

## Electronic Supplementary Information for:

### N-Heteroquinones: Quadruple Weak Hydrogen Bonds and N-Channel Transistors

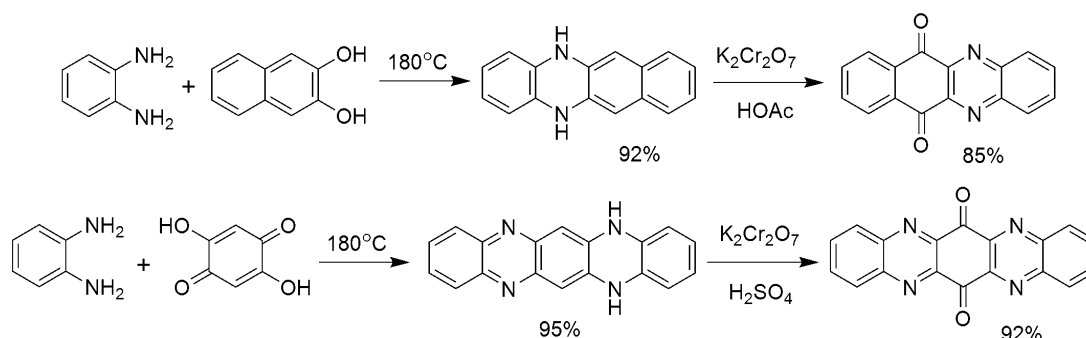
Qin Tang,<sup>1</sup> Zhixiong Liang,<sup>1</sup> Jing Liu,<sup>1</sup> Jianbin Xu,<sup>2</sup> Qian Miao\*,<sup>1,3</sup>

*Department of Chemistry,*<sup>1</sup> *Department of Electronic Engineering*<sup>2</sup> *and the*  
*Center of Novel Functional Molecules,*<sup>3</sup> *the Chinese University of Hong Kong,*  
*Shatin, New Territories, Hong Kong, China*

#### 1. Synthesis

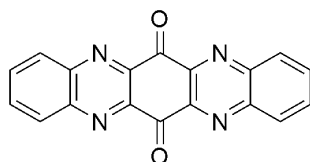
**General:** The reagents and starting materials employed were all commercially available and were used without any further purification. <sup>1</sup>H-NMR or <sup>13</sup>C-NMR spectra were recorded on a Bruker ADVANCE III 400MHz spectrometer. Mass spectra were recorded on a Thermo Finnigan MAT 95 XL spectrometer. Differential scanning calorimetry was carried on Perkin Elmer Differential Scanning Calorimeter 6. X-ray crystallography was carried on Bruker AXS Kappa ApexII Duo Diffractometer.

5,14-dihydro-5,7,12,14-tetraazapentacene and 5,12-dihydro-5,12-diazatetracene were prepared by following the reported procedures.<sup>1, 2</sup> TAPQ and DATQ were prepared by modifying the reported procedures.<sup>3</sup>



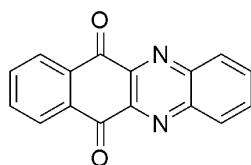
**Scheme S-1.** Synthesis routes of TAPQ and DATQ

1. Q. Tang; J. Liu; H.S. Chan and Q. Miao *Chem. Eur. J.* **2009**, *15*, 3965–3969
2. S. Miao; S.M. Brombosz; P.V.R. Schleyer; J.I. Wu; S. Barlow; S.R. Marder; K.I. Hardcastle and U.H.F. Bunz *J. Am. Chem. Soc.* **2008**, *130*, 7339–7344
3. a) G. M. Badger, R. Pettit, *J. Chem. Soc.* **1951**, 3211–3215; b) S. Miao; A.L. Appleton; N. Berger; S. Barlow; S.R. Marder; K.I. Hardcastle and U.H.F. Bunz *Chem. Eur. J.* **2009**, *15*, 4990–4993.



