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Electronic Supplementary Information

π-Extended Hexadeca-Substituted Cobalt Phthalocyanine as an Active Layer for Organic Field-Effect Transistors

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Table of Contents

General Information

All NMR spectra were recorded on Agilent VNMRS 500 MHz at 25 ^{o}C and chemical shifts were referenced internally using the residual solvent resonances. Mass spectra were measured on a MALDI (matrix assisted laser desorption ionization) BRUKER Microflex LT using Dithranol (DIT; 1,8-dihydroxy-9,10-dihydroanthracen-9-one) as the matrix. The elemental analysis was performed on a Costech ECS 4010 CHNS elemental analyzer. All reagents and solvents were of reagent grade quality obtained from commercial suppliers. Electrochemical measurements were carried out using a Gamry 600 Potentiostat/Galvanostat. The cell comprised inlets for a glassy carbon working electrode, a platinum wire counter electrode and a saturated calomel electrode (SCE) reference electrode. Typically, a 0.1 M solution of TBAP in CH_2Cl_2 containing the sample was purged with nitrogen for 20 min, and then the voltammograms were recorded at room temperature.

Single crystals of **4** was obtained slow slow diffusion of acetonitrile into a concentrated solution of **4** in chloroform/THF 100/1). Single crystal **4** was mounted on a MicroMount (MiTeGen). Crystallographic data of the compounds were recorded on a Bruker D8 VENTURE single crystal X-ray diffractometer equipped with PHOTON 100 CMOS detector and KryoFlex II low-temperature apparatus operating at 100K, using graphite monochromatized MoKα radiation (λ=0.71073 Å). All of the data were corrected for absorption effects using the multiscan method. The structures were solved by direct methods and refined on F^2 by fullmatrix least-squares using SHELXL 2014[1]. All the hydrogen atoms were added to their geometrically ideal positions. All non-hydrogen atoms were refined with anisotropic displacement parameters. Crystal data and structure refinement details are summarized in **Table S1.**

Fabrication and characterization of OFET

OFETs were fabricated on (100) oriented p-type silicon wafers in the bottom gate top contact configuration. After standard RCA cleaning of Si substrates, 250 nm Aluminum (Al) metal with a purity of 99.99% was thermally evaporated onto the back side of the Si wafer to form ohmic contact, followed by heat treatment at 500 °C for 5 min in dry nitrogen (N_2) atmosphere. Before spin coating of gate dielectric, the native oxide on the Si surface was removed in HF/H_2O (1:10) solution and then washed with de-ionized water and finally dried with N_2 gas. Thin film of gate dielectric, polymethylmethacrylate (PMMA), was obtained by spin coating process from a THF solution of PMMA. Thickness of the PMMA film was ~ 120 nm, determined by ellipsometric technique. After the PMMA film formation, in order to investigate the PMMA-p-Si interface gold (Au) metal contacts were deposited onto the PMMA surface by thermal evaporation of Au through a metal shadow mask. For OFET studies, a solution of **4** with a concentration of 5×10^{-4} M in DMF was spun on top of PMMA film at 2000 rpm for 90 s and the films were thermally treated at 110 °C for 20 min to evaporate the solvent. Finally, on the top of active layer (compound **4** in our case), Au source and drain electrodes with thickness of 200 nm was deposited by thermal evaporation through a metal shadow mask with a channel width (W) of 4 mm and a channel length (L) of 100 μm. Electrical measurements, transfer and output characteristics of the OFET device, were performed in ambient atmosphere using a Keithley 2400 source-meter and Keithley 617 programmable electrometer.

