Supporting Information

Toward Highly Fluorescence and Ultralow-Threshold Amplified Spontaneous Emission in Ordered Solid State From Twin-tapered Bi-1,3,4-oxadiazole Derivatives

Songnan Qu,[a] Haitao Wang,[b, c] Wanbin Zhu,[d] Jinsong Luo,[a] Yi Fan,[a] Liwei Song,[a] Hong-Xing Zhang*[b] and Xingyuan Liu*[a]

[a]State Key Laboratory of Luminescence and Applications, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033 (P. R. China)

[b] State Key Laboratory of Theoretical and Computational Chemistry, Institute of Theoretical Chemistry, Jilin University, Changchun 130023 (P. R. China)

[c] Key Laboratory of Automobile Materials (Jilin University), Ministry of Education, Institute of Materials Science and Engineering, Jilin University, Changchun 130012 (P. R. China)

[d]State Key Laboratory of Applied Optics, Chinese Academy of Sciences, Changchun 130033 (P. R. China)

E-mail: xingyuanliu@hotmail.com, Songnanqu@yahoo.cn, zhanghx@mail.jlu.edu.cn,

Experimental Section

BOXD-T3 was prepared following our previously published procedures.[18] BOXD-T3 vacuum deposited film was prepared by high-vacuum (6×10^{-5} Pa) thermal evaporation method. Film thicknesses were measured with an Ambios XP-1surface profiler. PL spectra were collected using a Hitachi F-4500 spectrometer and UV-visible absorption spectra were recorded on a Shimazu UV-3101PC spectrophotometer. Photoluminescence quantum yield in solid state is obtained in a calibrated integrating sphere (excitation wavelength: 340nm). Fluorescence lifetimes were measured using FL920 time-corrected single photon counting (TCSPC) system. FE-SEM observations were taken with a Hitachi S-4800 apparatus. The POM and fluorescence microscopy images were carried out with an Olympus BX51TRF microscope. The light source for fluorescence microscopy observation was a mercury lump with a fluorescent filter cube, which provides excitation in the range of 330-385 nm, and collects the emission at > 420 nm. Intensity of the fluorescence emission was measured using the built-in CCD camera along with the associated software. The emission spectra were detected using an Ocean Optics Maya2000 Pro Fiber Optic Spectrometer. X-ray diffraction (XRD) was carried out with a Bruker Advance D8 X-ray

diffractometer. ASE investigation was performed using a Nd:YAG laser with a repetition rate of 10 Hz and pulse duration of about 10 ns. The laser power was detected by Newport 2936C laser power meter. All computations were performed with the Gaussian 09 Program package.[1] The stimulated emission cross sections were calculated by equation:

$$\sigma_e(\nu) = \frac{\lambda^4 \varphi_f}{8\pi n^2 c_0 \tau_f} F(\nu)$$

Where F(ν) is the lineshape of the spectra which $\int_0^\infty F(\nu) d\nu = 1$, n is the refractive index of gain material, Φf is the quantum yield, τf is the fluorescence lifetime. For BOXD-T3 xerogel, solution processed aligned film and vacuum evaporated film, n was introduced to 1.6.

[1] Gaussian 09, Revision A.02, Frisch, M. J. G.; Trucks, W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B. G.; Petersson, A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O .; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2009**.

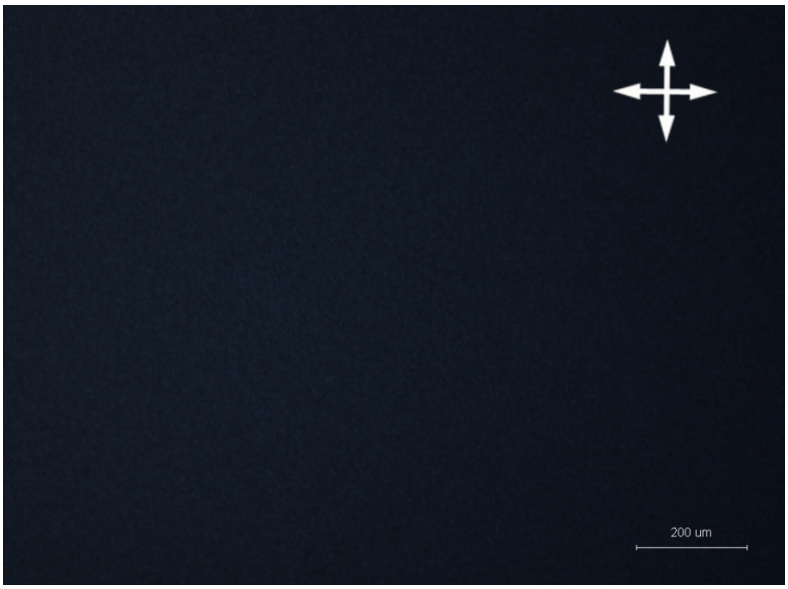


Figure S1. POM image of BOXD-T3 vacuum evaporated film on glass (white crossed arrows illustrated the crossed-polarizers).

