Supporting information

Dimerization Effect of Fluorene-Based Semiconductors on Conformational Planarization for Microcrystal Lasing

Chang-Jin Ou[1, 2], Can Zhu[3], Xue-Hua Ding[1], Lei Yang[2], Jin-Yi Lin[1,2, *], Zong-Yan Zuo[2], Ling-Hai Xie[2,*], Yan Qian[2], Chun-Xiang Xu[3,*], Jian-Feng Zhao[1], Wei Huang[1, 2, *]

[1] Key Laboratory of Flexible Electronics (KLOFE) & Institute of Advanced Materials (IAM), Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), Nanjing Tech University, Nanjing 211816, China

[2] Center for Molecular Systems and Organic Devices (CMSOD), Key Laboratory for Organic Electronics and Information Displays (KLOEID) & Institute of Advanced Materials (IAM), Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM)，Nanjing University of Posts & Telecommunications, Nanjing 210046, China

[3] State Key Laboratory of Bioelectronics, School of Electronic Science and Medical Engineering, Southeast University, Nanjing, China

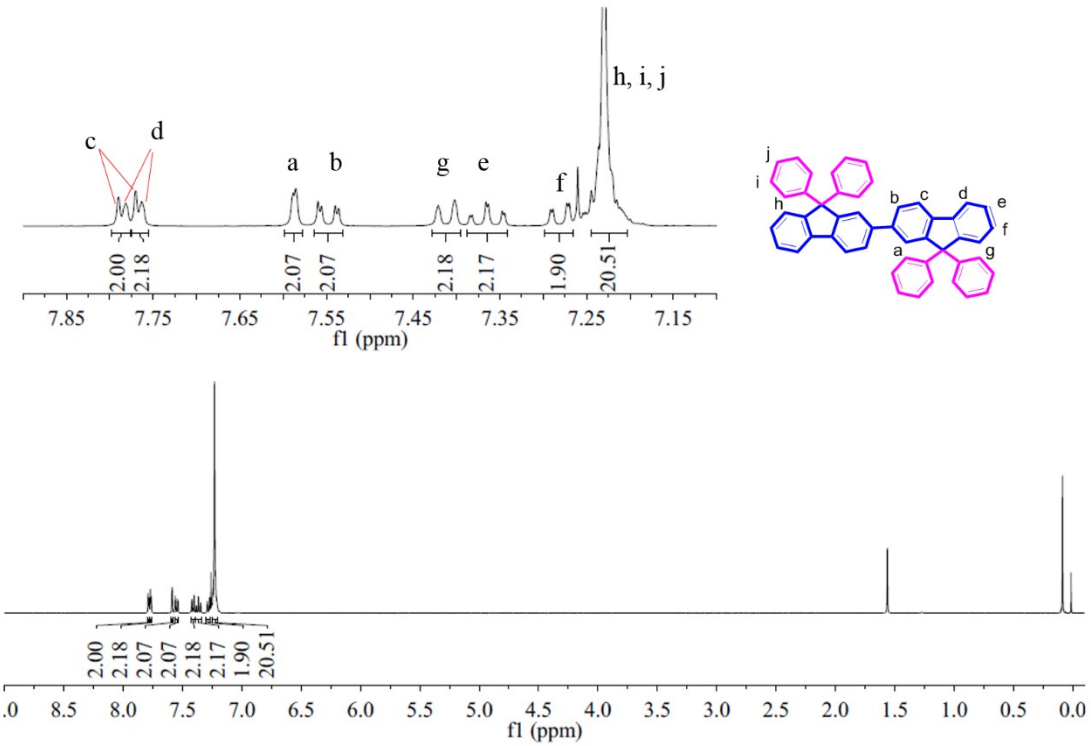

Figure S1. 1H NMR spectrum of BDPhF.

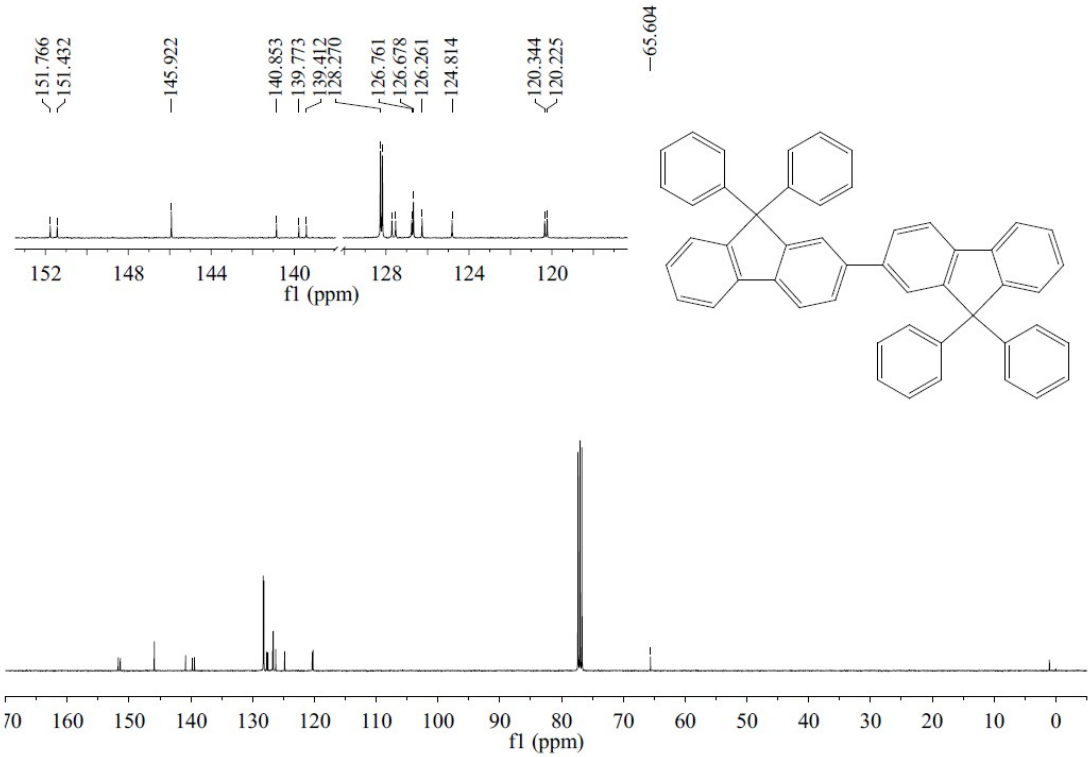

Figure S2. 13C NMR spectrum of BDPhF.

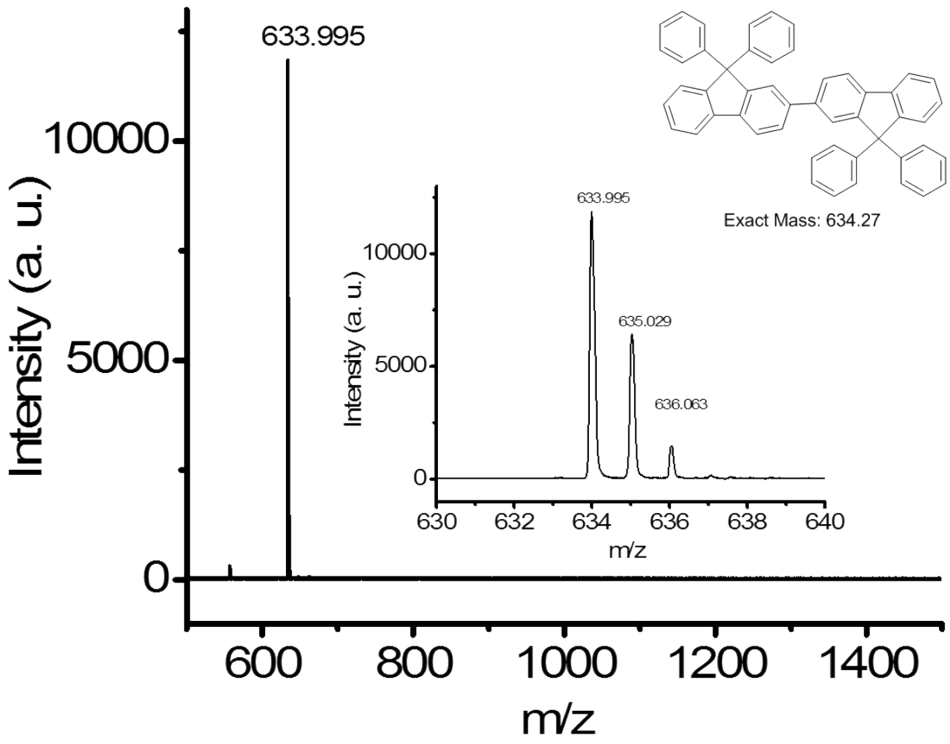

Figure S3. MALDI-TOF mass spectrum of BDPhF.

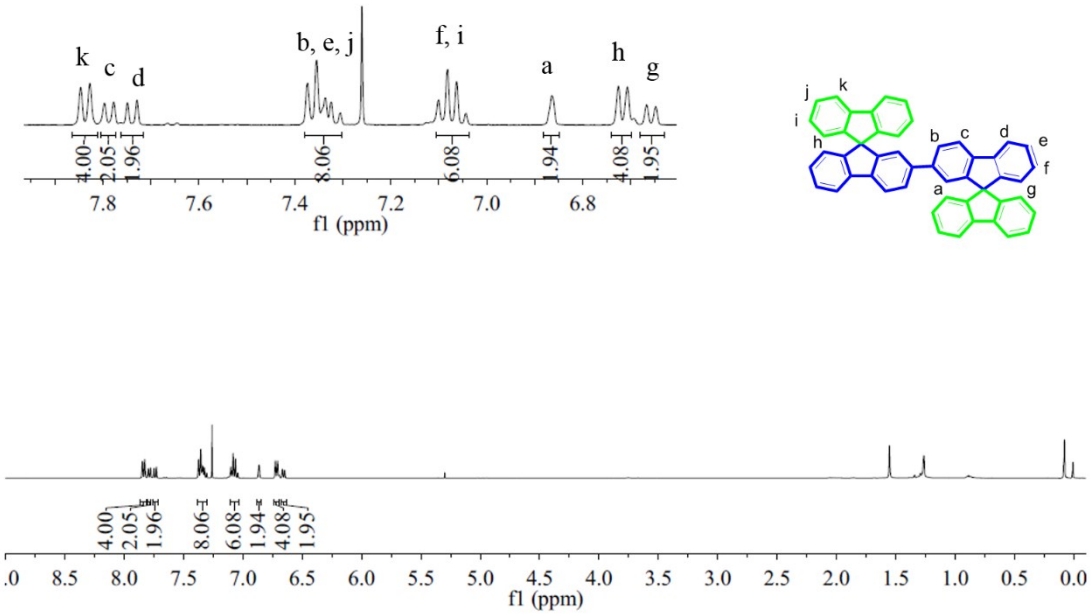

Figure S4. 1H NMR spectrum of BSBF.

