Electronic Supplementary Information for:

Vapochromic and Semiconducting Solids of a Bifunctional Hydrocarbon

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1. Crystal structure of 1

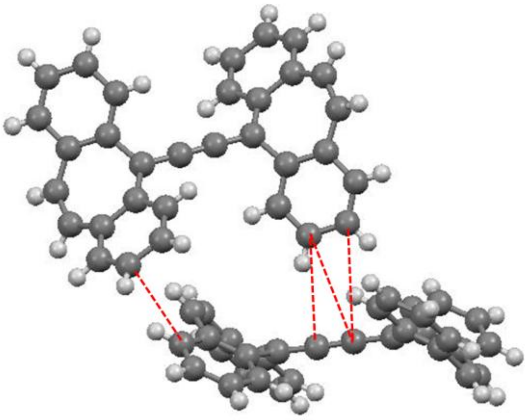
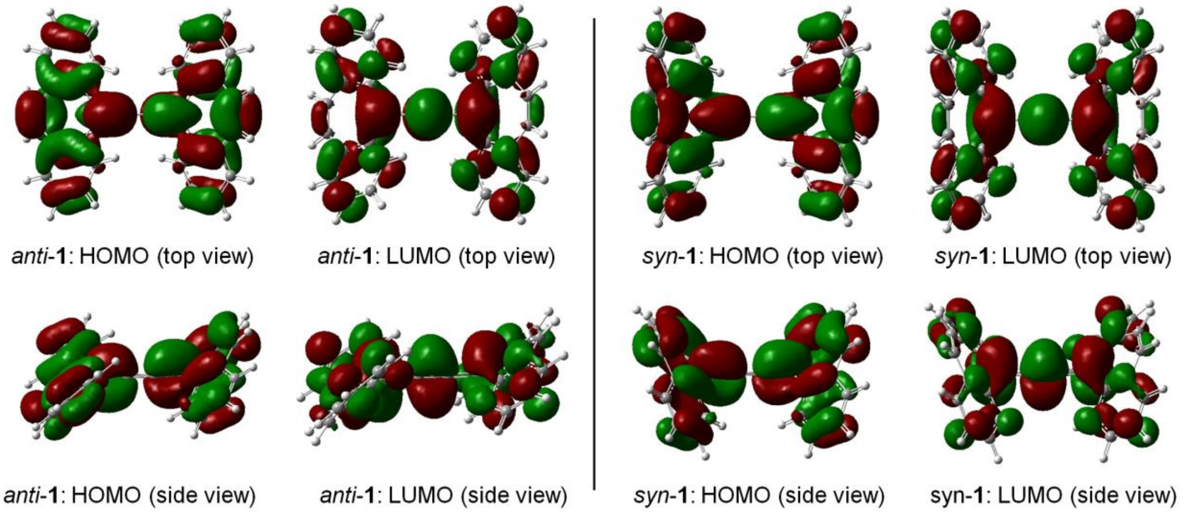


Figure S-1 Two nearest neighbouring molecules of *anti*-**1** in the single crystal of 3(*anti*-**1**) • *m*-xylene showing short C-C contacts within the range of 3.59 to 3.86 Å

2. Electronic Structure of 1

Density functional rheory (DFT) calculation: The frontier molecular orbitals of *syn*-**1** and *anti*-**1** were calculated using the hybrid density functional method B3LYP with a 6-311G** basis set.



anti-**1**: HOMO (top view) *anti*-**1**: LUMO (top view) *syn*-**1**: HOMO (top view) *syn*-**1**: LUMO (top view)

anti-**1**: HOMO (side view) *anti*-**1**: LUMO (side view) *syn*-**1**: HOMO (side view) syn-**1**: LUMO (side view)

Figure S-2. Calculated HOMOs and LUMOs of *syn*-**1** and *anti*-**1** showing the distribution of the positive and negative LCAO (linear combination of atomic orbitals) coefficients in red and green, respectively

Experimental methods: 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^{-1}. 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 psedo-reference. Ferrocene/ferrocenium was used as an internal standard, and potentials were recorded versus $FeCp_2^+/FeCp_2^0$. UV-vis spectra were recorded with a Varian CARY 1E UV-vis spectrophotometer.

