Supporting Information for:

Synthesis, Solution-Processed Thin Film Transistors and Solid Solutions of Silylethynylated Diazatetracenes

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1. Synthesis and Reactions

General: The reagents and starting materials employed were commercially available and used without any further purification if not specified elsewhere. Anhydrous and oxygen-free THF was purified by an Advanced Technology Pure-Solv PS-MD-4 system. ^{1}H NMR (400 MHz) or ^{13}C NMR (100 MHz) spectra were recorded on a Brucker ADVANCE III spectrometer. Mass spectra were recorded on a Therno Finnigan MAT 95 XL spectrometer. X-ray crystallography data were collected on a Bruker AXS Kappa ApexII Duo Diffractometer. Melting points were measured using a Nikon Polarizing Microscope ECLIPSE 50i POL equipped with an INTEC HCS302 heating stage without calibration.
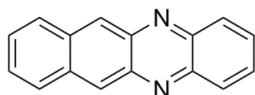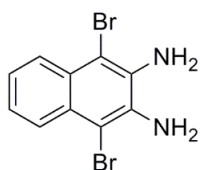

Benzo[b]phenazine was synthesized following the reported procedure.[1]
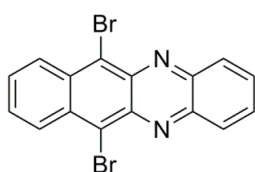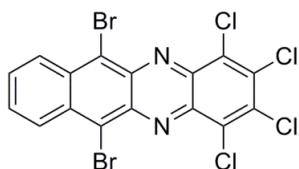

6, 11-dibromobenzo[b]phenazine

1.15g (5mmol) of benzo[b]phenazine was dissolved in 200 ml of chloroform at 0 °C. To the orange solution was added 0.52 ml (10 mmol) of Br_2 slowly. The resulting dark solution was allowed to warm to room temperature, and then stirred for 3 hours. The solution was then washed with an aqueous Na_2SO_3 solution, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by column chromatography using CH_2Cl_2/hexane (V/V=1:3) as the eluent yielding 6,11-dibromo-benzo[b]phenazine as dark purple solids (66%). Melting point: 254.6-255.8 °C. ^{1}H NMR (CDCl$_3$) δ (ppm): 8.75-8.73 (dd, 2H, J_1=3.2Hz, J_2=6.7Hz), 8.41-8.38 (dd, 2H, J_1=3.6Hz, J_2=6.7Hz), 7.91-7.89 (dd, 2H, J_1=3.2Hz, J_2=7.2Hz), 7.72-7.69 (dd, 2H, J_1=3.2Hz, J_2=7.2Hz). ^{13}C NMR (CDCl$_3$) δ (ppm): 145.0, 137.9, 133.7, 132.1, 130.0, 128.8, 128.6, 124.9. HRMS (EI$^+$) calcd. for $C_{16}H_8Br_2N_2$([M]$^+$): 387.9028, found: 387.9021.


1, 4-dibromonaphthalene-2, 3-diamine was synthesized following the reported procedure.[2]

1. S. Miao, S. M. Brombosz, P. v. R. Schleyer, J. I. Wu, S. Barlow, S. R. Marder, K. I. Hardcastle, U. H. F. Bunz, *J. Am. Chem. Soc.*, 2008, **130**, 7339–7344.
2. P. Wei, L. Duan, D. Zhang, J. Qiao, L. Wang, R. Wang, G. Dong, Y. Qiu, *J. Mater. Chem.*, 2008, **18**, 806–818.
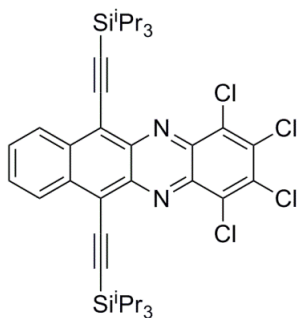
6, 11-dibromo-1, 2, 3, 4-tetrachlorobenzo[b]phenazine

A mixture of 316 mg (1 mmol, 1 eq) of 1,4-dibromonaphthalene-2,3-diamine and 246 mg (1 mmol,1 eq) of 3,4,5,6-tetrachloro-*o*-benzoquinone in 8 mL of chloroform, 8 mL of ethanol and 5 mL of acetic acid was refluxed overnight. The dark purple suspension was then cooled to room temperature and concentrated under reduced pressure. The resulting crude powder was suspended in ethanol (30 mL), filtered and washed with ethanol. 423 mg (80 %) of 6,11-dibromo-1,2,3,4-tetrachlorobenzo[b]phenazine was collected as dark purple powders. Melting point: 349-352 ℃. ^{1}H NMR (C$_2$D$_2$Cl$_4$, recorded at 383K) δ (ppm): 8.83-8.81(dd, 2H, J_1=3.2Hz, J_2=6.9Hz), 7.81-7.79 (dd, 2H, J_1=3.1Hz, J_2=6.9Hz).^{13}C NMR was not recorded due to poor solubility. HRMS (EI$^+$) calcd. for C$_{16}$H$_4$Cl$_4$Br$_2$N$_2$ ([M]$^+$): 525.7442, found: 525.7447.
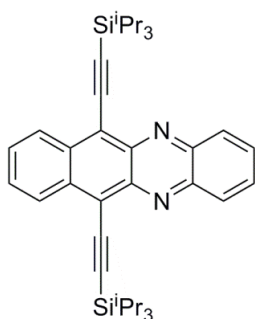
6, 11-bis((triisopropylsilyl)ethynyl)benzo[b]phenazine (1a)

Under an atmosphere of N$_2$, a mixture of 6, 11-dibromobenzo[b]phenazine (76.8 mg, 0.2 mmol), CuI (15 mg, 0.08 mmol), Pd(PPh$_3$)$_4$ (25 mg, 0.02 mmol) was dissolved in 5 ml of anhydrous and oxygen-free THF and 5 ml of diisopropylamine. Then (triisopropylsilyl) acetylene (0.18ml, 0.8mmol) was added to the solution. The reaction mixture was heated to reflux overnight under the same atmosphere of N$_2$. After cooled to room temperature, the mixture was filtered through a short pad of celite, and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography using CH$_2$Cl$_2$/hexane (V/V=1:4) as the eluent, yielding 104 mg (88%) of 6,11-bis ((triisopropylsilyl)ethynyl) benzo[b]phenazine (**1a**) as red solids. Melting point: 185-186 ℃. ^{1}H NMR (CDCl$_3$) δ (ppm): 8.75-8.73 (dd, 2H, J_1=3.2Hz, J_2=6.8Hz), 8.23-8.21 (dd, 2H, J_1= 3.4Hz, J_2= 6.8Hz), 7.82-7.80 (dd, 2H, J_1= 3.2Hz, J_2= 6.8Hz), 7.66-7.64 (dd, 2H, J_1= 3.1Hz, J_2= 6.8Hz), 1.33-1.32 (m, 42H, broad). ^{13}C NMR (CDCl$_3$) δ (ppm): 144.8, 141.5, 135.4, 131.2, 130.5, 128.1, 127.8, 121.0, 108.3, 103.1, 19.1, 11.8. HRMS (ESI$^+$) calcd. for C$_{38}$H$_{50}$N$_2$Si$_2$ ([M]$^+$): 590.3513, found: 590.3510.

