

## Supplementary Information

for

### Thermosalient effect of a diketopyrrolopyrrole dye between two polymorphs with different crystal systems and molecular arrangements

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## 1. Experimental Details

### 1.1 Materials and Instruments

All materials were used without further purification. 3,6-Bis(4-chlorophenyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione was obtained from DIC Co.  $K_2CO_3$  and 1-bromopropane were obtained from Tokyo Chemical Industry (TCI) Co. Dimethyl formamide (DMF) was purchased from Hayashi Pure Chemical (HPC) Ind. Ltd. Wako silica gel C-300 (45–75  $\mu\text{m}$ ) was used for the column chromatography. All solvents were obtained from Kanto Chemical Co.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Jeol ECX-400 MHz NMR instrument (Jeol Co.) with tetramethylsilane (TMS) as the internal standard. Elemental analyses (EA) of C, H, and N were performed with a CHNOS Elemental Analyzer Vario EL III (Elementar Co.). High-resolution mass spectrometry (HRMS) data were collected using a [LC] LaChromUltra/[MS] NanoFrontierLD (Hitachi High-Technologies Co.) spectrometer. Infrared (IR) spectra were collected on a JASCO FT/IR 6200 spectrophotometer.

### 1.2 Synthesis procedure of PR3

A suspension of 3,6-bis(4-chlorophenyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (pigment red 254) (1.78 g, 5.0 mmol) and  $K_2CO_3$  (2.81 g, 20mmol) in DMF (20 mL) was heated at 140°C under nitrogen. At this temperature and with vigorous stirring, a solution of 1-bromopropane (2.1 mL, 15 mmol) in DMF (6 mL) was added dropwise. The mixture was stirred at 120°C for 3 h. After cooling to room temperature,  $\text{CHCl}_3$  (100 mL) and distilled water (100 mL) were added. The  $\text{CHCl}_3$  layer was separated from the

aqueous layer and then washed with water several times using a separating funnel.

After evaporation of the organic solvent, silica gel column chromatography was carried out two times (toluene: ethyl acetate = 5:1, CHCl<sub>3</sub>: *n*-hexane = 7:3). The pure product was obtained as an orange solid (187 mg, yield 10.5%)

m.p.: 232-233°C, IR (KBr pellet):  $\nu$  2966.95, 1676.8, 1609.31, 1447.31, 1375, 844.669, 815.742, 737.639 cm<sup>-1</sup>, <sup>1</sup>H NMR (400 MHz, Chloroform-d)  $\delta$  7.77 (d, J = 8.7 Hz, 4H), 7.52 (d, J = 8.2 Hz, 4H), 3.72 (t, J = 7.3 Hz, 4H), 1.65 - 1.58 (m, 4H), 0.86 (t, J = 7.3 Hz, 6H). <sup>13</sup>C NMR (100 MHz, Chloroform-d),  $\delta$  (ppm): 11.26, 22.91, 43.53, 110.02, 126.62, 129.41, 130.04, 137.44, 147.44, 162.59. HRMS (ESI) calcd for C<sub>24</sub>H<sub>23</sub>C<sub>12</sub>N<sub>2</sub>O<sub>2</sub> ([M+H]<sup>+</sup>): 441.35; found: 441.11.

### 1.3 Single-crystal X-ray diffraction

The diffraction data of **PR3Y** and **PR3O** were collected at 223 and 293 K, respectively, on a Rigaku XtaLAB PRO using graphite monochromated Cu *K* $\alpha$  radiation ( $\lambda$  = 1.54187 Å). Data reduction was performed using CrysAlisPro software [1]. The structures were solved by a direct method using SHELXT [2] and refined by full-matrix least-squares methods based on  $F^2$  using SHELXL [3]. All non-hydrogen atoms were refined anisotropically. In the refinement of **PR3Y**, two C11 and C12 belonging to one propyl group were disordered over two sets of atomic sites having unequal occupancies. Therefore, the structural analysis was carried out by dividing into two parts without any restraints or constraints (part 1: C11A-C12A and part 2: C11B-C12B, respectively). And their occupancy factors were converged to 0.740(8) for part 1 and 0.260(8) for part 2,

respectively. The positions of all hydrogen atoms of **PR3Y** and **PR3O** were calculated geometrically and refined by the riding model. Structure analysis was performed using Olex 2 [4] and the CrystalStructure 4.2 crystallographic software package [5]. The crystal structures were visualised and evaluated using Mercury 3.9 [6].

