Block-like electroactive oligo(aniline)s: anisotropic structures with anisotropic function

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Instrumentation:

Proton and carbon nuclear magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded on JEOL Lambda 300 and Eclipse 400 spectrometers and were referenced with respect to residual solvent (DMSO-d_6).

Infrared spectroscopy was carried out on a Perkin Elmer Spectra 100 FTIR spectrometer.

UV/VIS/NIR spectra were obtained using a Perkin Elmer Lambda 19 UV/VIS/NIR spectrometer.

Mass spectra were recorded on Applied Biosystems QStar XL mass spectrometer.

Elemental analyses were carried out on a Euro Vector Euro EA 3000.

WAXS was carried out on a D8 Advance diffractometer.

SEM was carried out on Hitachi S-4800 at accelerating voltage of 3KV

TEM was carried out on Tecnai G^2 F20 U-TWIN at accelerating voltage of 120KV

AFM was carried out on Dimensional 3100, Veeco

Current voltage (I-V) characteristics were recorded using a Keithley 4200-SCS semiconductor parameter analyzer and a Micromanipulator 6150 probe station in a clean and shielded container at room temperature.

Conductivity measurements:

Sample preparation:

Pellets:

Undoped **TANI-C8** and **TANI-C8 (HCl)$_{0.5}$** (ES) powder was pressed using a steel die having 1.3 cm as diameter in a hydraulic press under a pressure of 10 tons.

Measurements:

Bulk:

The DC conductivity (σ_{dc} in S.cm^{-1}) of the HCl-doped **TANI-C8** pellet was measured by using a custom-built 4-probe (Collinear probe) measuring station with the help of Keithley digital sourcemeter (Model 2401). Measurements on **TANI-C8(HCl)$_{0.5}$** ES pellet were performed at ambient temperature

(≈ 20°C). In order to ensure that accurate values were obtained for the conductivity, the resistance measurements were averaged out of the results of three times for each pellet (two pellets). Pellet thickness was determined by recording SEM images of cross sections of the pellet on a JEOL JSM 5600LV SEM.

The following equation used to calculate the conductivity,

$$\sigma = 1 / \rho$$

$$\rho = (\pi\, tV / \ln 2\ I)\ k$$

where σ is DC conductivity in $S.cm^{-1}$, ρ is the specific resistivity in Ω cm. t is the thickness of the pellet in in cm. V is the applied voltage and I is the measured current, k is the correction factor based on the ratio of the probe spacing to conductive pellet diameter. Correction factor for pellet is 0.6462.[S1]

Anisotropic microstructures:

Device fabrication:

The microplates were spin-coated from aqueous solution on Si substrates, which was capped with a layer of SiO_2. Au electrodes (about 20 nm thick) were deposited on the microplates by thermal evaporation, using an organic ribbon as a shadow mask. The organic ribbon was then removed to obtain a conducting channel.[S2]

Measurements

The conductivity of the **TANI-C8** microplate was measured by using a Keithley 4200-SCS semiconductor parameter analyzer and a Micromanipulator 6150 probe station in a clean and shielded container at room temperature. The conductivity of the HCl-doped **TANI-C8** microplate was recorded after exposing the device to HCl vapour (2% HCl in N_2) over night. The channel length and thickness of the microplate was determined by AFM.

The following equation was used to calculate the conductivity,

$\sigma = 1 / \rho$

$\rho = RA / L$

σ: electrical conductivity

ρ: resistivity

R: resistance

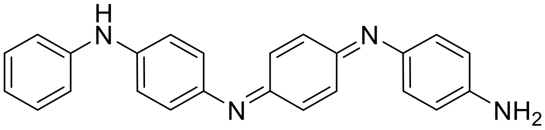
A: cross sectional area (A = channel length * thickness)

L: channel length

The conductivity characterization was performed more than 3 times, and each time 2 devices were fabricated. The values we presented here are recorded from the last characterization and are the average value of two devices.

Synthesis:

N-phenyl-1,4-phenylenediamine was purchased from Aldrich Chemical Co. and purified by recrystallization from a 3:1 mixture of iso-propanol and hexane. Triethylamine was purchased from Fisher Scientific Co. Octanoyl chloride and phenylhydrazine were purchased from Aldrich Chemical Co. and used as supplied. Dry ether was obtained by distillation using standard procedures or by passage through a column of anhydrous alumina using equipment from Anhydrous Engineering based on the Grubbs design.



