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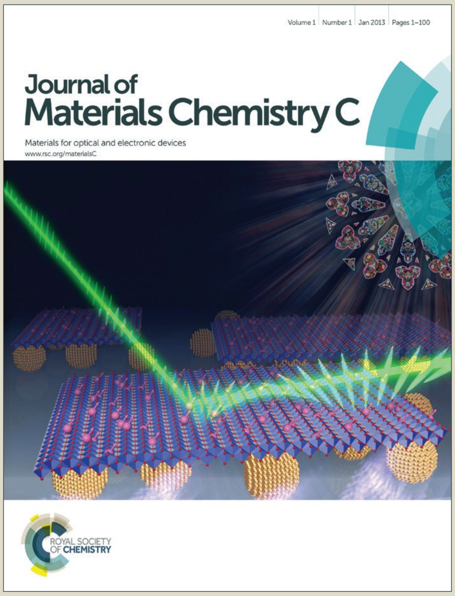

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Thermally induced reversible solid-state transformation of novel *s*-indacene 1,3,5,7-tetraone derivatives

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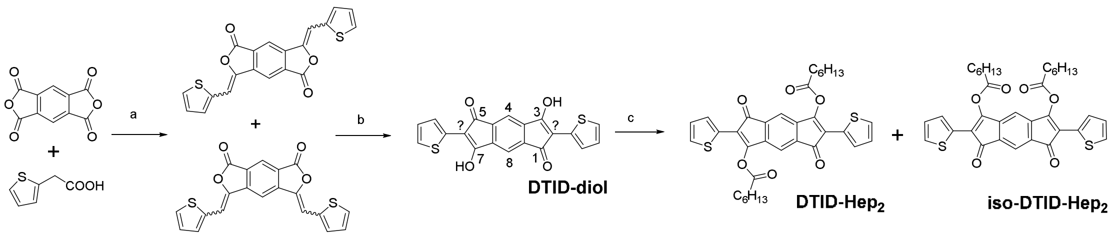
Abstract: Two novel *s*-indacene 1,3,5,7-tetraone derivatives, DTID-Hep$_2$ and iso-DTID-Hep$_2$ were synthesized and fully characterized. The controllable solid-state phase transformation of the crystals was studied. The unique thermal-induced polymorphic transformations suggest the two materials are interesting for potential applications not only in organic optoelectronics but also in switchable molecular actuators.

The discovery of new organic materials that exhibit reversible stimulus-responsive solid-state transformation have attracted special attention in recent years for their potential applications in molecular devices such as sensors, data storage and molecular actuators.[1-4] The mode of the organic molecular stacking characteristics can be altered by external stimulus, such as heating, light, grinding or exposure to chemical vapors. These are observed as changes in spectroscopic properties, electronic properties or mechanical properties.[5, 6] Polymorphic transformations in organic materials, including metal-organic frameworks, inorganic-organic hybrid materials and luminescent solids, have opened the way to develop novel functional materials for various potential applications.[1, 5, 7]

Molecularly stacked organic electronic materials were found to play a critical role in functional performance.[8] The molecular organizations can be changed by chemical modification of the semiconducting materials or controlling the preparation method of polymorphs.[9, 10] For instance, crystal packing and polymorphic transformation of the most representative organic semiconductors such as pentacene and related acenes have been studied for over 30 years.[8, 11] Studies on polymorphism of ogliothiophenes due to differential backbone arrangement have also been published,[12, 13] as well as those arising from long side-chain conformational changes under different preparation conditions.[14] However, few reports on reversible solid-state phase transformation of organic semiconducting materials have been reported.

Herein, we report the design of an *s*-indacene 1,3,5,7-tetraone analog of 1,3-indandione, composed of a symmetric tricyclic system consisting of a six-membered ring and two five-membered rings with carbonyl groups in the 1,3,5,7 positions. The planar structure and high electron affinity make it interesting in constructing organic electronics materials. The molecules 2,6-di(thiophen-2-yl)-s-indacene-*1,5*-dione-*3,7*-diol (DTID-diol) and its two derivatives have been synthesized and characterized: 2,6-di(thiophen-2-yl)-s-indacene-*1,5*-dione-*3,7*-diyl diheptanoate (DTID-Hep$_2$) and 3,5-dioxo-2,6-di(thiophen-2-yl)-*3,5*-dihydro-s-indacene-*1,7*-diyl diheptanoate (iso-DTID-Hep$_2$). Polymorphism in DTID-Hep$_2$ and iso-DTID-Hep$_2$ have been observed and the nature of the phase transformation between the polymorphs was investigated. Interestingly, iso-DTID-Hep$_2$ exhibits a thermally-induced reversible solid-state phase transformation, while DTID-Hep$_2$ has an irreversible phase transformation with significantly changed molecular packing.