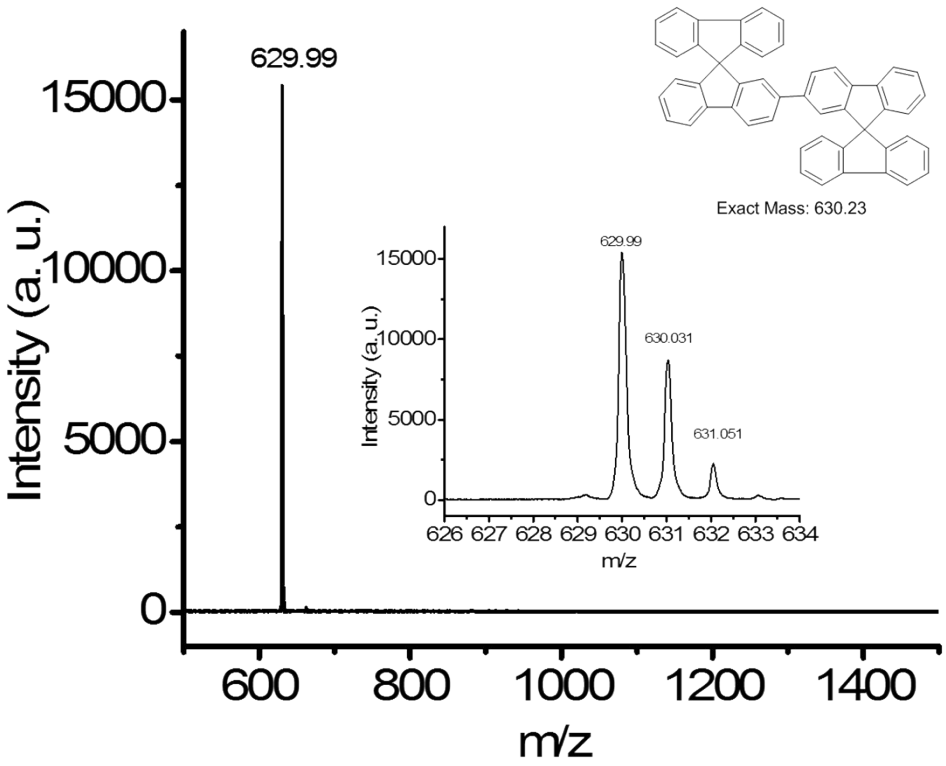

Figure S5. MALDI-TOF mass spectrum of BSBF.

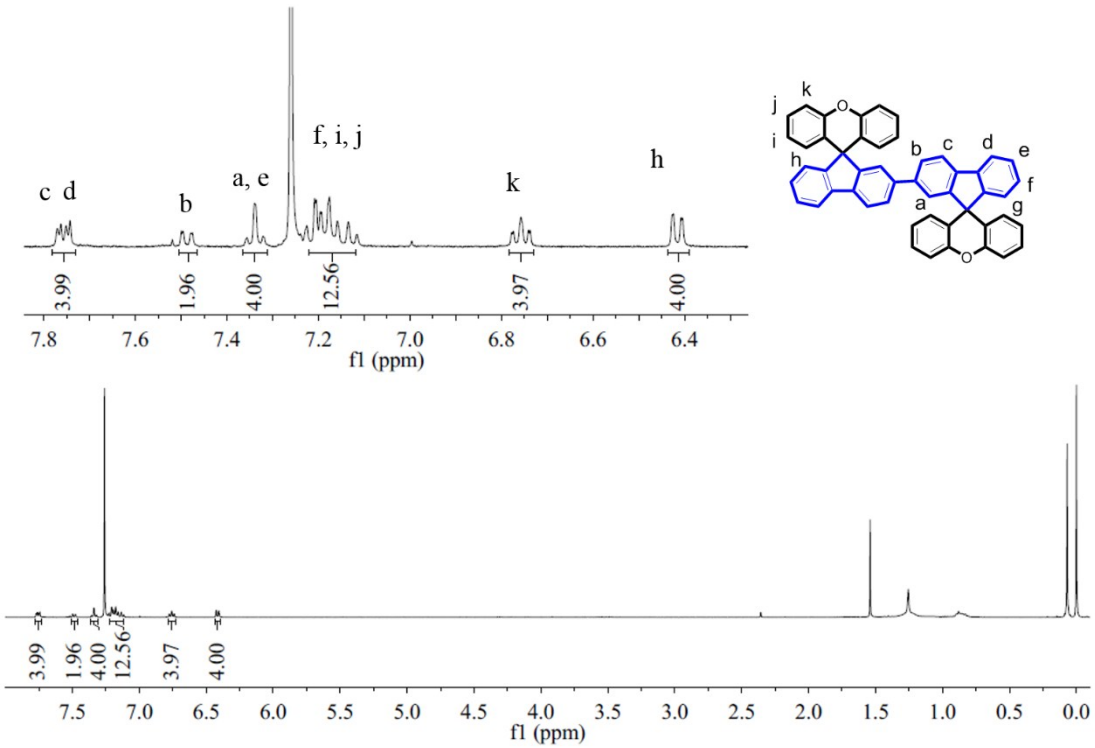

Figure S6. 1H NMR spectrum of BSFX.

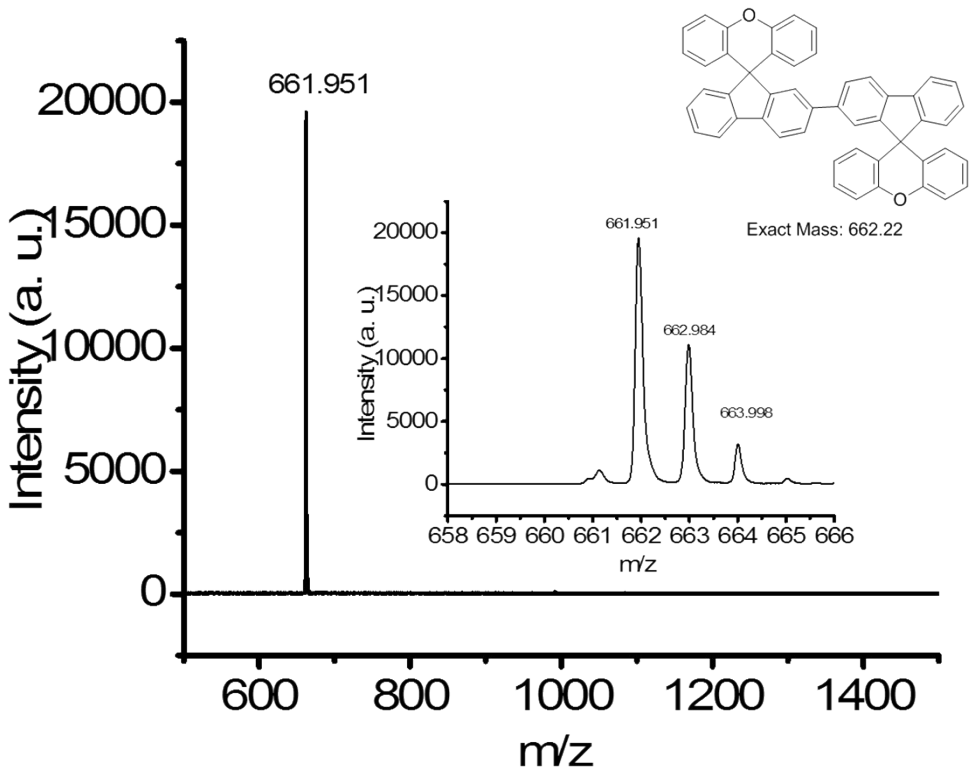

Figure S7. MALDI-TOF mass spectrum of BSFX.

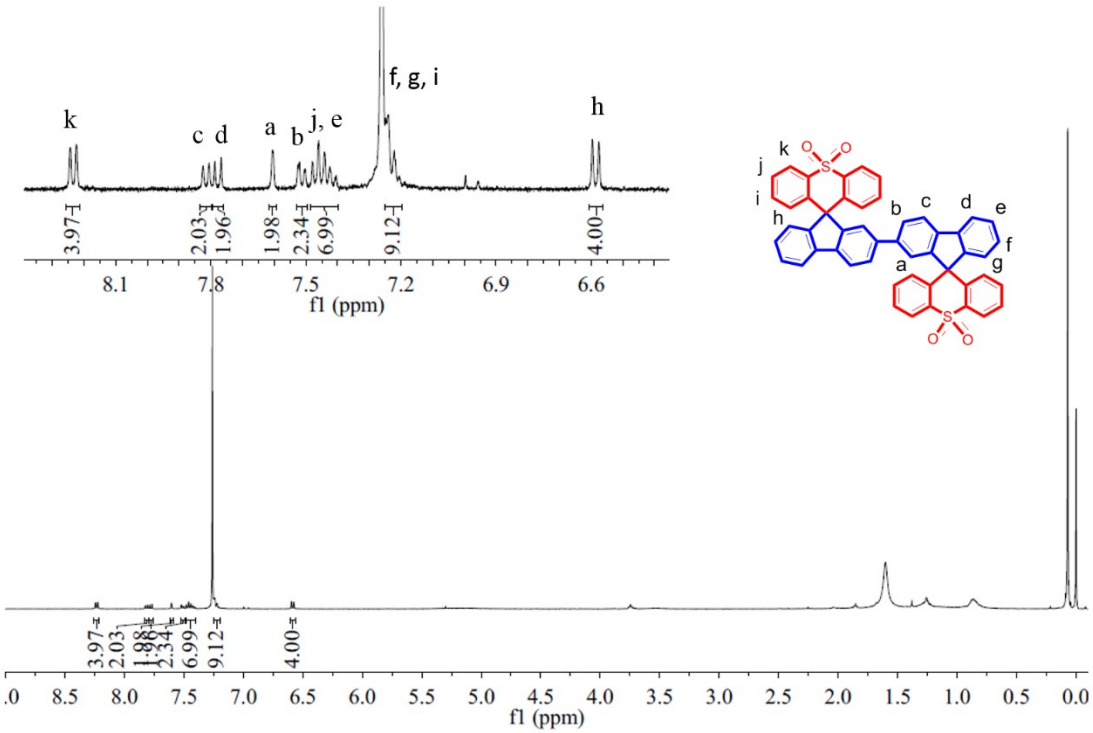

Figure S8. 1H NMR spectrum of BSFSO.

