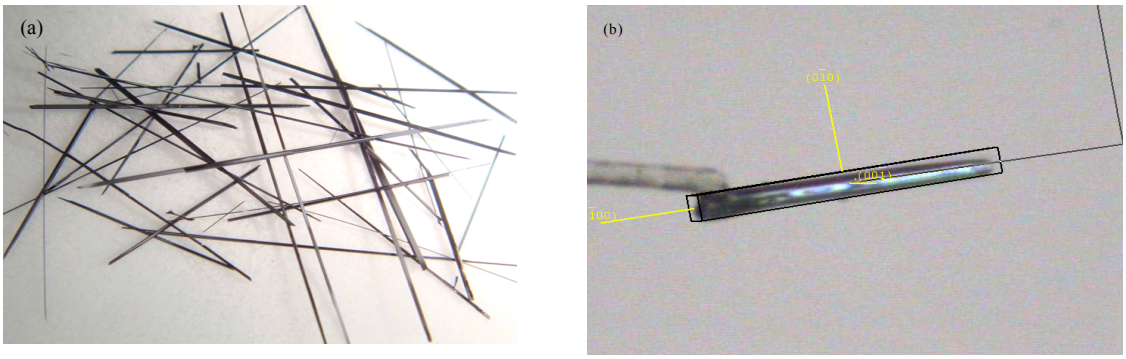


Figure S3. **(a)** Digital image of **TCDAP** single-crystal and **(b)** Unit cell crystal structure of TCDAP exhibiting short a-axis along the (-100), b-axis along (0-10) and long c-axis along (001).

Crystal structure analysis

To investigate the molecular structure and intermolecular interactions in the solid state, we performed single-crystal structure analysis using Bruker X8APEX X-ray diffractometer with Mo Kα radiation (λ = 0.71073 Å). The data were collected at 150.0(1) K and the structure was solved by SHELX 97 program (Table S1). Unit cell parameters are a = 3.919(5) Å, b = 12.184(5) Å, c = 16.985(5) Å, α = 90, β = 94.83, γ = 90, V = 808.1(11) Å^3, GOF = 1.056, R_1 = 0.0404, R_w = 0.0855 (for all reflection). Single-crystal size was 0.34 x 0.08 x 0.08 mm^3.