Unlike 1,3-indandione and its derivatives that drew the attention of researchers,[15-22] a literature search shows that only few *s*-indacene 1,3,5,7-tetraone analog of 1,3-indandione have been synthesized.[23-25] The low number of publications is probably due to the difficult synthesis of the *s*-indancene tetraone precursor and its poor solubility.[26] The first attempt to synthesize DTID-diol by a literature procedure failed.[27] The condensation of pyromellitic dianhydride and 2-thiophene acetic acid in presence of triethylamine in acetic anhydride, yielded a complex insoluble mixture. Only a trace amount of the desired compound was found by mass spectroscopy. The desired DTID-diol was successfully obtained with a modified condensation method (Scheme 1).[28] The reaction of pyromellitic dianhydride and thiophene acetic acid in N-Methyl-2-pyrrolidone (NMP) in the presence of sodium acetate, afforded a poorly soluble solid mixture. The mass spectrum for this solid showed only a single peak at 378.00 Da, indicating an isomeric mixture of indancene derivatives.[28, 29] Without further isolation, the solid mixture was converted to disodium salts of DTID-diol in good yield by a rearrangement reaction in sodium methoxide solution.[30, 31] Acidifying the disodium salt yielded DTID-diol as a black solid. Condensation between DTI-dione-diol and heptanoic acid in presence of N,N'-dicyclohexylcarbodiimide (DCC) afforded DTID-Hep$_2$ and its isomer iso-DTID-Hep$_2$.



Scheme 1. Synthetic route.(a): NMP, NaOAc, 205 °C, 3 h; (b): Na, MeOH, 60 °C, 15 min; (c): Heptanoic acid, DCC, Dimethylformamide, rt, 24 h.

The DTID-diol shows poor solubility in common organic solvents and its ^{1}H NMR spectrum in DMSO-d_6 shows two slightly broadened peaks (δ = 7.79 ppm and (δ = 7.22 ppm) and a triplet (δ = 6.99 ppm) corresponding to protons at the C-3, C-5, and C-4 positions of the thiophene ring, respectively. No signal was observed for the aliphatic protons at C-2 and C-6 (Scheme 1, structure positions labeled with a question mark) of the indacene ring, indicating that DTID-diol in DMSO exists mainly as the enolized tautomer. This structure was further confirmed by a FD-MS mass spectrometry that exhibited only a single peak at 378.00 Da (Calcd 378.00 Da). For DTID-Hep$_2$, the singlet peak at 7.11 ppm is from the two protons in the central benzene ring of the material, as expected for such a symmetric structure. For iso-DTID-Hep$_2$, the chemical shift of the two protons in the central benzene ring appeared as two singlet peaks at 7.59 ppm and 6.50 ppm. (**Figure 1a**)