### 5,7,11,14-tetraaza-6,13-pentacenequinone (TAPQ)

To a solution of 25ml of H<sub>2</sub>SO<sub>4</sub> in 100mL water was added 808mg (2.84 mmol) of 5,14-dihydro-5,7,12,14-tetraazapentacene,<sup>1</sup> and then 4g (13.6mmol) of potassium dichromate slowly. The resulting mixture was refluxed for 1 hour and then poured into 200mL of ice-water. The resulting yellow powder was filtered and washed with water and acetone subsequently. 813mg of TAPQ was collected in a yield of 92% after drying under vacuum. No peak was found up to 450°C in DSC for melting or decomposition. <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>) δ (ppm): 8.48 (dd, J<sub>1</sub>=3.2Hz, J<sub>2</sub>=6.4Hz, 4H), 8.18 (dd, J<sub>1</sub>=3.2Hz, J<sub>2</sub>=6.4Hz, 4H); <sup>13</sup>C-NMR was not taken due to the low solubility; HRMS (EI+): cald. For ([M]<sup>+</sup>): 312.0642, found: 312.0649.



### 6,11-diaza-5,12-tetracenequinone (DATQ)

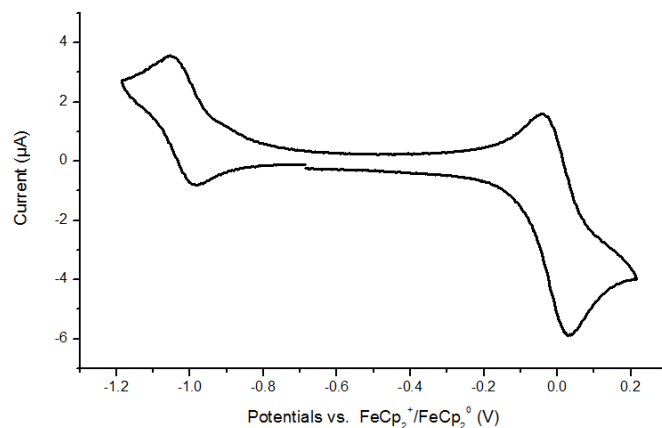
Potassium dichromate (1g) was added slowly into a warm solution of 5,12-dihydro-5,12-diazatetracene<sup>2</sup> (232mg, 1mmol) in 30mL of acetic acid. The solution was then refluxed for 1 hour. After the reaction mixture was cooled down, DATQ was collected as yellow crystals (222mg, 85%) by filtration and wash with acetone. mp: 320°C with decomposition. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ (ppm): 8.53 (dd, J<sub>1</sub>=3.2Hz, J<sub>2</sub>=6.4Hz, 2H), 8.51 (dd, J<sub>1</sub>=3.2Hz, J<sub>2</sub>=6.4Hz, 2H), 8.05 (dd, J<sub>1</sub>=3.2Hz, J<sub>2</sub>=6.4Hz, 2H), 7.94 (dd, J<sub>1</sub>=3.2Hz, J<sub>2</sub>=6.4Hz, 2H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ (ppm): 180.273, 143.315, 143.224, 134.417, 132.979, 130.283, 127.482; HRMS (EI+): cald. For ([M]<sup>+</sup>): 260.0580, found: 260.0574.

## 2. Cyclic Voltammetry

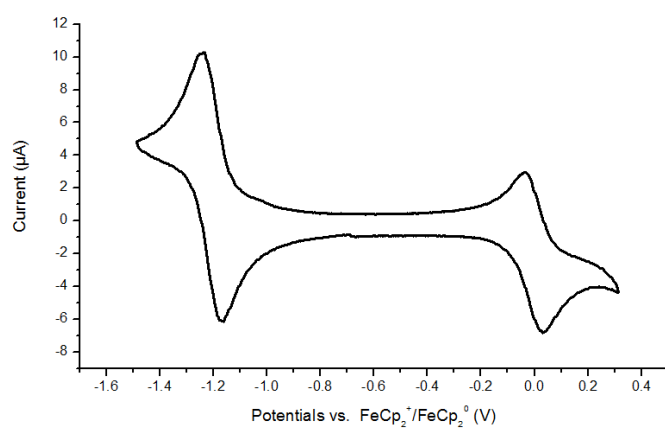
The cyclic voltammetry was performed in a solution in anhydrous DMF with 0.1M tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) as the supporting electrolyte, at a scan rate of 50mV s<sup>-1</sup>. A platinum bead was used as a working electrode, with a platinum wire as an auxiliary electrode and a silver wire is used as a pseudo-reference. Ferrocene/ferrocenium was used as the internal standard. Potentials were referenced to FeCp<sub>2</sub><sup>+</sup>/FeCp<sub>2</sub><sup>0</sup>, which has a HOMO level of -4.8eV.