***N*^{1}-(4-aminophenyl)-*N*^{4}-(4-(phenylamino)phenyl)benzene-1,4-diamine in the EB state**. To a 1 L round-bottom flask (RBF) containing dianiline (9.2 g) was charged diethyl ether (400 mL) to dissolve the solid. A portion of hydrochloric acid (75 mL, 2M) was added dropwise into the ether solution under strong stirring. The precipitated dianiline salt was collected by filtration and dried under dynamic vacuum for 48 h. To a two-neck 250 mL round-bottom flask was charged the dianiline salt (2.56 g, 10.0 mmol, 1 eq.) and hydrochloric acid (50 mL, 0.1M). After 30 min of strong stirring using an overhead mechanical stirrer, a portion of ferric chloride hexahydrate (2.70 g, 10.0 mmol, 1 eq.) in hydrochloric acid (10 mL, 0.1M) was added very quickly through a funnel into the RBF, and a colour change from gray to black-green was observed. The mixture was stirred for another 2 h. The precipitate was collected by centrifugation and washed with HCl (0.1 M) for 5 times. The precipitate was then treated with a mixture of ammonium hydroxide solution (50 mL, 2M) and acetone (300 mL) for 30 min. Then the acetone was removed under reduced pressure. The precipitate was collected by filtration and flushed with diethyl ether and air-dried to afford the product, in the emeraldine base state, as a purple powder (1.79 mg, 49%): Anal. Calcd for $C_{24}H_{20}N_4$: C, 78.66; H, 6.05; N, 15.29. Found: C, 77.91; H, 6.09; N, 14.65. HRMS Calcd for $C_{24}H_{20}N_4$: 364.1688. Found: 364.1683.

Preparation of undoped and redoped TANI-C8:

TANI-C8 (EB):

A solution of ammonium persulfate (91.3 mg, 0.4 mmol, 1 eq.) in hydrochloric acid (20 mL, 2 M) was added dropwise to a DMF (20 mL) solution of the **TANI-C8** leucoemeraldine base state (196.9 mg, 0.4 mmol, 1 eq.) under stirring for 30 min. The resulting solution was poured into stirred deionised water

(100 mL). The deep green precipitate was collected by centrifugation and treated with a mixture of ammonium hydroxide solution (30 mL, 2 M) and acetone (200 mL) for 6 h. After removal of acetone under reduced pressure, the residue was filtered to afford the product, in the emeraldine oxidation state **TANI-C8**, as a purple powder.

TANI-C8(HCl)$_{0.5}$ (ES):$^{S3\text{-}4}$

To a 100 mL RBF containing **TANI-C8** (EB) (100 mg) was charged with HCl (40 mL, 1M) and the resultant green reaction mixture was stirred at room temperature for 72 h. Aqueous HCl was removed by centrifugation and the green solid was washed with diethyl ether (5 mL) to get the bulk ES. Then the green solid was dried under vacuum for 24 h.

Preparation of anisotropic microstructure:

Tetrahydrofuran (THF) was purchased form Sinopharm Chemical Reagent Co. Ltd., and all chemicals were used as received. The **TANI-C8** microplates were prepared through a self-assembly process in a mixture of THF/H_2O where THF was used as good solvent and H_2O as poor solvent. A typical preparation process was as follows: **TANI-C8** was pre-dissolved in THF as 5 mg/mL solution. 160 μL of this **TANI-C8** solution was diluted with various volumes of THF corresponding to different good solvent to poor solvent ratio from 10% : 90% to 90% : 10%. Then different volumes of deionized water were added as poor solvent, followed by immediate mixing. The total volume of the solution was 4 mL. The mixture was left standing for 12 hours for self-assembly and microplates were formed and precipitated. SEM and TEM samples were prepared by dropping cast on silicon wafer and carbon coated copper grid. The microplate solution was drop cast to quartz plates for solid-state UV-Vis-NIR characterization. XRD data was obtained from microplate precipitates, which were dried in vacuum for 48 h at room temperature. Data of **TANI-C8(HCl)** were recorded form the samples, which were exposed to HCl vapour (2% HCl in N_2) over night.

