Supplementary material (ESI) for Journal of Materials Chemistry


# Supporting Information for Self-assemblies of Highly luminescent Bi-1,3,4-oxadiazole Derivatives through Electron Donor-Acceptor Interactions in Three-Dimensional Crystal, Two-Dimensional Layers and Mesophases

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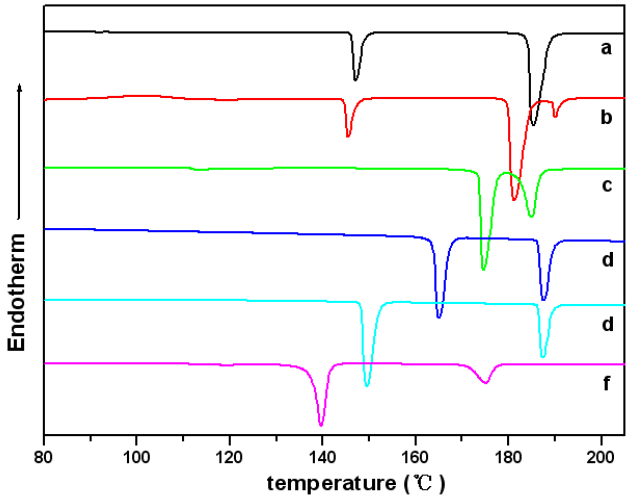
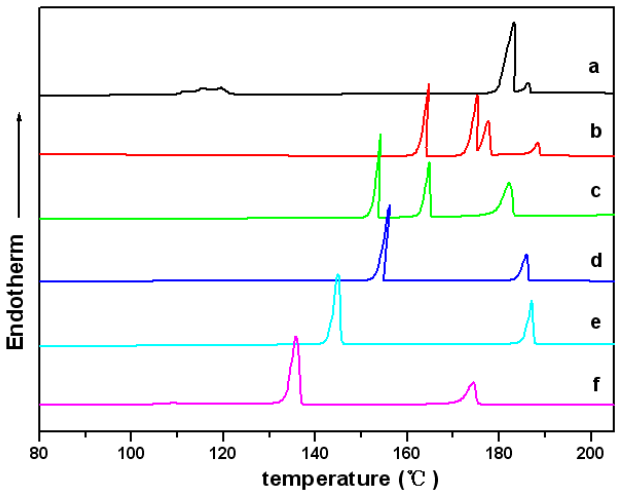
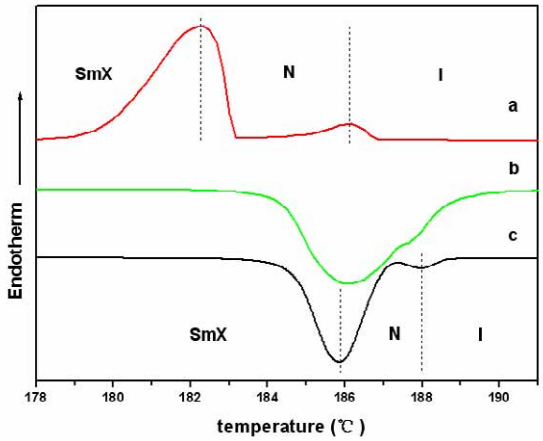