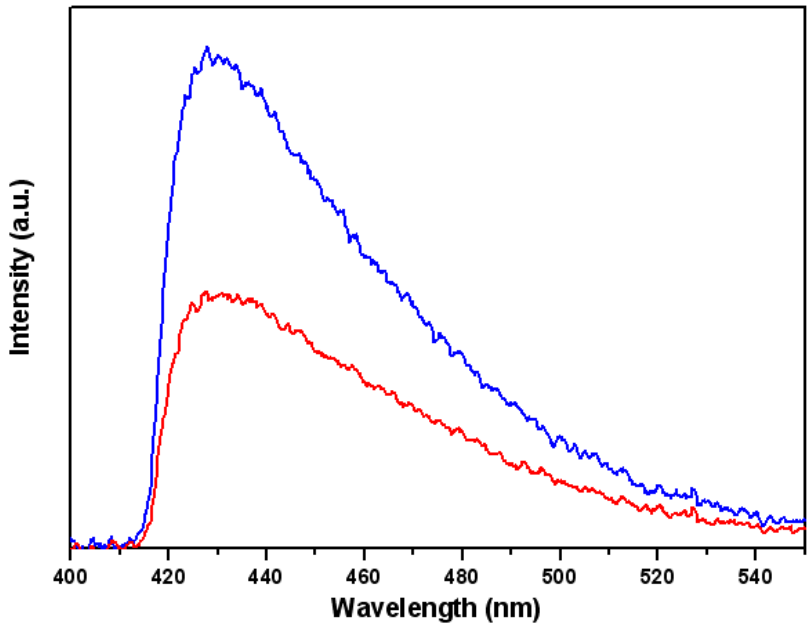


Figure S2. Fluorescent emission spectra of BOXD-T3 solution processed aligned film under polarized UV excitation (blue line: polarizer perpendicular to the growth direction; red line: polarizer parallel to the growth direction).

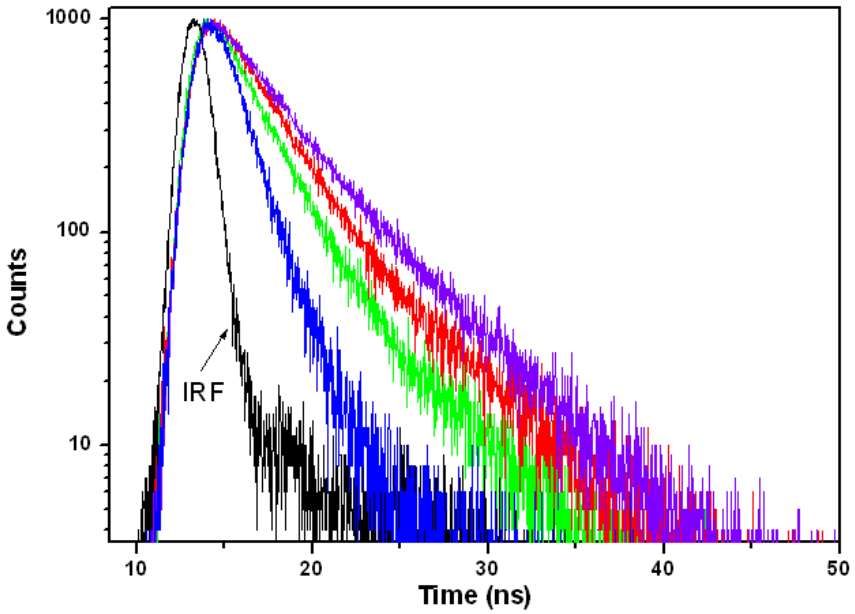


Figure S3. Time-resolved fluorescence signals of BOXD-T3 in cyclohexane solution at 1 × 10-3 mol/L (blue line), in solution processed aligned film (green line), xerogel (red line) and vacuum evaporated film (violent line). IRF = instrument response function.