UV-Vis Spectra of 3 and 4

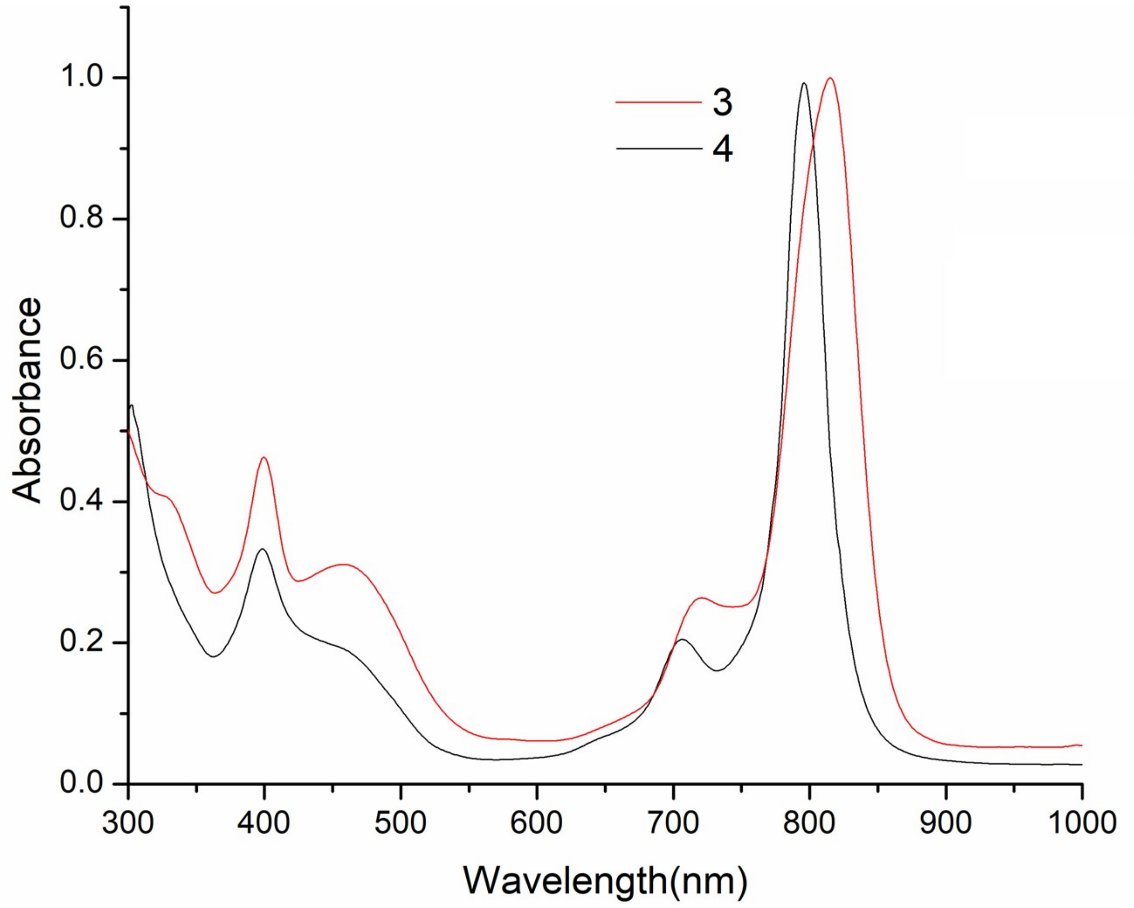

Fig. S1 UV-Vis spectrum of **3** and **4** in $CHCl_3$.

NMR spectra of 3 and 4

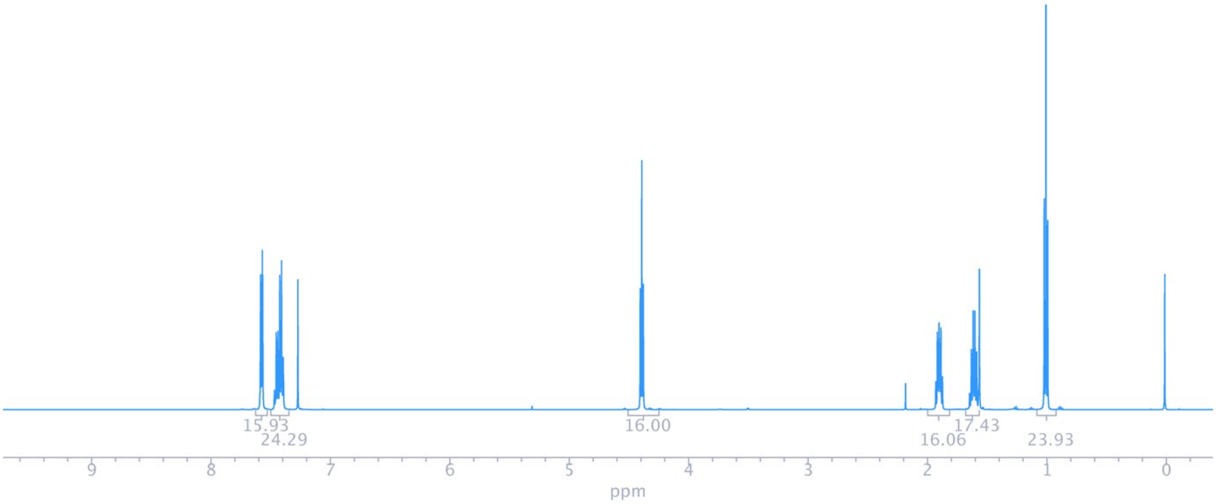

Fig. S2 ^{1}H NMR spectrum of **2** in CDCl$_3$.