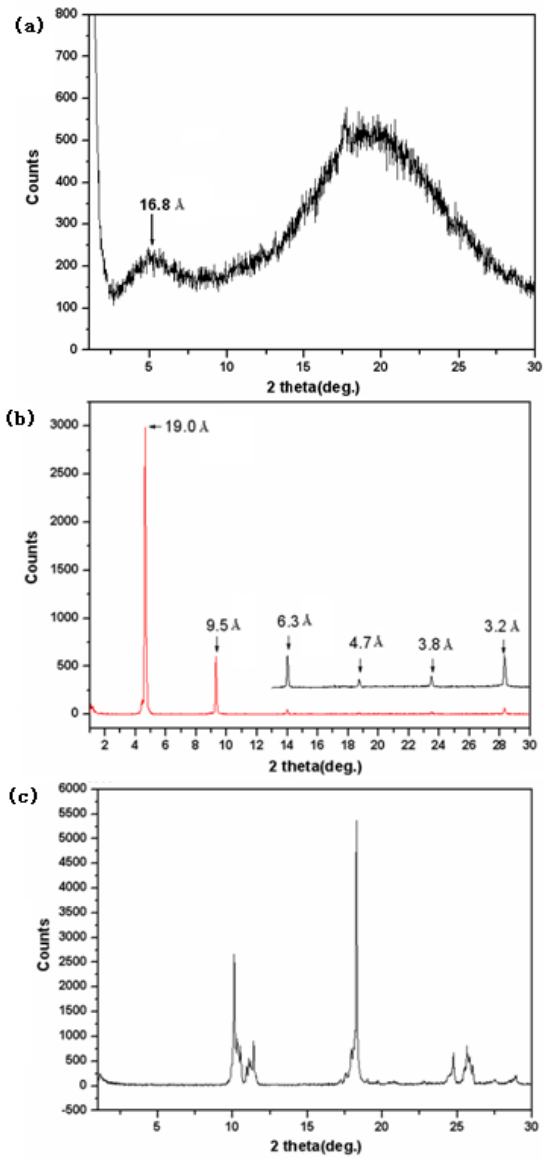

**S-Figure 1.** DSC curves of (a) BOXD-5, (b) BOXD-6, (c) BOXD-7, (d) BOXD-8, (e) BOXD-10, (f) BOXD-16 on the second heating run (heating rate: 10 ℃/min).



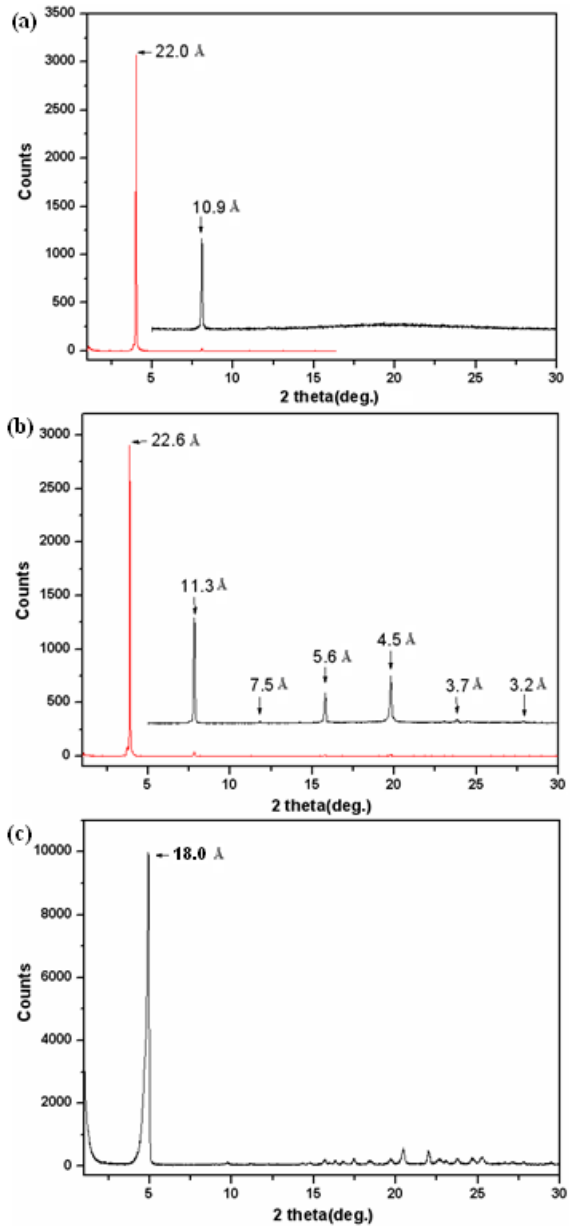

**S-Figure 2.** DSC curves of (a) BOXD-5, (b) BOXD-6, (c) BOXD-7, (d) BOXD-8, (e) BOXD-10, (f) BOXD-16 on the first cooling run (cooling rate: 10 ℃/min).



