Supplementary Information

Polymorph- and molecular alignment-dependent lasing behaviors of cyano-substituted thiophene/phenylene co-oligomer

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S1. Polarized light microscopy observations of BP2T-CN orange-emitting crystals.

The fluorescence micrographs of BP2T-CN orange-emitting crystal is shown in Fig.S1. Figures S1(a) and S1(b)/S1(c) show the non-polarized and polarized fluorescence microscope images, respectively. The luminescence intensity was maximum or minimum when 115°-or 25°-polarized light was irradiated to the crystal. No polycrystalline domains can be seen from the polarized microscopy images. This means that BP2T-CN orange-emitting sample is the single crystal.

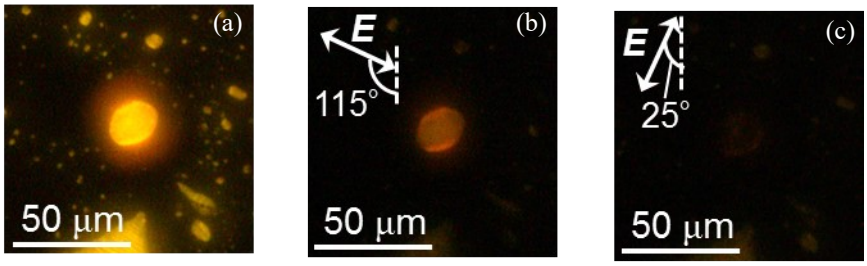

Figure S1. The non-polarized (a) and polarized fluorescence micrographs (b, c) of BP2T-CN orange-emitting crystal.

S2. X-ray diffraction analysis for orange- and green-emitting crystals.

Molecular structures and crystal structures for orange- and green-emitting crystals are shown in Fig. S2. The crystal structure data was obtained for orange-emitting crystal ($P2_1$, a = 18.47 Å, b =7.271 Å, c = 18.56Å, α = 90˚, β = 100.57˚, γ = 90˚ Z = 4) and green-emitting crystals ($P2_1$, a = 18.40 Å, b = 7.240 Å, c = 18.44 Å, α = 90˚, β = 100.57˚, γ = 90˚, Z = 4), respectively. As results of x-ray diffraction measurements, there were no impurities, crystal structure change, and the mixture of amorphous and monoclinic phase crystal for orange- and green-emitting crystals. Therefore, the red-shifting in the PL spectrum of the orange-emitting crystal compared to the green-emitting crystal is attributed to smaller slip angle (angle between two adjacent molecules forming a diagonal pair and (100) plane).

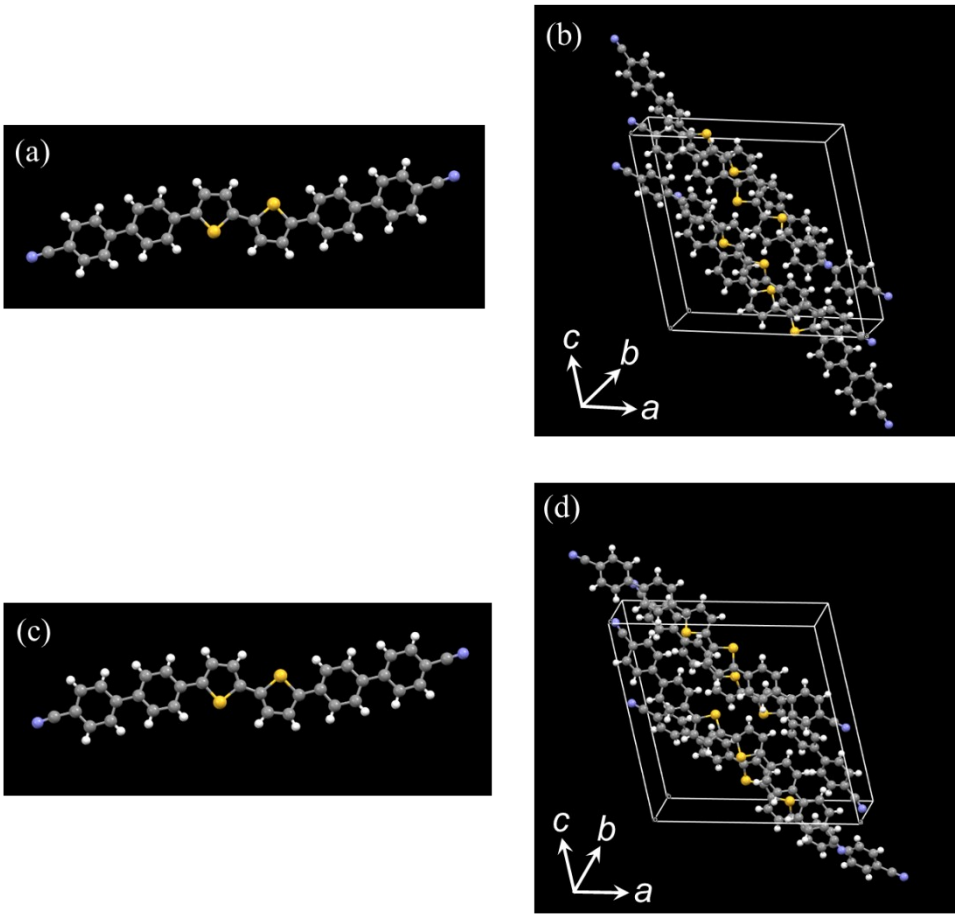

Figure S2. Molecular structures and crystal structures for orange- (a, b) and green-emitting crystals (c, d).