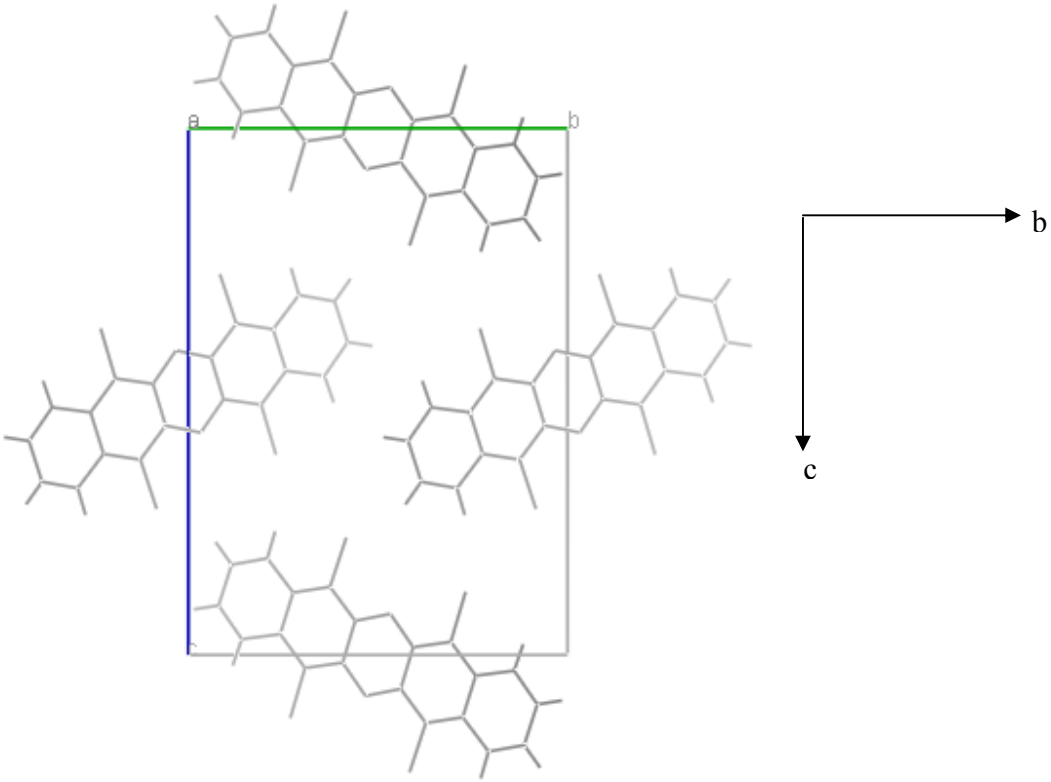


Figure S4. Unit cell of a **TCDAP** single-crystal.

Device Fabrication Procedure

Top-contact/top-gate device configuration was used to fabricate **TCDAP** single-crystal FET. The glass substrate was cleaned before device fabrication with a Piranha solution (H_2SO_4 : H_2O_2 = 4:1 v/v) then thoroughly washed with de-ionized water and blow dry with nitrogen. Water based colloidal graphite was used as electrodes and parylene used as gate dielectric. The bare glass substrate and octadecyltrichlorosilane (ODTS) self-assemble monolayer treated substrate were used to fabricate **TCDAP** single-crystal FETs. First, single-crystal was placed on the substrate and then colloidal graphite was painted on the crystal surface as source and drain then dried at room temperature. Thin film of parylene was deposited onto the single-crystal with preformed source-drain electrodes in a homemade reactor. Finally colloidal graphite was painted on top of the parylene over the region between the source and drain as a gate electrode. The measured film thickness was 1.50 – 2.50 μm. The typical channel length (L) and channel width (W) were 0.50 – 1.00 mm and 0.10 – 0.20 mm respectively.

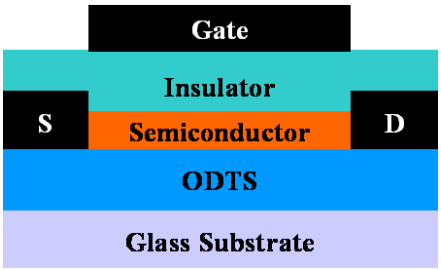
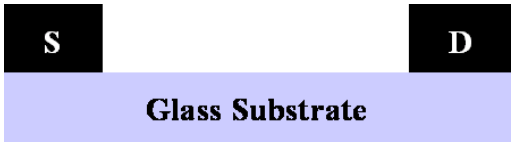


Figure S5. Schematic diagram of **TCDAP** FET on ODTS-modified glass substrate.

To fabricate devices without semiconductors, colloidal graphite was used as source and drain electrodes on bare glass substrate and on ODTS modified glass substrate.



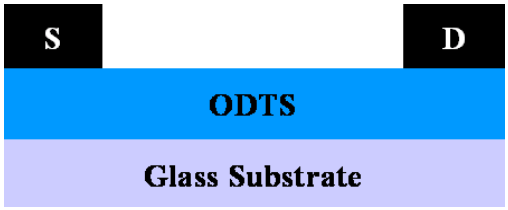


Figure S6. Schematic diagram of devices without semiconductor, gate electrode and insulator on bare glass and on ODTS modified glass substrate.

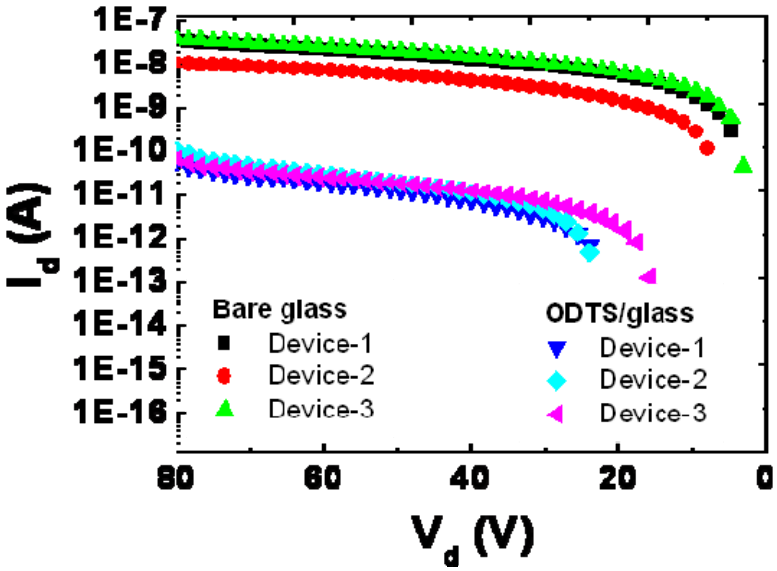


Figure S7. *I_d vs. V_d* curves measured for three electrode patterns without semiconductor on bare glass and ODTS-modified glass substrate**.**

Table S1: Crystallographic data for TCDAP.