1, 2, 3, 4-tetrachloro-6, 11-bis ((triisopropylsilyl)ethynyl)benzo[b]phenazine (1b)

Under an atmosphere of N_2, a mixture of 6, 11-dibromo-1, 2, 3, 4- tetrachlorobenzo [b]phenazine (356 mg, 0.68 mmol), CuI (12.9 mg, 0.068 mmol), Pd(PPh$_3$)$_4$ (42.5 mg, 0.034 mmol) was dissolved in 5 ml of oxygen-free THF and 5 ml of diisopropylamine. Then 0.37 ml (1.7 mmol, 2.5 eq) of (triisopropylsilyl) acetylene was added to the solution. The reaction mixture was heated to reflux overnight under the atmosphere of N_2. After cooled to room temperature, the mixture was filtered through a short pad of celite, and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography using CH$_2$Cl$_2$/hexane (V/V=1:6) as the eluent, yielding 397 mg (80%) of 1,2,3,4-tetrachloro-6,11-bis((triisopropylsilyl)ethynyl)benzo[b]phenazine (**1b**) as dark blue solids. Melting point: 179.5 °C (measured by differential scanning calorimetry). ^{1}H-NMR (CDCl$_3$) δ(ppm): 8.79-8.77 (dd, 2H, J_1= 3.2 Hz, J_2= 6.8 Hz), 7.73-7.70 (dd, 2H, J_1= 3.2 Hz, J_2= 6.8 Hz), 1.29-1.27 (m, 42H, broad). ^{13}C NMR (CDCl$_3$) δ (ppm): 140.7, 139.4, 136.7, 134.7, 132.4, 129.2, 128.0, 121.5, 109.8, 102.0, 19.1, 11.7. HRMS (ESI[+]) cald. for C$_{38}$H$_{47}$Cl$_4$N$_2$Si$_2$ ([M+H][+]): 729.2004, found: 729.1999.

Note: It was reported that **1b** melted with decomposition at 179 °C.[3] However, as confirmed by ^{1}H NMR spectrum from a solution of the melt, **1b** does not change when melting at 179.5 °C although it shows an unusually wide peak for melting in the DSC heating trace.
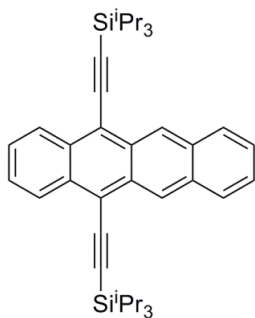

5,12-bis((triisopropylsilyl)ethynyl)tetracene (**2**) was synthesized following the reported procedure.[4]

3. A. L. Appleton, S. M. Brombosz, S. Barlow, J. S. Sears, J. L. Brédas, S. R. Marder, U. H. F. Bunz, *Nat. Commun.*, 2010, **1**, Article 91.
4. S. A. Odom, S. R. Parkin, J. E. Anthony, *Org. Lett*., 2003, **5**, 4245–4248.

2. Characterization of 1a, 1b and 2

(1) UV-vis Absorption Spectroscopy

The solution UV-vis spectra were recorded on a Varian CARY 1E UV-vis spectrophotometer.
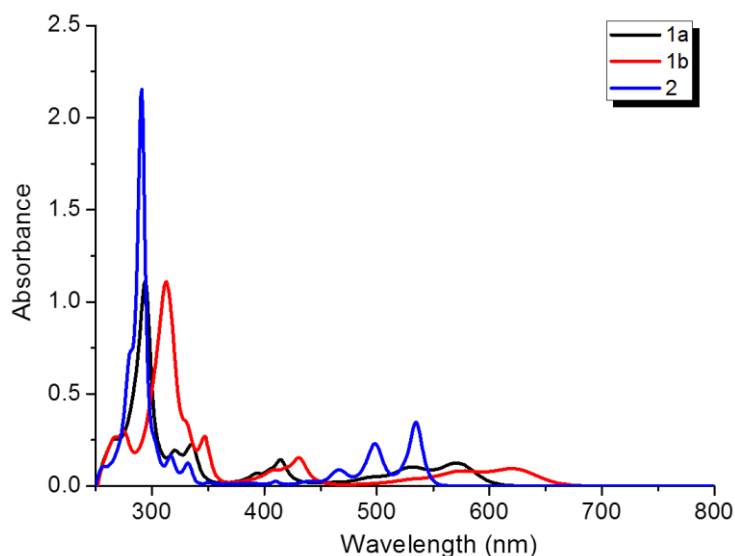

Figure S1 UV-vis spetra of **1a**, **1b** and **2** from solutions in dichloromethane (1×10^{-5} M).
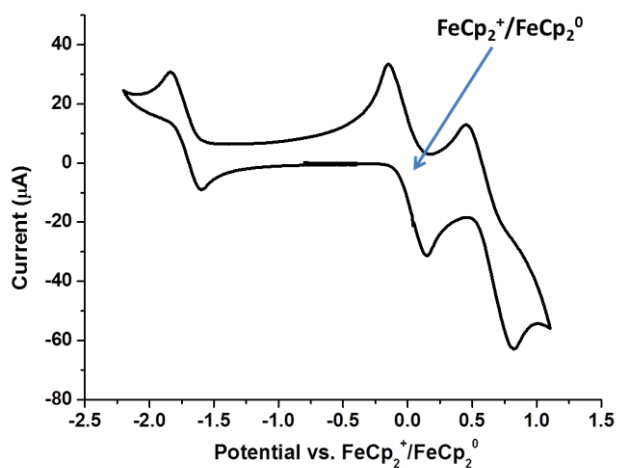
(2) Cyclic Voltammetry