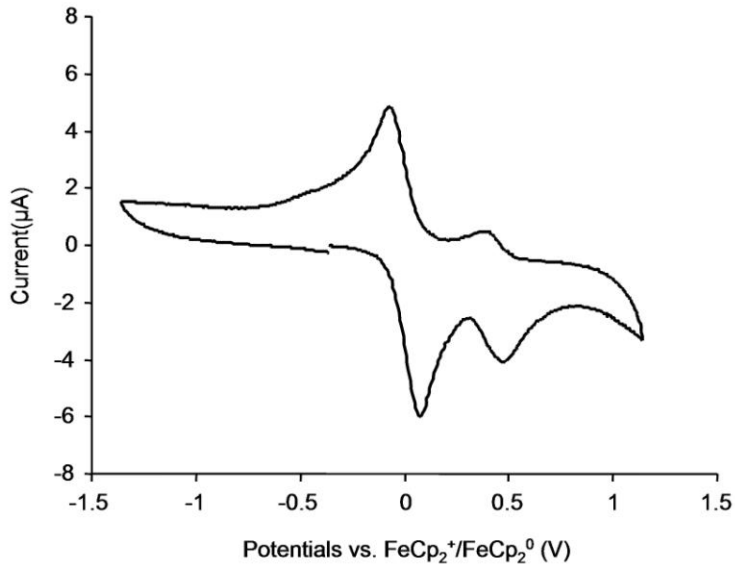


Figure S-3. Cyclic voltammogram of **1**

Table S-1. Oxidation potentials[a], absorption edge[b] and HOMO energy levels of **1**

E_{ox} vs. Fc^+/Fc	Absorption Edge	Optical Gap_{exp}	$HOMO_{exp}$[c]	$HOMO_{cal}$[d]	$LUMO_{cal}$[d]
0.42 V	506 nm	2.45 eV	−5.22 eV	*anti*: −5.19 eV *syn*: −5.24 eV	*anti*: −2.16 eV *syn*: −2.12 eV

[a] Cyclic voltammetry was performed in a solution of anhydrous CH_2Cl_2 with 0.1M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) as supporting electrolyte and at a scan rate of 50mV s^{-1}. [b] The UV-vis absorption spectra were recorded from solutions in CH_2Cl_2 of 5×10^{-5}mol/L. [c] Estimated from $E_{HOMO} = -4.80 - E_{ox}$ (eV). [d] Calculated using the hybrid density functional method B3LYP with a 6-31+1G** basis set.

3. Experimental details for vapochromism of 1

Vapochromic experiment: The red crystalline powders of *syn*-**1** used for vapochromism experiments were prepared by grinding guest-free crystals of *syn*-**1**, which were freshly recrystallized from ethyl acetate. A small vial containing red powders of *syn*-**1** was placed in a sealed container, which was filled with 0.5 mL of liquid organic compounds as shown in Figure S-6a at room temperature.

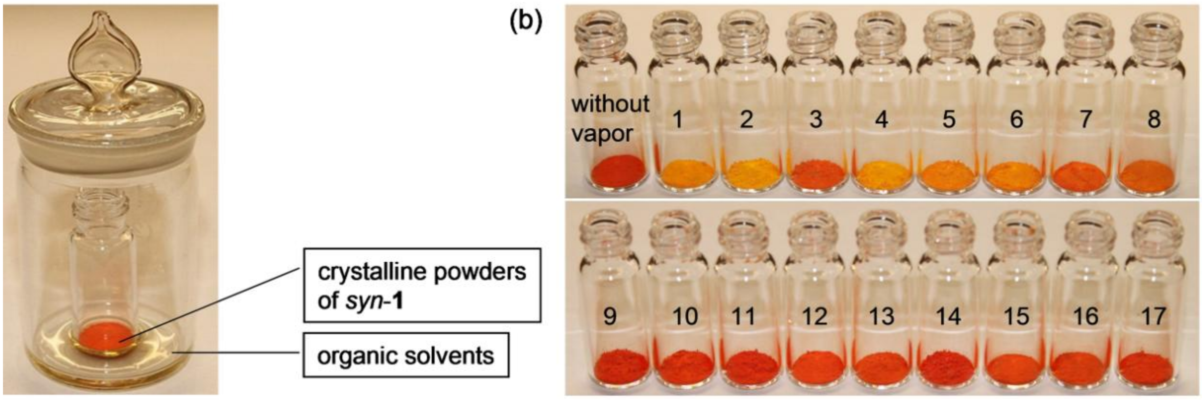


Figure S-4. (a) The experimental set-up for the vapochromic behaviors of cumulene **1**; (b) graphs for crystalline powders of *syn*-**1** after being exposed to varied organic vapors for 120 hours (1: toluene, 2: *m*-xylene, 3: *p*-xylene, 4: *o*-bromotoluene, 5: bromobenzene, 6: *o*-dibromobenzene, 7: benzene, 8: mesitylene, 9: ethyl acetate, 10: hexane, 11: THF, 12: acetone, 13: ethanol, 14: chloroform, 15: acetic acid, 16: DMSO, 17: DMF)

^{1}H-NMR and Powder X-ray diffraction (XRD) analysis for vapochromic behavior of cumulene 1

Vapochromic behavior was monitored by powder X-ray diffraction with powder samples exposed to *m*-xylene for certain periods of time. Powder X-ray diffractions were recorded on a SmartLab X-Ray Refractometer.

