

## Supplementary Information

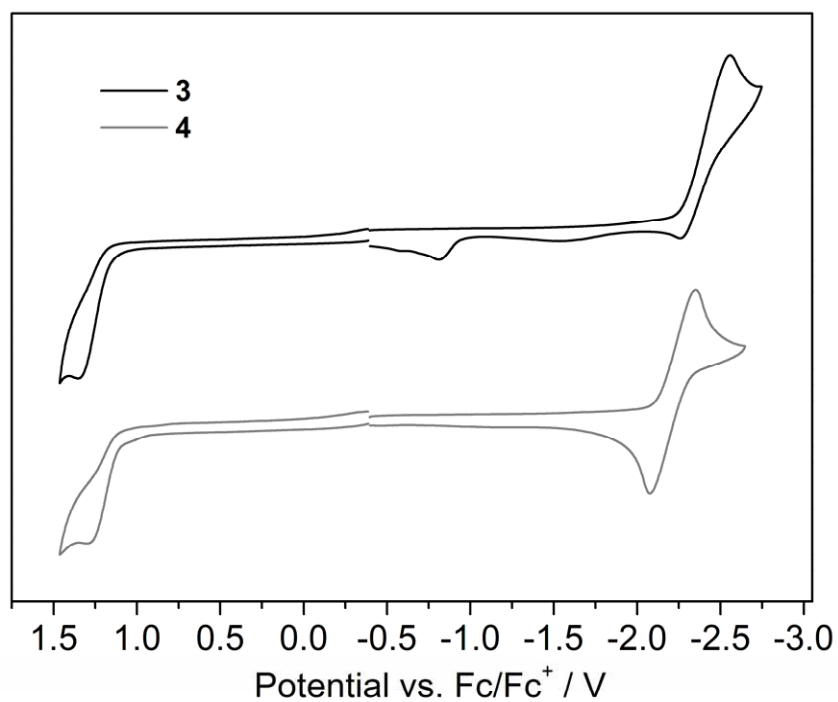
### **Brightly Fluorescent Red Organic Solids Bearing Boron-Bridged $\pi$ -Conjugated Skeletons**

**Di Li,<sup>a</sup> Kai Wang,<sup>a</sup> Shuo Huang,<sup>a</sup> Songnan Qu,<sup>b</sup> Xingyuan Liu,<sup>b</sup> Qingxin Zhu,<sup>c</sup>  
Hongyu Zhang,<sup>a\*</sup> and Yue Wang,<sup>a</sup>**