Summary of electrochemical potentials and estimated LUMO energy:

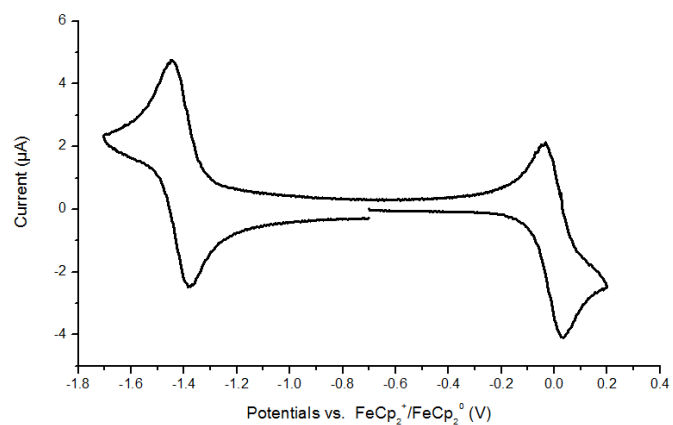
Compound	E <sub>red</sub> <sup>1/2</sup> (V)	LUMO (eV)
TAPQ	-1.020	-3.780
DATQ	-1.203	-3.600
5,12-tetracenequinone	-1.409	-3.392
6,13-pentacenequinone	-1.508	-3.293



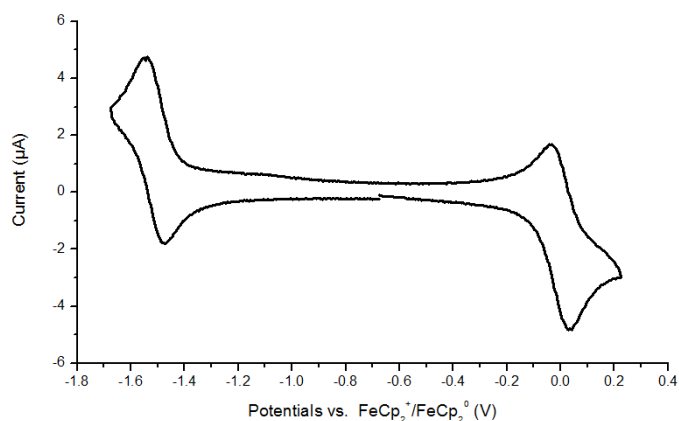
**Figure S-1.** Cyclic voltammogram of TAPQ



**Figure S-2.** Cyclic voltammogram of DATQ



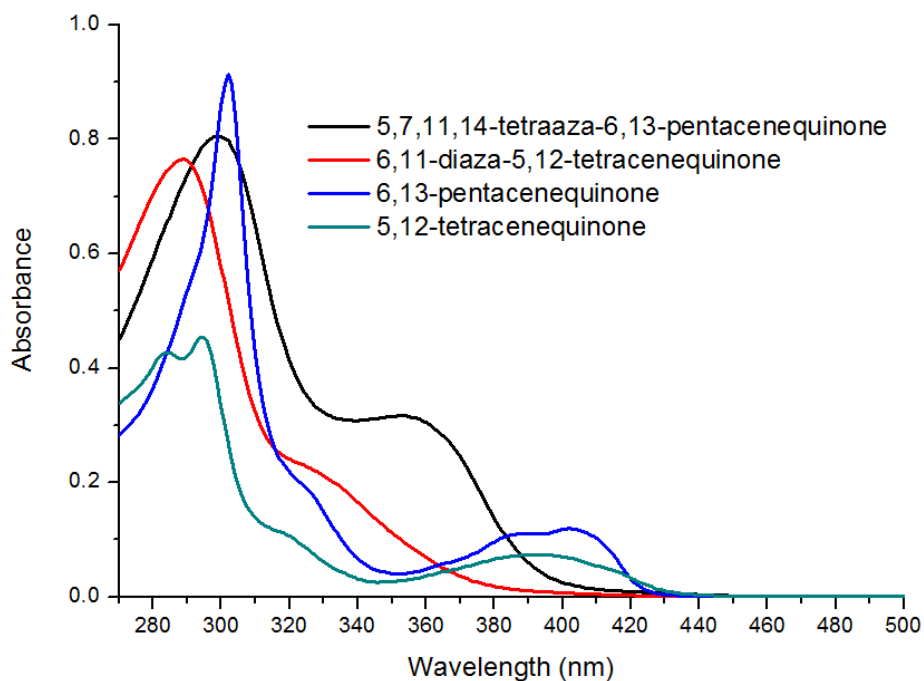
**Figure S-3.** Cyclic voltammogram of 5,12-tetracenequinone