S3. Differential scanning calorimetry (DSC) purity analysis and thermogravimetry-differential thermal analysis (TG-DTA) for powder and crystals of BP2T-CN.

The van't Hoff plot (temperature versus reciprocal of the melt fraction (*F*)) for orange-emitting BP2T-CN crystals was obtained by differential scanning calorimetry (DSC) purity analysis (Figure S3(a)). The procedures of data analysis were based on the following literatures.[1, 2] The purity *P* of orange-emitting BP2T-CN crystals was determined using the slope S_2 of the data plots for after linearization (black closed circles) in Figure S3(a) and the following equation:

$$P = 100 \times \left(1 + \frac{\Delta H_f \times S_2}{RT_0{}^2}\right)$$

, where R, T_0, and ΔH_f are gas constant, melting point of sample, and heat of melting obtained from total peak area × (1+correction %), respectively. As a result of data analysis, the purity of the orange-emitting BP2T-CN crystals was determined to be 99.64 %.

Thermogravimetry-differential thermal analysis (TG-DTA) was also performed on a powder and crystals of BP2T-CN. The TG-DTA spectra for powder and crystals were shown in Figures S3(b) and S3(c). From the TG curves for powder and crystals, the materials were chemically stable up to approximately 450 °C without any noticeable weight loss. The first peaks at 320 °C (powder) and 319 °C (crystals) in DTA curves show the melting point of the materials. Decomposition temperatures were decided to be 484 °C (powder) and 482 °C (crystals) by gravimetrical reduction points of TG-DTA curves, respectively. Therefore, since the decomposition does not occur under the crystal fabrication condition at ~360 °C using a gas burner, the orange emissions from the BP2T-CN crystals are attributed to smaller slip angle.

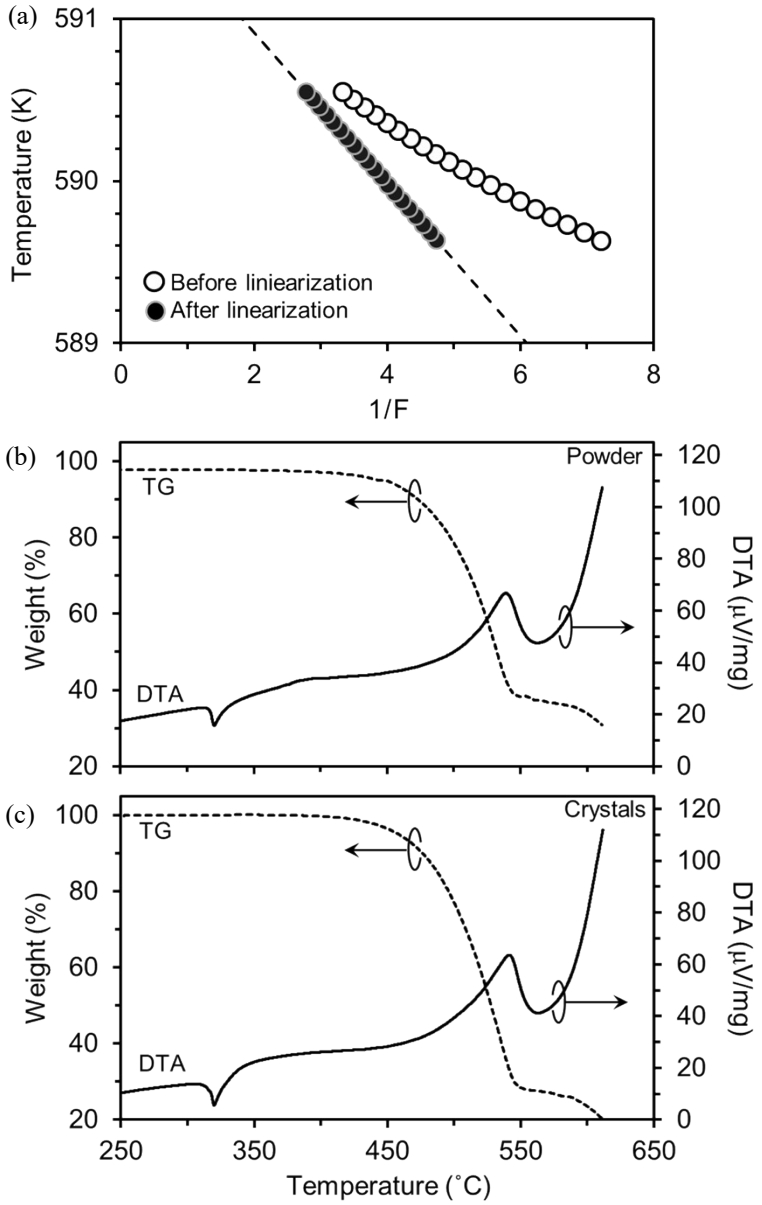

Figure S3. (a) DSC purity analysis for orange-emitting crystals. (b) The TG-DTA spectra for powder (b) and crystals

References

1. K. Yoshii, *Chem. Pharm. Bull*., 1997, **45**, 338-343.
2. A. Książczak, T. Książczak and T. Zielenkiewicz, *J. Therm. Anal. Cal*., 2004, **77**, 233–242.