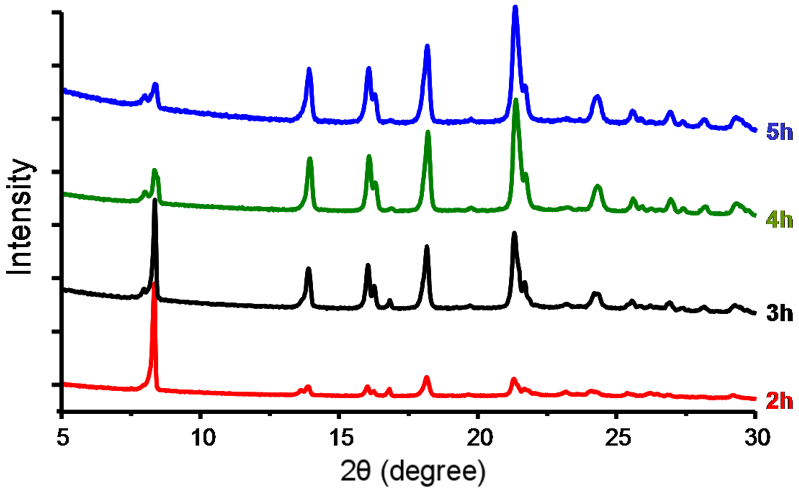
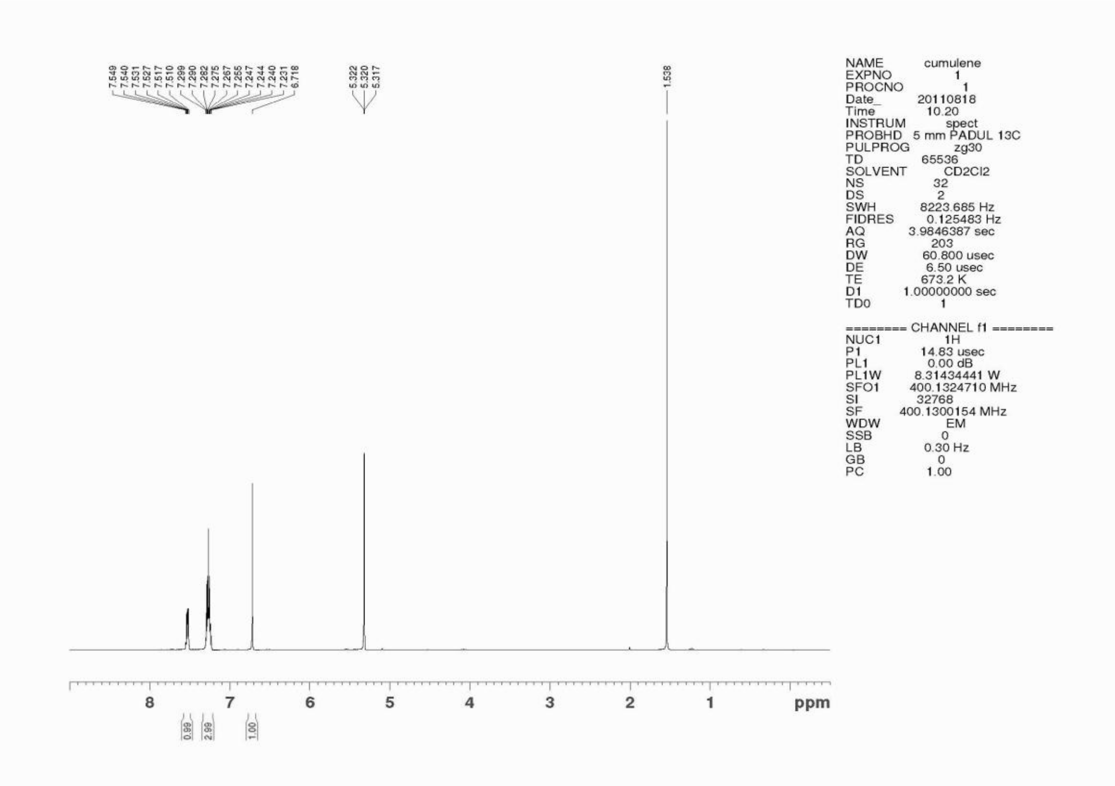


Figure S-5. X-Ray diffractions from *syn*-**1** powders after being exposed to *m*-xylene for 2, 3 4, and 5 hours

After being exposed to various organic vapors for 6 hours or 120 hours, the resulting powders were completely dried under vacuum and dissolved in CD_2Cl_2 for ^1H-NMR analysis. The ^1H-NMR spectra were recorded on a Bruker AVANCE III 400MHz spectrometer.