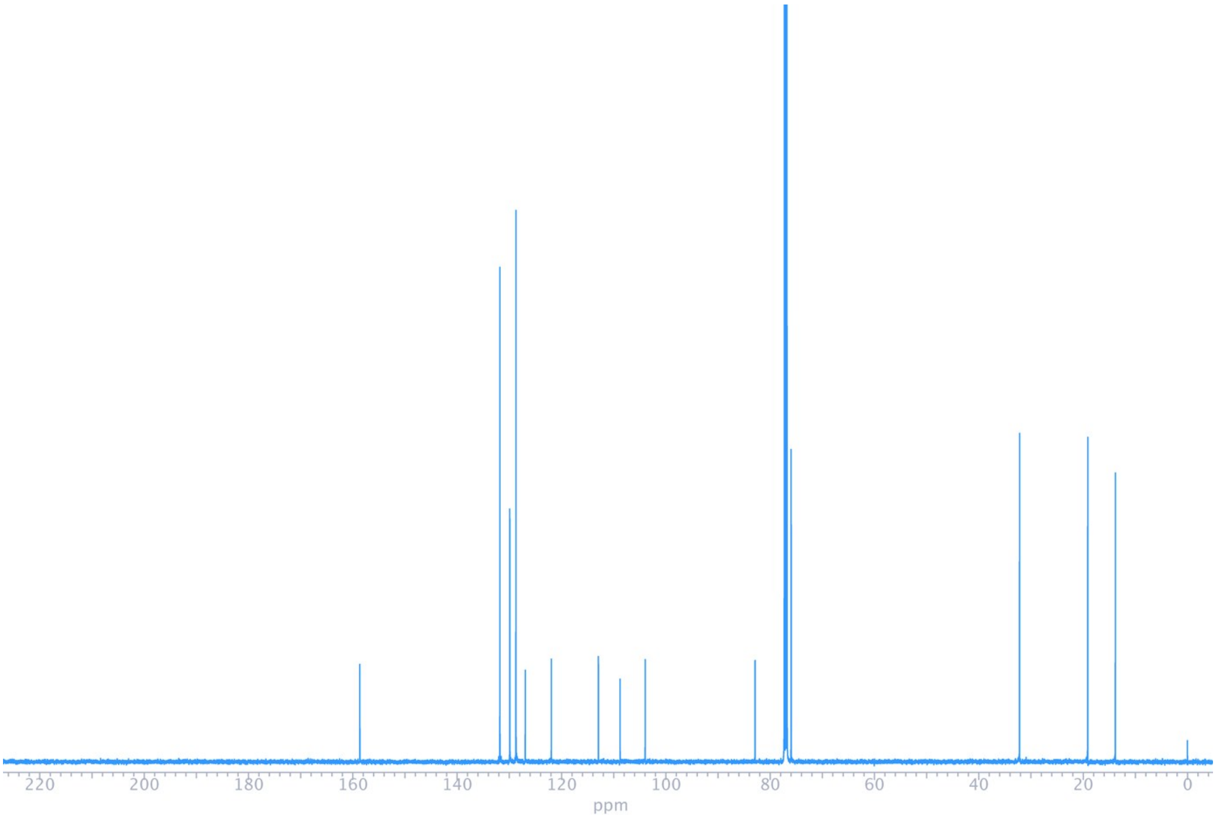

Fig. S3 ^{13}C NMR spectrum of **2** in CDCl$_3$.

