Supporting Information

Rapidly Reversible Organic Crystalline Switch for Conversion of Heat into Mechanical Energy

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Materials

1-bromodecane, silver nitrate, ammonium hydroxide, D-(+)-Glucose, potassium carbonate, 1-methyl-2-pyrrolidone (NMP), 1,4,5,8-naphthalenetetracarboxylic dianhydride, chloroform, hydrochloric acid, N,N'-dimethylformamide (DMF), 4-aminophenol, and sodium chloride were purchased from Sigma-Aldrich (St. Louis, MO, USA), or Thermo Fisher Scientific (Waltham, MA, USA) and used without further modification.

Instrumentation

Scanning Electron Microscopy

Crystals were selected for SEM and adhered to the sample holder pins with double-sided copper tape and imaged on a ZEISS Supra 40 Scanning Electron Microscope (Zeiss, Oberkochen, Germany) with an accelerating voltage of 2.5 kV and a working distance of 6.7 to 15.3 mm.

Digital Scanning Calorimetry

Thermal properties of DNDI samples were analyzed with differential scanning calorimetry (DSC) using a TA Instruments Q2000. The crystals were heated from 20 °C to 60 °C then back to 20 °C for 200 cycles at a heating rate of 20 °C/min, under a flow of nitrogen (40 mL/min). The crystals were recovered from the pan afterwards for further analysis.

Electrical Measurement

Voltage was supplied with a Global Specialties 1325 (Global Specialties, Yorba Linda, CA, USA) or a Longwei Electric 302D (Longwei Electric, No.50 Tangxia Industrial Zone, Dongguan, China) power supply. Voltage measurements were recorded on a Tektronix DPO 3014 oscilloscope (Tektronix, Beaverton, OR, USA) or a Keysight 34465A multimeter (Keysight Technologies, Santa Rosa, CA, USA).

Methods

Synthesis

NDI-Phenol

NDI-Phenol was synthesized according to a literature protocol.[1] A mixture of 1,4,5,8-naphthalenetetracarboxylic dianhydride (4.582 g, 2.119 mmol and 4-aminophenol (4.627 g, 4.240 mmol) was heated under reflux at 130 °C for 24 h. The reaction product was then collected under filtration and washed with DMF.

DNDI

DNDI was synthesized based on a literature protocol.[2] NDI-Phenol (2. 00 g, 4.4 mmol), 1-bromodecane (19.448 g, 88 mmol) and K_2CO_3 (4.8 g, 8.7 mmol) were stirred in NMP (80 mL) at 70 °C for 6 h. The reaction mixture was poured into diluted HCl, the precipitate was filtered off, and dried in vacuum. The crude product was purified by flash column chromatography on silica in isocratic chloroform and allowed to crystallize in the fraction tubes.

Hot Stage Microscopy

A polarized optical microscope was set up with a heat gun and a cooling apparatus each pointed at the underside of the stage. The cooling apparatus consisted of a vacuum flask partially filled with water and embedded in an ice bath with an air hose delivering air to the top of the flask and another air hose delivering cooled air from the flask stem to the underside of the stage. Alternating use of the heat gun and cooling apparatus allowed a range of temperatures from approximately 5 °C to 70 °C in a reasonable cycle time of less than five minutes.

Silver Coating

Selected DNDI crystals were added to a scintillation vial and 5 mL 1 M silver nitrate and 0.2 g (D)-glucose added. 5 drops of ammonium hydroxide was added and the vial capped and gently heated while swirling until the silver mirror appeared on the inside of the vial surface. The vial was then left on a rotisserie to gently tumble for 2 days. The vial contents were vacuum filtered and rinsed with water. Silver flakes were picked out and the silvered crystals were carefully collected into a separate vial for storage. Selected silvered crystals were mounted on double-sided copper tape for examination by SEM.