**Figure S-4.** Cyclic voltammogram of 6,13-pentacenequinone

### 3. UV-vis spectrum

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



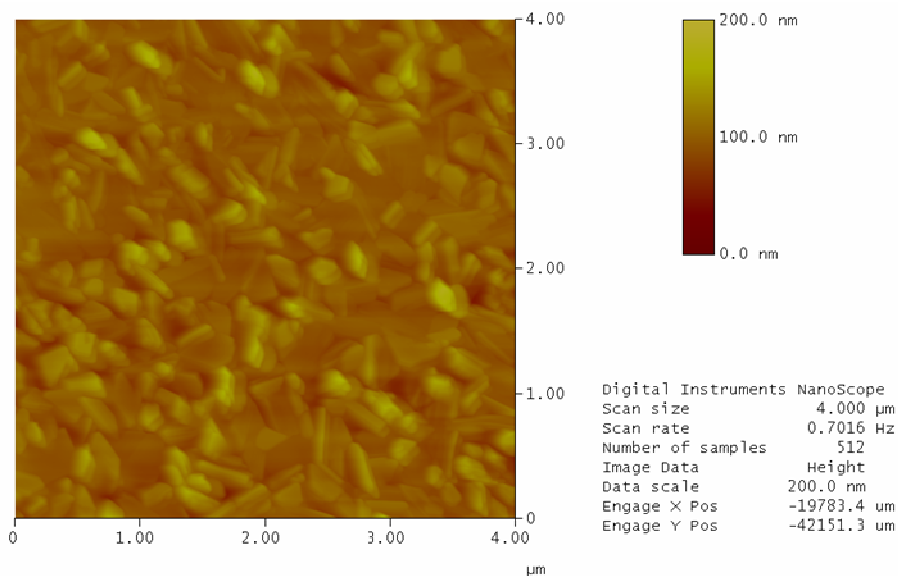
**Figure S-5.** Absorbance spectra of DATQ, TAPQ, 5,12-tetracenequinone and 6,13-pentacenequinone in DMF at a concentration of  $1 \times 10^{-5}$  mol/L.

Summary of optical gap by absorbance spectra:

Compound	Optical gap	Edge-wavelength
6,11-diaza-5,12-tetracenequinone (DATQ)	3.33 eV	372nm
5,7,11,14-tetraaza-6,13-pentacenequinone(TAPQ)	3.15 eV	395nm
5,12-tetracenequinone	2.82 eV	440nm
6,13-pentacenequinone	2.92 eV	425nm

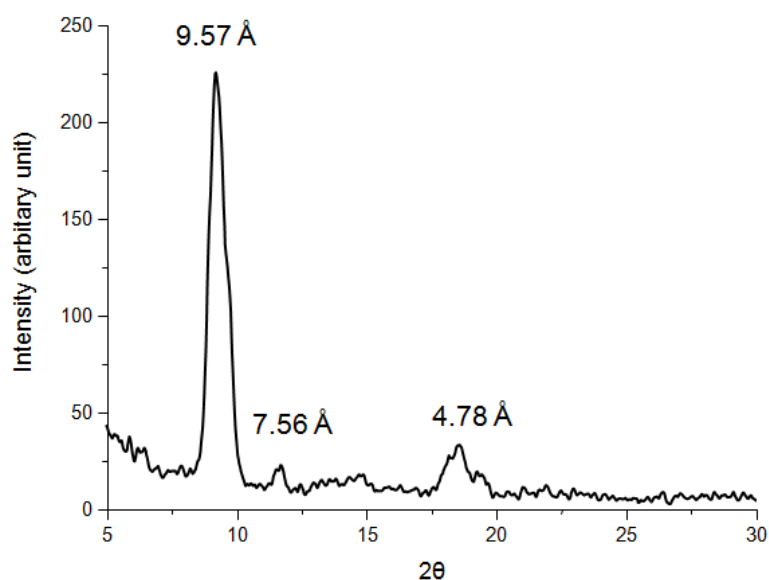
#### 4. AFM study on TAPQ polycrystalline films