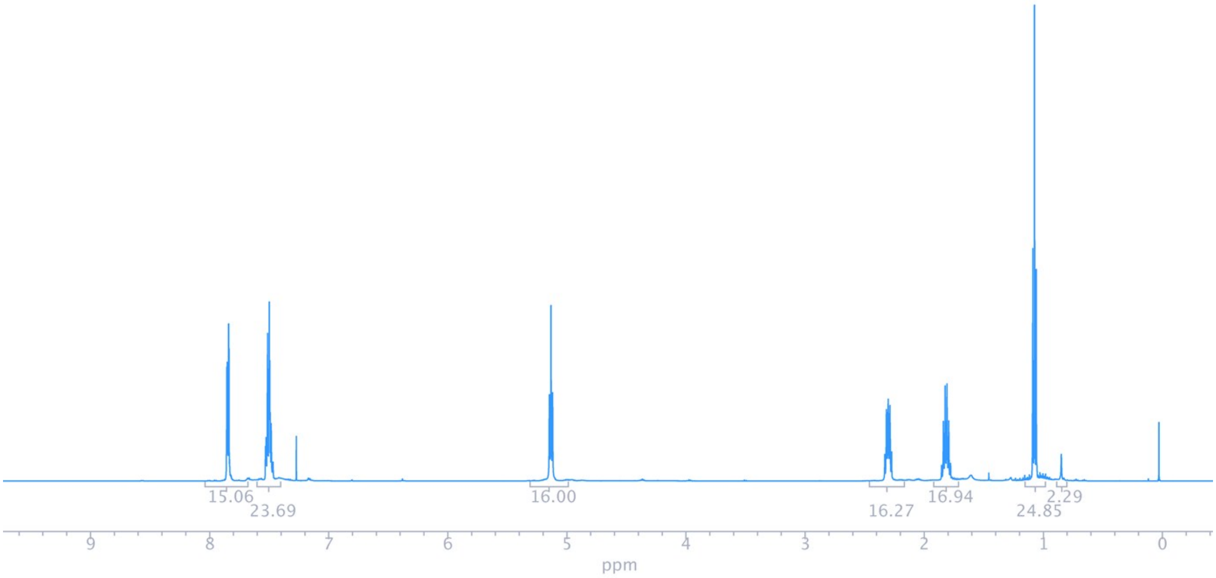

Fig. S4 ^{1}H NMR spectrum of **3** in $CDCl_3$.

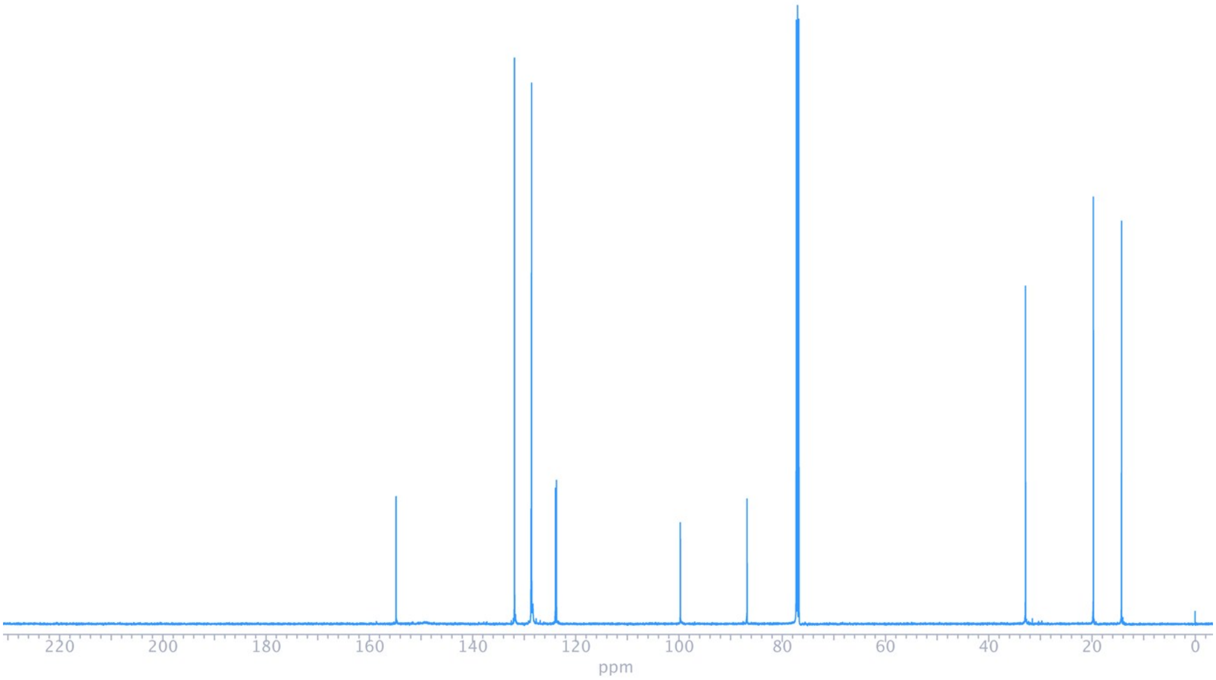

Fig. S5 ^{13}C NMR spectrum of **3** in $CDCl_3$.