The cyclic voltammetry was performed in a solution of anhydrous CH_2Cl_2 with 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) as supporting electrolyte, at a scan rate of 50mV/s. A platinum bead was used as a working electrode, a platinum wire was used as an auxiliary electrode, and a silver wire was used as a pseudo-reference. Ferrocene/ferrocenium was used as an internal standard, and potentials were recorded versus $FeCp_2^+/FeCp_2^0$.
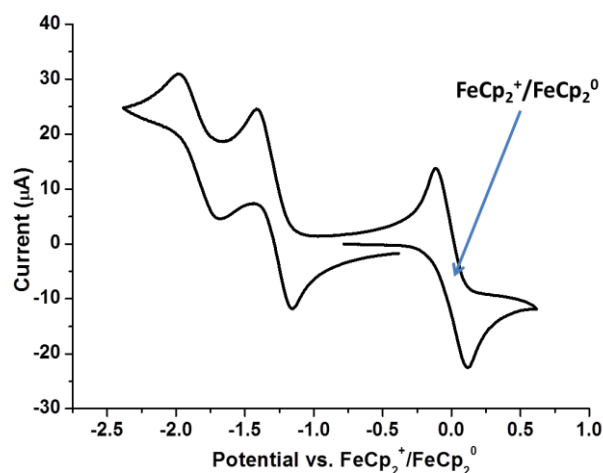
Figure S2 Cyclic voltammogram of **1a** recorded in CH_2Cl_2 with $FeCp_2^+/FeCp_2^0$ as the internal standard.
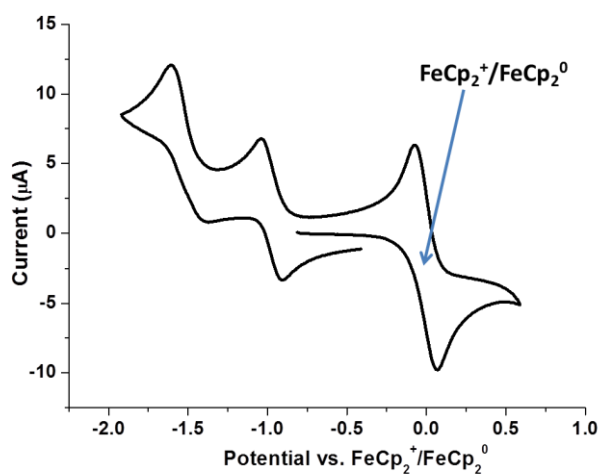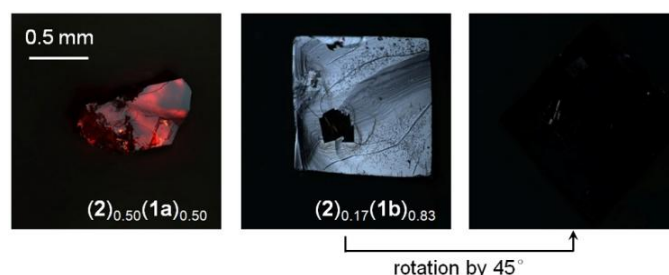
Figure S3 Cyclic voltammogram of **1b** recorded in CH_2Cl_2 with $FeCp_2^+/FeCp_2^0$ as the internal standard.
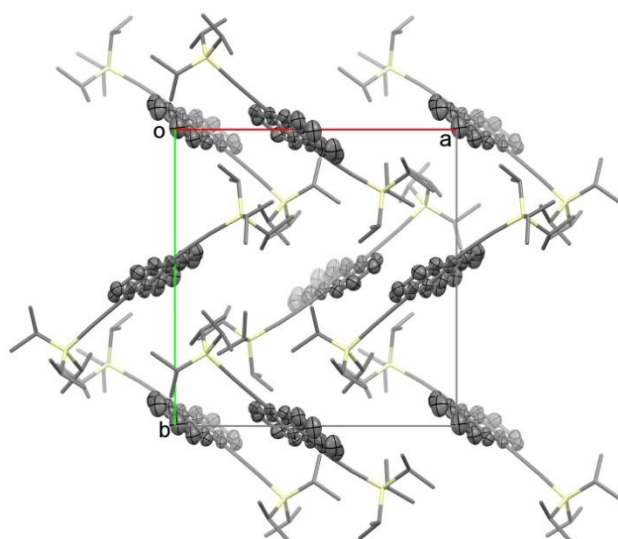

Figure S4 Cyclic voltammogram of **2** recorded in CH_2Cl_2 with $FeCp_2^+/FeCp_2^0$ as the internal standard.

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3. Characterization of the solid solutions

Figure S5 Reflection polarized-light micrographs of single co-crystals

Crystallography

Figure S6 Molecular packing of **2** in a unit cell. (Atoms in the tetracyclic backbone are shown as ellipsoids at 50% probability level and silylethynyl substituents are shown as capped sticks, hydrogen atoms are removed for clarification.)

Table S1 Summary of crystallographic data of **1a**, **1b, 2** and solid solutions of $(2)_x(1a)_{1-x}$ and $(2)_x(1b)_{1-x}$.

|	**1a** [1] only	**1b** only	**2** only	$(2)_{0.61}(1a)_{0.39}$	$(2)_{0.19}(1b)_{0.81}$	$(2)_{0.14}(1b)_{0.86}$
Space Group	P-1	C 2/c	P 2_1 2_1 2_1	P 2_1 2_1 2_1	C 2/c	C 2/c
Unit Cell Lengths (Å)	a = 7.3968 b = 13.8925 c = 18.4277	a = 35.551 b = 15.1706 c = 14.9907	a = 14.4346 b = 15.1821 c = 17.0101	a = 14.4307 b = 15.1331 c = 16.975	a = 35.4482 b = 15.1828 c = 14.9575	a = 35.3907 b = 15.1394 c = 14.9478
Unit Cell Angles (°)	α= 112.065 β = 95.624 γ = 90.53	α = 90.00 β= 104.265 γ = 90.00	α = 90.00 β = 90.00 γ = 90.00	α = 90.00 β = 90.00 γ = 90.00	α = 90.00 β = 103.908 γ = 90.00	α = 90.00 β = 104.143 γ = 90.00
Volume per molecule (Å^3)	1744.3	7835.65	3727.72	3707.02	7814.16	7766.18
R-factor	0.1484	0.0806	0.0580	0.1491	0.0751	0.0603
Packing Motif	2D π-stacking	2D π-stacking	herringbone	herringbone	2D π-stacking	2D π-stacking

