## **Supporting Information**

## **Disproportionation-induced solid-state fluorescence**

## in 6,13-dihydropentacenes

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**Fig. S1.** <sup>1</sup>H NMR spectrum of **3a** after heating at 250 °C.



Fig. S2. <sup>1</sup>H NMR spectrum of **3a** after heating at 250 °C upon exposure to air.



**Fig. S3.** The differential scanning calorimetry (DSC) DSC (Differential Scanning Calorimetry) measurement of **3a** (scan rate = 10 °C/min).



Fig. S4. Apparent fluorescence color change of a 3b with the increasing temperature and polarized optical microscopy images of 3b.



Fig. S5. Fluorescence spectra of a thin film of 3a with increasing temperature.



Fig. S6. Fluorescence spectra of 3a in CHCl<sub>3</sub> solution as function of concentration ( $\lambda_{ex} = 275$  nm).



Fig. S7. ORTEP drawings of 3b (thermal ellipsoids at 50% probability).



Fig. S8. ORTEP drawings of 3c (thermal ellipsoids at 50% probability).



**Fig. S9.** Fluorescence spectra of solid of **3b** upon photoirradiation ( $\lambda_{ex} > 300$  nm).



**Fig. S10.** XRD pattern of **3a** after annealing at 230 °C (orange line), at 230 °C (green line), and before annealing (bule line).



Fig. S11. FT-IR spectrum of 2.



Fig. S12. <sup>1</sup>H NMR spectrum of 3a in CDCl<sub>3</sub>.



Fig. S13. <sup>1</sup>H NMR spectrum of 3a in CDCl<sub>3</sub>.



Fig. S14. <sup>1</sup>H NMR spectrum of 3b in CDCl<sub>3</sub>.



Fig. S15. <sup>13</sup>C NMR spectrum of **3b** in CDCl<sub>3</sub>.



Fig. S16. <sup>1</sup>H NMR spectrum of 3c in CDCl<sub>3</sub>.



Fig. S17. <sup>13</sup>C NMR spectrum of **3c** in CDCl<sub>3</sub>.