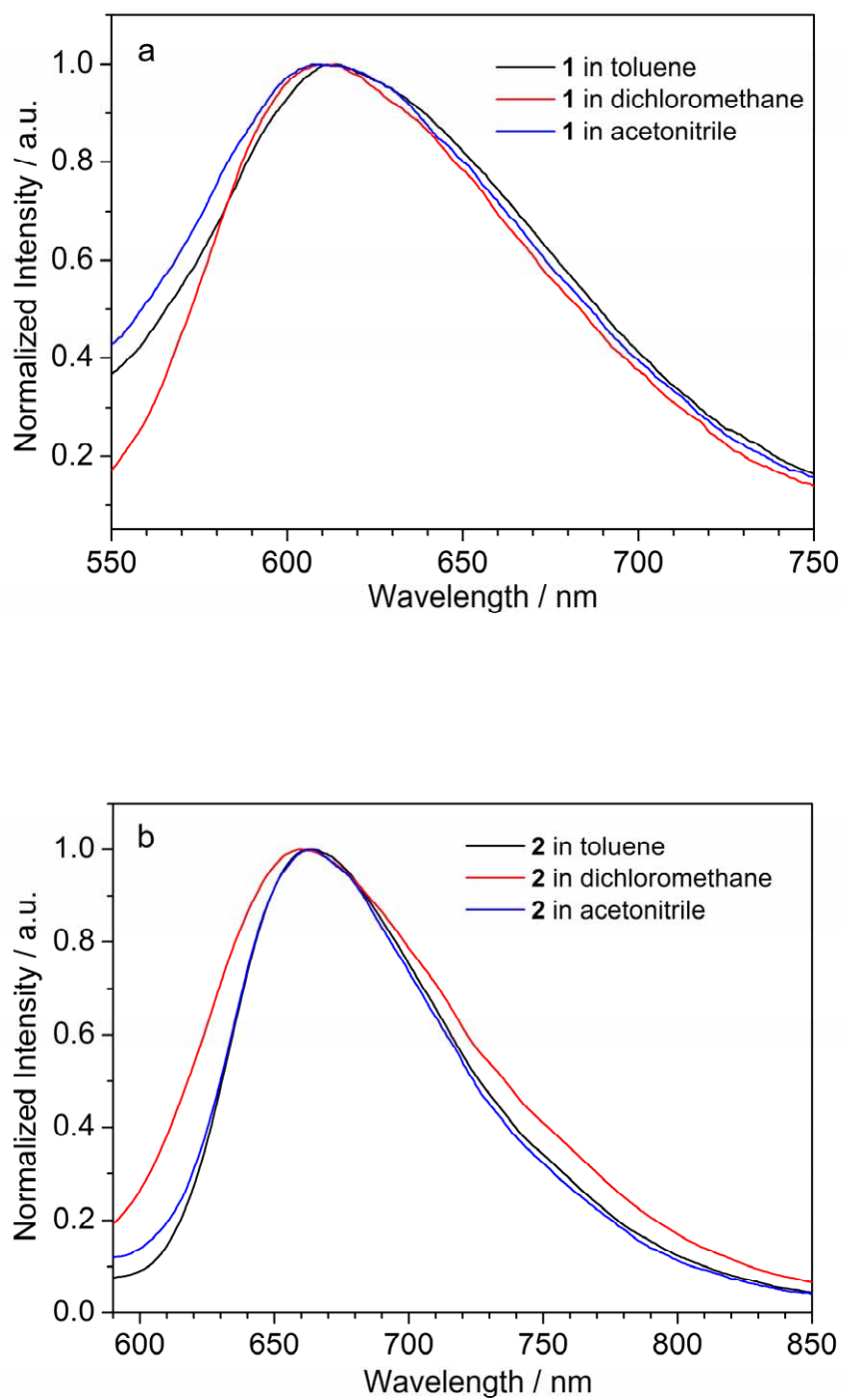
<sup>a</sup> State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin University, Changchun 130012, P. R. China. E-mail: hongyuzhang@jlu.edu.cn (H. Zhang); Tel: +86-431-85168496

<sup>b</sup> Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, P.R. China.