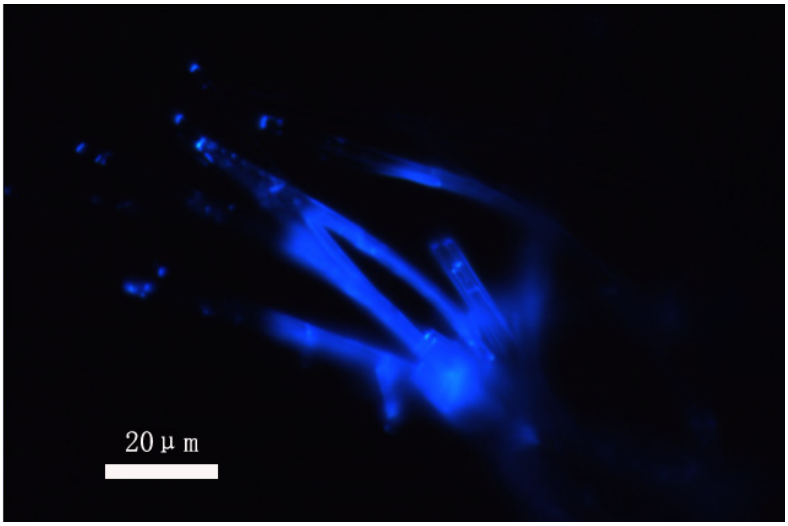
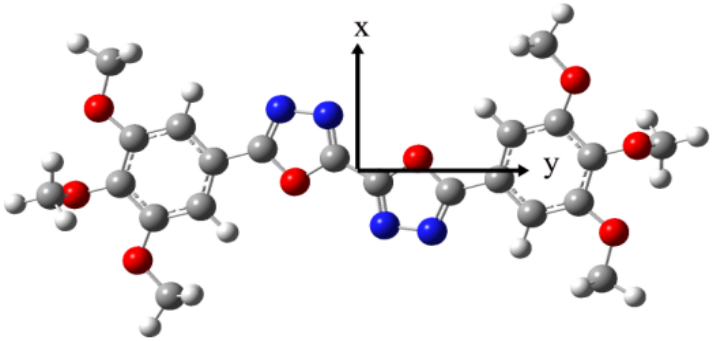


Figure S4. Photoluminescence microscopy image of BOXD-T3 xerogel from 2 wt % gel in DMSO with the excitation UV lights refined into a ~50 μm spot.

S-Table 1. Main geometrical parameters of BOXD-t1 obtained with B3LYP methods for ground state and CI-singles method for excited state together with 6-311+G** basis set; LUMO and HOMO levels of BOXD-T1 in ground state and excited state with B3LYP methods with 6-311+G** basis set.

	Ground state	Excited state
	B3LYP/6-311+G**	CIS/6-311+G**
Bond lengths (Å)		
2-6 (C-C)	1.44212	1.39443
6-10 (C-N)	1.29677	1.31786
7-9 (C-N)	1.30358	1.31182
9-10 (N-N)	1.38361	1.31118
6-8 (C-O)	1.35796	1.34484
7-8 (C-O)	1.36473	1.34268
7-19 (C-C)	1.45131	1.42061
19-20 (C-C)	1.40066	1.40849
19-21 (C-C)	1.38959	1.39349
20-22 (C-C)	1.38773	1.36760
21-24 (C-C)	1.39657	1.38160
22-26 (C-C)	1.41963	1.41828

24-26 (C-C)	1.41236	1.40353
26-27 (C-O)	1.36295	1.34015
27-28 (C-C)	1.43230	1.41215
22-40 (C-O)	1.36935	1.34865
40-49 (C-C)	1.42353	1.40293
24-39 (C-O)	1.36332	1.34571
39-53 (C-C)	1.43127	1.40927
Angles		
6-8-7(C-O-C)	102.50586	103.02331
8-6-10(N-C-O)	112.76525	111.12067
8-7-9(N-C-O)	111.66945	110.77705
6-10-9(C-N-N)	106.13464	106.95360
7-9-10(C-N-N)	106.92480	108.12538
26-27-28(C-O-C)	125.55509	127.52618
22-40-49(C-O-C)	118.64399	120.01173
24-39-53(C-O-C)	125.84261	127.35991
Dihedral angles		
13-11-1-5(C-C-C-N)	180.00000	-179.98859
3-2-6-8(O-C-C-O)	180.00000	-179.98141
9-7-19-21(N-C-C-C)	180.00000	-179.99192
	B3LYP/6-311+G**	
HOMO	-5.72 eV	-5.45
LUMO	-2.09 eV	-2.17 eV



S-Table 2. Calculated ground to excited state transition electric dipole moments (Au) of BOXD-T1:

State	x	y	z	Dip. S.	Osc.
1	0.0287	-3.8382	0.1526	14.7559	1.5198
2	0.0000	0.0000	0.0000	0.0000	0.0000
3	-0.2082	0.3490	-0.0455	0.1672	0.0204
4	0.0000	0.0000	0.0000	0.0000	0.0000
5	-0.0143	0.0026	0.0924	0.0087	0.0012
6	0.0000	0.0000	0.0000	0.0000	0.0000