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PROCNO            1
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Time          10.20
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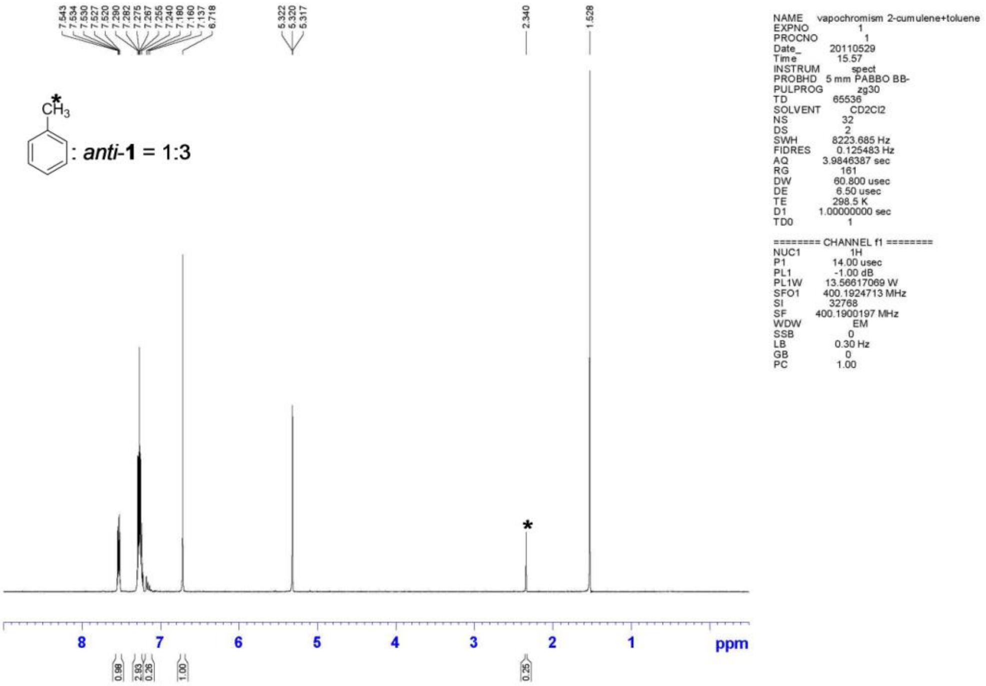
PULPROG        zg30
TD            65536
SOLVENT      CD2Cl2
NS               32
DS                2
SWH        8223.685 Hz
FIDRES     0.125483 Hz
AQ        3.9846387 sec
RG              203
DW           60.800 usec
DE             6.50 usec
TE            673.2 K
D1       1.00000000 sec
TD0               1