X-ray diffraction (XRD): XRD data were recorded on a SmartLab X-Ray Refractometer from powders, which were prepared from solution-grown crystals by grinding.
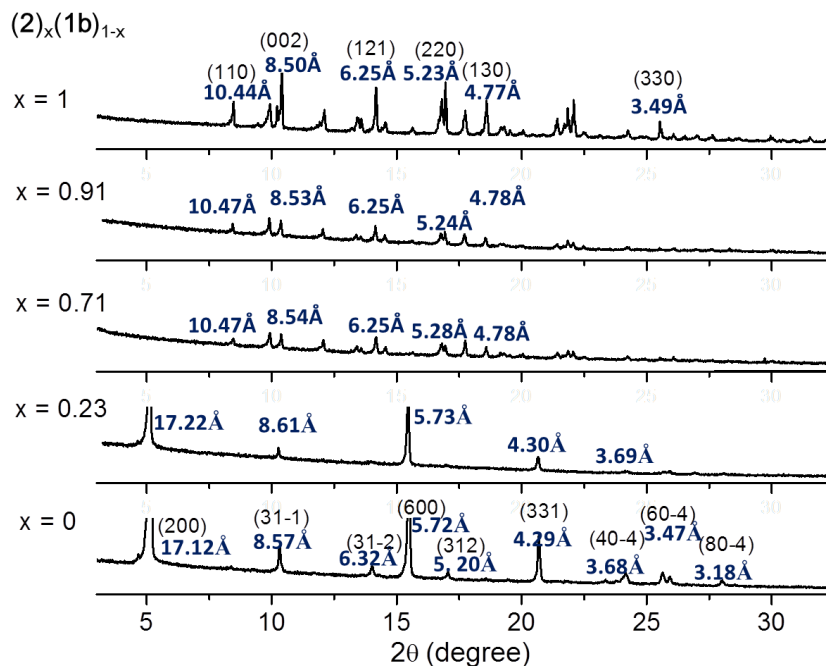
Figure S7 X-ray diffractions from ground powders of **2**, **1b** and the solid solutions $(2)_x(1b)_{1-x}$.
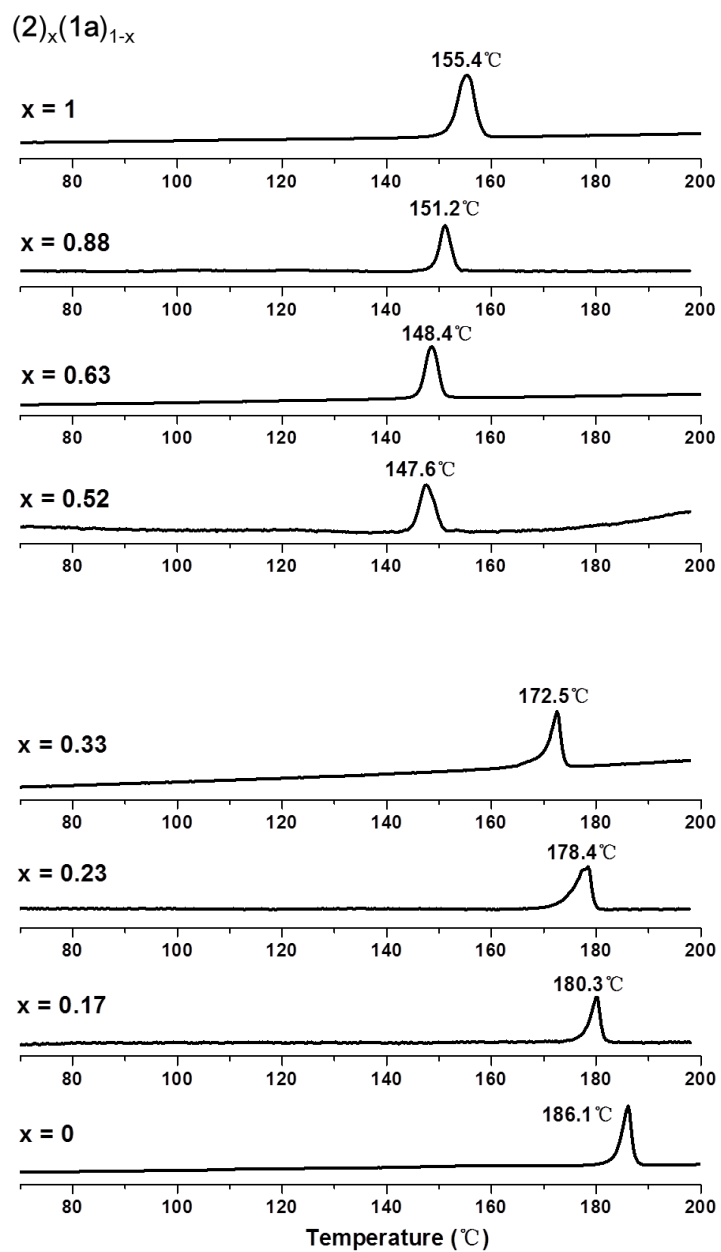
Differential scanning calorimetry (DSC):
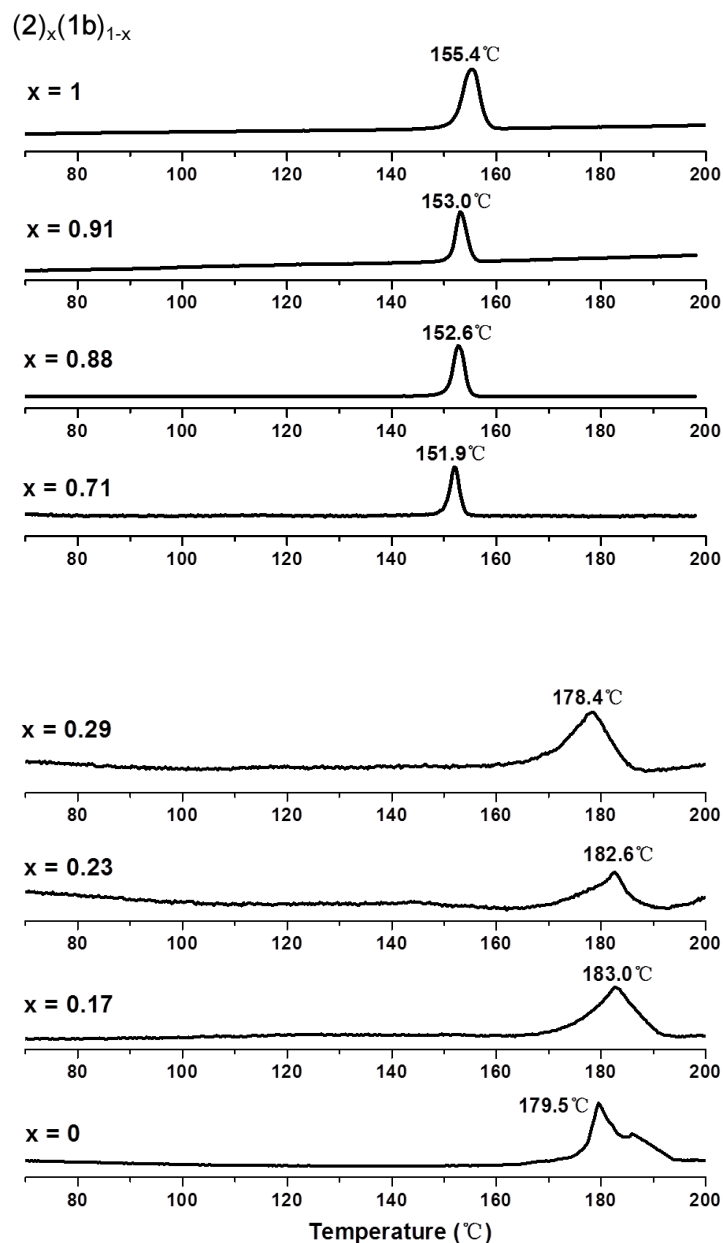DSC data were recorded on a PERKIN ELMER DSC 6 equipment under a N_2 flow.
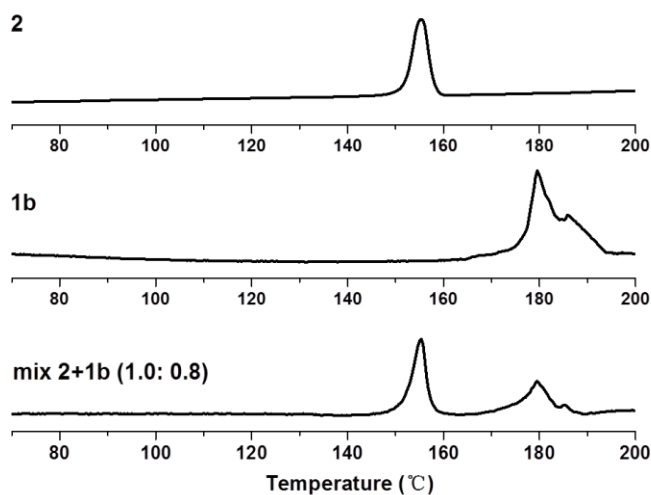
Figure S8 DSC thermograms (heating cycle) showing **2**, **1b** and a mixture of **2** with **1b.**

Figure S9 DSC thermograms (heating cycle) of **2**, **1a** and the solid solutions $(2)_x(1a)_{1-x}$ with the melting point marked for each sample.