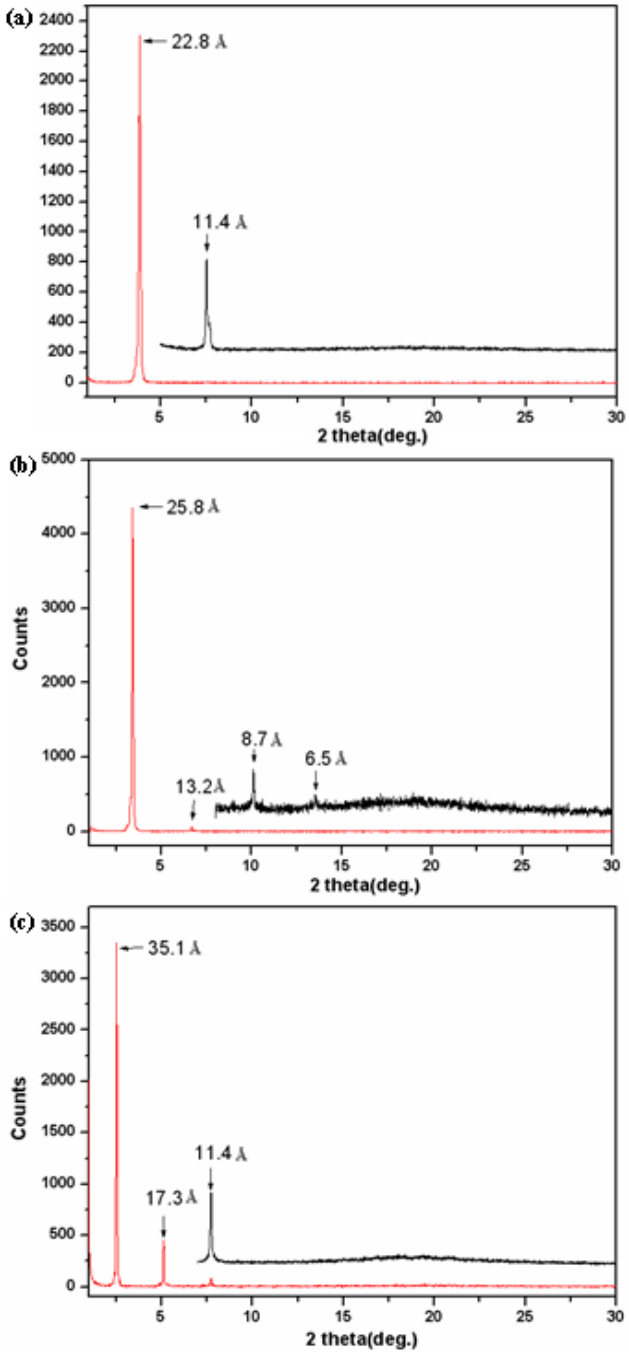

**S-Figure 3.** DSC curves of BOXD-5 (a) on the first cooling run (10 ℃/min), (b) second heating run (10 ℃/min) and on the second heating run (2 ℃/min).