Electrical Actuation

A circuit was set up and soldered to a breadboard consisting of a terminal for power supply, a 270 Ω resistor, a red LED, terminals for current measurement, electrodes for the crystal switch contacts, and a terminal for return power supply. The crystal switch contacts consisted of filter paper strips moistened by saturated sodium chloride solution. The LED indicated a closed circuit, the resistor protected the LED from overcurrent, and the current was monitored as the power supply voltage was increased until the crystal actuated. Originally, copper tape was used for the electrodes, but the silvered DNDI crystals did not make good contact so we instead used liquid electrolyte electrodes that consisted of Whatman #1 filter paper cut into an “L” shape and moistened with a saturated NaCl solution. Two acrylic blocks were placed such that there was an air gap between the electrodes that the silvered crystal bridged, ensuring that the only electrical circuit path was across the crystal and not liquid electrolytes that have seeped away from the electrodes. During the course of the electrical measurements, the electrodes were occasionally moistened with fresh NaCl solution to maintain conductivity.

Force Measurements

A squared metal rod was machined to fit snugly between the fins of an aluminum heatsink with a setscrew to hold it down firmly in the trench to act as an adjustable backstop for expanding crystals. A thermocouple was glued into the next trench over for temperature monitoring. The heatsink assembly was clamped firmly in place and a Honeywell FSG005WNPB force sensor (Honeywell, Golden Valley, MN, USA) was glued to an adjustable stage and clamped at the end of the backstopped trench. Selected crystals were placed in the trench such that they would re-expand against the backstop and protrude outwards from the end of the trench against the force sensor. An Opti-TekScope digital USB microscope camera (Opti-TekScope, Chandler, AZ, USA) was mounted above the assembly to monitor alignment and to record crystal lengths. A soldering iron heated to 850 °C was applied to a neighboring trench to heat the aluminum and the crystal

by conduction until the thermal threshold was passed and the crystal contracted. The backstop was carefully adjusted such that the contracted crystals was butted up against it, and all of the expansion force would be applied in the opposite direction, that is, into the sensor. The assembly was cooled by placing a chunk of ice against the bottom surface of the heatsink away from the crystal until the crystal re-expanded. The sensor values were converted to Newtons according to the manufacturer's data sheet. The trench width was determined with a microscope calibration slide, and this width was then used to determine individual crystal lengths by pixel count from the microscope images.

List of associated supplementary files

Movie D1. DNDI crystal contracting and expanding in multiple cycles.

Movie D2. DNDI crystal under polarized light showing propagation of wavefronts.

Movie D3. A silvered DNDI crystal delaminating from the silver coating upon heating on a hot plate.

Movie D4. Electrical actuation of a silvered DNDI crystal across saturated NaCl electrodes upon voltage increase.

Computational Details:

Molecular Cluster Modeling:

Four cluster modeling systems were created due to the extended nature of the bulk DNDI crystal structure: (a) single layer; (b) bilayer; (c) three layers; and (4) four layers molecular structures. These models were completed on the linker of interest coordinated to a pair of benzene rings, which are attached to the $-OCH_2CH_2CH_2CH_3$ groups bound to either end of the organic main linker as depicted in Figure S1-S3. To truncate the system, the ligating oxygen atoms at both the ends that are not part of the included linker were added as $-OCH_2CH_2CH_2CH_3$ in order to conserve charge as well as make it neutral, and one -H atom was added in the $-OCH_2CH_2CH_2CH_3$ groups to truncate and neutralize the system.

Thermodynamics.

The periodic crystal structure and four cluster modeling systems (1-4 layers molecular structures) were created and shown in Figure S1, S2. All the calculations were performed using unrestricted hybrid DFT at the UB3LYP-D3 level, with the correlation-consistent polarization double ζ-quality (cc-pVDZ) atomic basis sets for all atoms.[3-5] The harmonic vibrational frequencies at the optimized geometries were analyzed to confirm stable minima. Thermochemistry calculations were performed at 298K and 333K considering mono-, bi- and tri-layer molecular models (Figure 1b-d, 2b-d). The threshold used for evaluating the convergence of the energy, forces, and electron density was 10^{-7} a.u. for each parameter. All the calculations were performed with the electronic structure quantum chemistry program code Gaussian09. [5]