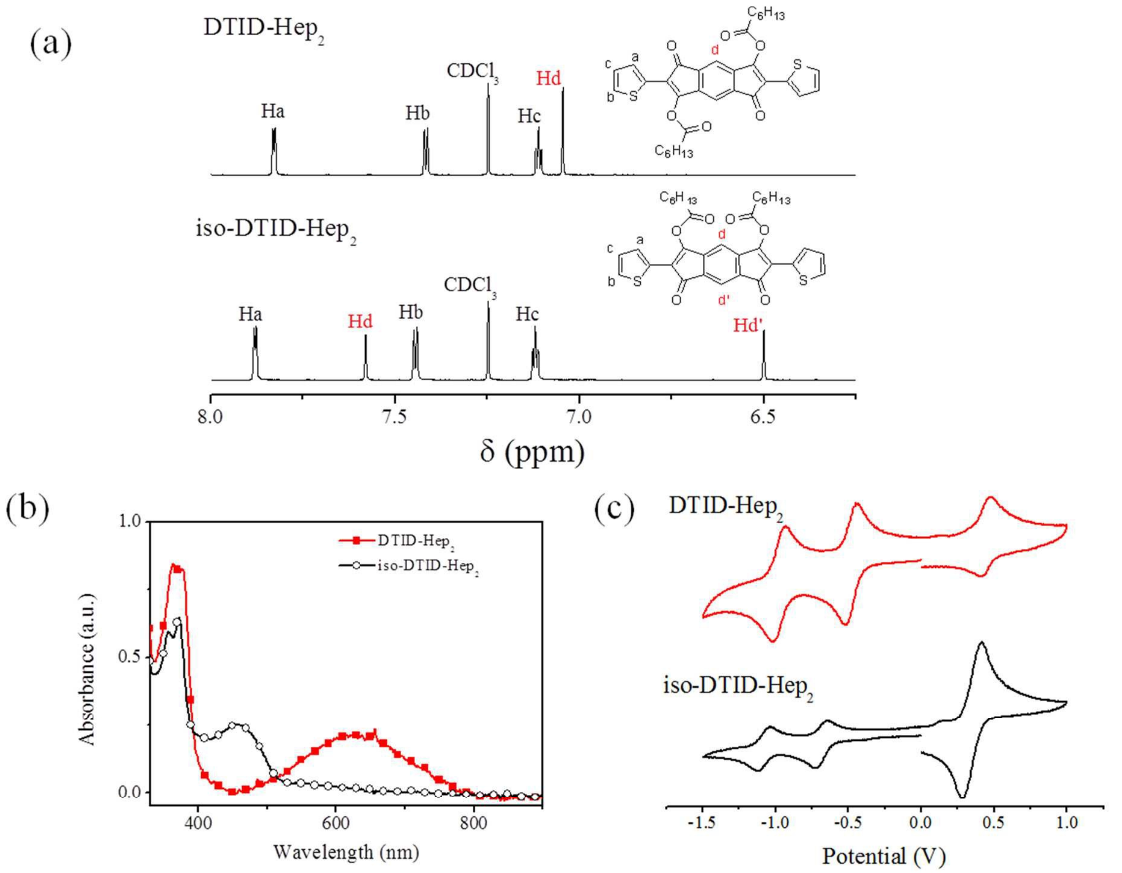
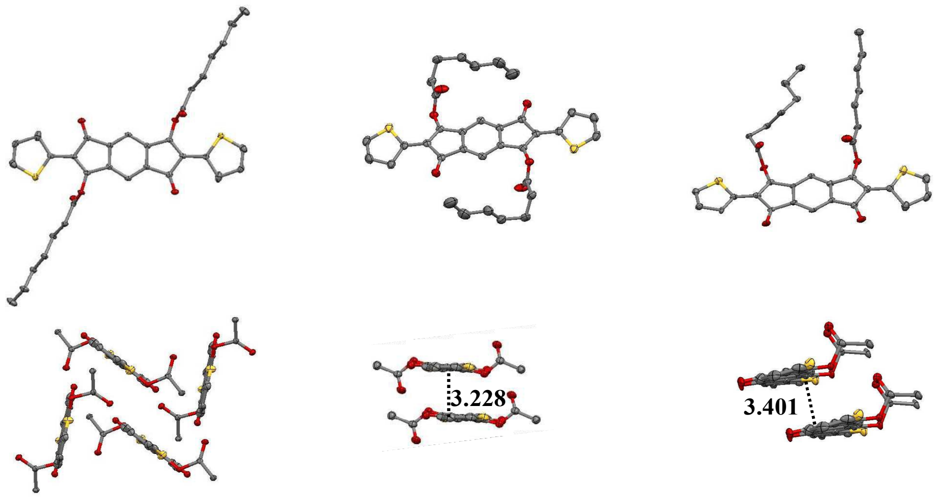


Figure 1. (a) ^{1}HNMR spectra of DTID-Hep$_2$ and iso-DTID-Hep$_2$ in CDCl$_3$. (b) UV/Vis absorption spectra of DTID-Hep$_2$ and iso-DTID-Hep$_2$ in dichloromethane (DCM). (c) Cyclic voltammogram of DTID-Hep$_2$ and iso-DTID-Hep$_2$ in DCM, 0.1 M tetrabutylammonium tetrafluoroborate, with Fc/Fc$^+$ as internal reference (~ 0.4 eV).