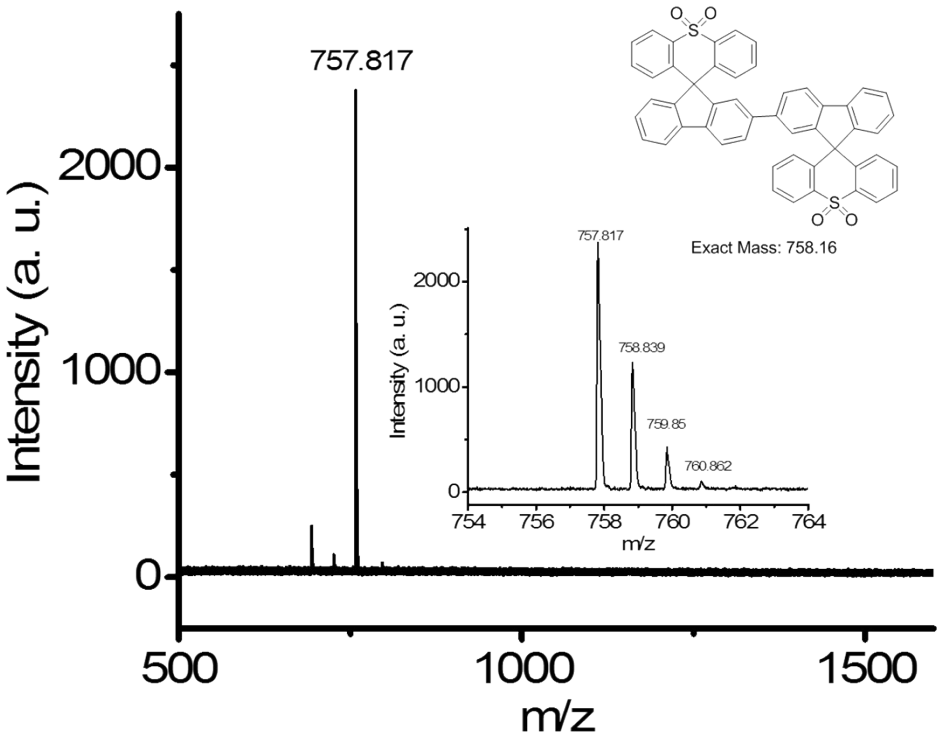

Figure S9. MALDI-TOF mass spectrum of BSFXSO.

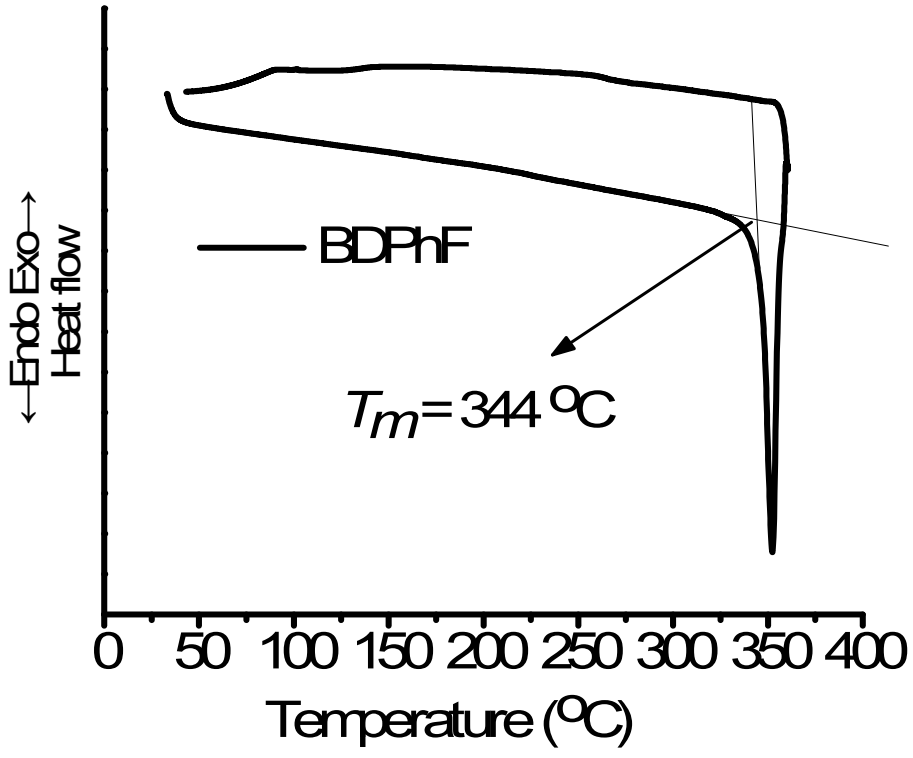

Figure S10. DSC curve of BDPhF.

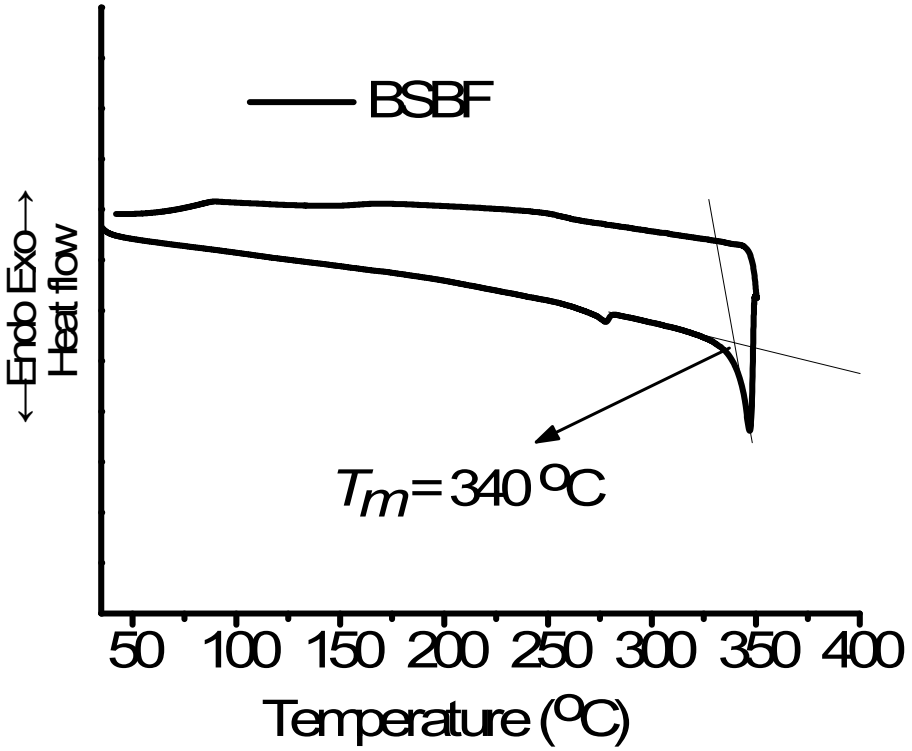

Figure S11. DSC curve of BSBF.

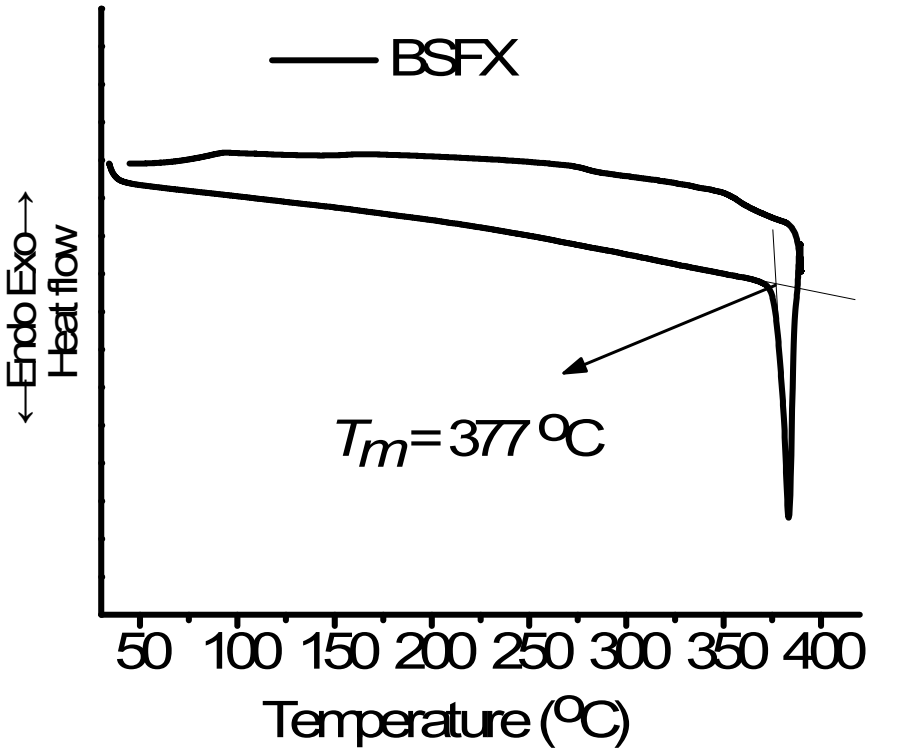

Figure S12. DSC curve of BSFX.