A rigid scan has been performed by using the 1-,2-,3-, and 4-layer systems. The rotation of the benzene ring is defined as a continuous transition where the spatial alignment of the crystal is changed by tuning around a rotational axis, C1-C2-N1-C3 (Figure S3, left). Taking the optimized equilibrium structures, the benzene group was rotated around the axis of the DNDI crystal to scan the potential energy curve (PEC) in the range of 0° to 180° with 10° increments. We found one global minimum is the equilibrium position with the dihedral angle of 80.0°. Two most unstable positions are at the dihedral angle 0.0° and 180.0°. Thus, the rotational energy barrier has been computed as the energy difference between the most stable and unstable positions of the rotational groups (Figure S3, right). This estimated rotational barrier is $\Delta E^{\dagger}$ = 13.6 – 14.4 $kJ.mol^{-1}$ for the molecules surrounded by 1-,2-,3-layers of DNDI molecules.

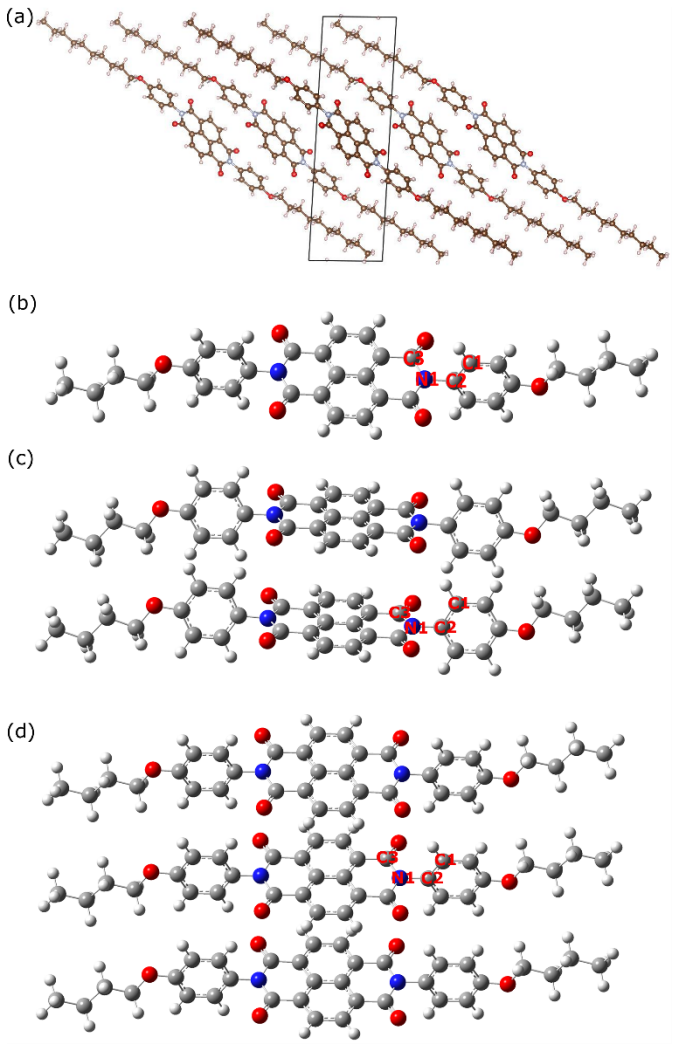

Figure S1. DNDI structures at 298K. (a) Crystal structure of DNDI crystal at this temperature. Molecular models for the optimized structure defined as (b) mono-; (c) bi- and (d) tri- layers of the same crystal. Accordingly, the thermochemical calculations of these models are performed at temperature of the crystal.