======== CHANNEL f1 ========
NUC1             1H
P1            14.83 usec
PL1            0.00 dB
PL1W     8.31434441 W
SFO1    400.1324710 MHz
SI            32768
SF      400.1300154 MHz
WDW              EM
SSB               0
LB             0.30 Hz
GB                0
PC             1.00
```

Figure S-6. ^1H NMR spectrum of **1** in CD_2Cl_2 (prepared from the red crystals of *syn*-**1**)



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PROCNO            1
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PULPROG        zg30
TD            65536
SOLVENT      CD2Cl2
NS               32
DS                2
SWH        8223.685 Hz
FIDRES     0.125483 Hz
AQ        3.9846387 sec
RG              161
DW           60.800 usec
DE             6.50 usec
TE            298.5 K
D1       1.00000000 sec
TD0               1

======== CHANNEL f1 ========
NUC1             1H
P1            14.00 usec
PL1           -1.00 dB
PL1W    13.56617069 W
SFO1    400.1924713 MHz
SI            32768
SF      400.1900197 MHz
WDW              EM
SSB               0
LB             0.30 Hz
GB                0
PC             1.00
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Figure S-7. ^1H NMR spectrum from sample 1 of the vapochromic experiment (powders of *syn*-**1** that were exposed to a saturated vapor of **toluene** for **6 hours**) in CD_2Cl_2