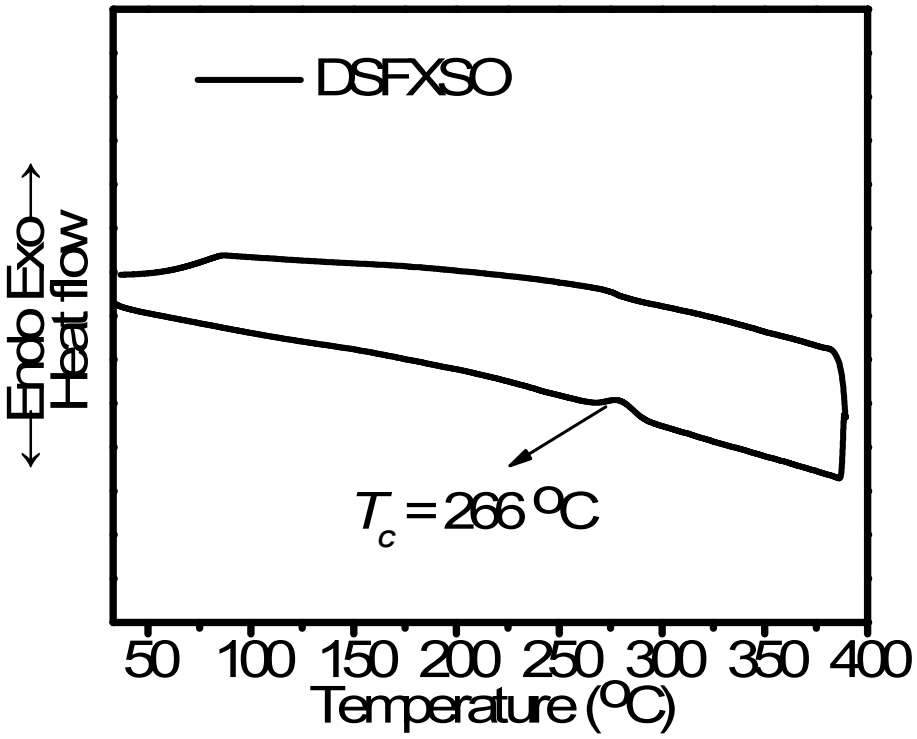

Figure S13. DSC curve of BSFXSO.

Table S1. Crystal parameters of bifluorene derivatives.

name	BDPhF	BSBF	BSFX	BSFSO
CCDC No.	1487810	1487806	1097103	1497102
formula	$C_{50}H_{34}$	$C_{50}H_{30}$	$C_{50}H_{30}O_2 \cdot C_7H_8$	$C_{50}H_{30}O_4S_2 \cdot 2C_6H_7Cl$
fw[g/mol]	634.77	630.74	754.86	983.96
crystal colar	colorless	colorless	colorless	colorless
crystal size [mm]	0.53*0.42*0.31	0.65*0.42*0.33	0.56*0.34*0.15	0.26*0.26*0.11
T [K]	101	100	102	298
lattice type	triclinic	monoclinic	triclinic	monoclinic
space group	P -1	P 21/n	P -1	P 21/c
a [Å]	8.8611(11)	9.4833(8)	9.052(6)	12.7364(17)
b [Å]	9.3197(12)	10.8649(9)	9.102(7)	11.5702(16)
c [Å]	12.2678(14)	15.1455(14)	12.453(9)	16.337(2)
α [°]	91.850(3)	90	83.587(13)	90
β [°]	96.029(3)	91.177(2)	80.720(14)	105.965(4)
γ [°]	115.276(2）	90	71.417(14)	90
V [Å^3]	833.70(18)	1560.2(2)	956.4(12)	2316.4(6)
Z	1	2	1	2
ρ_{calcd} [g/cm3]	1.264	1.343	1.309	1.411
F(000)	334	660	395	1020
absorption coefficient [mm^{-1}]	0.072	0.076	0.078	0.284
measured	7238	13460	6698	19619
observed	5386	9466	3706	4491
θ range [°]	2.56-28.25	2.21-28.23	2.37-28.43	2.52-28.24
R1	0.0452	0.0421	0.1216	0.0865
ωR2	0.1155	0.1086	0.3476	0.1899
completeness	0.982	0.995	0.997	0.999
S	1.062	1.04	1.633	1.021

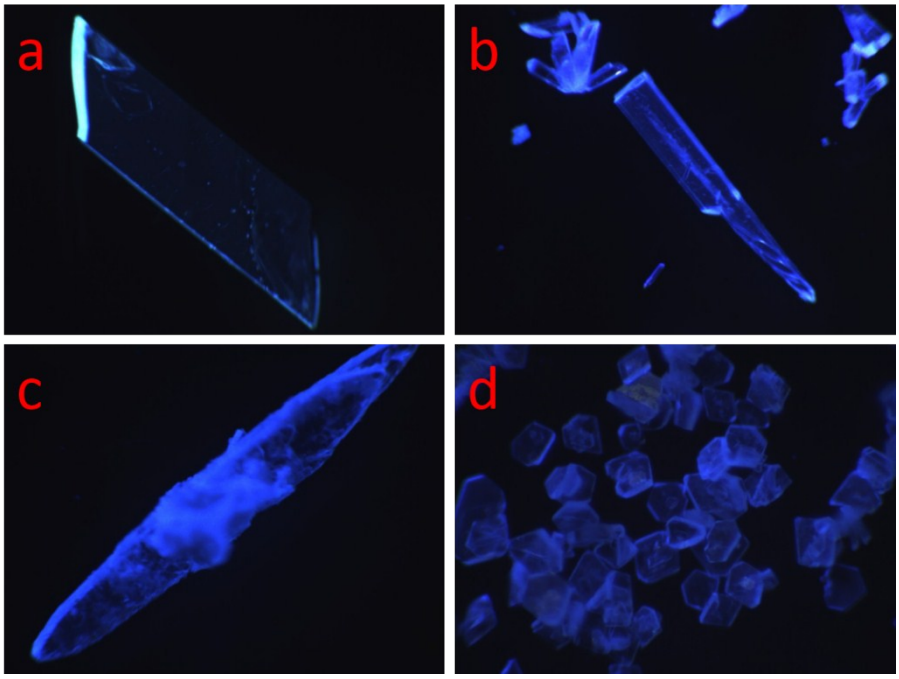

Figure S14. Photo images of diarylfluorene dimmer crystals, the crystal was excited by UV lamb. (a) BDPhF single crystal. The crystal is plate showed a greenish-blue color. (b) BSBF single crystal. (c) BSFX single crystal. The most of BSFX crystal were twined. (d) BSFSO single crystal. BDPhF, BSBF, BSFX and BSFSO crystallized from dichloromethane-ethanol, dichloromethane-ethanol, toluene and chlorobenzene-ethanol, respectively.

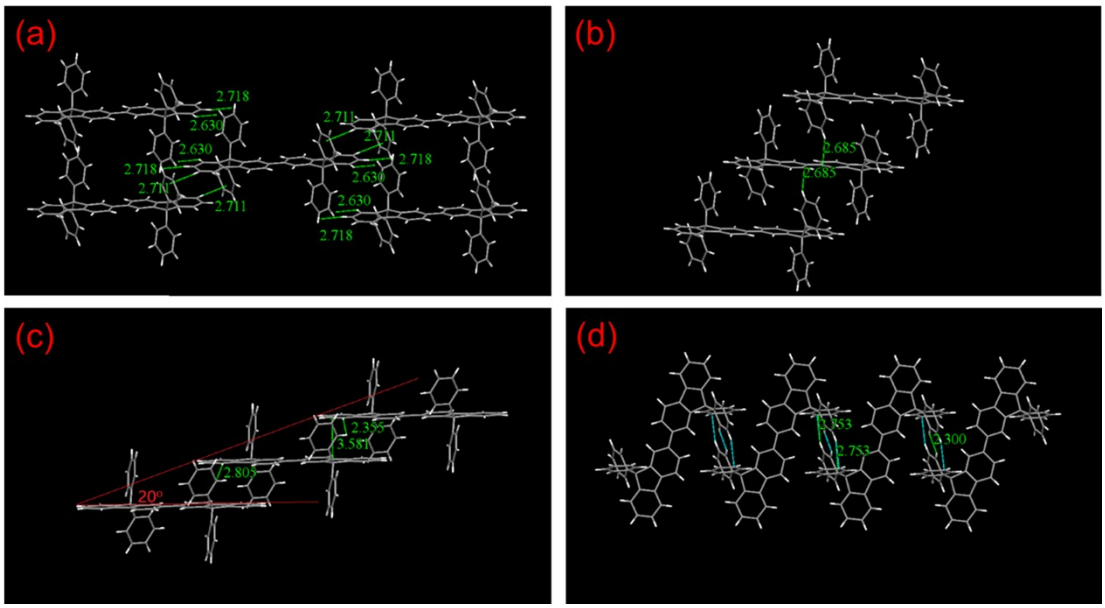

Figure S15. Intermolecular interactions in BDPhF crystal. (a) and (b) C-H···π interactions (c) J-aggregate in BDPhF crystal, the pitch angle of BDPhF is about 20°, and the distance of π-π interaction is 3.581 Å. (d) C-H···π interactions and H···H interaction.