Physical Characterisation Data:

X-ray diffraction studies:

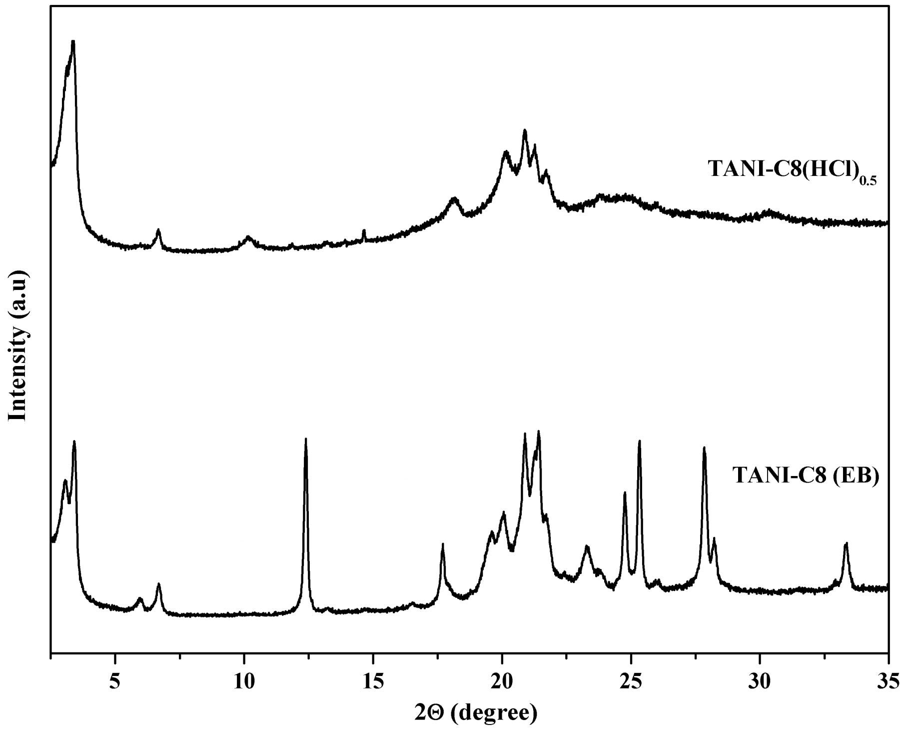
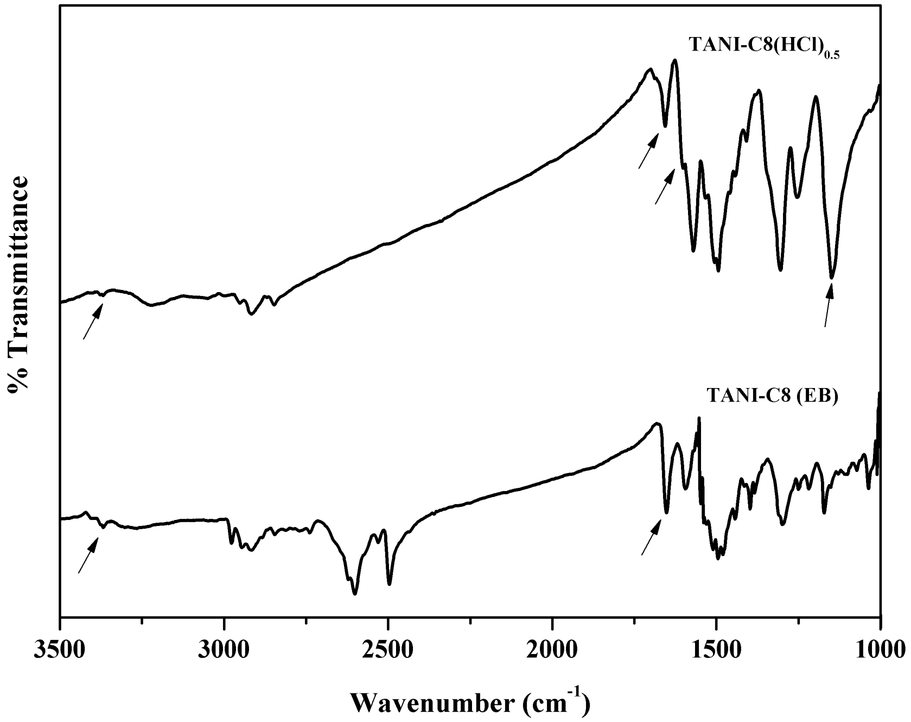


Figure S-1: XRD of the bulk **TANI-C8(HCl)$_{0.5}$** and **TANI-C8** (EB state).

See table S-2 below for tentative indexation.