#### 1.4 Hot-stage microscopy (HSM)

The thermal behaviour of **PR3Y** crystals was observed by using a conventional microscope with a hot stage. The video was recorded at the time of the heating and it continued from 170°C until melting.

#### 1.5 Differential scanning calorimetry (DSC)

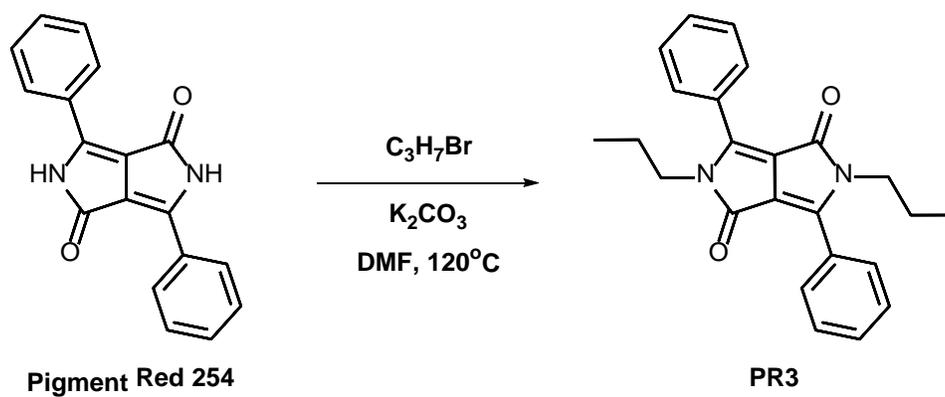
DSC was conducted in crimped aluminium pans using a Rigaku Thermo plus2 DSC8230 at a heating rate of 10 K min<sup>-1</sup>. The typical weight of the sample was 2–4 mg.

#### 1.6 Powder X-ray diffraction (PXRD)

PXRD was performed using Rigaku R-Axis Rapid imaging plate diffractometer with a graphite monochromatic Cu  $K\alpha$  radiation ( $\lambda = 1.54187 \text{ \AA}$ ) source at room temperature.

Measurements were conducted in the  $2\theta$  range from 5° to 35°. (observed  $2\theta = 11.22^\circ$ ,  $15.13^\circ$ ,  $19.40^\circ$ ,  $23.14^\circ$  for **PR3Y**;  $12.89^\circ$ ,  $14.52^\circ$ ,  $18.92^\circ$ ,  $22.50^\circ$  for **PR3O** and after the

transition of **PR3Y**) Before measurement, the crystals of each polymorph were ground into a powdered form.