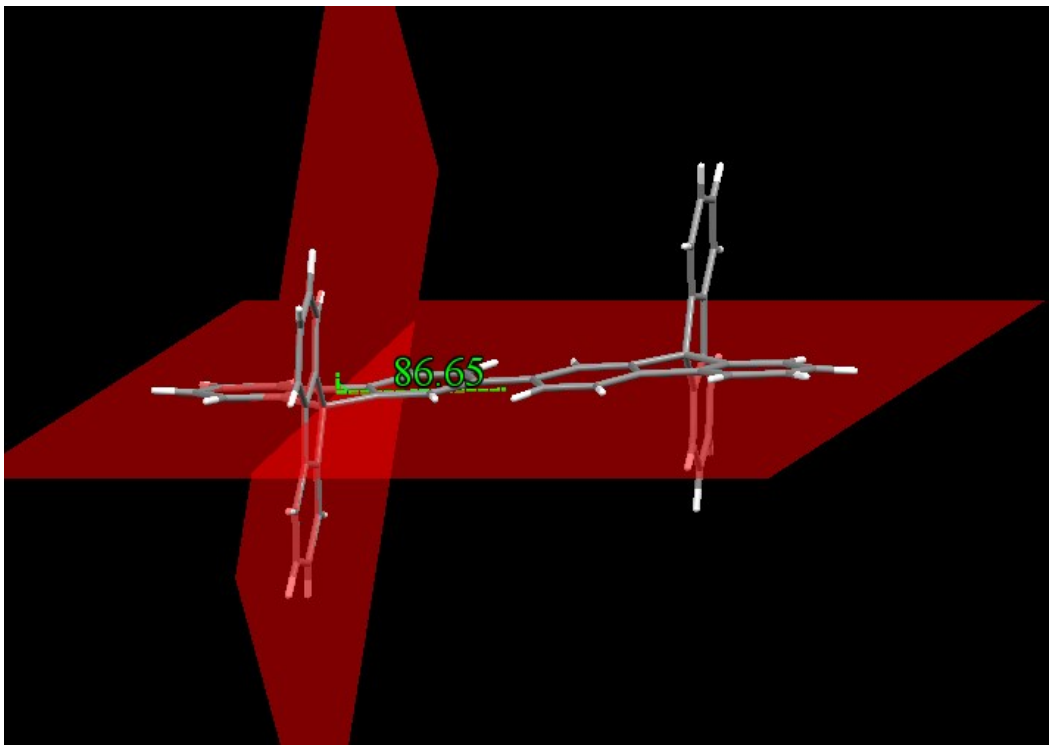

Figure S16. Dihedral angle between nonconjugated fluorene and conjugated backbone in BSBF.

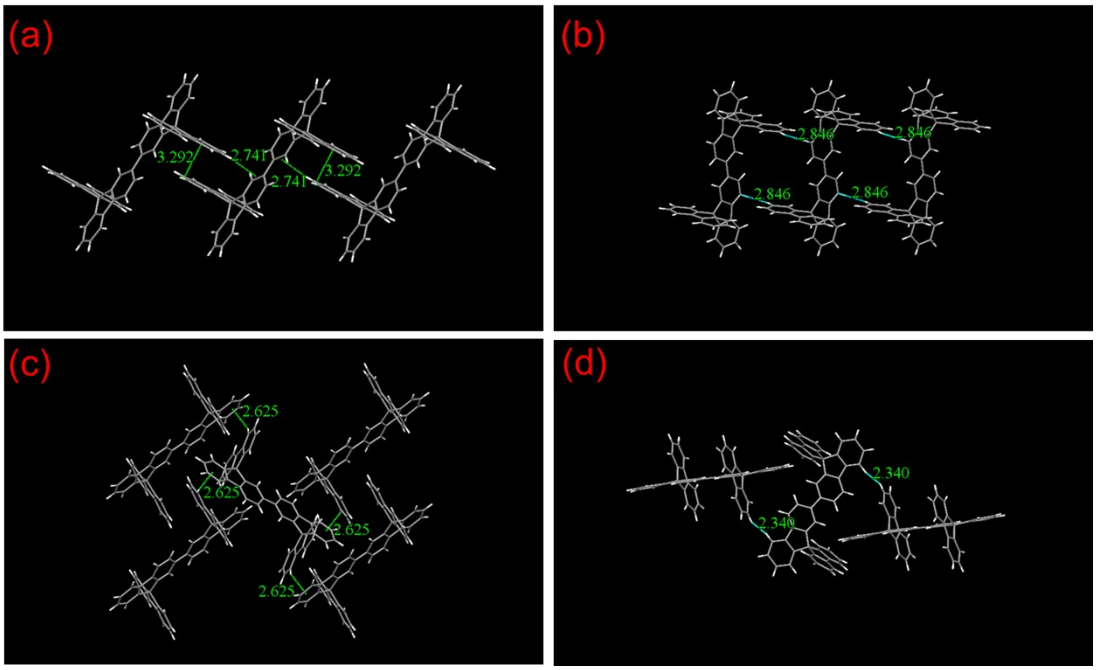

Figure S17. Intermolecular interactions in BSBF crystal. (a) π-π interactions between non-conjugated lateral fluorene moieties of BSBF, and C-H···π interactions. (b) and (c) C-H···π interactions. (d) H···H interactions

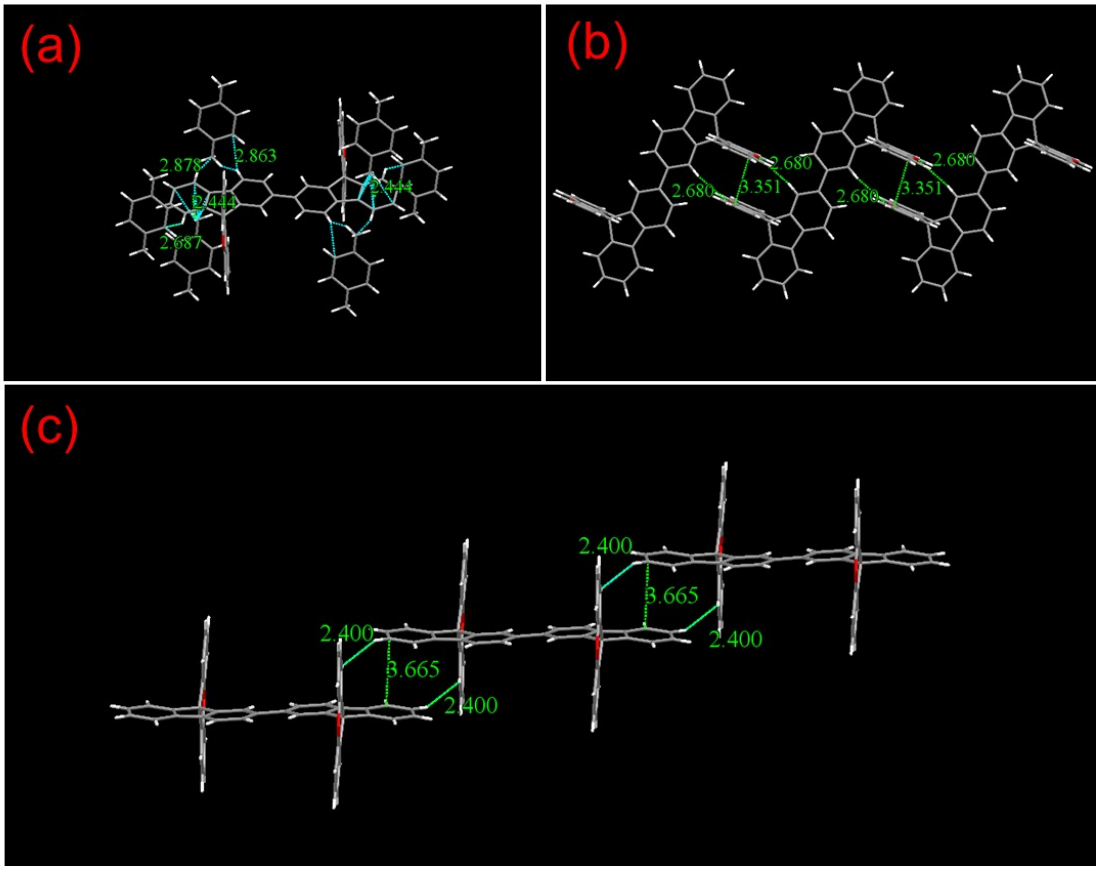

Figure S18. Intermolecular interactions in BSFX crystal. (a) The interactions between toluene molecules with BSFX. (b) π-π interactions between xanthene moieties of BSFX, and C-H···O hydrogen bonds. (c) head-to-tail arrangement (J-aggregate) with a π-π interaction distance of 3.665 Å.

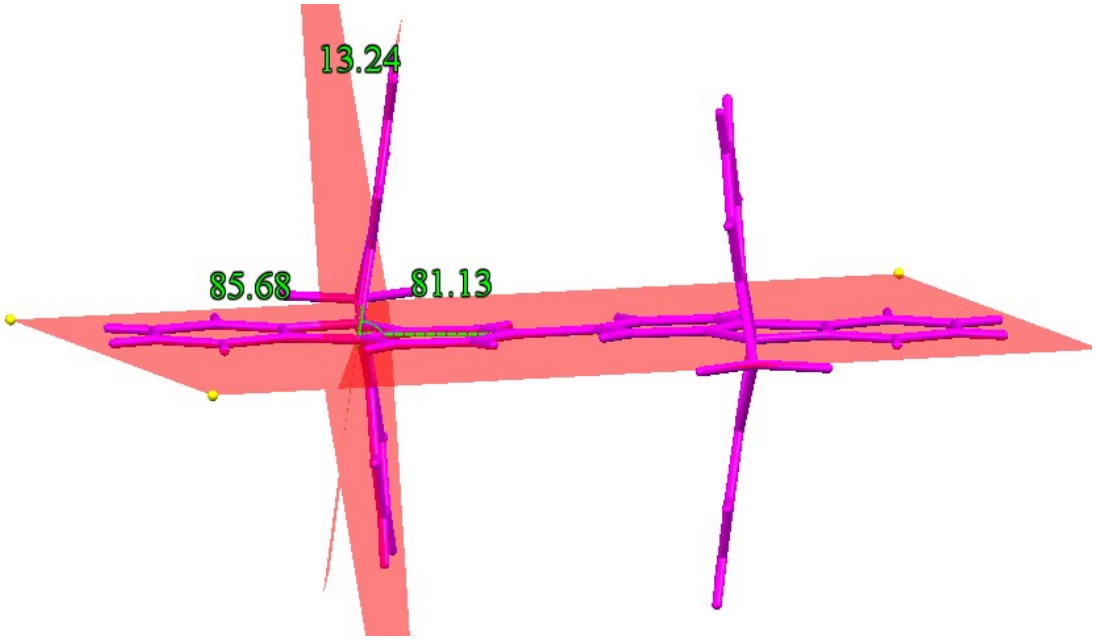

Figure S19. Dihedral angles of BSFSO between phenyl groups in thioxanthene and conjugated backbone, and between phenyl groups. The dihedral angle is 13.2° between

the two benzene rings of thioxanthene-10,10-dioxide group.