Formula	C_{20} H_8 Cl_4 N_2
Formula weight	418.08
Temperature	150.0(1) K

Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 3.919(5) Å	α = 90.000(5)°.
	b = 12.184(5) Å	β = 94.834(5)°.
	c = 16.985(5) Å	γ = 90.000(5)°.
Volume	808.1(11) $Å^3$	
Z	4	
Density (calculated)	1.718 Mg/m^3	
Absorption coefficient	0.739 mm^{-1}	
F(000)	420	
Crystal size	0.34 x 0.08 x 0.08 mm^3	
Theta range for data collection	2.06 to 25.02°.	
Index ranges	-4<=h<=4, -14<=k<=14, -19<=l<=20	
Reflections collected	5277	
Independent reflections	1405 [R(int) = 0.0333]	
Completeness to theta = 25.02°	97.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7452 and 0.6537	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1405 / 0 / 118	
Goodness-of-fit on F^2	1.056	
Final R indices [I>2sigma(I)]	R1 = 0.0305, wR2 = 0.0795	
R indices (all data)	R1 = 0.0404, wR2 = 0.0855	

Largest diff. peak and hole	0.319 and -0.205 e.Å^{-3}

Table S2: Bond lengths [Å] and angles [°] for TCDAP.

Cl(1)-C(1)	1.727(2)
Cl(2)-C(6)	1.727(2)
N-C(8)#1	1.341(3)
N-C(7)	1.350(3)
C(1)-C(9)	1.392(3)
C(1)-C(7)	1.416(3)
C(2)-C(3)	1.355(3)
C(2)-C(9)	1.433(3)
C(2)-H(2)	0.9300
C(3)-C(4)	1.415(4)
C(3)-H(3)	0.9300
C(4)-C(5)	1.359(3)
C(4)-H(4)	0.9300
C(5)-C(10)	1.436(3)
C(5)-H(5)	0.9300
C(6)-C(10)	1.397(3)
C(6)-C(8)	1.422(3)
C(7)-C(8)	1.449(3)
C(8)-N#1	1.341(3)
C(9)-C(10)	1.445(3)
C(8)#1-N-C(7)	117.22(19)

C(9)-C(1)-C(7)	121.7(2)
C(9)-C(1)-Cl(1)	120.39(18)
C(7)-C(1)-Cl(1)	117.90(17)
C(3)-C(2)-C(9)	121.0(2)
C(3)-C(2)-H(2)	119.5
C(9)-C(2)-H(2)	119.5
C(2)-C(3)-C(4)	120.7(2)
C(2)-C(3)-H(3)	119.6
C(4)-C(3)-H(3)	119.6
C(5)-C(4)-C(3)	120.9(2)
C(5)-C(4)-H(4)	119.6
C(3)-C(4)-H(4)	119.6
C(4)-C(5)-C(10)	120.8(2)
C(4)-C(5)-H(5)	119.6
C(10)-C(5)-H(5)	119.6
C(10)-C(6)-C(8)	121.6(2)
C(10)-C(6)-Cl(2)	120.43(17)
C(8)-C(6)-Cl(2)	117.91(17)
N-C(7)-C(1)	119.6(2)
N-C(7)-C(8)	121.3(2)
C(1)-C(7)-C(8)	119.14(19)
N#1-C(8)-C(6)	119.9(2)
N#1-C(8)-C(7)	121.53(19)
C(6)-C(8)-C(7)	118.5(2)

C(1)-C(9)-C(2)	122.2(2)
C(1)-C(9)-C(10)	119.4(2)
C(2)-C(9)-C(10)	118.4(2)
C(6)-C(10)-C(5)	122.3(2)
C(6)-C(10)-C(9)	119.51(19)
C(5)-C(10)-C(9)	118.2(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+2,-z+1