As shown in **Figure 1b**, DTID-Hep$_2$ and iso-DTID-Hep$_2$ exhibit a strong absorption peak at about 350 nm and a broad peak in the visible range (450 nm to 800 nm for DTID-Hep$_2$ and 400 nm to 510 nm for iso-DTID-Hep$_2$, respectively). The red-shifted absorption peak in the visible range of DTID-Hep$_2$ can be ascribed to the longer conjugation length of the molecule where π-electrons are apt to delocalize through the longitudinal axis of the molecule. i.e., the two thiophene moieties are in conjugation in DTID-Hep$_2$ but not in iso-DTID-Hep$_2$. The optical band gaps of DTID-Hep$_2$ and iso-DTI-Hep$_2$ are ~1.6 eV and ~2.3 eV, respectively. The electrochemical properties of DTID-Hep$_2$ and iso-DTID-Hep$_2$ were examined by cyclic voltammetry (**Figure 1c**). Two-reversible similar reduction waves were observed for DTID-Hep$_2$ and iso-DTID-Hep$_2$ in DCM, suggesting the LUMO values of -4.0 eV and -3.9 eV, respectively. The low-lying LUMO of the molecules makes them interesting candidates for n-type transistors and electron acceptors in organic electronics.[32-34]

Single crystals of DTID-Hep$_2$ and iso-DTID-Hep$_2$ were grown and analyzed using X-ray crystallography. From DCM/ethanol, DTID-Hep$_2$ forms a monoclinic unit cell, space group P 2_1/c (**Form 1**). The molecule is packed in a herringbone-type pattern with fully extended heptanoyl side-chains and no π-π interactions between the backbones **(Figure 2a)**. A unique polymorphism from side-chain conformation changes was observed from DCM/ethanol/Hexane **(Figure 2b)**. It forms a monoclinic unit cell, space group C2/c (**Form 2**). The backbone of DTID-Hep$_2$ is nearly planar with two disordered side chains and a dihedral angle between the outer thiophene rings with the central planar indacene ring of 5.8°. It exhibits a face-to-face slipped π-stacking motif with a short inter-planar packing distance 3.228 Å (please refer to Figure S4). This short intermolecular contact should provide an efficient pathway for charge transport. The iso-DTID-Hep$_2$ grown from DCM/ethanol forms an orthorhombic unit cell, space group P $2_1 2_1 2$. It has a nearly planar backbone with the two outer thiophene rings slightly twisted, exhibiting a face-to-face π-stacking (please refer to Figure S4 and Figure 2c). One of the thiophene units is disordered due to two possible (*syn* and *anti*) conformers. The inter-planar packing distance of iso-DTID-Hep$_2$ is 3.401 Å.



(a) Form 1, DTID-Hep$_2$ (b) Form 2, DTID-Hep$_2$ (c) iso-DTID-Hep$_2$

Figure 2. Crystal structure of DTID-Hep$_2$ (a), Form 2 of DTID-Hep$_2$ (b) and iso-DTID-Hep$_2$ (c). In Form 2 of DTID-Hep$_2$ (b), a conformer of the disordered side chains were omitted for clarity. In the lower row, the long side chains were omitted for clarity. Thermal ellipsoids are shown at 50% probability level (red and yellow color represents oxygen and sulfur atom, respectively)

The DSC data of DTID-Hep$_2$ (mp: 176-179 °C) showed an irreversible sharp endothermic peak at about 150 ^{o}C, while the DSC of iso-DTID-Hep$_2$ (mp: 195-197 °C) exhibited a weak broad endothermic peak at about 85 ^{o}C in the heating part of the cycle and a weak broad exothermic peak at about 65 ^{o}C upon cooling (**Figure S1**). To observe the phase transition processes, a hot-stage cross-polarized optical microscope was used to record the images. The phase transition of DTID-Hep$_2$ crystals occurred at about 150 ^{o}C in the first heating process, along with color change from bright yellowish to blue. The new phase grew along the longitudinal direction of the crystalline needle until the whole needle eventually irreversibly changed (**Figure 3, A-D**). While for iso-DTID-Hep$_2$, the orange color of the fiber gradually faded into dark grey-green along the longitudinal direction at about 85 ^{o}C in the heating process (**Figure 3, E-G**), as the phase transition occurred. In contrast, during the cooling process, at about 65 ^{o}C, the fiber color reversibly changed back form dark grey-green into bright orange (**Figure 3, H-J**).