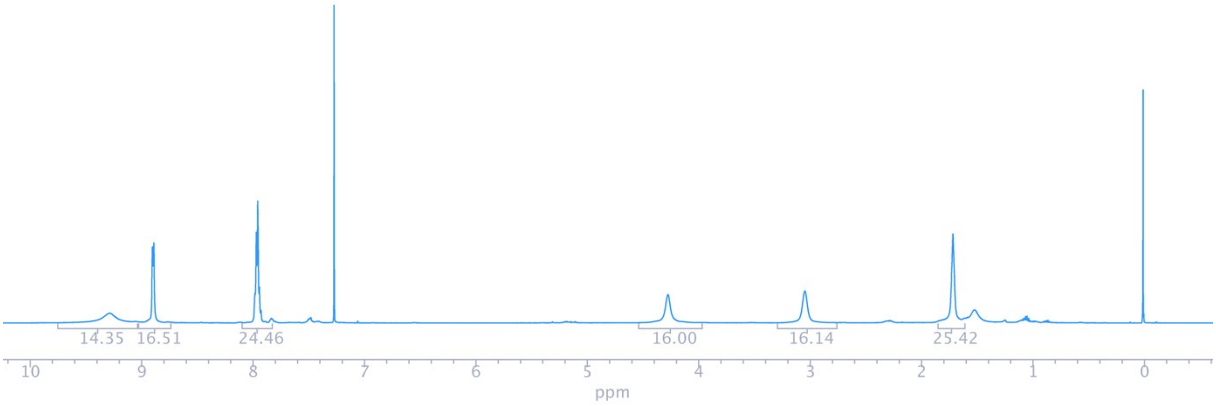

Fig. S6 ^{1}H NMR spectrum of **4** in $CDCl_3$.

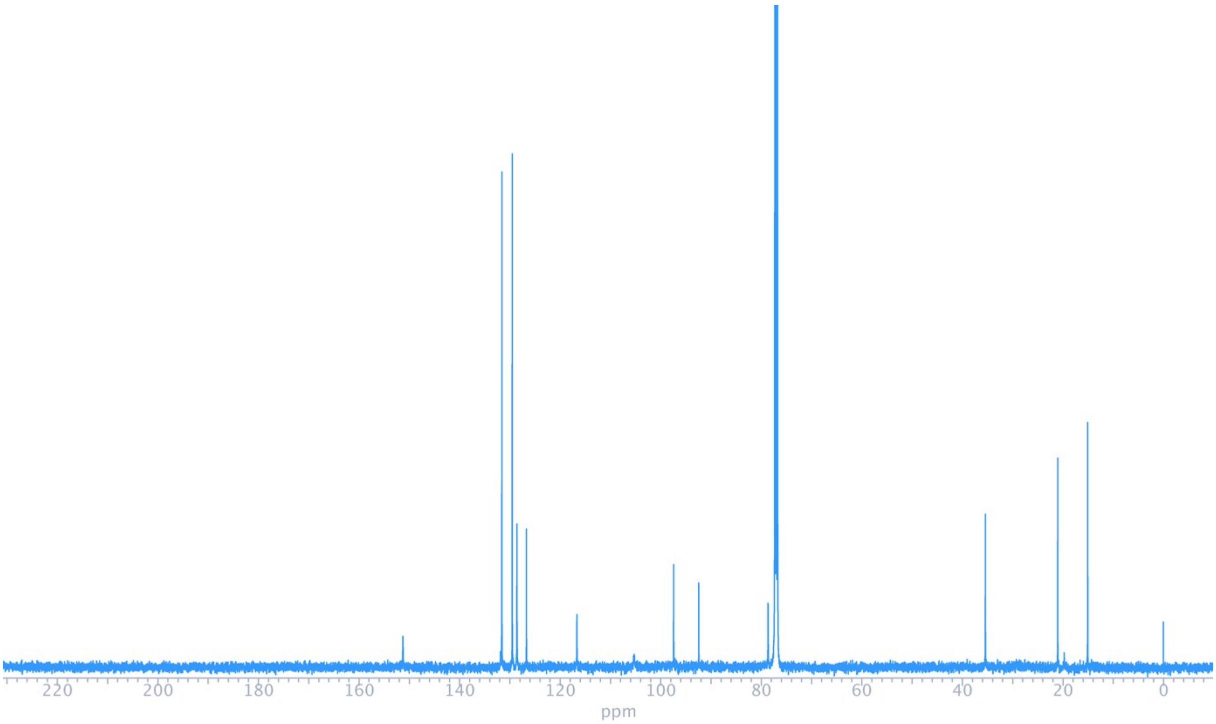

Fig. S7 ^{13}C NMR spectrum of **4** in $CDCl_3$.