**S-Figure 4.** Powder X-ray diffraction patterns of BOXD-5 (a) at 185 ℃; (b) 175 ℃, (c) 20 ℃ on the cooling run.



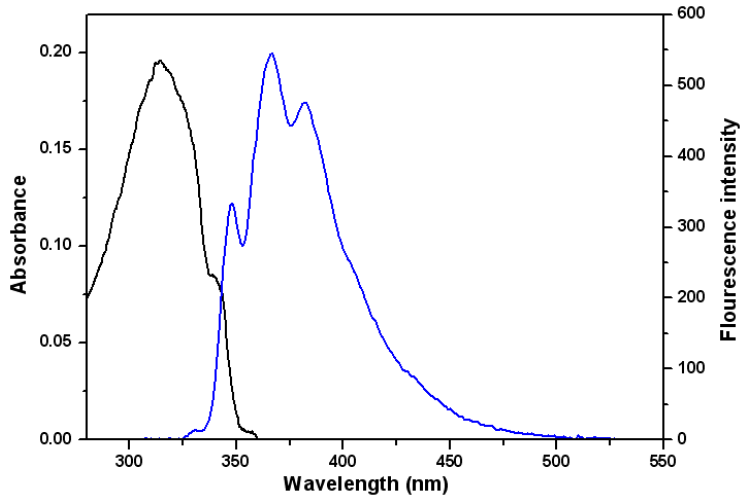

**S-Figure 5.** Powder X-ray diffraction patterns of BOXD-7 (a) at 175 ℃; (b) 160 ℃, (c) 20 ℃ on the cooling run.



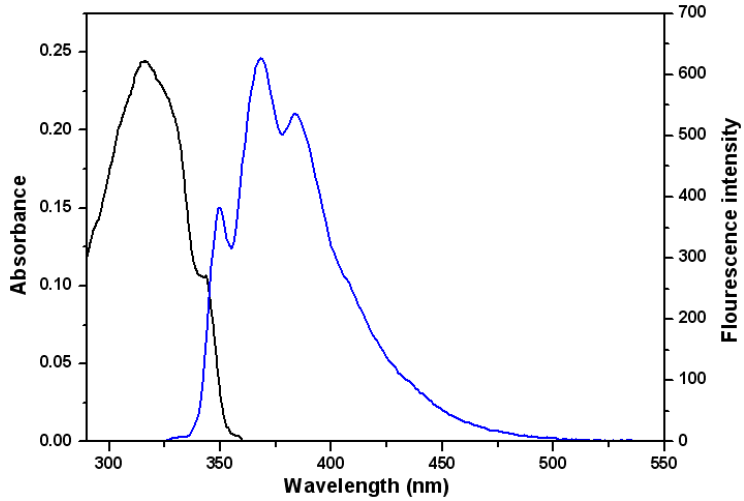

**S-Figure 6.** Powder X-ray diffraction patterns of (a) BOXD-8 at 180 ℃; (b) BOXD-10 at 160 ℃, (c) BOXD-16 at 165 ℃ on the cooling run.

**S-Table 1.** Photophysical Properties of (BOXD-n, n=1, 3, 6, 16) in cyclohexane ($1\times10^{-5}$mol/L).

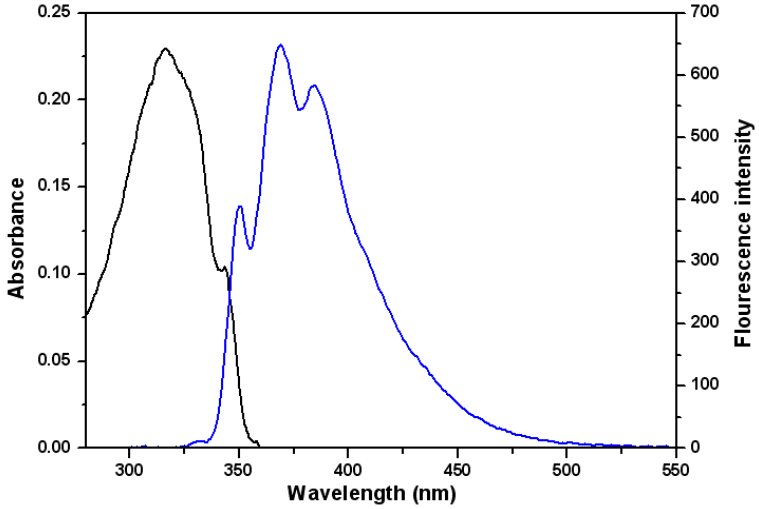
| Compound | $\lambda_{max}$ abs/nm | $\lambda_{max}$ EM/nm | $\Phi_F$ |
|---|---|---|---|
| BOXD-1 | 315 | 348, 366, 382 | 0.94 |
| BOXD-3 | 316 | 350, 368, 384 | 0.93 |
| BOXD-6 | 316 | 350, 368, 384 | 0.92 |
| BOXD-16 | 316 | 350, 368, 384 | 0.92 |