**Scheme S1.** Synthesis route of **PR3**

**Table S1.** Crystallographic data of two polymorphs of **PR3**

	<b>PR3Y</b>	<b>PR3O</b>
Formula	<b>C<sub>24</sub> H<sub>22</sub> Cl<sub>2</sub> N<sub>2</sub> O<sub>2</sub></b>	<b>C<sub>24</sub> H<sub>22</sub> Cl<sub>2</sub> N<sub>2</sub> O<sub>2</sub></b>
Crystal size / mm	<b>0.294×0.14×0.055</b>	<b>0.649×0.358×0.197</b>
Radiation	<b>Cu K<math>\alpha</math></b>	<b>Cu K<math>\alpha</math></b>
Crystal system	<b>Triclinic</b>	<b>Monoclinic</b>
Space group	<b><i>P</i>-1</b>	<b><i>P</i> 2<sub>1</sub>/<i>c</i></b>
<i>a</i> / Å	<b>9.7334(2)</b>	<b>11.31549(16)</b>
<i>b</i> / Å	<b>9.9244(2)</b>	<b>9.66903(15)</b>
<i>c</i> / Å	<b>12.4910(3)</b>	<b>9.86401(15)</b>
<i>α</i> / °	<b>89.585(2)</b>	<b>90</b>
<i>β</i> / °	<b>69.561(2)</b>	<b>96.4687(13)</b>
<i>γ</i> / °	<b>67.774(2)</b>	<b>90</b>
<i>V</i> / Å <sup>3</sup>	<b>1035.74(4)</b>	<b>1072.35(3)</b>
<i>Z</i>	<b>2</b>	<b>2</b>
Temperature/ K	<b>223</b>	<b>293</b>
<i>D</i> <sub>calc</sub> / g cm <sup>-3</sup>	<b>1.415</b>	<b>1.367</b>
Reflections collected	<b>9651</b>	<b>5661</b>
Independent reflections	<b>3580</b>	<b>1868</b>
<i>R</i> <sub>int</sub>	<b>0.027</b>	<b>0.031</b>
<i>R</i> -factor	<b>0.045</b>	<b>0.0496</b>
<i>wR</i> <sub>2</sub> (all data)	<b>0.1215</b>	<b>0.1397</b>
CCDC No.	<b>1828028</b>	<b>1828027</b>
Colour	<b>yellow</b>	<b>orange</b>

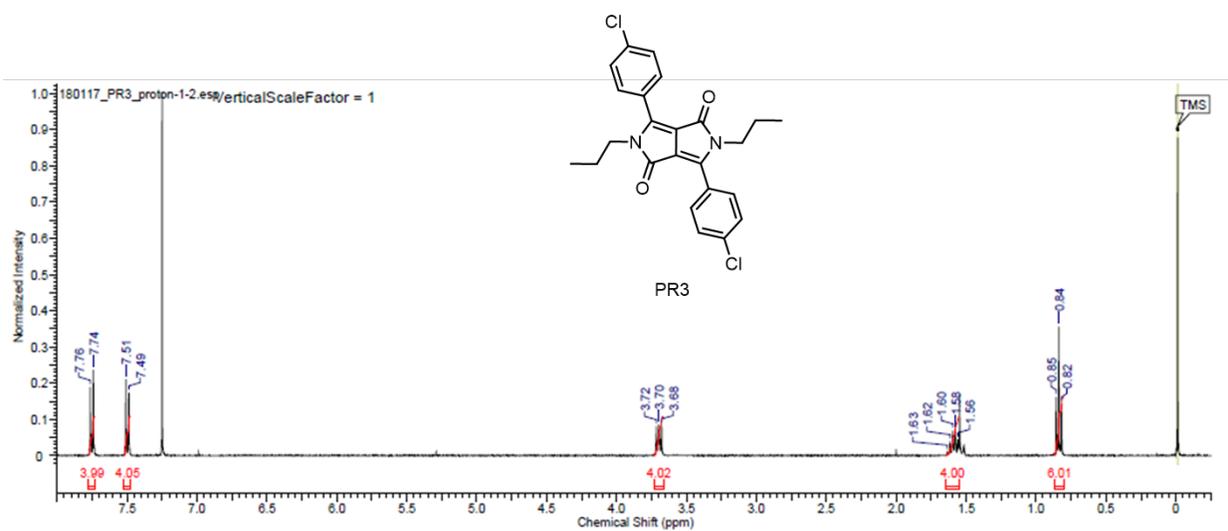


Figure S1. <sup>1</sup>H-NMR spectra of PR3.