FT-IR spectra of TANI-C8 (ES) and (EB) state



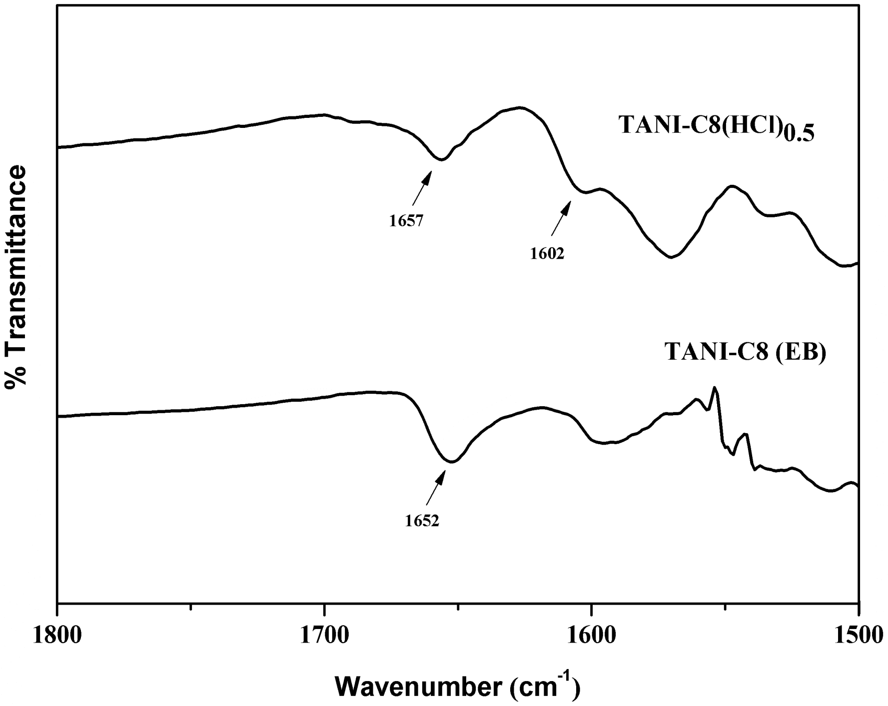


Figure S-2: FT-IR spectra of **TANI-C8(HCl)$_{0.5}$** and **TANI-C8** (EB) in the range from a) 4000 – 650 cm^{-1} and b) 1800 – 650 cm^{-1}, as taken in CCl$_4$.