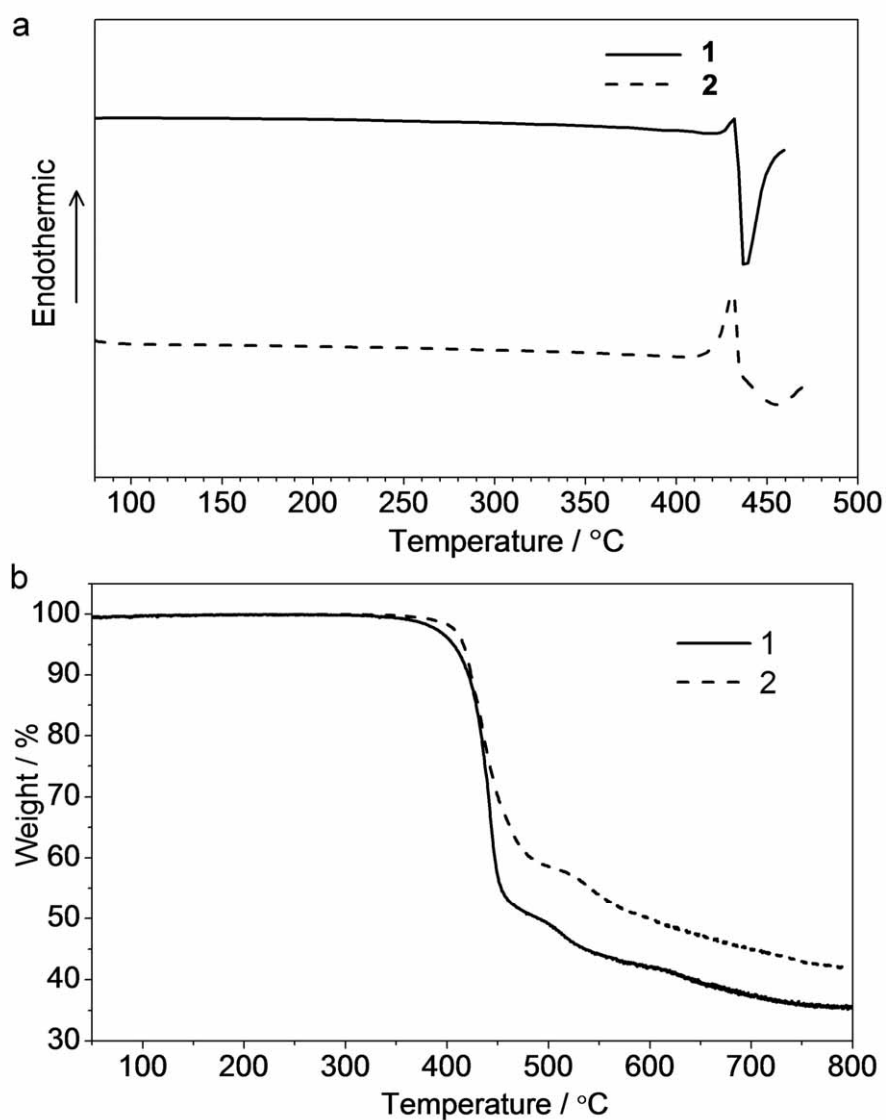
<sup>c</sup> State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, P. R. China.



**Fig. S1** Cyclic voltammograms of **3** (black line) and **4** (gray line) in CH<sub>2</sub>Cl<sub>2</sub> (oxidation, 1 mM) and THF (reduction, 1 mM), measured with TBAP (0.1 M) as a supporting electrolyte at a scan rate of 100 mV s<sup>-1</sup>



**Fig. S2** Emission spectra of **1** (a) and **2** (b) in toluene, dichloromethane and acetonitrile.



**Fig. S3** (a) DSC curves of **1** and **2** at a heating rate of 10 °C/min. (The second cycles were not carried out because **1** and **2** underwent a partial decomposition procedure during the first heating process.) and (b) TGA curves of **1** and **2** at a heating rate of 10 °C/min.

**Table S1.** Crystal data for complexes **1**<sup>a</sup> and **2**<sup>b</sup>.

	<b>1</b>	<b>2</b>
formula	C <sub>44</sub> H <sub>30</sub> B <sub>2</sub> N <sub>2</sub> O <sub>4</sub>	C <sub>44</sub> H <sub>30</sub> B <sub>2</sub> N <sub>2</sub> O <sub>2</sub> S <sub>2</sub>
fw	672.32	704.44
crystal system	triclinic	triclinic
space group	P <sub>-1</sub>	P <sub>-1</sub>
<i>a</i> (Å)	8.220(5)	9.813(7)
<i>b</i> (Å)	8.960(7)	10.072(6)
<i>c</i> (Å)	13.113(7)	10.185(6)
<i>α</i> (deg)	74.48(2)	85.79(2)
<i>β</i> (deg)	75.97(2)	77.07(2)
<i>γ</i> (deg)	65.43(3)	63.68(2)
<i>V</i> (Å <sup>3</sup> )	836.7(10)	879.0(9)
<i>Z</i>	1	1
<i>D<sub>c</sub></i> (g cm <sup>-3</sup> )	1.334	1.331
<i>θ</i> <sub>max</sub> (deg)	27.48	27.47
no. of reflns meads	8244	8711
no. of reflns used	3776	3993
no. of parameters	236	235
<i>R</i> <sub>int</sub>	0.0889	0.0484
final <i>R</i> [ <i>I</i> > 2σ( <i>I</i> )]		
R1	0.0786	0.0549
wR	0.1304	0.1064
<i>R</i> (all data)		
R1	0.1801	0.1013
wR2	0.1631	0.1230
GOF on <i>F</i> <sup>2</sup>	1.015	1.017