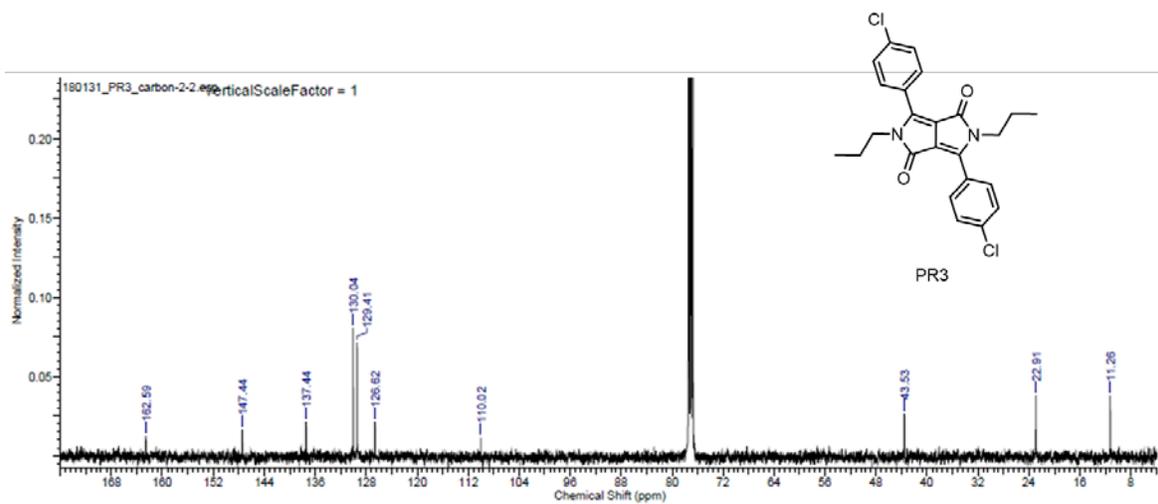
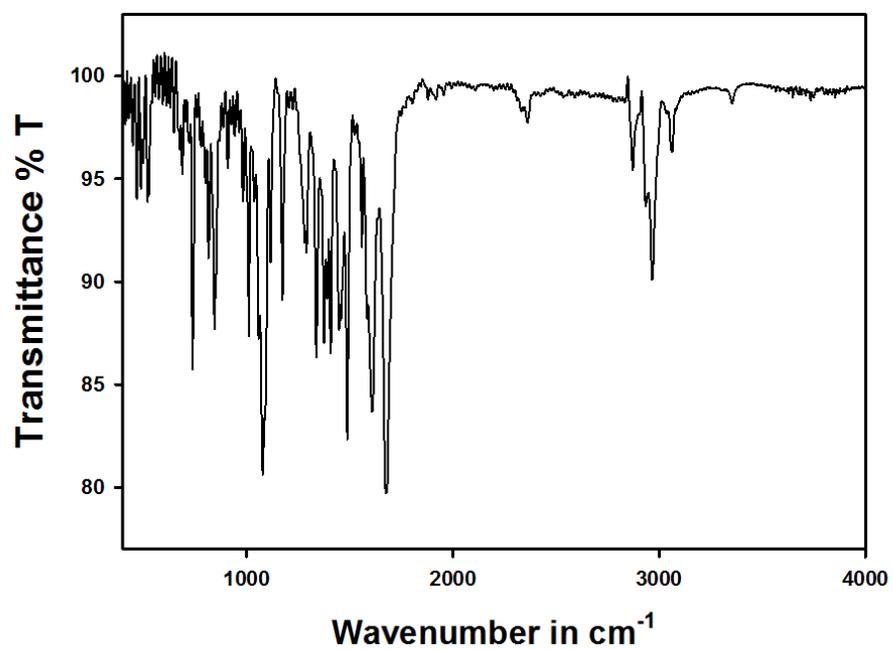
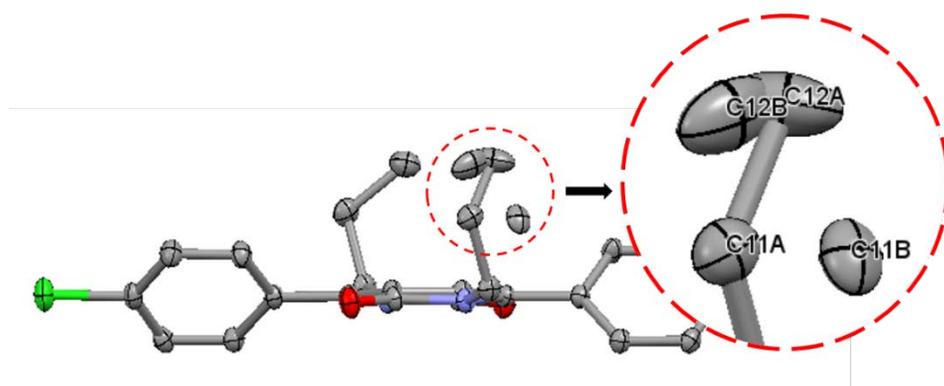