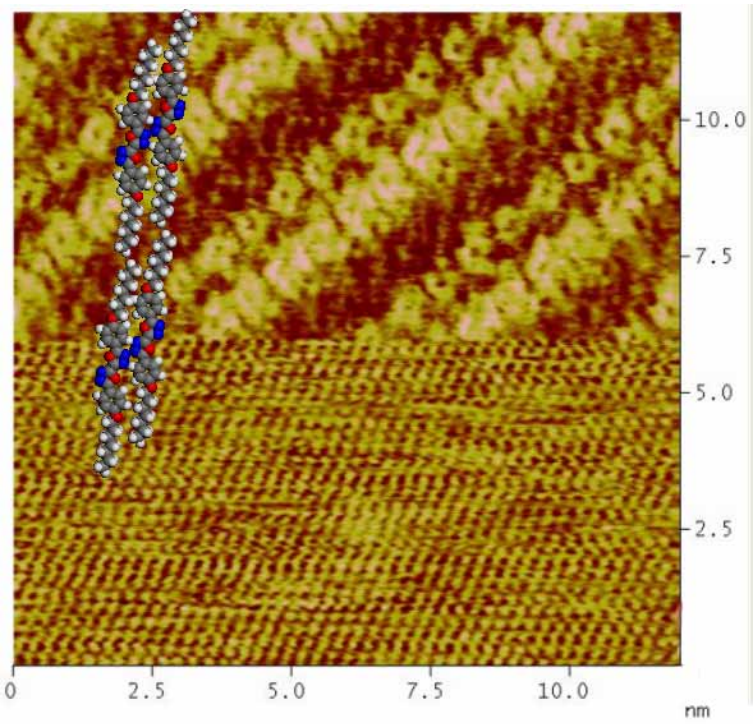

**S-Figure 7.** UV-vis (black) and PL spectra (blue) of BOXD-1 in cyclohexane ($1 \times 10^{-5}$mol/L) at room temperature.