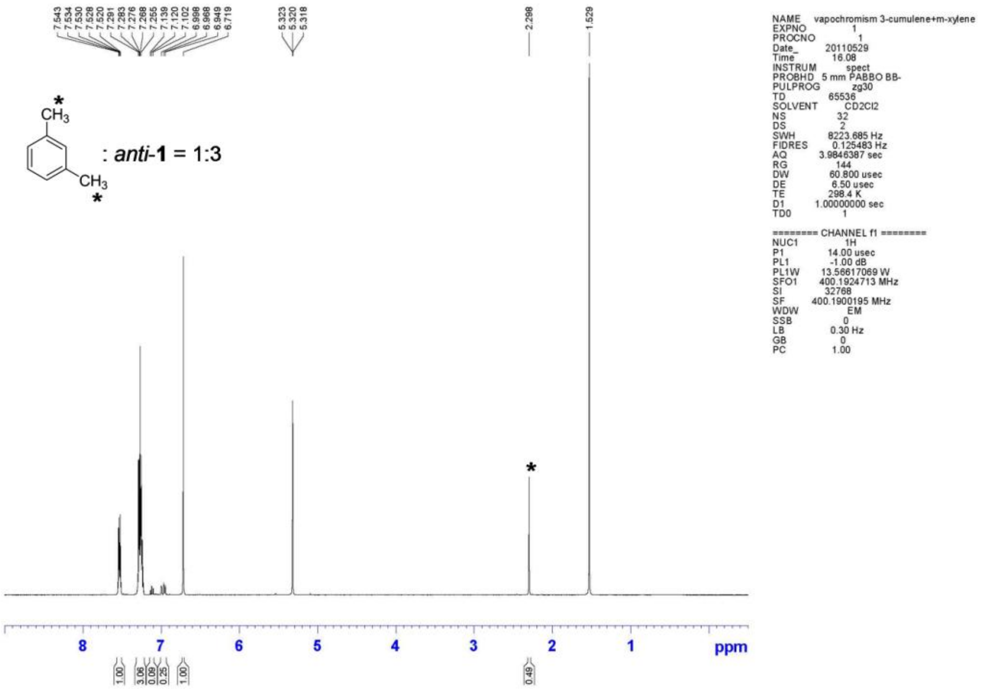

Figure S-8. ^{1}H NMR spectrum from sample 2 of the vapochromic experiment (powders of *syn*-**1** that were exposed to a saturated vapor of ***m*-xylene** for **6 hours**) in CD_2Cl_2

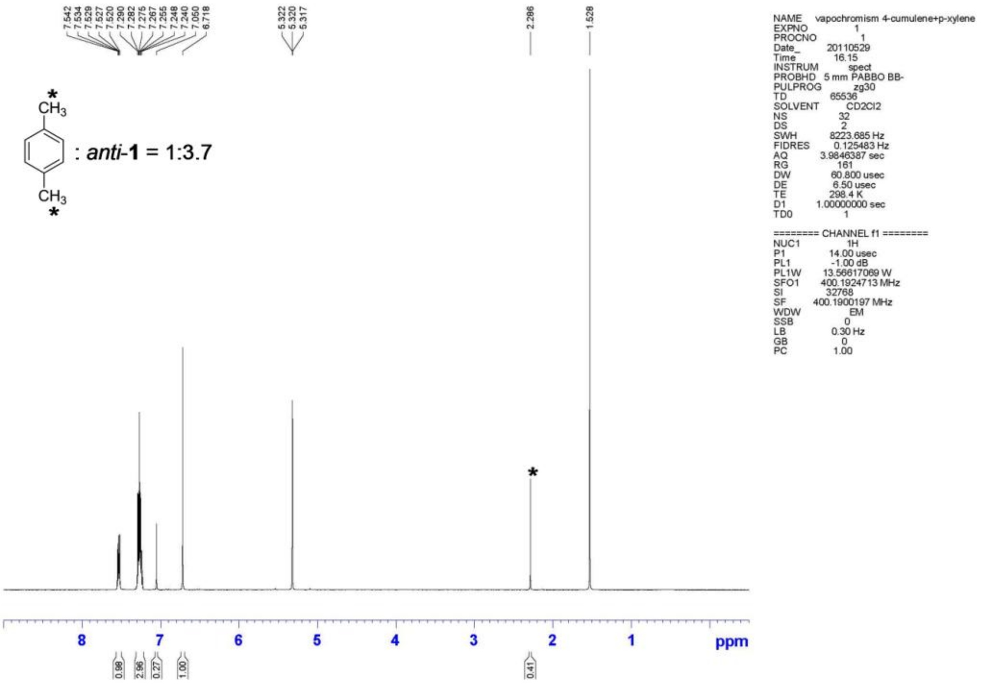

Figure S-9. ^{1}H NMR spectrum from sample 3 of the vapochromic experiment (powders of *syn*-**1** that were exposed to a saturated vapor of ***p*-xylene** for **120 hours**) in CD_2Cl_2

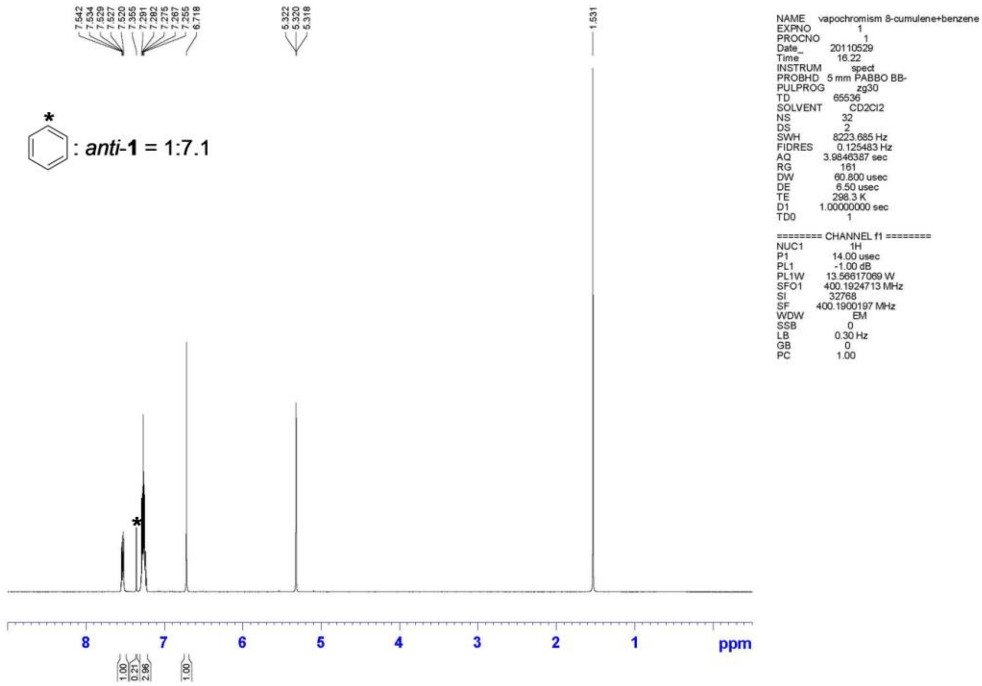

Figure S-10. ^{1}H NMR spectrum from sample 7 of the vapochromic experiment (powders of *syn*-**1** that were exposed to a saturated vapor of **benzene** for **120 hours**) in CD_2Cl_2

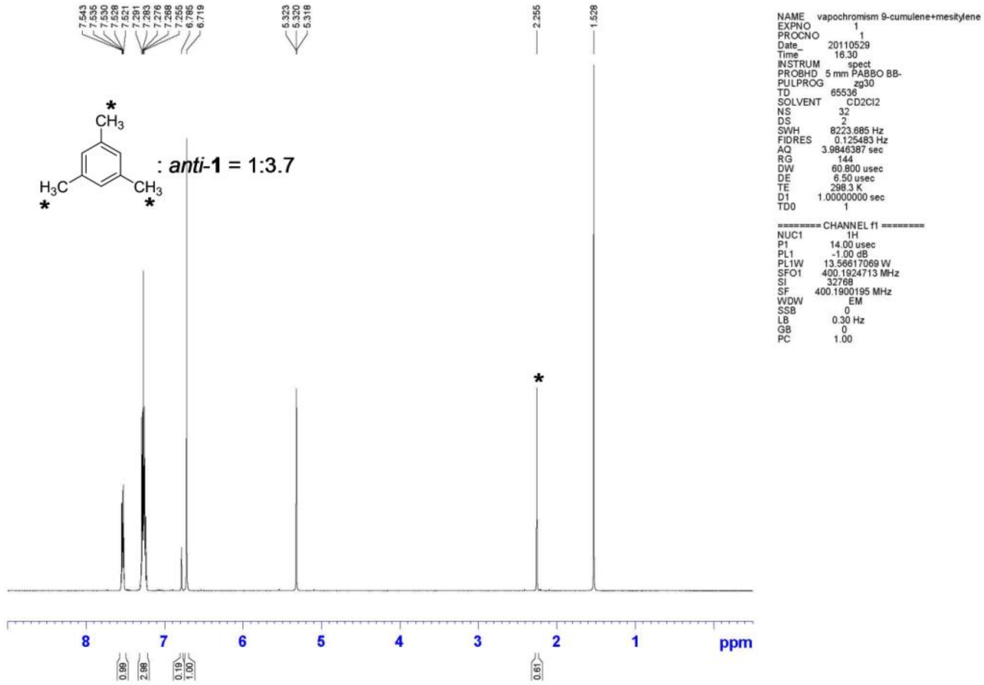

Figure S-11. ^{1}H NMR spectrum from sample 8 of the vapochromic experiment (powders of *syn*-**1** that were exposed to a saturated vapor of **mesitylene** for **120 hours**) in CD_2Cl_2

4. Fabrication and Characterization of Thin Films and Thin Film Transistors

The dielectric SiO_2 surface was modified with octadecyltrimethoxysilane (OTMS) by following the reported procedures (Ito, Y.; Virkar, A. A.; Mannsfeld, S.; Oh, J. H.; Toney, M.; Locklin, A.; Bao, Z. *J. Am. Chem. Soc.* **2009**, *131*, 9396–9404).