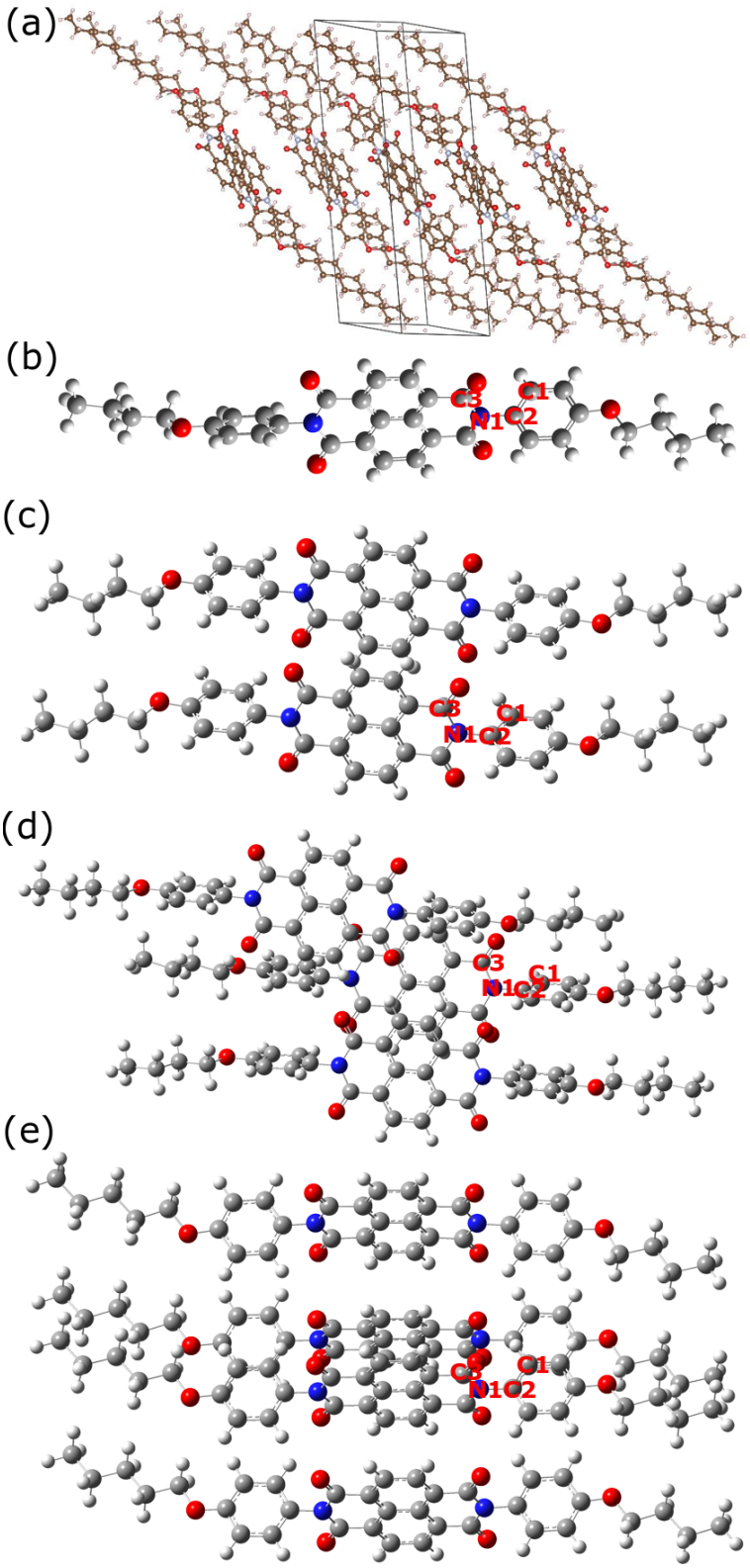

Figure S2. DNDI structures at 333K. (a) Crystal structure of DNDI crystal at this temperature. Molecular models for the optimized structure defined as (b) mono-; (c) bi- and (d) tri- layers of the same crystal. Accordingly, the thermochemical calculations of these models are performed at temperature of the crystal.