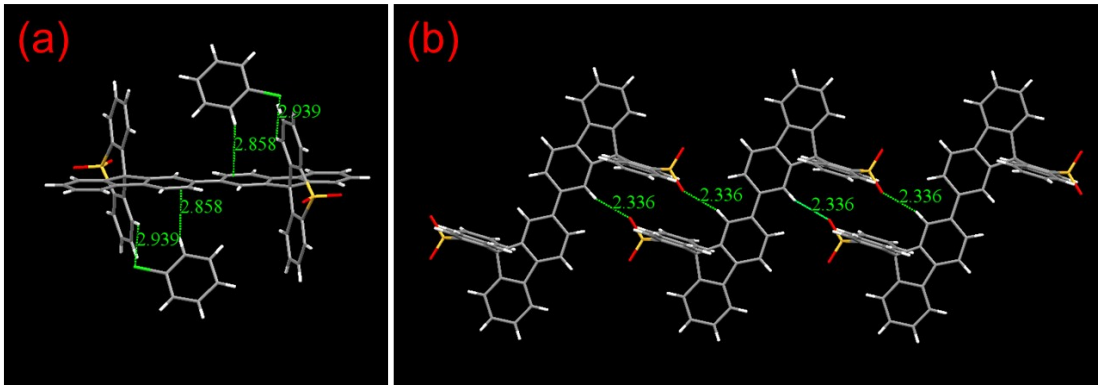

Figure S20. Intermolecular interactions in BSFSO crystal. (a) The interactions between chlorobenzene molecules with BSFXSO. (b) C-H···O hydrogen bonds involving sulfone group.

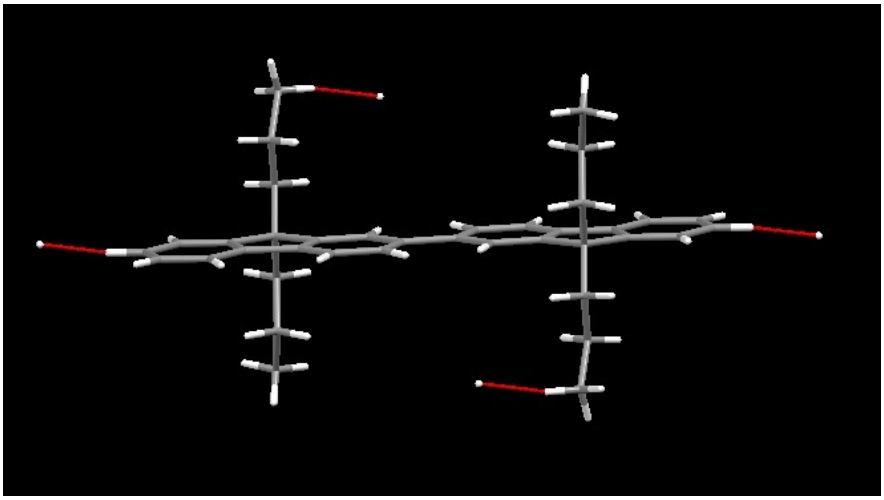

Figure S21. Symmetric interactions between the two fluorene units of 2,2'-bi(9,9'-dipropylfluorene) (CCDC: 201721).

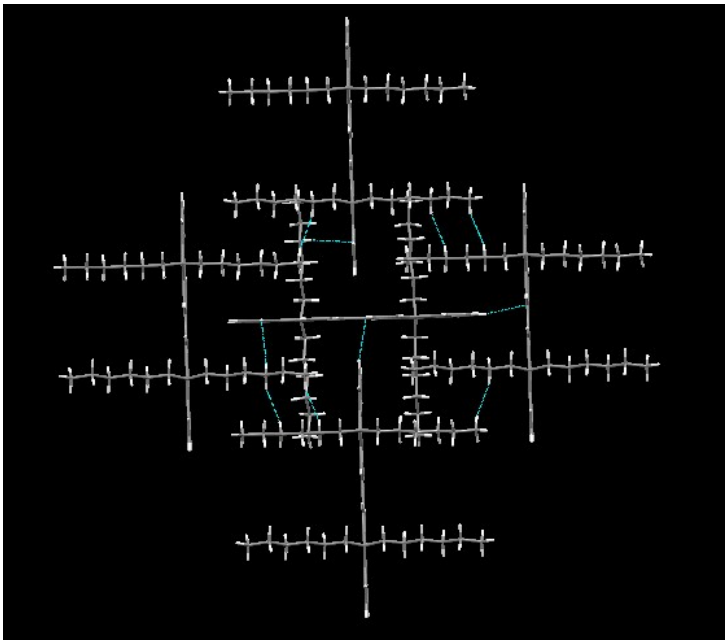

Figure S22. Quasi-symmetric interactions between the two fluorene units of 2,2'-bi(9,9'-dihexylfluorene) (CCDC: 143328 and 663945).

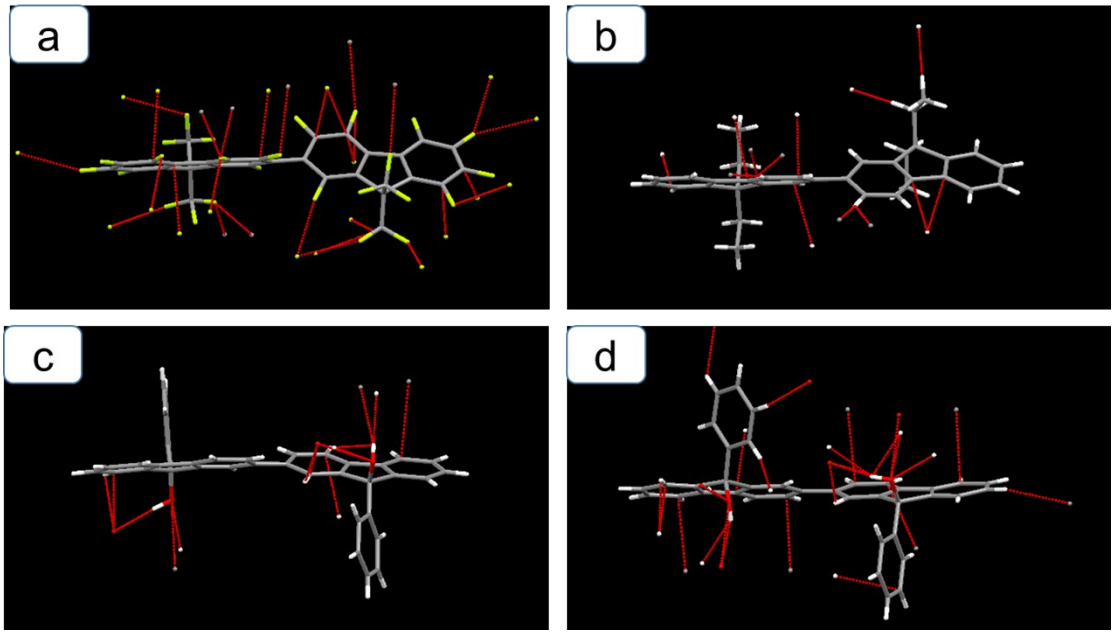

Figure S23. Intermolecular interactions of the reported fluorene dimmers. All the dimmers adopt torsional conformation, and display asymmetric interactions between the fluorene units. (a) perfluoro-substituted 2,2'-bi(9,9'-dimethylfluorene) (CCDC: 677181). (b) 2,2'-bi(9,9'-diethylfluorene) (CCDC: 982343). (c) and (d) two crystal polymorphs of 2,2‘-(9-hydroxyl-9'-phenhylfluorene) (CCDC: 1061802 and 1061803).

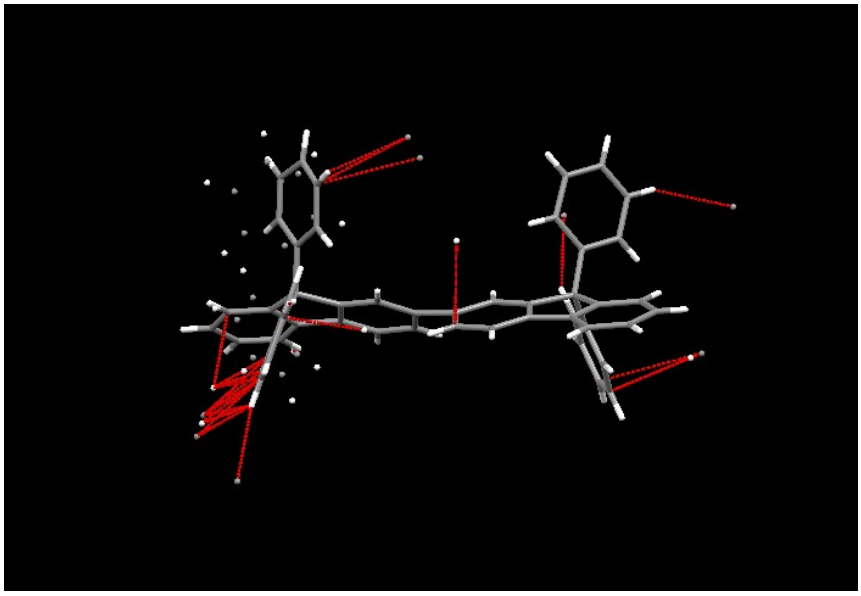

Figure S24. Asymmetric interactions between the two fluorene units of 2,2'-bi(9,9'-diphenylfluorene), there are chloroform molecules in crystal lattice, the torsional angle is -140.05°.

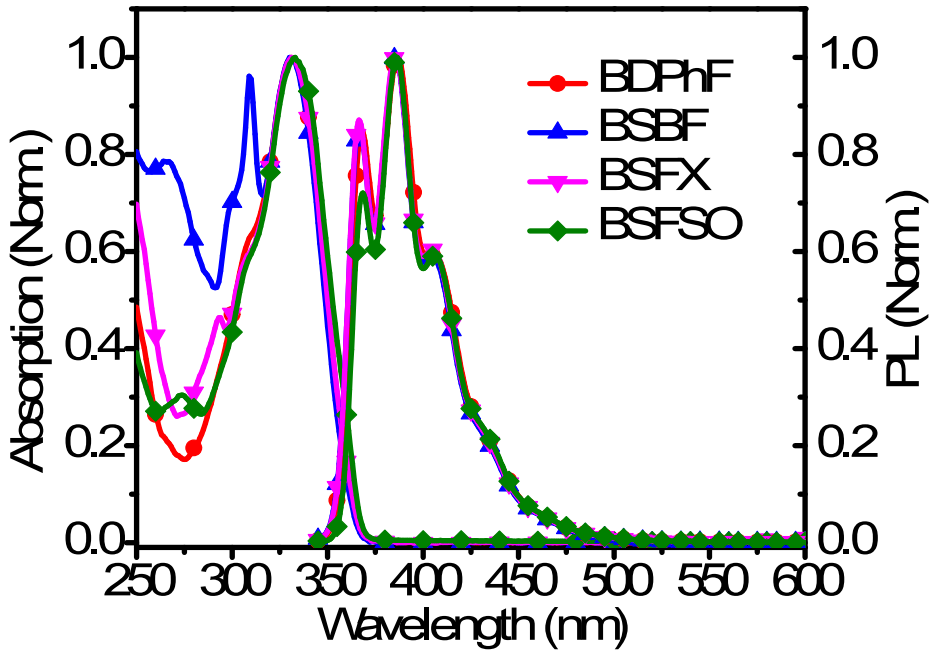

Figure S25. Absorption and emission spectra of bifluorene derivatives in dichloromethane solution.

