## **Electronic supplementary Information (ESI)**

Charge Transfer (CT) Mechanochromism: Dramatic CT Absorption Change of

Crystalline *π*-Conjugated Oligomers Containing TCNQ Upon Mechanical Grinding

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## Section 1. Materials and methods

Squaric acid (> Tokyo Kasei Kogyo, Co., > 98%), 1,3-diaminopyrene (Wako Chemicals Co., 99.5%), and 1,6-diaminopyrene (Wako Chemicals Co., 99.5%) was used as received. Anhydrous toluene (99.0%) and *n*-butanol (> 99%) were purchased from Kanto Chemicals. Other reagents were used as received without further purification.

Fourier transform Infrared (FT-IR) spectra were recorded on a JASCO model FT-IR-6100 infrared spectrometer. UV-Vis-IR diffuse reflectance spectrum (Kubelka-Munk spectrum) was recorded on a JASCO model V-670 spectrometer equipped with integration sphere model IJN-727. Powder X-ray diffraction (PXRD) data were recorded on a Rigaku model RINT Ultima III diffractometer by depositing powder on glass substrate, from  $2\theta = 1.5^{\circ}$  up to  $60^{\circ}$  with  $0.02^{\circ}$  increment. Molecular modeling and Pawley refinement were carried out using Reflex, a software package for crystal determination from XRPD pattern. The optimization of the oligomers was carried out at the B3LYP level of theory with a range of basis sets (6-31G(d)) utilizing Gaussian 03 suite of programs, and these of model compounds were calculated at the B3LYP/6-31G(d) level of theory.

## Section 2. Synthetic procedures

**Oligo(sq-alt-1,3py).** To a 50 mL glass tube, squaric acid (11.4 mg, 0.10 mmol) and 1,3diaminopyrene (23.4 mg, 0.10 mmol) were added. A mixture of n-butanol (3 mL) and toluene (7 mL) was added, and the reaction mixture was refluxed for 2 days. After the reaction mixture was cooled to room temperature, the resulting polymer was purified by precipitation into methanol (100 mL), and the product was dried under reduced pressure. The poly(sq-alt-1,3ampy) (yield = 65%) was obtained as a bright orange solid.

Elemental analysis (%) calcd. for  $(C_{24}O_4N_4H_{14})_n$  (theoretical formula for an infinite oligo(sqalt-1,3py)) C (68.24), H (3.34), N (13,26), found C (69.51), H (3.34), N (12.44).

**Oligo(sq-alt-1,6py).** To a 50 mL glass tube, squaric acid (11.4 mg, 0.10 mmol) and 1,6diaminopyrene (23.4 mg, 0.10 mmol) were added. A mixture of n-butanol (3 mL) and toluene (7 mL) was added, and the reaction mixture was refluxed for 2 days. After the reaction mixture was cooled to room temperature, the resulting polymer was purified by precipitation into methanol (100 mL), and the product was dried under reduced pressure. The poly(sq-alt-1,6ampy) (yield = 72%) was obtained as a bright orange solid.

Elemental analysis (%) calcd. for  $(C_{24}O_4N_4H_{14})_n$  (theoretical formula for an infinite oligo(sq*alt*-1,6py)) C (68.24), H (3.34), N (13,26), found C (69.01), H (3.22), N (13.2).

**Oligo(sq-alt-1,3py)-TCNQ.** To a 50 mL glass tube, squaric acid (11.4 mg, 0.10 mmol), 1,3diaminopyrene (23.4 mg, 0.10 mmol), TCNQ (20.1 mg, 0.10 mmol) were added. A mixture of nbutanol (3 mL) and toluene (7 mL) was added, and the reaction mixture was refluxed for 2 days. After the reaction mixture was cooled to room temperature, the resulting polymer was purified by precipitation into methanol (100 mL), and the product was dried under reduced pressure. The oligo(sq-*alt*-1,3ampy) (yield = 54%) was obtained as a bright orange solid.

Elemental analysis (%) calcd. for  $(C_{39}O_4N_8H_{26})_n$  (theoretical formula for an infinite oligo(sq*alt*-1,3py)-TCNQ) C (69.84), H (3.91), N (16.71), found C (72.22), H (4.28), N (11.03).

**Oligo(sq-alt-1,6py)-TCNQ.** To a 50 mL glass tube, squaric acid (11.4 mg, 0.10 mmol), 1,3diaminopyrene (23.4 mg, 0.10 mmol), TCNQ (20.1 mg, 0.10 mmol) were added. A mixture of nbutanol (3 mL) and toluene (7 mL) was added, and the reaction mixture was refluxed for 2 days. After the reaction mixture was cooled to room temperature, the resulting polymer was purified by precipitation into methanol (100 mL), and the product was dried under reduced pressure. The oligo(sq-*alt*-1,6ampy) (yield = 78%) was obtained as a bright orange solid.

Elemental analysis (%) calcd. for  $(C_{39}O_4N_8H_{26})_n$  (theoretical formula for an infinite oligo(sq*alt*-1,6py)-TCNQ) C (69.84), H (3.91), N (16.71), found C (71.84), H (3.91), N (15.11).

Section 3. FT-IR spectra of oligomers and CT-oligomers



Fig. S1 IR spectra of (a) oligo(sq-*alt*-1,3ampy), (b) oligo(sq-*alt*-1,6ampy), (c) oligo(sq-*alt*-1,3ampy)-TCNQ, and (d) oligo(sq-*alt*-1,6ampy)-TCNQ.

## Section 4. DFT calculation of model compounds



Fig. S2 Molecular orbital diagrams for HOMO and LUMO of model compounds (B3LYP/6-311G(d)// B3LYP/6-311G(d)).

Section 5. PXRD patterns of oligomer before and after grinding



Fig. S3. XRD patterns of (a) oligo(sq-*alt*-1,6py)-TCNQ and (b) grinding oligo(sq-*alt*-1,6py)-TCNQ.





Fig. S4. XRD patterns of oligo(sq-alt-1,6py)-TCNB (red dotted curve) and grinding oligo(sq-alt-1,6py)-TCNB (red curve).