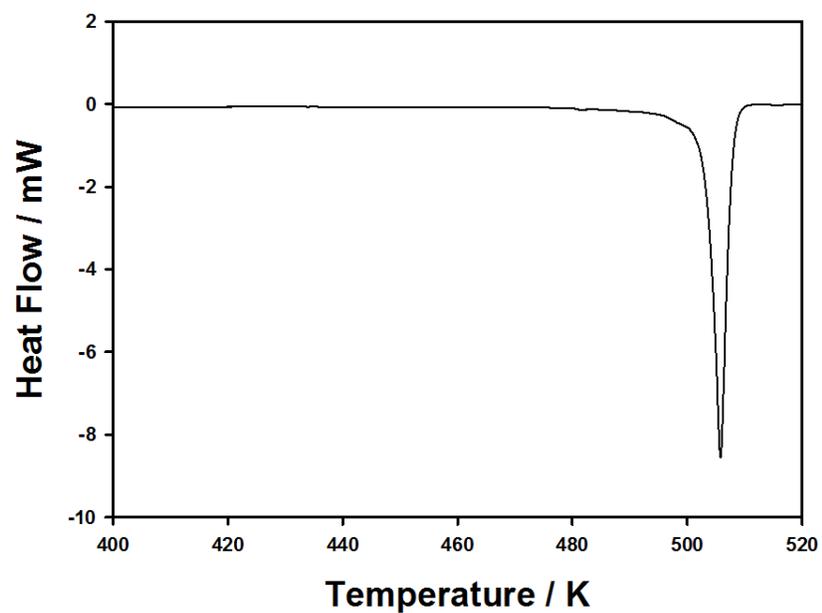
Figure S2.  $^{13}\text{C}$ -NMR spectra of PR3.