Figure S10 DSC thermograms (heating cycle) showing **2**, **1b** and the solid solutions $(\mathbf{2})_x(\mathbf{1b})_{1-x}$ with the melting point marked for each sample.

4. Fabrication and characterization of solution-processed thin films and transistors

(1) Thin film formation and fabrication of OTFTs

A thin layer of AlO_y/TiO_x was spin-cast onto a highly doped silicon wafer following the reported solution-based procedure to form dielectrics.[5] To form SAMs of the phosphonic acids **3**, the AlO_y/TiO_x-coated Si wafer was soaked in a solution of **3** in isopropanol (0.3 mM) at room temperature for 12 hours, rinsed with isopropanol subsequently and dried with a flow

5. Y. Su, C. Wang, W. Xie, F. Xie, J. Chen, N. Zhao, J. Xu, *ACS Appl. Mater. Interfaces* 2011, **3**, 4662–4667.

of nitrogen.[6] Thin films of pristine **1a, 1b, 2** and the solid solutions of $(2)_x(1a)_{1-x}$, $(2)_x(1b)_{1-x}$ were formed by immersing the silicon substrate into a 1 mg/mL solution in dichloromethane and acetone (1:1 by volume) and then pulling it up with a constant speed of 10μm/s. A layer of gold was subsequently deposited by thermal evaporation under vacuum onto the films through a shadow mask to form top-contact source and drain electrodes. The resulting devices had highly doped silicon as the gate electrode and the SAM-modified AlO_y/TiO_x as dielectrics. The **3**-modified AlO_y/TiO_x has a capacitance per unit area (C_i) of 250 ± 18 nF/cm^2 as measured at a frequency of 100 Hz from a metal-insulator-metal structure, which had vacuum-deposited gold (0.2 mm $\times$ 1 mm) as the top electrode and a highly doped silicon substrate as the bottom electrode.[6]

(2) Characterization of the thin films deposited from pristine 1a, 1b and 2

Reflected polarized-light micrographs were obtained using a Nikon 50IPOL microscope.
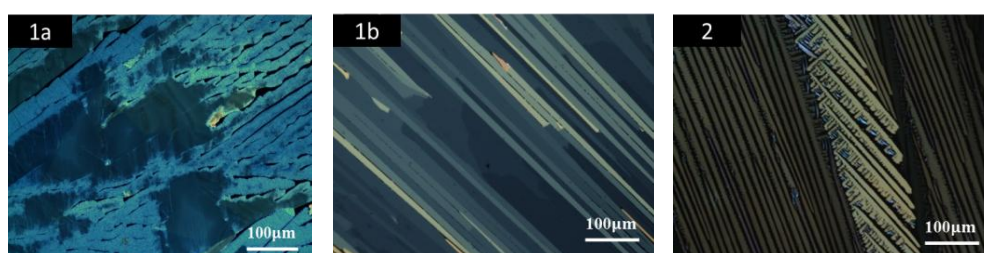
Figure S11 Reflected polarized-light micrographs for the dip-coated films of **1a**, **1b**, and **2** from the solutions in dichloromethane and acetone (1:1) on **3**-modified AlO_y/TiO_x dielectrics.
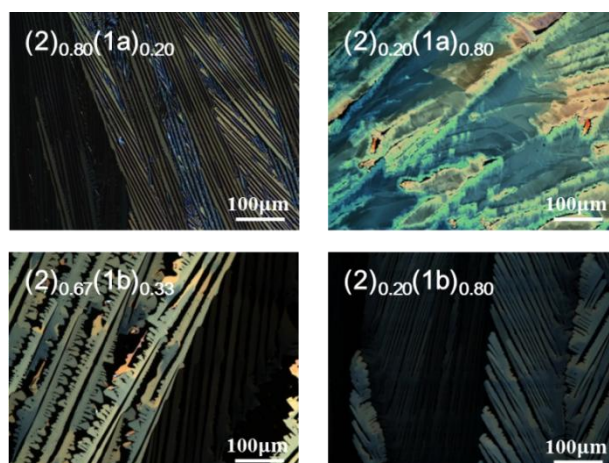
X-ray diffractions from thin films were recorded on a SmartLab X-Ray Refractometer.
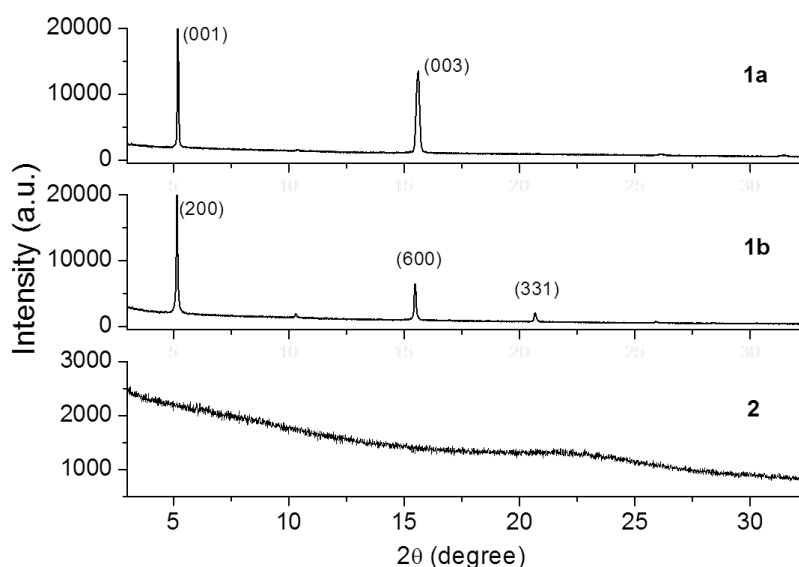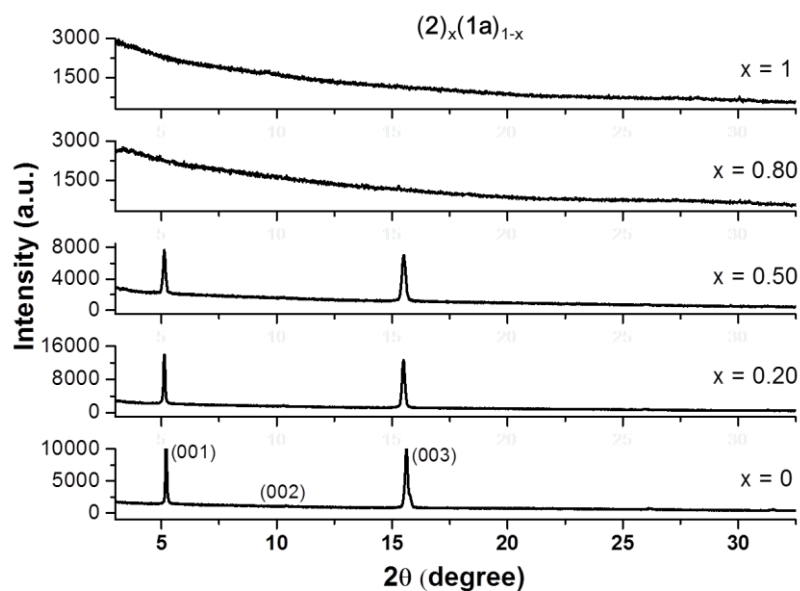