X-ray structure of **4**

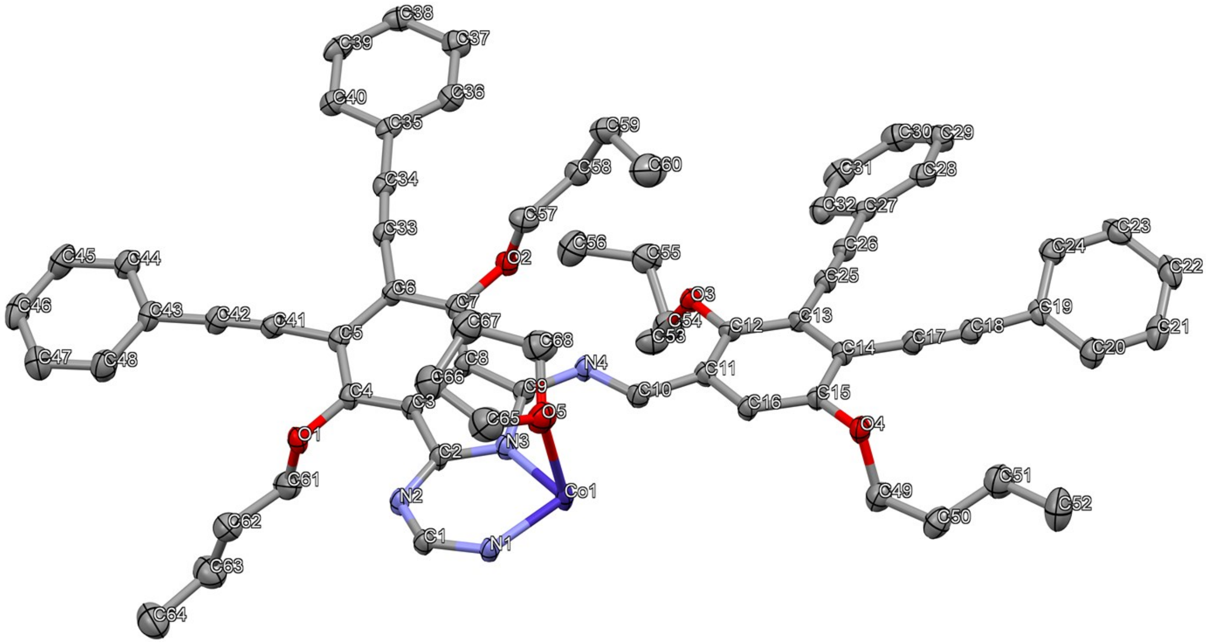

Fig. S8 Asymmetric unit structure of **4** with atomic numbering.

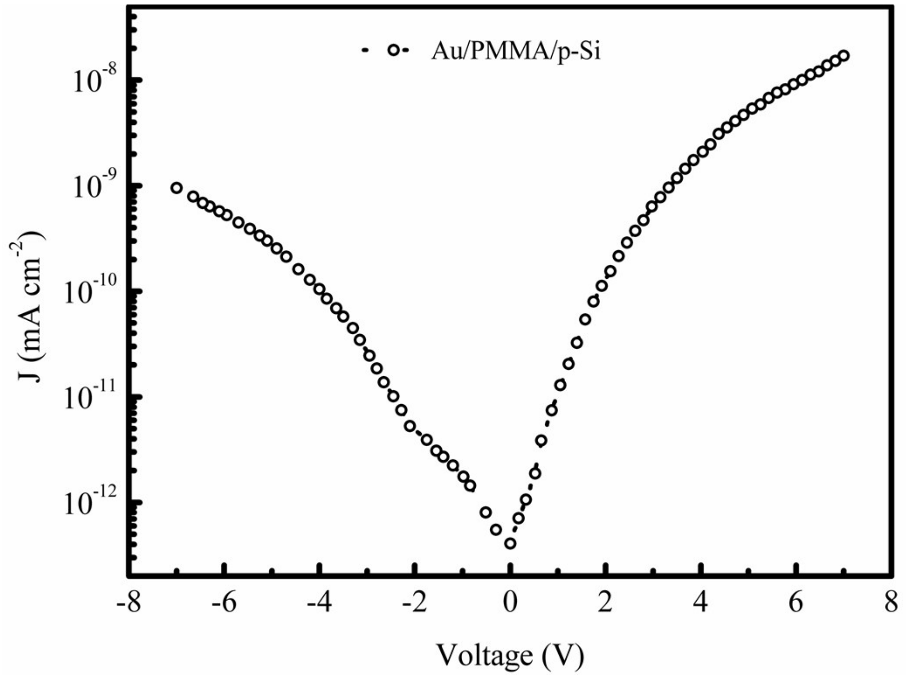

Fig. S9 J-V characteristic of the Au/PMMA/p-Si structure.