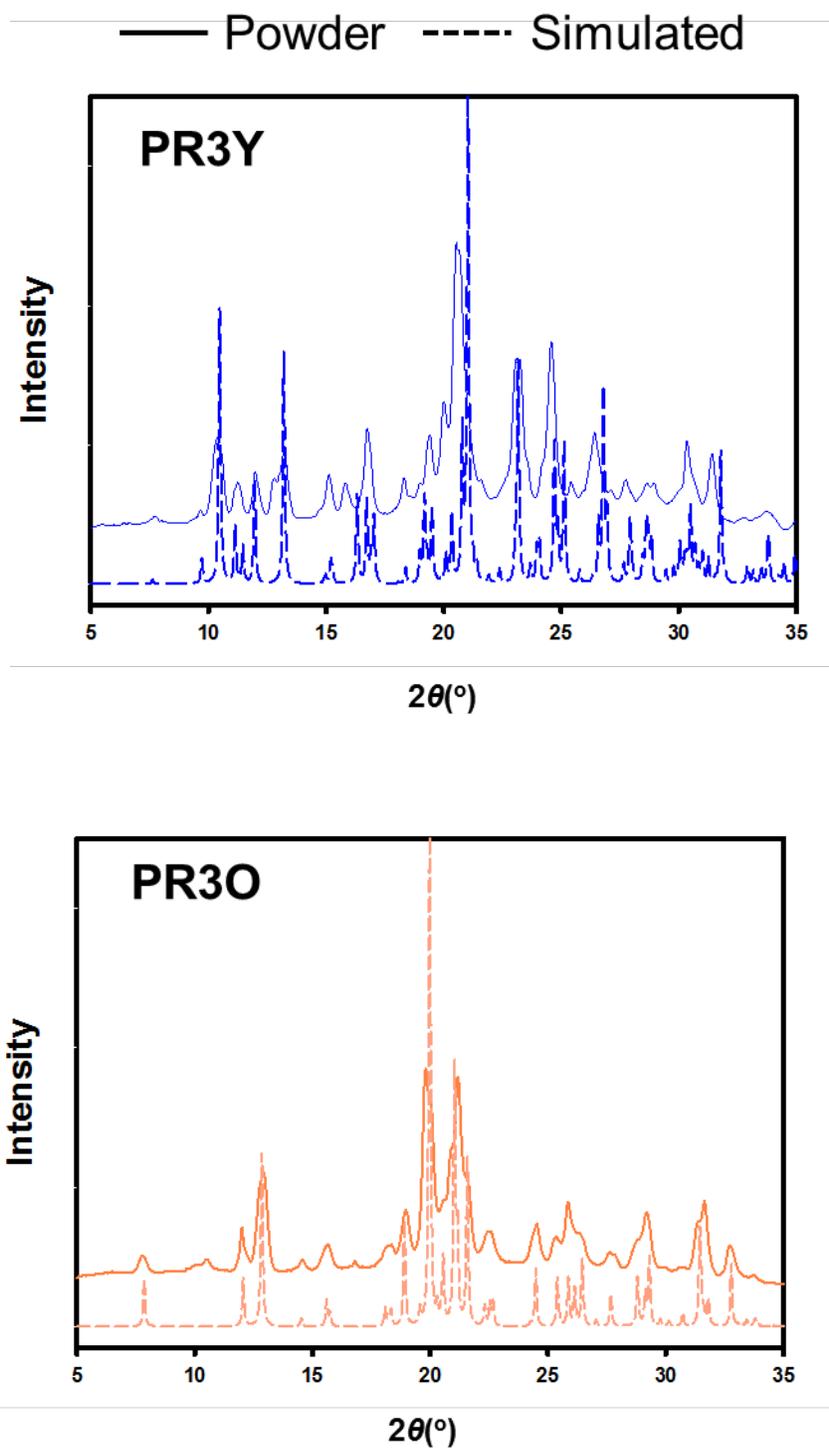
**Figure S3.** Fourier transform infrared (FTIR) spectra of **PR3**.



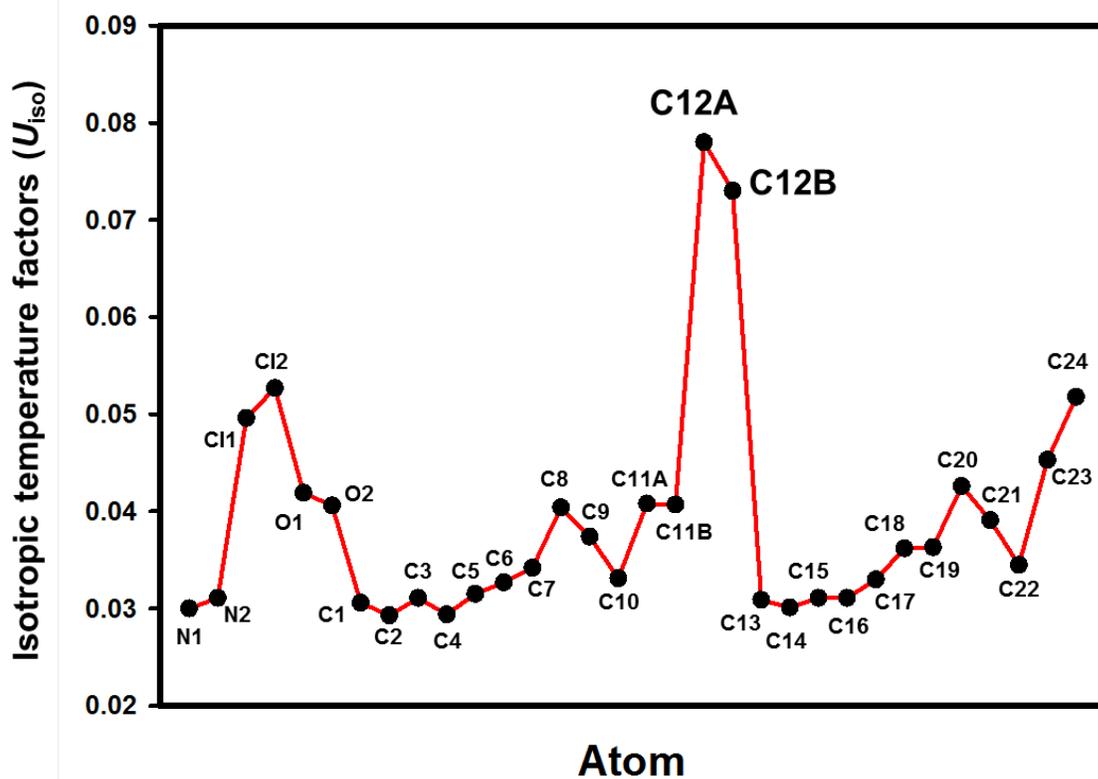
**Figure S4.** Molecular conformation of **PR3Y**. Red dotted circle indicates the disorder of one of the propyl substituents.