Figure S12 X-ray diffractions of dip-coated films of **1a**, **1b** and **2** on the **3**-modified AlO_y/TiO_x

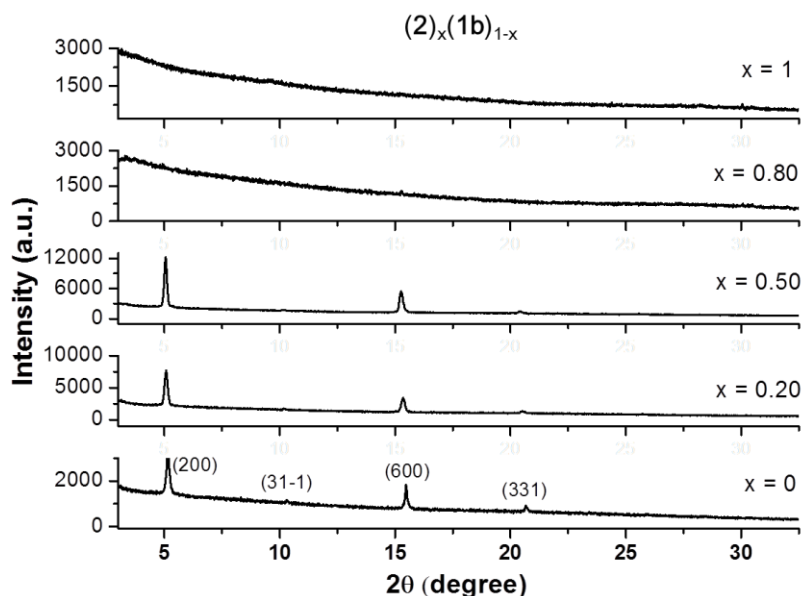6. D. Liu, X. Xu, Y. Su, Z. He, J. Xu, Q. Miao, *Angew. Chem. Int. Ed.*, 2013, **52**, 6222–6227.

(3) Characterization of the thin films deposited from mixed solutions

Figure S13 Reflected polarized-light micrographs for typical dip-coated films of $(2)_x(1a)_{1-x}$, $(2)_x(1b)_{1-x}$ on the **3**-modified AlO_y/TiO_x.

Figure S14 X-ray diffraction patterns of dip-coated films of **2**, **1a** and $(2)_x(1a)_{1-x}$ on the **3**-modified AlO_y/TiO_x.

**Figure S15** X-ray diffraction patterns of dip-coated films of **2**, **1b** and $(2)_x(1b)_{1-x}$ on the **3**-modified AlO_y/TiO_x.

(4) Electrical Characterization of Thin Film Transistors:

The current-voltage measurement was carried out on a JANIS ST-500-20-4TX probe station with a Keithley 4200 Semiconductor Characterization System at room temperature with a background pressure of 1.0×10^{-5} torr or lower if not specified elsewhere.

The field effect mobility of these OTFTs in the saturation regime were extracted from transfer I-V curves using the equation: $I_{DS} = (\mu W C_i / 2L)(V_G - V_T)^2$, where I_{DS} is the drain current, μ is field effect mobility, C_i (250 nF/cm^2) is the capacitance per unit area for the **3**-modified AlO_y/TiO_x, W is the channel width, L is the channel length, and V_G and V_T are the gate and threshold voltage, respectively.
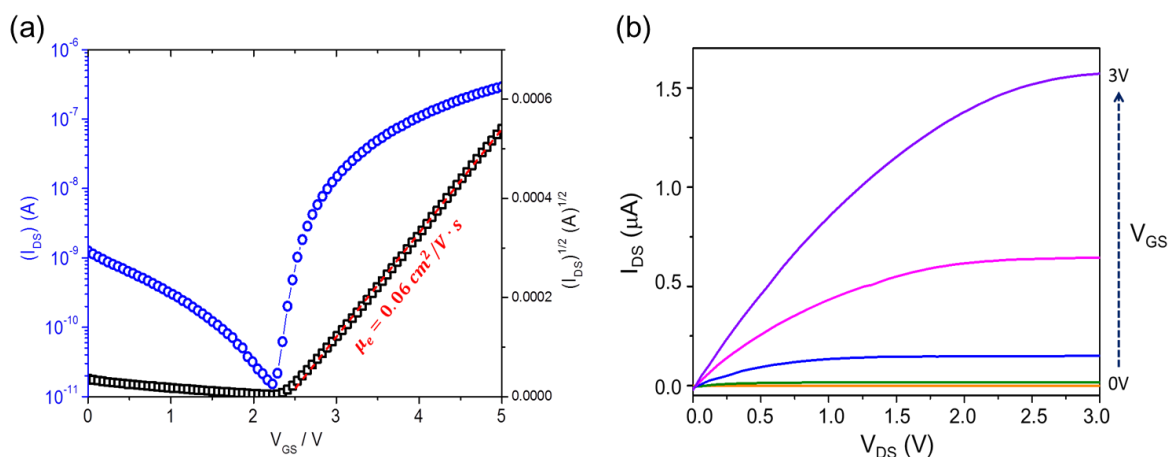
Figure S16 (a) Drain current (I_{DS}) versus gate voltage (V_G) with drain voltage (V_{DS}) at 5 V for a typical dip-coated OTFT of **1a** with an active channel of W = 1 mm and L = 150 μm as measured under vacuum showing an electron mobility of 0.06 cm^2/Vs. (b) Output I-V curves of a typical dip-coated OTFT of **1b** with an active channel of W = 1 mm and L = 100 μm as measured under vacuum.

