Supplementary Material (ESI) for Dalton Transactions

Diboron-Containing Fluorophores with Extended Ladder-Type π-Conjugated Skeleton

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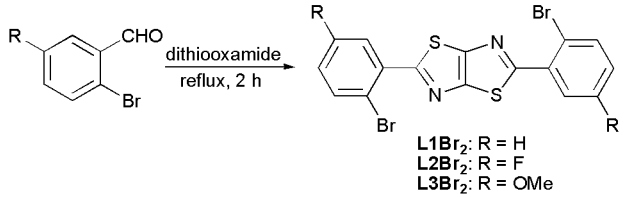
Content

Synthesis of the starting materials



Scheme S1: Synthtic procedure of the starting materials

2,5-bis(2-bromophenyl)thiazolo[5,4-d]thiazole ($L1Br_2$). A mixture of dithiooxamide (300 mg, 2.5 mmol) and 2-bromobenzaldehyde (4.63 g, 25 mmol) was heated to reflux temperature, and then it was cooled and diluted with ethanol after heating for 2 hours. The crude product was washed with ether and recrystallized from cyclohexanone to give yellow crystals (400 mg, 35% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 8.06 (d, J = 8.1 Hz, 2 H), 7.76 (d, J = 7.8 Hz, 2 H), 7.46 (t, J = 7.5 Hz, 2 H), 7.33 (t, J = 7.2 Hz, 2 H). Ms m/z: 451.8 $[M]^+$ (calcd: 451.9). Anal. Calcd (%) for $C_{16}H_8Br_2N_2S_2$: C, 42.50; H, 1.78; N, 6.20; S, 14.18. Found: C, 42.37; H, 1.93; N, 6.21; S, 14.41.

2,5-bis(2-bromo-5-fluorophenyl)thiazolo[5,4-d]thiazole ($L2Br_2$). In the same manner described for $L1Br_2$, compound $L2Br_2$ was provided as green crystals (20% yield) using 2-bromo-5-fluorobenzaldehyde as the initial material. Ms m/z: 487.8 $[M]^+$ (calcd: 487.8). Anal. Calcd (%) for $C_{16}H_6Br_2F_2N_2S_2$: C, 39.37; H, 1.24; N, 5.74; S, 13.14. Found: C, 39.67; H, 1.43; N, 5.92; S, 13.35. ^{1}H NMR spectrum of $L2Br_2$ was not recorded due to its poor solubility in organic solvents.

2,5-bis(2-bromo-5-methoxyphenyl)thiazolo[5,4-d]thiazole ($L3Br_2$). In the same manner described for $L1Br_2$, compound $L3Br_2$ was provided using 2-bromo-5-methoxybenzaldehyde as the initial material and purified by vacuum sublimation to give yellow green solids (10% yield). Ms m/z: 512.8 $[M]^+$ (calcd: 511.9). Anal. Calcd (%) for $C_{18}H_{12}Br_2N_2O_2S_2$: C, 42.21; H, 2.36; N, 5.47; S, 12.52. Found: C, 42.47; H, 2.34; N, 5.54; S, 12.56. ^{1}H NMR spectrum of $L3Br_2$ was not recorded due to its poor solubility in organic solvents.