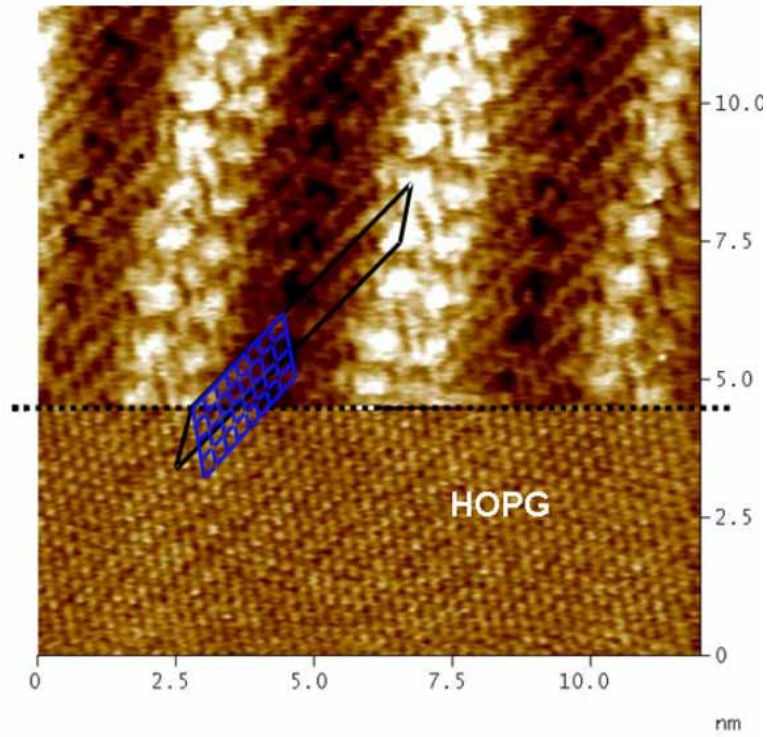

**S-Figure 8.** UV-vis (black) and PL spectra (blue) of BOXD-3 in cyclohexane ($1 \times 10^{-5}$mol/L) at room temperature.




**S-Figure 9.** UV-vis (black) and PL spectra (blue) of BOXD-16 in cyclohexane ($1 \times 10^{-5}$mol/L) at room temperature.




**S-Figure 10.** A hybrid STM image of BOXD-7 with superimposed molecular models




**S-Figure 11.** A hybrid STM image of BOXD-16 showing the mismatch between the adlayer and substrate symmetry

**Computational Details**

Molecular geometries (BOXD-n) were optimized with the Dmol[3] suite of MS Modeling 3.0. The generalized gradient approximation (GGA) method was employed which associated with the PW91

functional for correlation and the 'DNP' basis set. To obtain a high accuracy result, both 'Integration accuracy' and 'SCF tolerance' options were set to "fine".

The face-to-face interaction was estimated by calculating the energy difference between two nearest neighbours of BOXD-1 molecules in the stack which axes is parallel to **a** direction (Figure 2 (c)) and two isolated BOXD-1 molecules. And the estimate of edge-to-edge interaction was obtained by calculating the energy difference between two adjacent BOXD-1 molecules in the (**a** + **b**) direction (Figure 2 (d)) and two isolated BOXD-1 molecules. The face-to-face interaction between the two molecules in this case was about 15.2 kJ $mol^{-1}$ and the edge-to-edge interaction between the two molecules was about 14.7 kJ $mol^{-1}$. Both values were obtained by the accurate DFT method mentioned above.

**S-Table 2.** Crystal data and structure refinement for BOXD-1.

| Identification code | BOXD-1 |
|---|---|
| Empirical formula | C18 H14 N4 O4 |
| Formula weight | 350.33 |
| Temperature | 293(2) K |
| Wavelength | 0.71073 Å |
| Crystal system, space group | Monoclinic, $P2_1/n$ |
| Unit cell dimensions | a = 6.419(1) Å  α = 90°. |
| | b = 8.268(2) Å  β = 92.69(3)°. |
| | c = 15.213(3) Å  γ = 90°. |
| Volume | 806.5(3) $Å^3$ |
| Z, Calculated density | 2, 1.443 $Mg/m^3$ |
| Absorption coefficient | 0.105 $mm^{-1}$ |
| F(000) | 364 |
| Crystal size | 0.36 x 0.16 x 0.13 $mm^3$ |
| Theta range for data collection | 3.39 to 27.47 deg. |
| Limiting indices | -8<=h<=8, -10<=k<=10, -19<=l<=19 |
| Reflections collected / unique | 7435 / 1814 [R(int) = 0.0285] |
| Completeness to theta = 27.47 | 97.9 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.9869 and 0.9634 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 1814 / 0 / 146 |
| Goodness-of-fit on $F^2$ | 1.087 |
| Final R indices [I>2sigma(I) ] | R1 = 0.0368, wR2 = 0.0916 |
| R indices (all data) | R1 = 0.0580, wR2 = 0.0983 |
| Largest diff. peak and hole | 0.204 and -0.123 e $Å^{-3}$ |