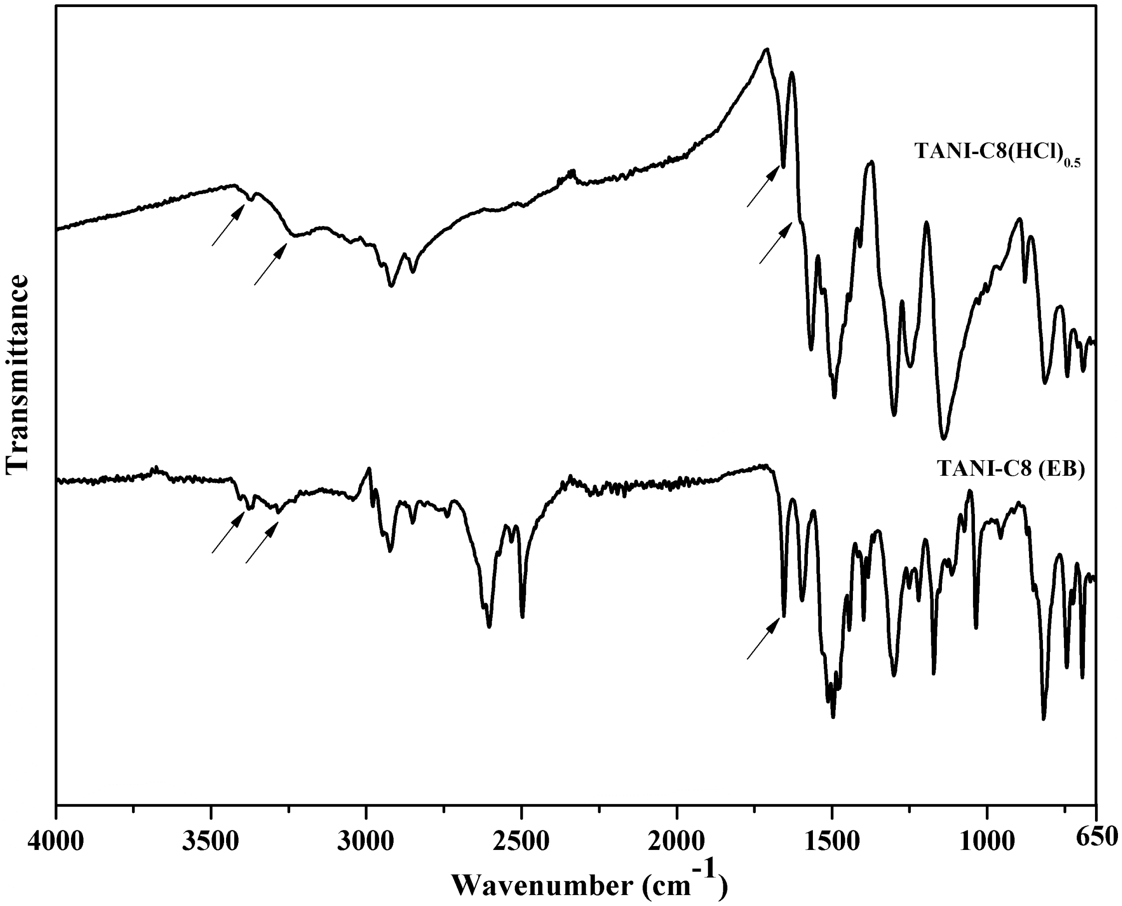


Figure S-3: FT-IR spectra of **TANI-C8(HCl)$_{0.5}$** and **TANI-C8** (EB) in the solid state.

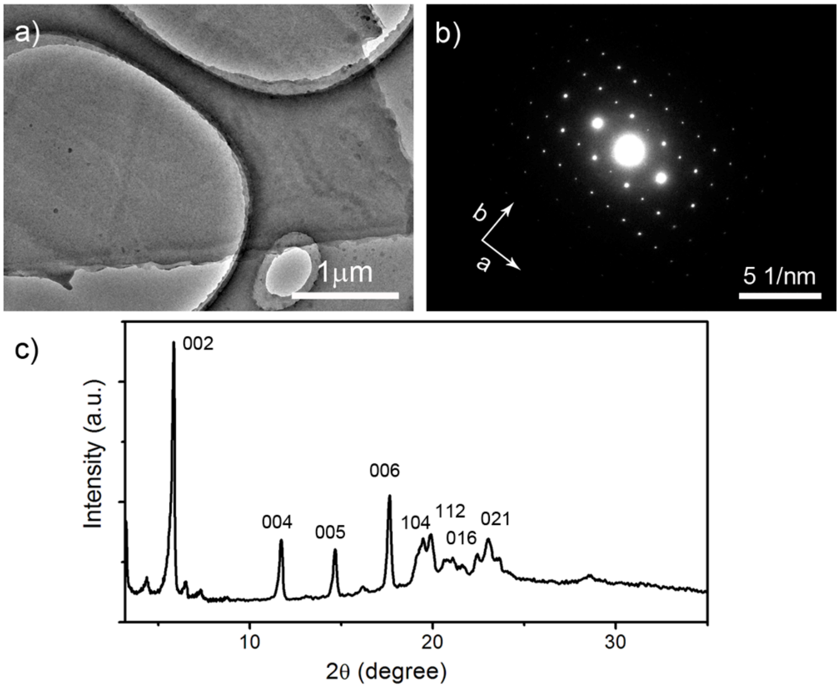


Figure. S-4 (a) TEM image (b) SAED patterns and (c) WAXS spectrum of redoped **TANI-C8** (HCl)(ES) anisotropic microplates.

XRD indexation data of TANI-C8

Table S1: Microplates

TANI-C8 (EB)

assigned peaks	2θ	d value (A°)
002	5.816	15.1210
004	11.705	7.5445
005	14.678	6.0298
006	17.628	5.0288
104	19.441	4.5620
112	19.852	4.4670
016	20.638	4.3002
021	22.961	3.8697

TANI-C8 (HCl)

assigned peaks	2θ	d value (A°)
002	5.809	15.2221
004	11.677	7.5705
005	14.559	6.0534
006	17.572	5.0404
104	19.396	4.5714
112	19.845	4.4711
016	20.691	4.2907
021	23.017	3.8601

Table S2: Bulk doped materials

TANI-C8 $(HCl)_{0.5}$

assigned peaks	2θ	d value (A°)
001	3.332	26.5325
002	6.619	13.3519
n.a.	10.027	8.8276
100	14.619	6.0588
003	17.98	4.9335
111	20.055	4.4285
013	20.845	4.2624
n.a.	20.937	4.2443
n.a.	21.35	4.1617
020	24.041	3.7018
n.a.	29.8	2.9981

References:

S1. H. Topsoe, <*http://www.four-point-probes.com/haldor.html>*, 1968.
S2. L. Jiang, J. Gao, E. Wang, H. Li, Z. Wang, W. Hu and L. Jiang, *Advanced Materials*, 2008, **20**, 2735-2740.
S3. A. G. MacDiarmid, J. Feng and W. J. Zhang, 2000, pp. US Patent, 6160177.
S4. W. J. Zhang, J. Feng, A. G. MacDiarmid and A. J. Epstein, *Synthetic Metals*, 1997, **84**, 119-120.