The semiconductor thin films were deposited using an Edwards Auto 306 vacuum coater with a Turbomolecular pump at a pressure of 1.0×10^{-6} torr or lower, with a deposition rate of ca. 2 nm/min to desired thickness. During vacuum deposition the distance between source and substrate was 18.5cm. Top contact drain and source gold electrodes were vacuum-deposited through a shadow mask onto the films in the same vacuum chamber, and the resulting semiconducting channels were 50μm(L)×1mm(W), 100μm(L)×1mm(W), 150μm(L)×1mm(W), 50μm(L)×2mm(W) and 100μm(L)×2mm(W). In these transistors highly n-doped silicon functioned as gate electrode and SiO_2 of 300nm thick was treated with octadecyltrimethoxysilane functioned as dielectrics.

UV-vis absorption spectroscopy: The UV-vis spectrum for a thin film of 40 nm thick was recorded with a Varian CARY 1E UV-vis spectrophotometer.

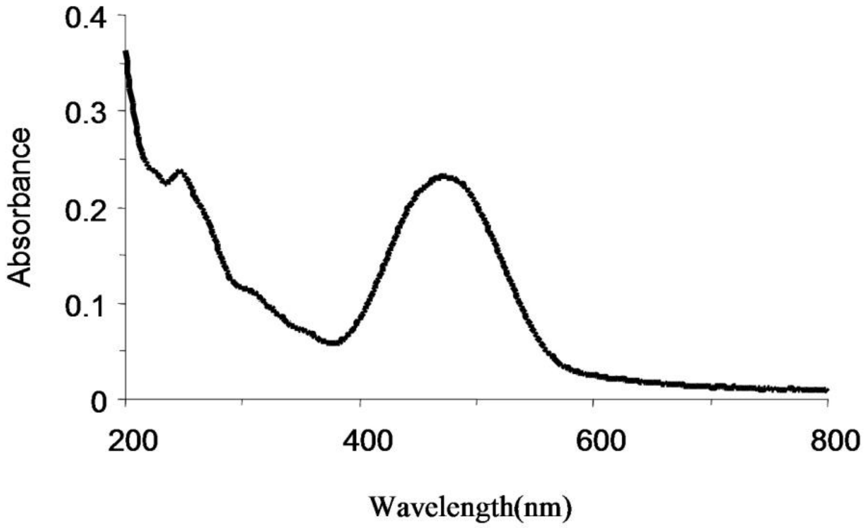

Figure S-12. Absorption spectra of **1** in a thin film of 40nm thick on quartz

Atomic Force Microscopy (AFM): Thin films deposited on OTMS treated SiO_2/Si were used for AFM studies. The topographic images were obtained using a Nanoscope IIIa Multimode Microscope from Digital Instruments. The AFM images were collected using tapping mode and in air under ambient conditions. The topographic images were collected from multiple samples, and for each sample, different regions were scanned to ensure reproducibility.