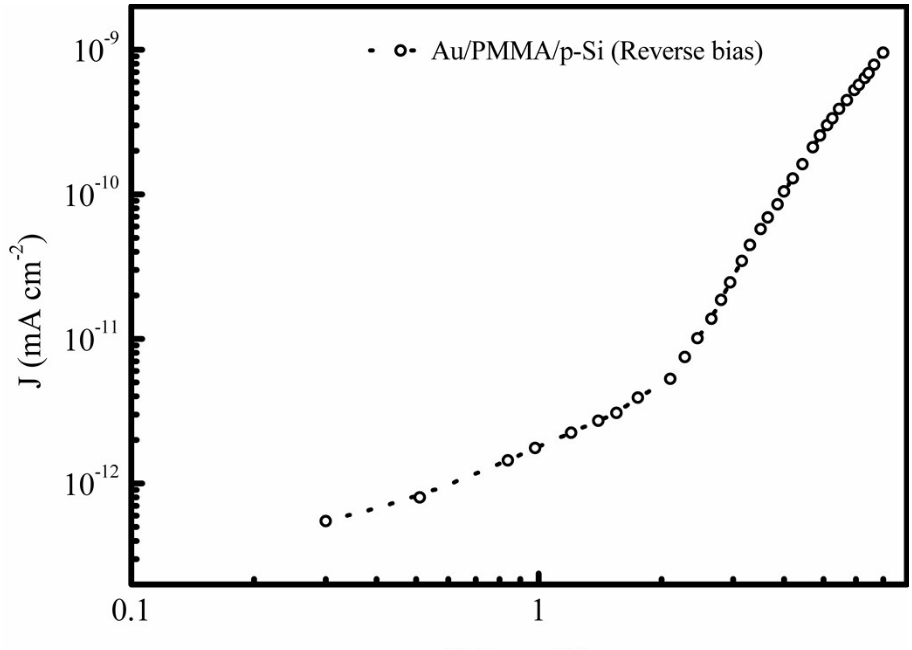

Fig. S10 Reverse bias J-V characteristic of the device.