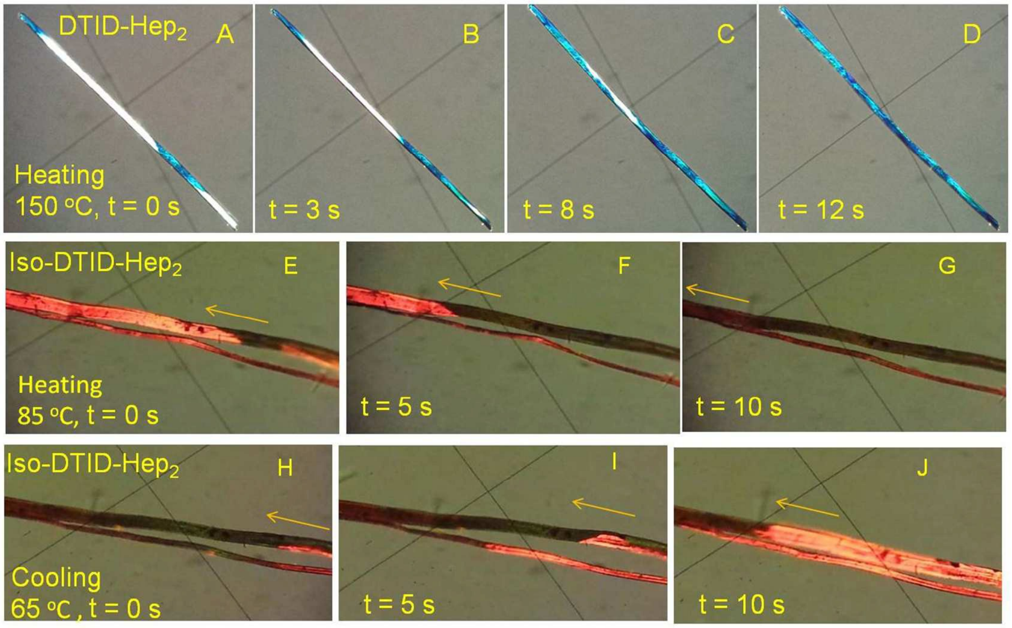


Figure 3. Cross-polarized optical microscope images of DTID-Hep$_2$ at 150 °C (from t= 0 s to 12 s) in heating process (A-D), and iso-DTID-Hep$_2$ at 85 °C (from t= 0 s to 10 s) in heating process (E-G), and at 65°C (from t = 0 s to 10 s) in cooling process (H-J).

The powder XRD of DTID-Hep$_2$ and iso-DTID-Hep$_2$ changed significantly upon heating. The experimental pattern of DTID-Hep$_2$ (**Form 1**) at 30 °C, before heating, matches well with its simulated XRD pattern **(Figure 4a)**. Upon heating to 160 °C, the pattern clearly changed, where the main diffraction shifted from 5.1° to 6.9° and a more amorphous halo, probably originating from the random conformation change of the localized heptanoyl side-chains at high temperature. This pattern is maintained when the sample is cooled back to 30 °C, indicating the thermally irreversible conformational changes. However, for iso-DTID-Hep$_2$, the reversible XRD pattern conversion suggests that the phase transformation is a thermally-induced reversible crystal-to-crystal transformation. The experimental pattern changed significantly when heating from 80 °C to 90 °C, along with a new diffraction peak at 5.7°, while two diffraction peaks at 5.3° and 6.3° disappeared, shown in **Figure 4b**. Interestingly, the diffraction pattern changed reversibly back to the original one when cooling the sample back to 60 °C. These changes are consistent with the DSC and optical microscope results, proving that iso-DTID-Hep$_2$ exhibits a thermally induced-reversible crystal-to-crystal transformation.