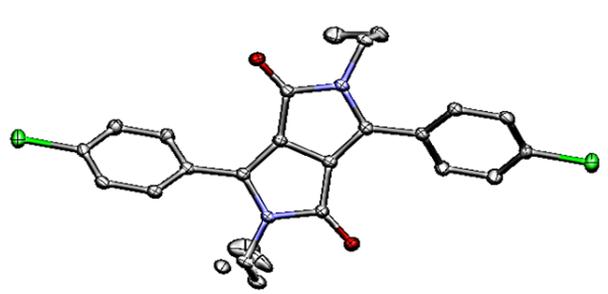
**Figure S5.** DSC curve of **PR3O**. No specific phase transition peak was observed. The endothermic peak around 505 K is a melting point.



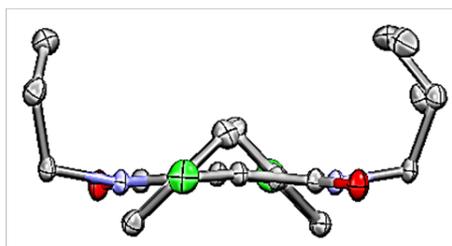
**Figure S6.** Powder (solid line) and simulated (dashed line)  $2\theta$  values of PXRD of **PR3Y** and **PR3O**.



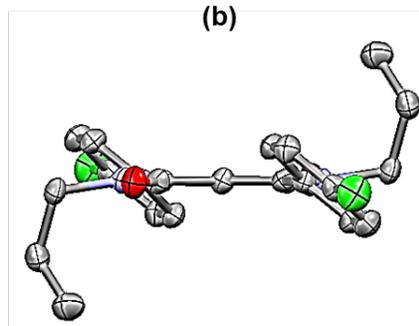
**Figure S7.** Isotropic temperature factors ( $U_{iso}$ ) of the PR3Y correlated with all atoms in  $-50^{\circ}\text{C}$ .



(a)



(b)



**Figure S8.** ORTEP diagrams of the molecular geometries showing with displacement ellipsoids at the 30% probability level. H atoms are omitted for clarity. (a) **PR3Y**, (b) **PR3O**.

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No.	Name	Weight [mg]	Date	Time	Info	O2	Prot. [%]	C/N Ratio	Content [%]	Peak Area	Daily Factor
14	PR3	3.0760	16.01.18	13:58	Su	1	0.000	10.30	N: 6.236 C: 64.20 S: 0.699 H: 4.997	6236 45890 221 8605	1.0094 0.9899 0.9909 1.3110

**Elemental Analysis of PR3.**

## References

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- [2] SHELXT Version 2014/5: Sheldrick, G. M. (2014). *Acta Cryst.* A70, C1437.
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- [4] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339-341.
- [5] Rigaku (2017). CrystalStructure. Version 4.2. Rigaku Corporation, Tokyo, Japan.
- [6] C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler and J. van de Streek, *J. Appl. Cryst.*, 2006, **39**, 453-457.