Thin films of TAPQ (ca. 60nm thick) deposited at 100°C on OTMS treated SiO<sub>2</sub>/Si were used for AFM studies. The topographic images were obtained using a Nanoscope IIIa Multimode Microscope from Digital Instruments. All 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.

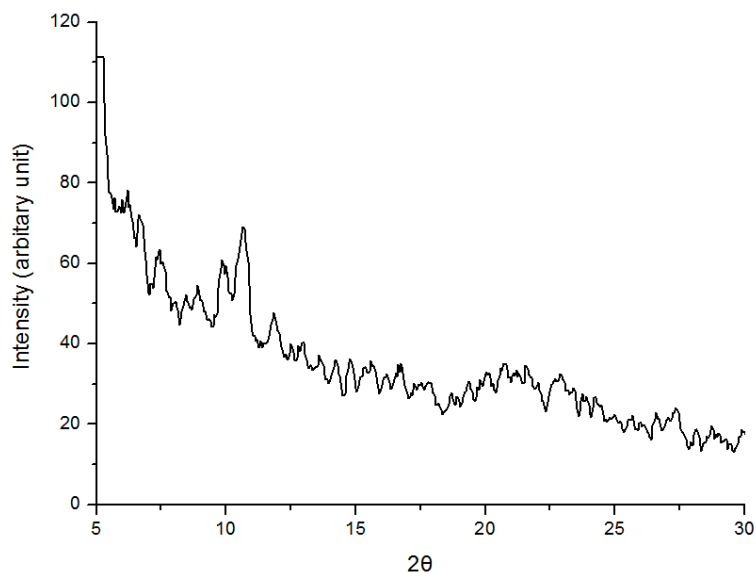


#### 5. Thin Film X-ray Diffraction

X-ray diffraction was carried on Philips Xpert XRD.



**Figure S-6.** X-ray diffraction of a 60nm-thick film of TAPQ



**Figure S-7.** X-ray diffraction of a 60nm-thick film of DATQ

## 6. Device Fabrication and transistor measurements

For transistor fabrication TAPQ was purified through physical vapor transport in a high pure nitrogen flow (flow rate larger than 250mL/min) at outside temperature 320°C measured by a thermocouple. All thin films were vacuum-deposited by an Edward Auto 306 vacuum coater with the Turbomolecular pump at a pressure of  $1.0 \times 10^{-6}$  torr or lower, with a deposition rate of ca. 1 Å/s to desired thickness. During vacuum deposition the distance between source and substrate was 18.5cm. Different substrate temperatures for deposition were achieved using a radiant heater and measured with a thermocouple. 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 50mm(L)×1mm(W), 100mm(L)×1mm(W), 50mm(L)×2mm(W) and 100mm(L)×2mm(W). In these transistors highly n-doped silicon functioned as gate electrode and SiO<sub>2</sub> of 300nm thick was treated with octadecyltrimethoxysilane functioned as dielectrics.