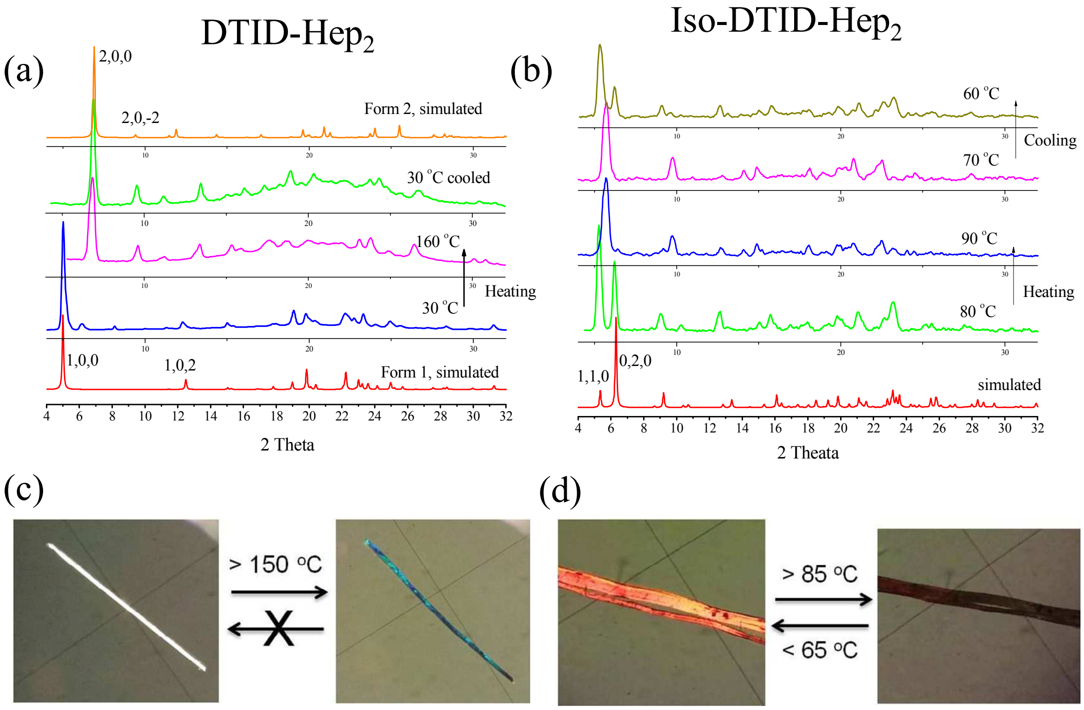


Figure 4. Experimental and simulated X-ray diffraction (XRD) data of DTID-Hep$_2$ (a), and iso-DTID-Hep$_2$ (b). Schematic thermally-induced phase transformation of DTID-Hep$_2$ (c), and iso-DTID-Hep$_2$ (d).

In conclusion, two novel s-indacene-tetraone derivatives, DTID-Hep$_2$ and iso-DTID-Hep$_2$, were easily synthesized and fully characterized. The reversible electron accepting properties and low-lying LUMO of DTID-Hep$_2$ and iso-DTID-Hep$_2$ indicate these molecules are good electron acceptors. Polymorphism in DTID-Hep$_2$ and iso-DTID-Hep$_2$ have been observed and the thermally-induced phase transformations between the polymorphs have been investigated. The unique thermally-induced polymorphic transformations suggest that the these materials are interesting for potential applications not only in organic optoelectronics but also in switchable molecular actuators.

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Supporting Information Available. Detailed synthesis procedures and characterization.

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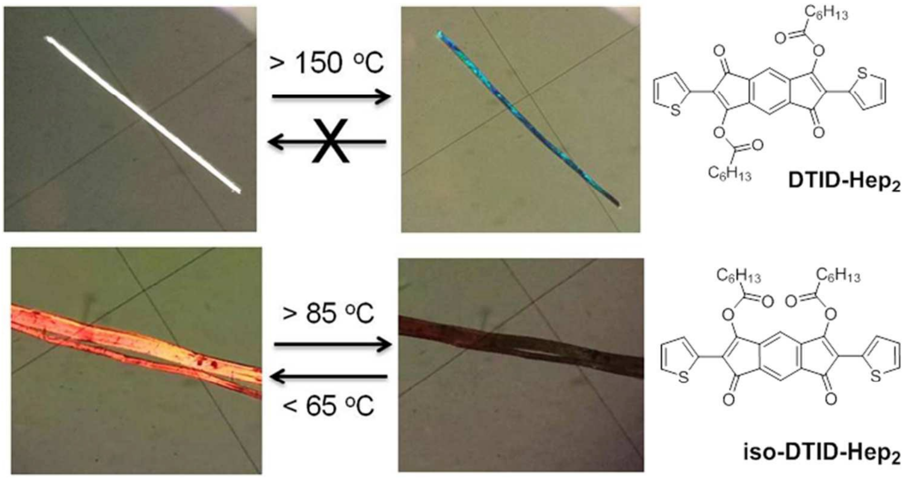

Novel electronic-efficient *s*-indacene 1,3,5,7-tetraone derivatives were synthesized, which exhibit unique thermal-induced polymorphic transformation.