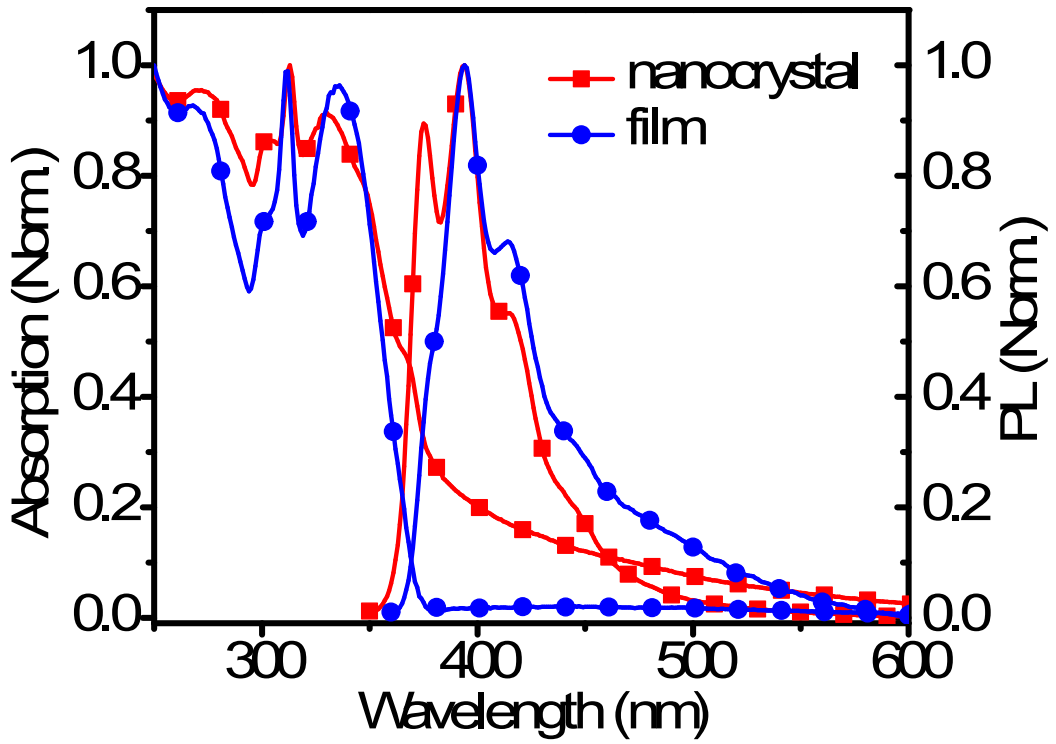

Figure S26. Absorption and emission spectra of amorphous film and nanocrystal of BSBF. The nanocrystals were dispersed in deionized water, and the excitation wavelength is 330 nm.

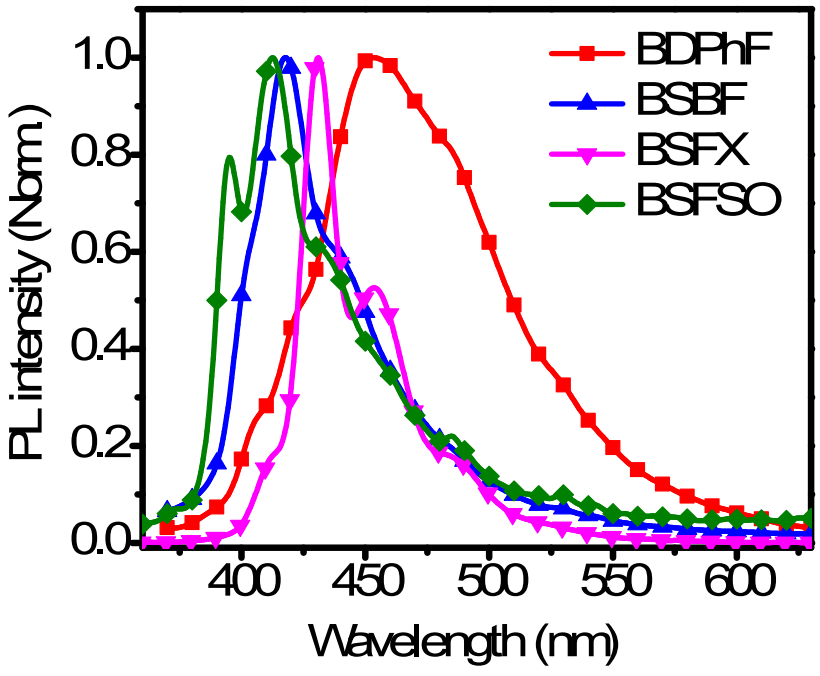

Figure S27. PL spectra of bifluorene macrocrystals. Due to large size of crystal, self-

absorption effect significantly affects PL profile of single crystals.

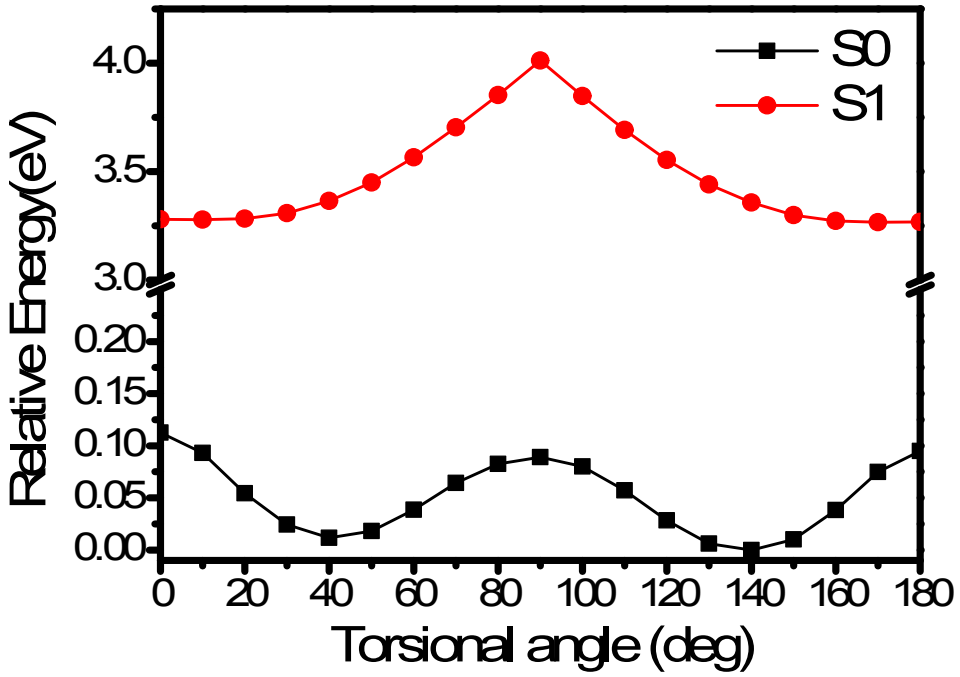

Figure S28. Potential curves of BSBF with respect to torsion of the fluorene-fluorene link. Note that symmetry considerations dictate that the opposite torsion gives the same potential curves. The minimal energy of ground state (S_0) is at torsion angles ±40º and ±140º. The minimal energy of the first excited state (S_1) is at torsional angles ±10º and ±170º. The S_0 molecular structures and energies are calculated at B3LYP/3-21G level; the S_1 molecular structures are optimized via TD-B3LYP/3-21G method. The S_1 energy is the sum of S_0 energy (based on the TDDFT-optimized S_1 structure) calculated at the B3LYP/3-21G level and the excitation energy computed via TD-B3LYP/3-21G method.

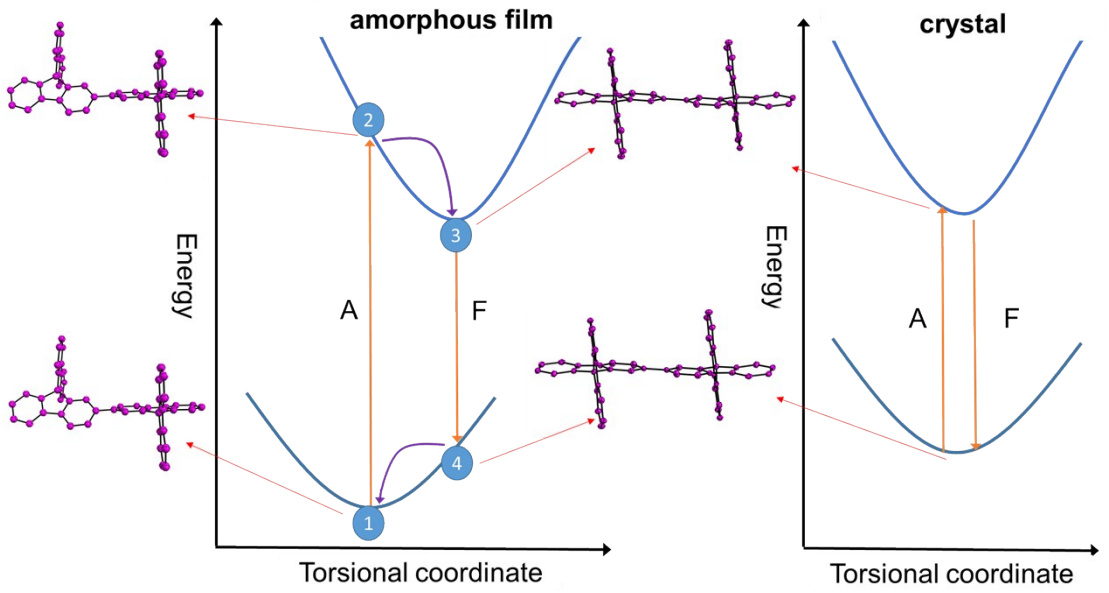

Figure S29. Schematic diagram of molecular photo-excited dynamics of BSBF in amorphous film and crystal. The processes of 1→2 and 3→4 are vertical absorption and emission. The processes of 2→3 and 4→1 are conformational relaxation. First, the stable and torsional BSBF (1) is excited to excited electronic state (2), since electronic process is very fast, they keep similar conformation after absorption or emission. Then (2) undergoes a conformational planarization process to the most stable excited state (3). The excited state (3) is deactivated to non-equilibrium ground state (4) via emitting fluorescence. Finally, (4) backs to stable ground state (1) via conformational relaxation.