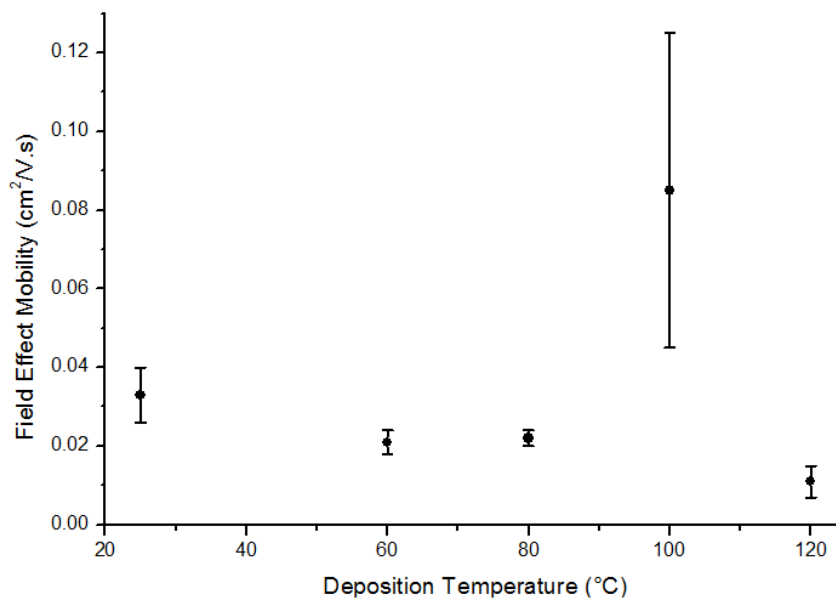
The method of fabrication of octadecyltrimethoxysilane (OTMS) surface on SiO<sub>2</sub> dielectric was fabricated by following the reported procedure:<sup>4</sup> 3mM OTMS solution in trichloroethylene (TCE) was cast to oxygen plasma cleaned SiO<sub>2</sub>/Si wafer washed by piranha solution (70:30 H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub>) first. The solution was allowed to partially assemble for 10s then the substrate was spun at 3000 rpm for 10s. Following spin-casting the substrate was put in a closed container with a small vial which containing 10mL of ammonium hydroxide solution (30% in water) for 10h at room temperature. The substrate were then rinsed with DI water and sonicated in toluene for 10 minutes.

The current-voltage measurement for n-type thin-film transistors was carried out on JANIS

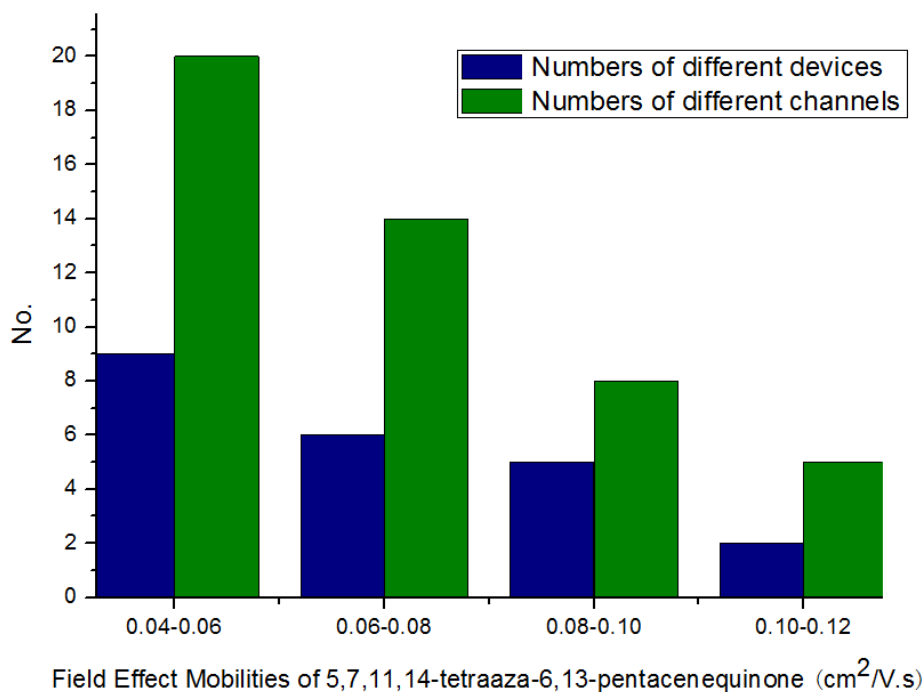
---

4. Y. Ito; A.A. Virkar; S. Mannsfeld; J.H. Oh; M. Toney; A. Locklin and Z. Bao *J. Am. Chem. Soc.* **2009**, *131*, 9396–9404.