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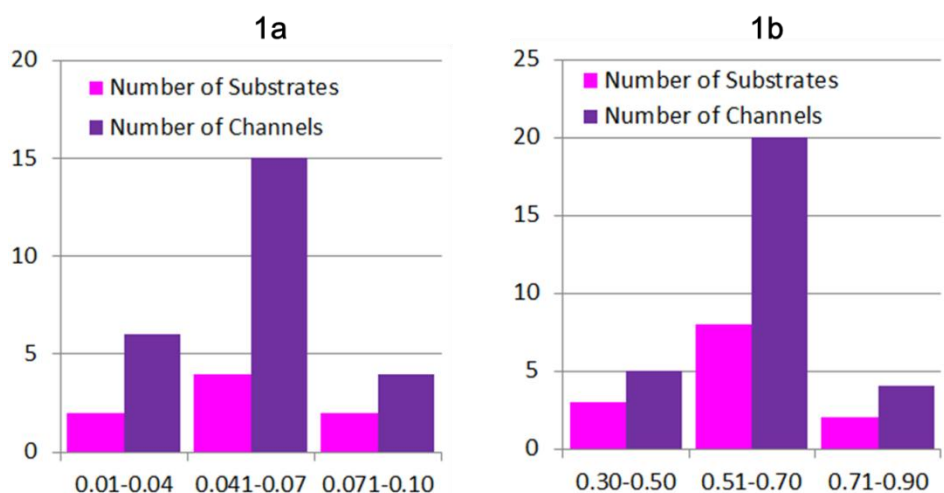
Figure S17 The statistics of measured field-effect mobilities for solution-processed OTFTs of **1a** and **1b**.

5. Photoluminescence

Photoluminescence spectra were recorded on a FLS920P fluorescence spectrometer (Edinburgh Instrument) equipped with a R928P photomultiplier (Hamamatsu) with a 450 W xenon arc lamp as the excitation source. The absolute fluorescence quantum yields were determined by standard procedure using the same fluorescence spectrometer equipped with an integrating sphere with its inner face coated with BENFLEC® (Edinburgh Instrument). Spectral correction curves were provided by Edinburgh Instrument. All optical measurements were performed at room temperature under ambient conditions. The fluorescence quantum yields (Φ) were determined by a calibrated integrating sphere system.
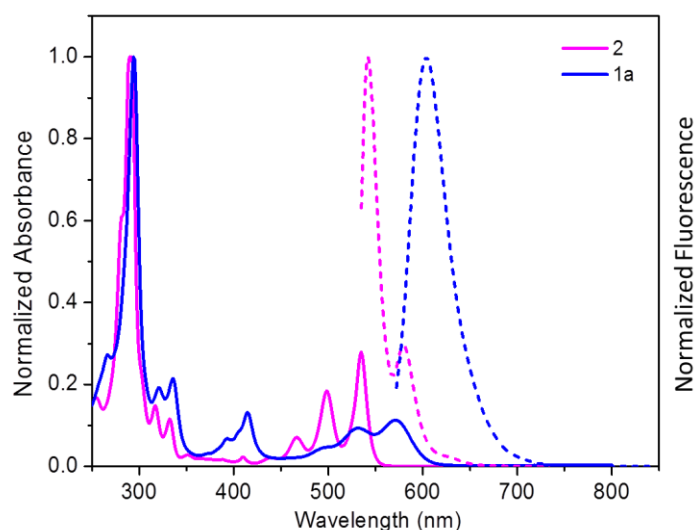
Figure S18 Normalized UV-vis absorption (solid line) and fluorescence emission (dashed line) spectra of **2** and **1a** respectively from solutions in dichloromethane (1×10^{-5} M).
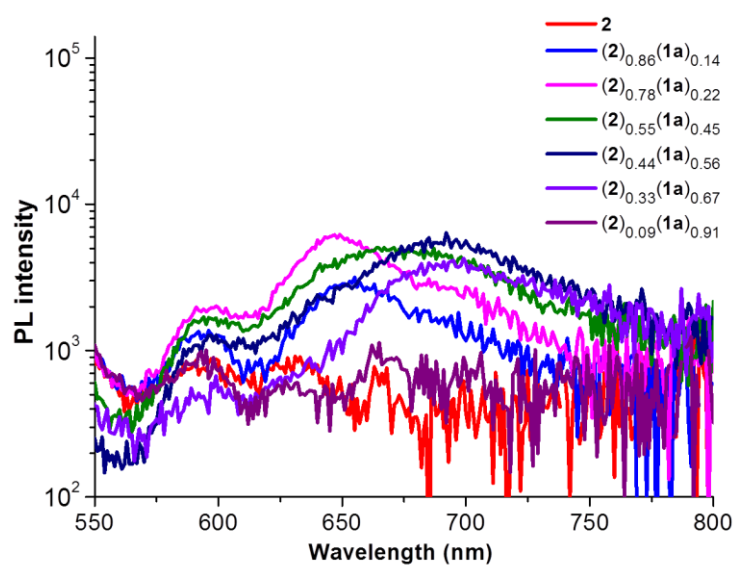
Figure S19 Photoluminescence spectra of **2** and the solid solutions $(\mathbf{2})_x(\mathbf{1a})_{1-x}$, excited at the maximum excitation of **2**.