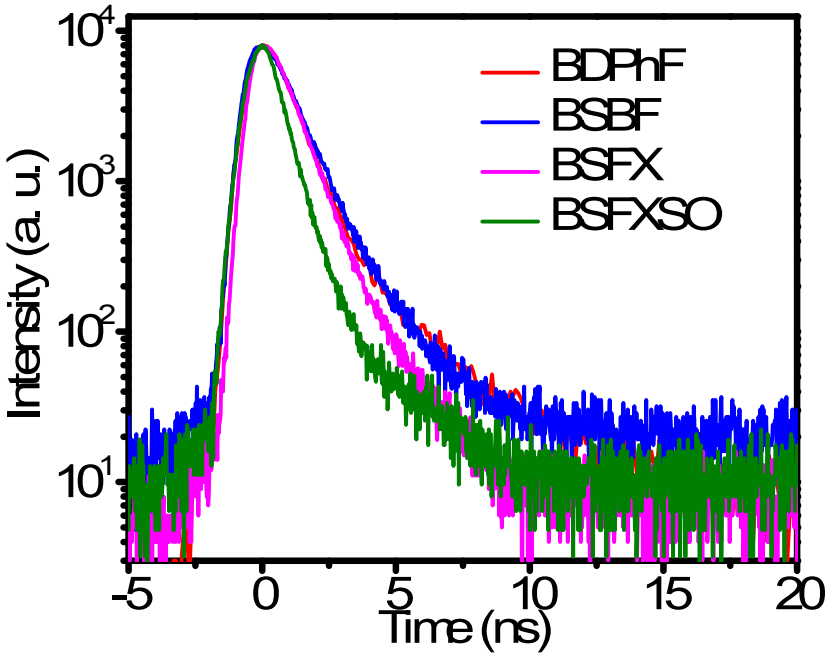

Figure S30. Transient PL decay curves of single crystals of the dimers. The lifetimes are 1.42, 1.21, 0.82 and 0.79 ns for BDPhF, BSBF, BSFX and BSFXSO.

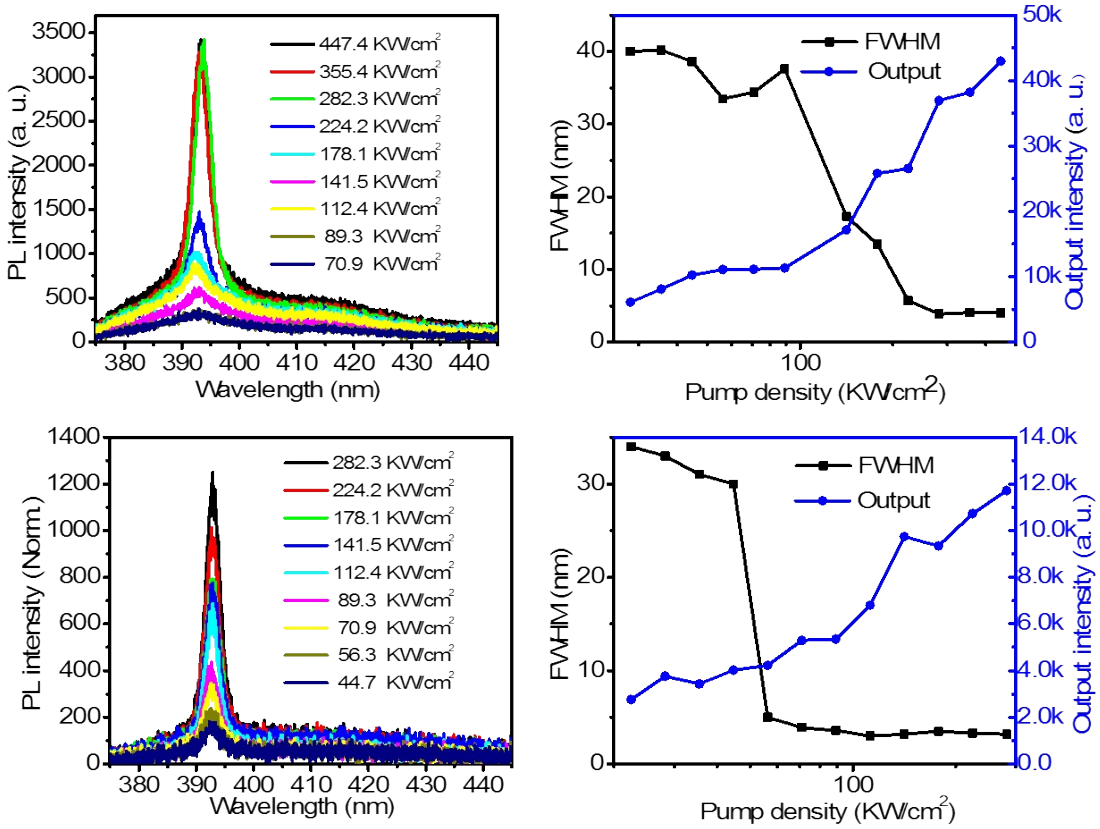

Figure S31. PL spectra of BDPhF film (a) and BSBF film (c) as the function of pump fluence. The change of PL intensity and FWHM of 0-1 emission band of BDPhF film (b) and BSBF film (d) as the increase of pump fluence.

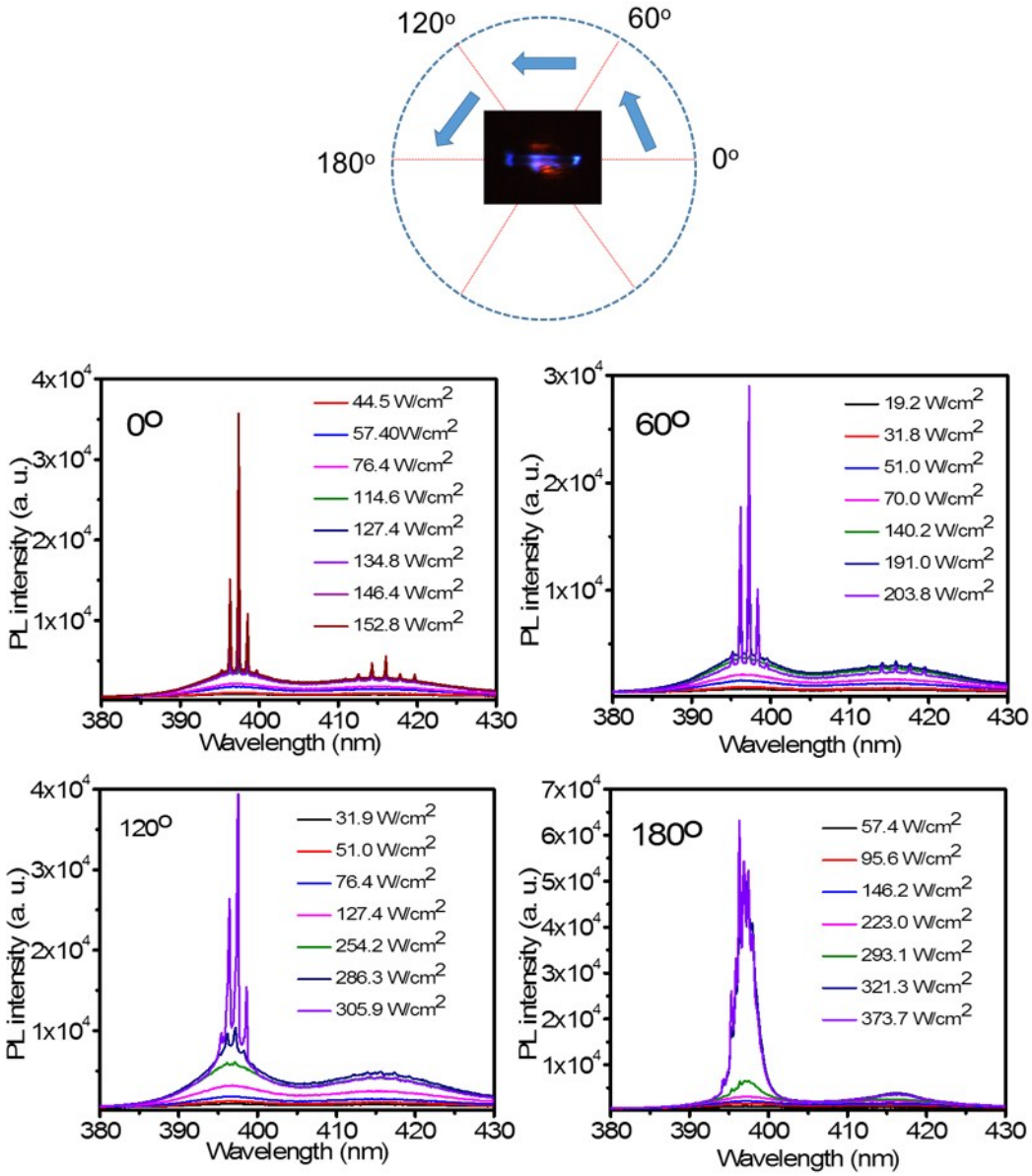

Figure S32. The schematic diagram of rotation direction of the BSBF microcrystal, and the pump fluence-dependent PL spectra at ~0, 60, 120 and 180°.