<sup>a</sup> Summary of Data CCDC 823398

<sup>b</sup> Summary of Data CCDC 823399

**Table S2.** Selected bond lengths (Å) and angles (deg) for complexes **1** and **2**.

Complex 1			
B(1)-O(2)	1.511(4)	O(2)-B(1)-N(1)#1	102.8(2)
B(1)-C(17)	1.593(4)	C(17)-B(1)-N(1)#1	110.0(3)
B(1)-C(11)	1.601(5)	C(11)-B(1)-N(1)#1	107.4(2)
B(1)-N(1)#1	1.630(4)	C(6)-C(1)-O(1)	108.2(3)
C(6)-N(1)	1.414(4)	C(1)-C(6)-N(1)	106.6(2)
C(7)-N(1)	1.312(4)	N(1)-C(7)-O(1)	113.3(3)
C(7)-O(1)	1.346(4)	N(1)-C(7)-C(8)	124.4(3)
C(7)-C(8)	1.431(4)	O(1)-C(7)-C(8)	122.2(3)
C(8)-C(10)#1	1.408(4)	C(7)-N(1)-C(6)	106.4(3)
C(10)-O(2)	1.350(3)	C(7)-N(1)-B(1)#1	119.0(2)
C(1)-C(6)	1.379(4)	C(6)-N(1)-B(1)#1	134.4(2)
C(1)-O(1)	1.396(3)	C(7)-O(1)-C(1)	105.4(2)
O(2)-B(1)-C(17)	111.4(2)	C(10)-O(2)-B(1)	119.4(2)
O(2)-B(1)-C(11)	109.7(3)	C(10)#1-C(8)-C(7)	115.3(3)
C(17)-B(1)-C(11)	114.8(3)	O(2)-C(10)-C(8)#1	121.7(3)
C(9)-C(8)-C(7)	122.6(3)	O(2)-C(10)-C(9)	120.4(3)
Complex 2			
B(1)-O(1)	1.495(3)	C(17)-B(1)-N(1)	108.97(18)
B(1)-C(17)	1.603(3)	C(11)-B(1)-N(1)	108.49(18)
B(1)-C(11)	1.606(3)	C(6)-C(1)-S(1)	110.60(16)
B(1)-N(1)	1.646(3)	C(1)-C(6)-N(1)	112.90(19)
C(1)-S(1)	1.731(2)	N(1)-C(7)-C(8)	122.4(2)
C(6)-N(1)	1.410(3)	N(1)-C(7)-S(1)	114.53(16)
C(7)-N(1)	1.324(3)	C(8)-C(7)-S(1)	123.08(16)
C(7)-S(1)	1.718(2)	C(9)-C(8)-C(7)	117.23(19)
C(9)-O(1)	1.339(2)	C(10)#1-C(8)-C(7)	121.7(2)
C(7)-C(8)	1.447(3)	O(1)-C(9)-C(10)	119.8(2)
C(8)-C(9)	1.403(3)	O(1)-C(9)-C(8)	121.27(18)
C(1)-C(6)	1.389(3)	C(7)-N(1)-C(6)	111.79(18)
O(1)-B(1)-C(17)	105.41(18)	C(7)-N(1)-B(1)	120.44(17)
O(1)-B(1)-C(11)	111.20(18)	C(6)-N(1)-B(1)	127.77(17)
C(17)-B(1)-C(11)	117.53(18)	C(9)-O(1)-B(1)	121.97(17)
O(1)-B(1)-N(1)	104.44(16)	C(7)-S(1)-C(1)	90.17(11)