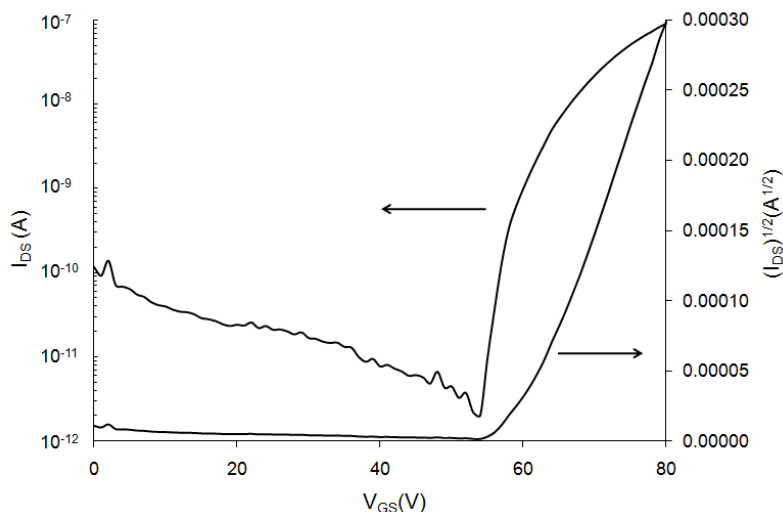
ST-500-20-4TX probe station at background pressure of  $1.0 \times 10^{-6}$  torr or lower at room temperature. For test under vacuum, samples were placed into the probe station at least 20mins before test. Keithley 4200 Semiconductor Characterization System was used for all measurements.



**Figure S-9.** Summary of thin film transistor performance of TAPQ deposited at different substrate temperatures and tested under high vacuum