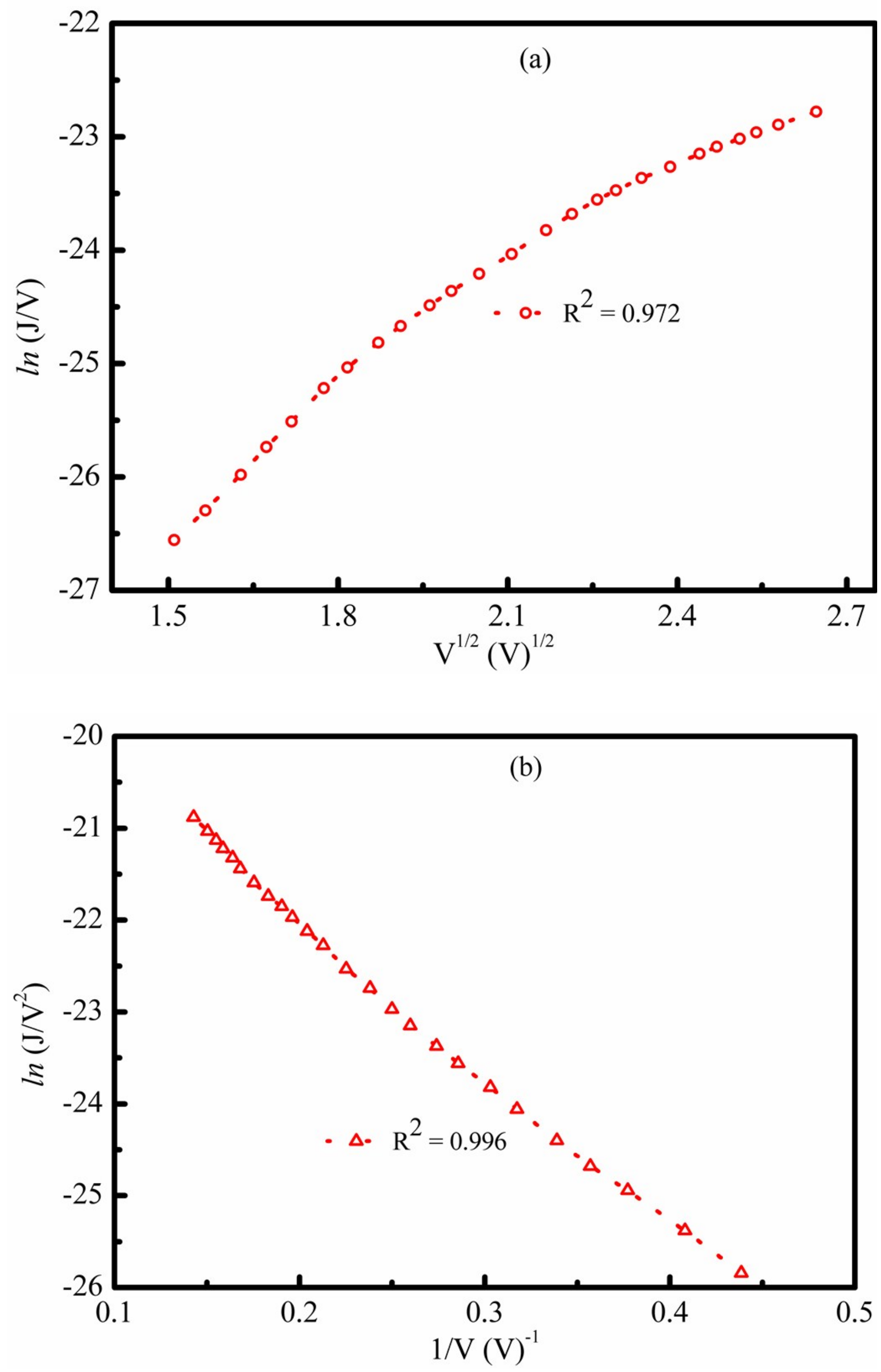

Fig. S11 Modelling of the J-V data according to (a) Pole-Frenkel emission (b) Fowler–Nordheim tunelling.

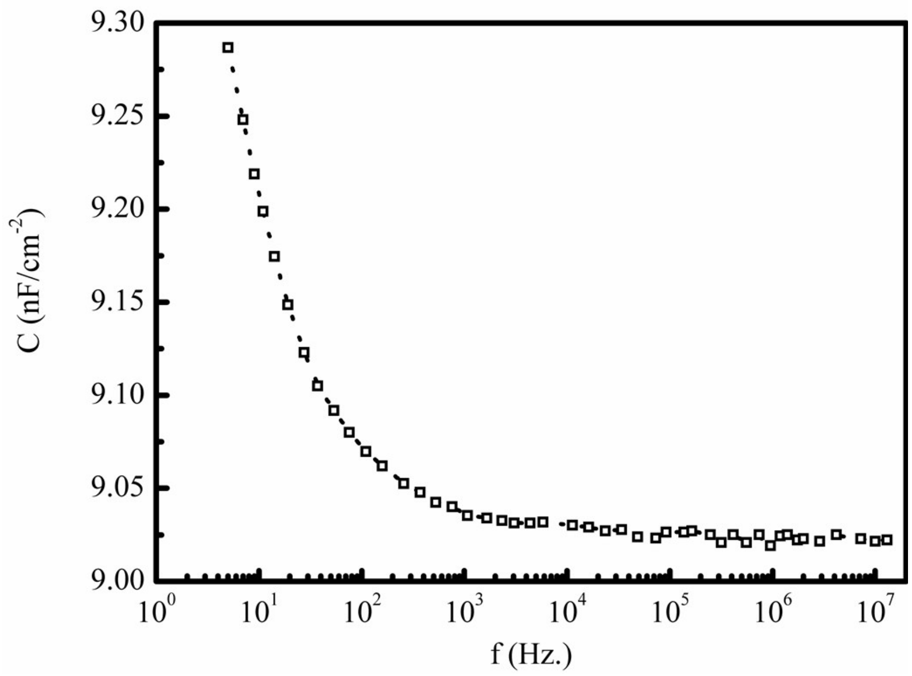

Fig. S12 Frequency dependence of the capacitance density for the Au/PMMA/p-Si structure.

Table S1. Crystal data and structure refinement details for compounds 4

	4

	4
CCDC number	1825468
Empirical formula	$C_{136}H_{128}CoN_8O_{10}$
Formula weight (g/mol)	2093.39
T(K)	100
λ(Å)	0.71073
Crystal system, space group	Triclinic, P -1
Unit cell dimensions: (Å, °)	
a	8.0365(6)
b	18.6296(14)
c	20.1267(15)
α	66.46(2)
β	83.003(3)
γ	82.317(3)
V(Å3)	2723.0(4)
Z	1
Absorbtion coefficient (mm^{-1})	0.225
Dcalc (g/cm^3)	1.273
F(000)	1107
Crystal size (mm)	0.12x0.18x0.24
θ Range for data collection (°)	2.21–25.24°
	$-9 \leqslant h \leqslant 9$
Index ranges	$-22 \leqslant k \leqslant 22$
	$-24 \leqslant l \leqslant 24$
Reflections collected	72585
Independent reflections	6718
Max. and min. transmission	0.746 and 0.648
Final R indices [$I \geqslant 2\sigma(I)$]	$R1 = 0.0634$, $wR2 = 0.1455$
R indices (all data)	$R1 = 0.1123$, $wR2 = 0.1713$
Goodness-of-fit on F^2	1.038
Largest difference in peak and hole (e Å^{-3})	0.737/−0.407

References

1. G. Sheldrick, *Acta Crystallographica Section C* **2015**, *71*, 3-8.