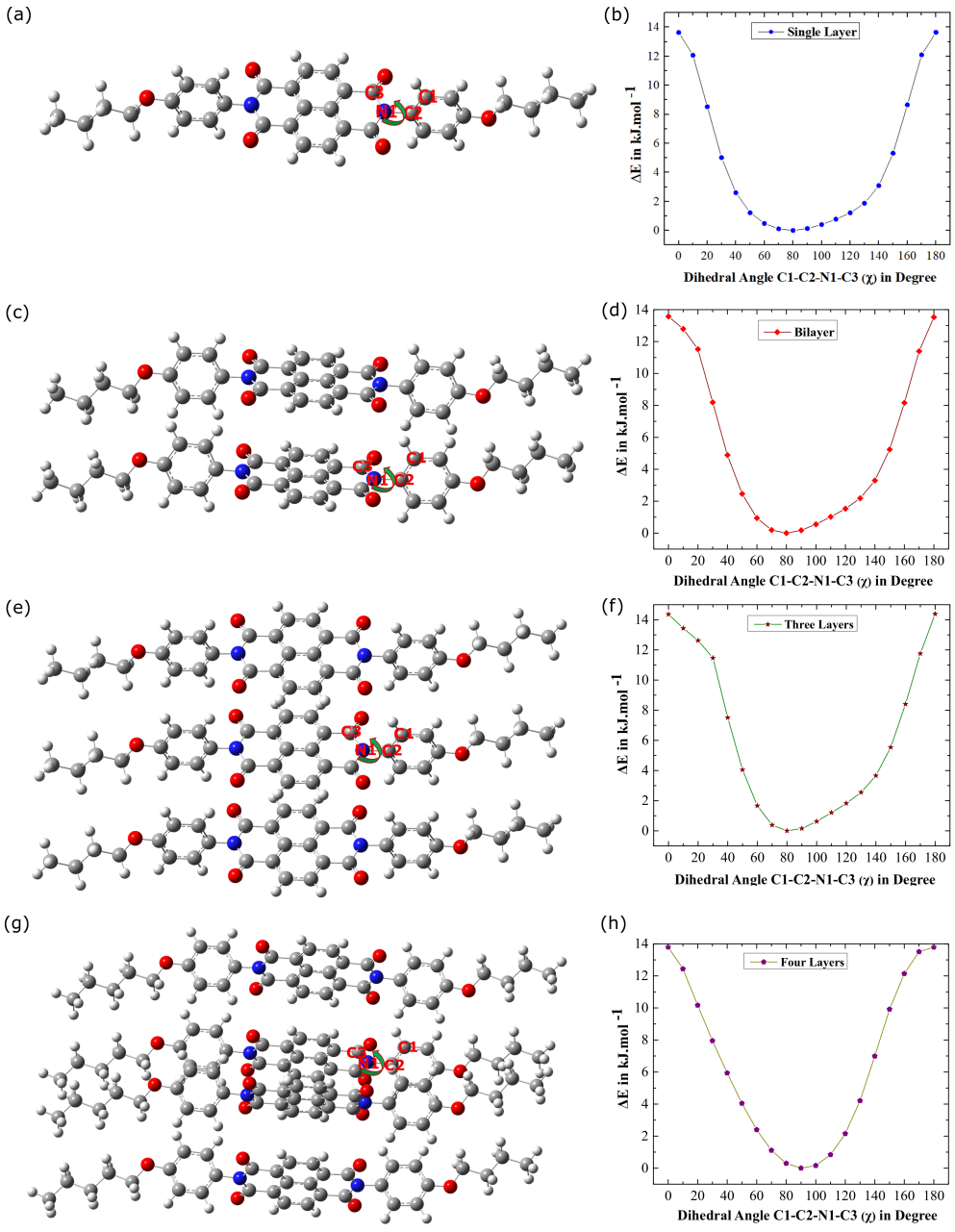

Figure S3. Left-to-right: molecular models surrounded by 1-3 layers to study the neighboring effect on the (right) rotational barrier. Top-bottom: 1-, 2-, 3-, 4-Layers models were optimized the same level of theory. The rotational dihedral angle χ is represented by C1-C2-N1-C3.

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