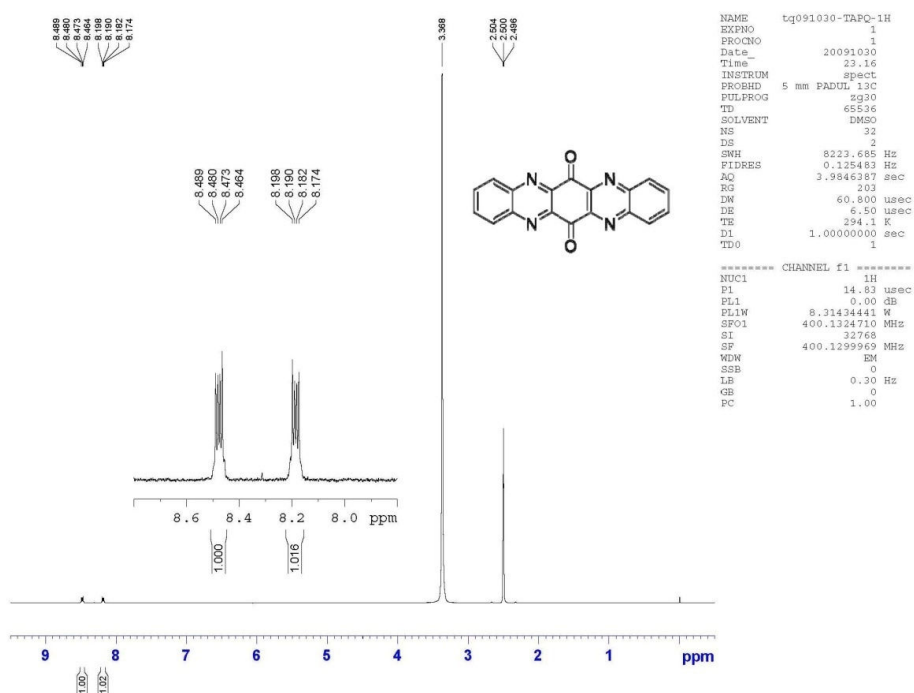


**Figure S-10.** Summary of thin film transistor performance of TAPQ deposited at 100°C and tested under high vacuum



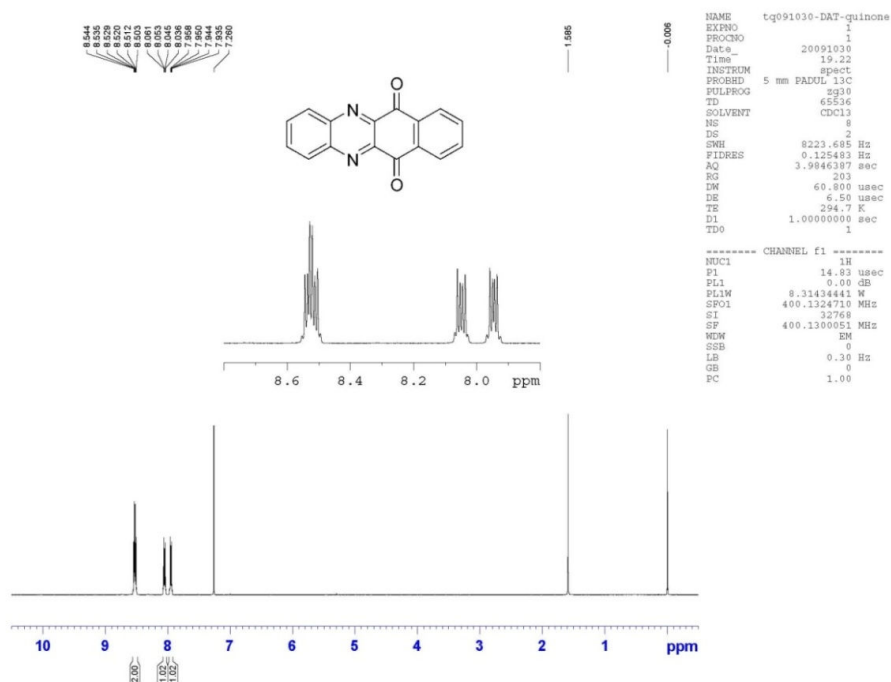
**Figure S-11.** Drain current ( $I_{DS}$ ) versus gate voltage ( $V_{GS}$ ) with  $V_{DS}=80V$  measured *in air* from the thin film transistors of TAPQ deposited on OTMS-treated  $SiO_2$  at substrate temperature of  $100^\circ C$  with channel dimension  $W=1mm$  and  $L=150 \mu m$ . This device has an electron mobility of  $0.003cm^2/V.s$  as measured from the saturation regime.

## 7. NMR spectra

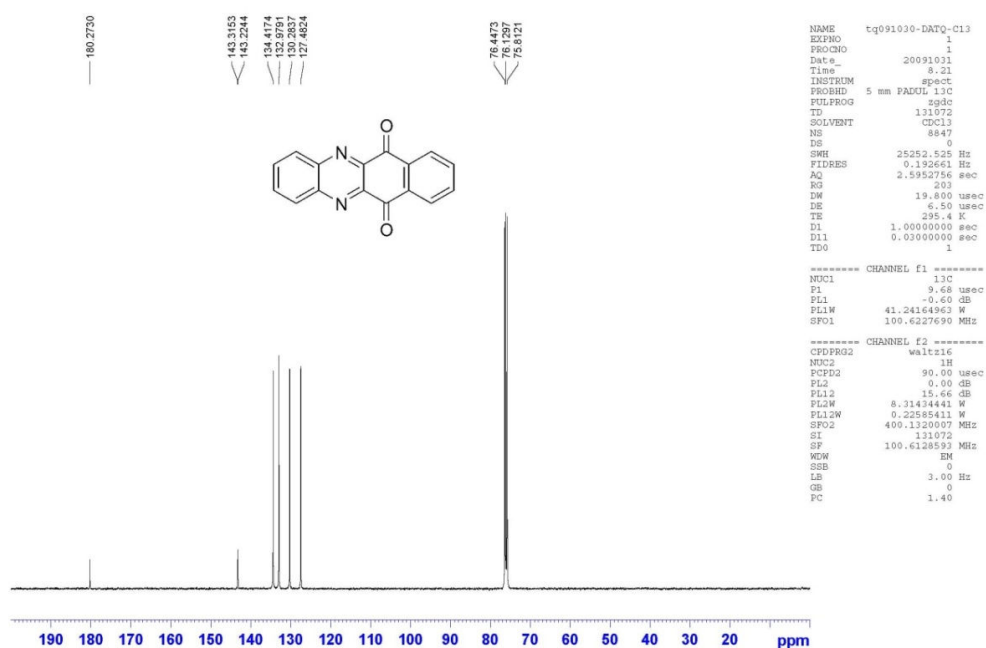


$^1H$ -NMR of 5,7,11,14-tetraaza-6,13-pentacenequinone





<sup>1</sup>H-NMR of 6,11-diaza-5,12-tetracenequinone



<sup>13</sup>C-NMR of 6,11-diaza-5,12-tetracenequinone