6. NMR Spectra

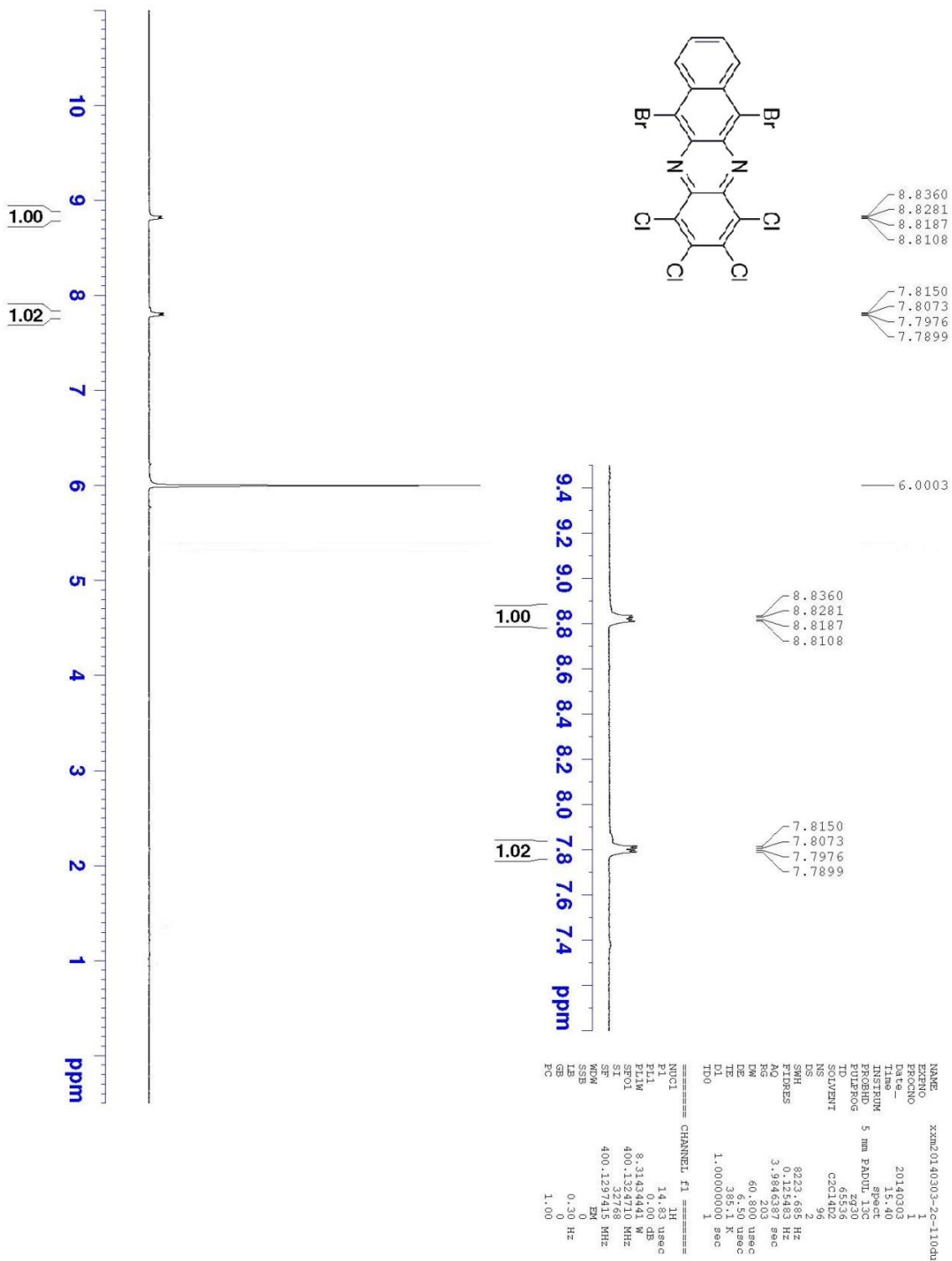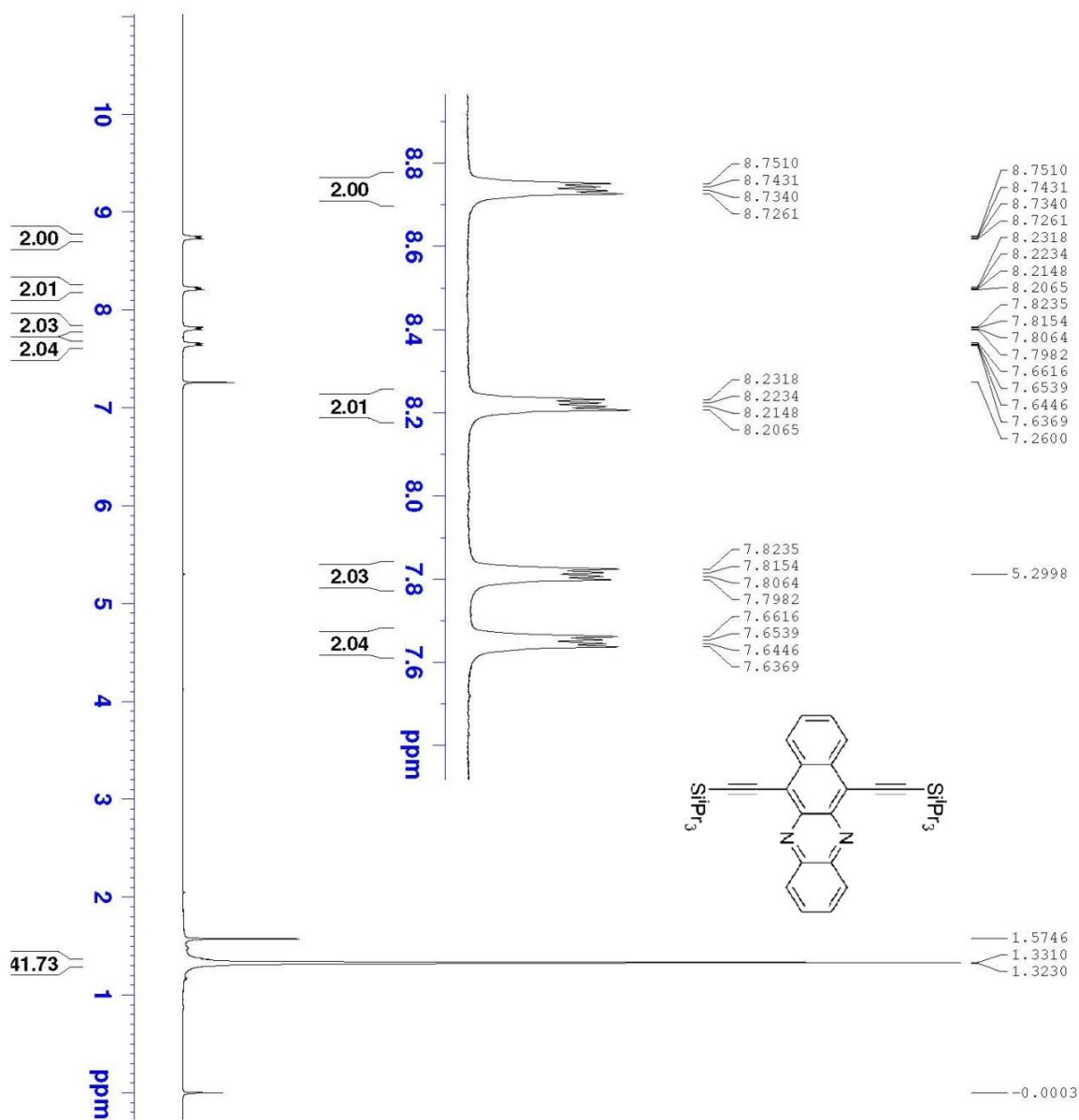^{1}H NMR spectrum of 6, 11-dibromobenzo[b]phenazine in CDCl$_3$

^{13}C NMR spectrum of 6, 11-dibromobenzo[b]phenazine in CDCl$_3$

17

8.8360
8.8281
8.8187
8.8108

7.8150
7.8073
7.7976
7.7899

6.0003

1.00

1.02

9.4 9.2 9.0 8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 ppm

8.8360
8.8281
8.8187
8.8108

7.8150
7.8073
7.7976
7.7899

10 9 8 7 6 5 4 3 2 1 ppm

^{1}H NMR spectrum (C$_2$D$_2$Cl$_4$-d_2) of 6, 11-dibromo-1, 2, 3, 4-tetrachlorobenzo[b]phenazine recorded at 383K

^{1}H NMR spectrum of **1a**

^{13}C NMR spectrum of **1a**

^{1}H NMR spectrum of **1b**

Peak labels (ppm):
- 140.6566
- 139.4144
- 136.7157
- 134.7401
- 132.4060
- 129.1696
- 127.9637
- 121.4932
- 109.8186
- 102.0390
- 77.4762
- 77.1593
- 76.8414
- 19.0800
- 11.6990

^{13}C NMR spectrum of **1b**

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