X-ray diffraction (XRD): XRD data were recorded with a SmartLab X-Ray Refractometer from the 40 nm-thick thin films, which were vacuum-deposited on OTMS-treated SiO_2 surface at a substrate temperature of 25°C.

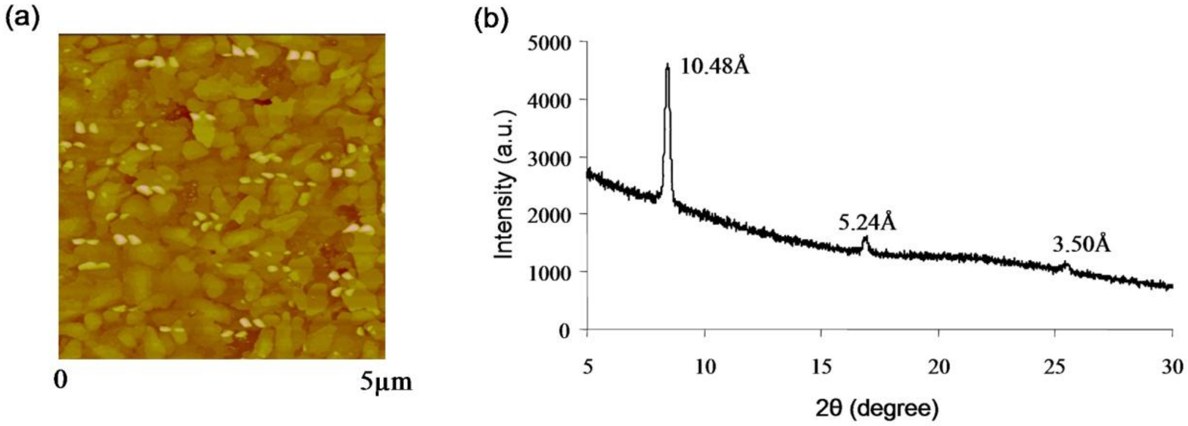

Figure S-13. (a) AFM image and (b) X-ray diffractions from of a 40 nm-thick film of **1**

Electrical Characterization: The current-voltage measurement was carried out on a probe station with a Keithley 4200 Semiconductor Characterization System at room temperature in ambient air.

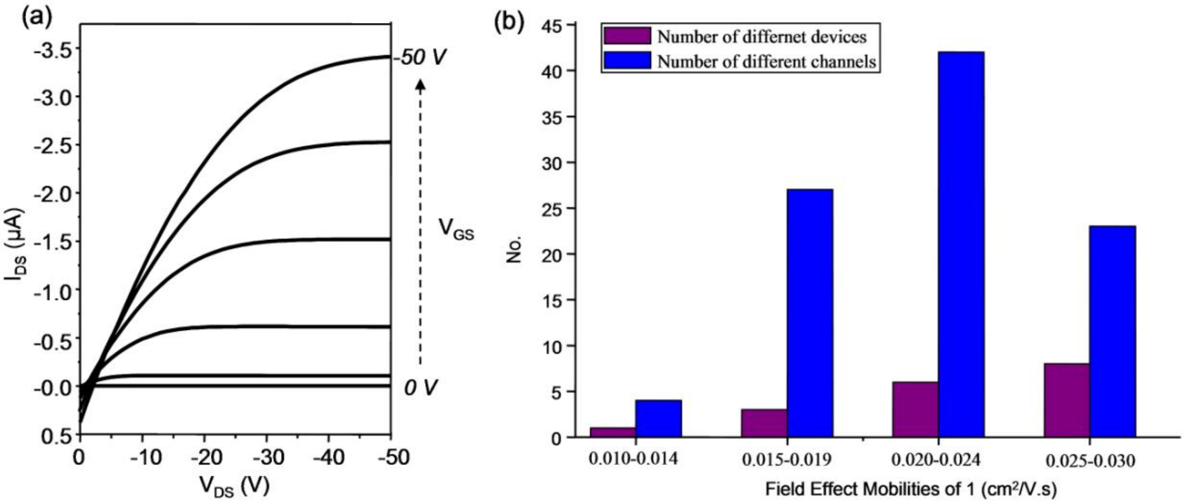

Figure S-14. (a) Drain current (I_{DS}) versus drain voltage (V_{DS}) with varying gated voltage (V_{GS}, from 0 to −50 V in −10 V steps) for organic thin film transistors of **1** deposited on OTMS-treated SiO_2 at substrate temperature of room temperature with channel dimension of $W = 1$ mm and $L = 50$ μm and (b) Summary of thin film transistor performance of **1** deposited under high vacuum at room temperature.

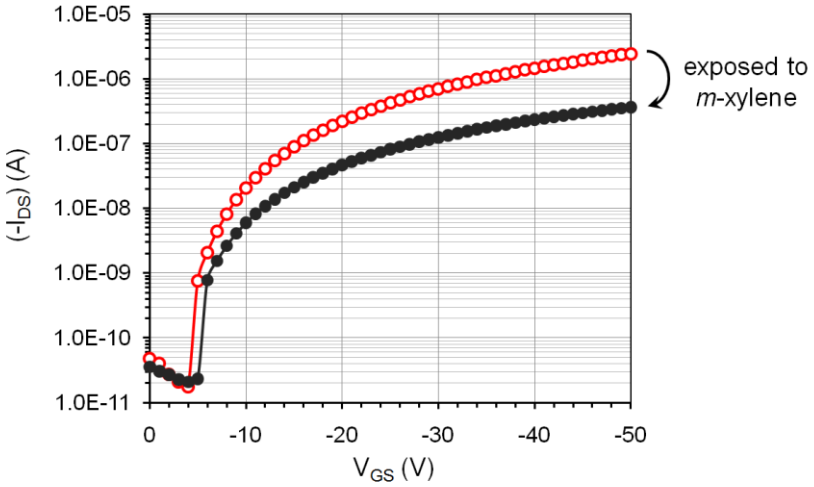

Figure S-15. Drain current (I_{DS}) versus gate voltage (V_{GS}) with drain voltage (V_{DS}) of −50 V for an OTFT of **1** with the active channel of W = 1 mm and L = 50 μm before and after exposed to a saturated vapor of *m*-xylene for about 10 minutes (red trace: before exposure, black trace: after exposure).