## Supporting Information Spontaneous Formation of Aligned Large Area Ordered $\pi$ -Conjugated Film with Polarized Fluorescence and Amplified Spontaneous Emission Based on Liquid Crystalline Bi-1,3,4-oxadiazole derivative

Songnan Qu,<sup>a</sup> Hongyu Zhang,<sup>b</sup> Yuejia Ma,<sup>a</sup> Junsheng Cao,<sup>a</sup> Shaohang Wu<sup>a</sup> and Xingyuan Liu\*<sup>a</sup>

<sup>a</sup> State Key Laboratory of Luminescence and Applications, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033 (P. R. China).
<sup>b</sup>Key Laboratory for Supramolecular Structure and Materials of Ministry of Education, College of Chemistry, Jilin University, Changchun 130012, P. R. China.



**Figure S1**. DSC curves of BOXD-5 on the first cooling run (red line) and on the second heating run (green line) (rate: 10 °C/min).



**Figure S2.** POM images of BOXD-5 aligned large area  $\pi$ -conjugated film sandwiched between untreated glass slides (a) before laser pumping, (b) after high energy pumping; POM images of (c) laser damaged BOXD-5 aligned large area  $\pi$ -conjugated film after removing the cover glass and (d) the removed cover glass; POM image of the BOXD-5 film (e) after recovering the same cover glass and (f) after heating-cooling thermal process (white crossed arrows illustrated the crossed-polarizers).



**Figure S3.** POM images of BOXD-5 aligned large area  $\pi$ -conjugated film prepared by parallelly moving off the covered glass along the same direction in its nematic phase and quickly cooling in the air at room temperature (white crossed arrows illustrated the crossed-polarizers).



**Figure S4.** (a) Polarized photoluminescence (PL) spectra taken with maximal and minimal intense, (b) polarized excited PL spectra taken with maximal and minimal intense of BOXD-5 aligned large area  $\pi$ -conjugated film sandwiched between untreated glass slides (excitation in the range of 330-385 nm, and collected the emissions longer than 420 nm).



**Figure S5.** POM image of BOXD-5 vacuum evaporated film on glass (white crossed arrows illustrated the crossed-polarizers).



**Figure. S6.** Excitation intensities and PL spectra of glass substrate as reference and BOXD-5 aligned ordered film and vacuum evaporated film on glass for photoluminescence quantum yield calculations.



| S-Table 1. | Calculated | ground | to | excited | state | transition | electric | dipole | moments | (Au) | of |
|------------|------------|--------|----|---------|-------|------------|----------|--------|---------|------|----|
| BOXD-5:    |            |        |    |         |       |            |          |        |         |      |    |

| state | Х       | Y       | Z      | Dip. S  | Osc.   |
|-------|---------|---------|--------|---------|--------|
| 1     | -4.2228 | -0.3292 | 0.0000 | 17.9401 | 1.6937 |
| 2     | 0.0000  | 0.0000  | 0.0000 | 0.0000  | 0.0000 |
| 3     | -0.3929 | 0.0860  | 0.0000 | 0.1617  | 0.0214 |
| 4     | 0.0000  | 0.0000  | 0.0000 | 0.0000  | 0.0000 |
| 5     | 0.3154  | -0.6745 | 0.0000 | 0.5545  | 0.0769 |
| 6     | 0.0000  | 0.0000  | 0.0000 | 0.0000  | 0.0000 |