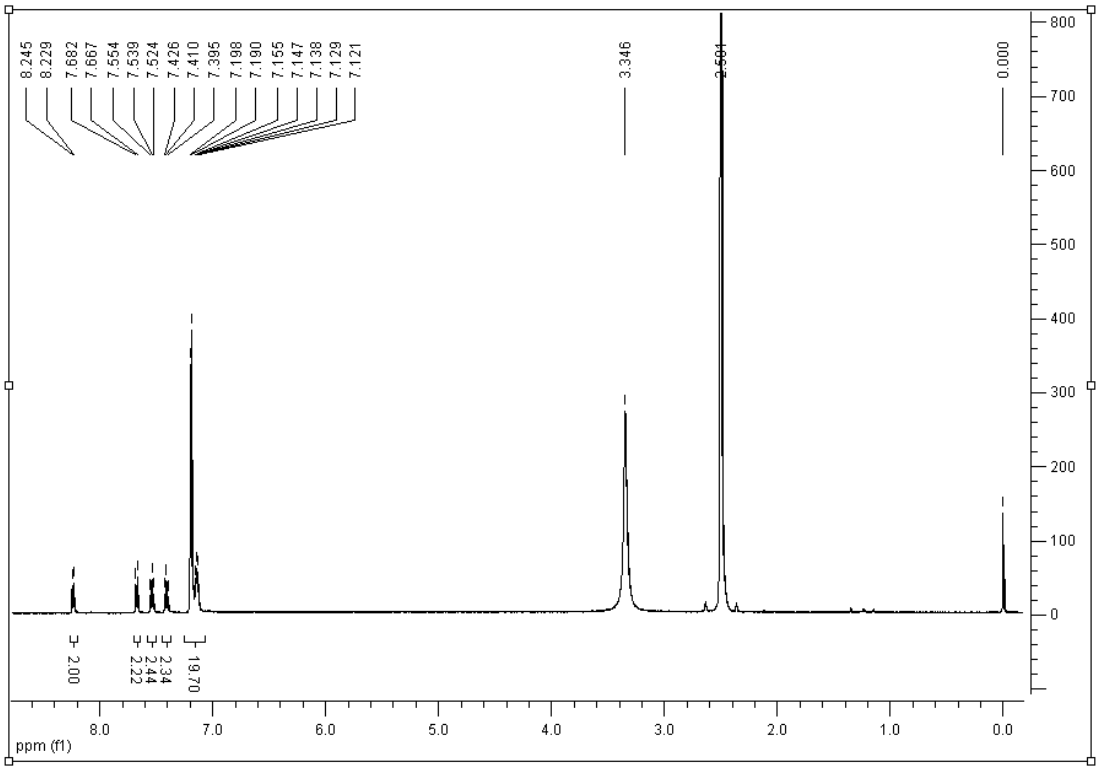


Fig. S1 ^{1}H NMR spectrum of compound **1**.

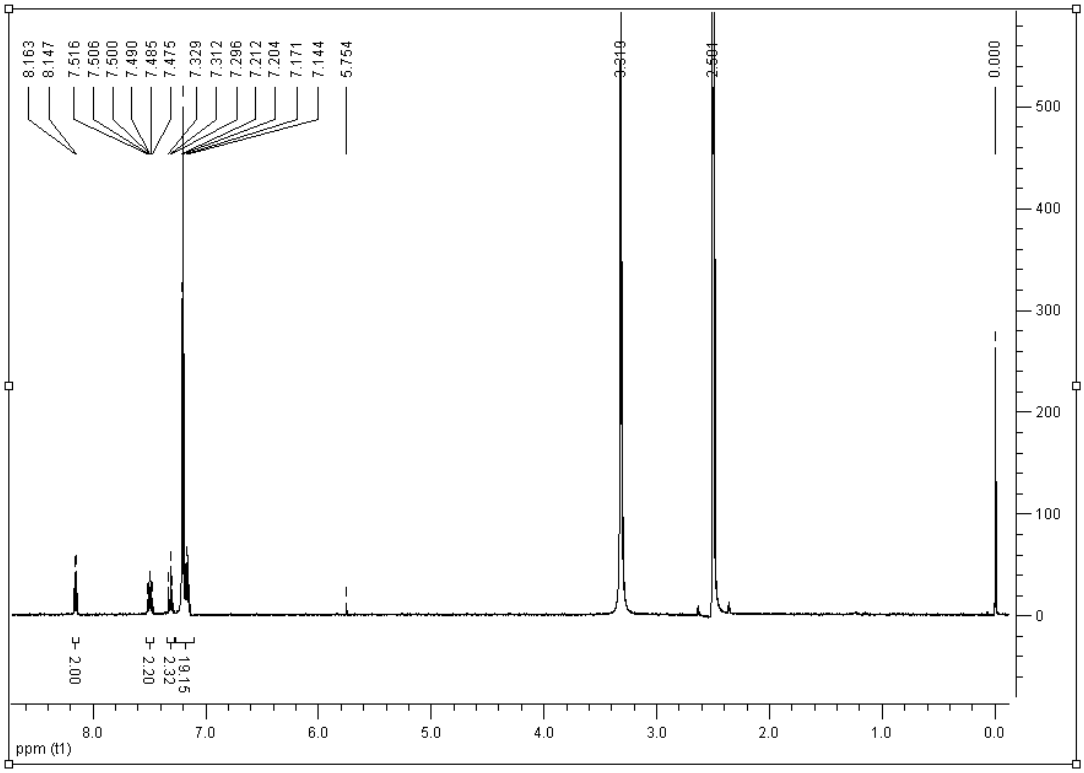


Fig. S2 ^{1}H NMR spectrum of compound **2**.

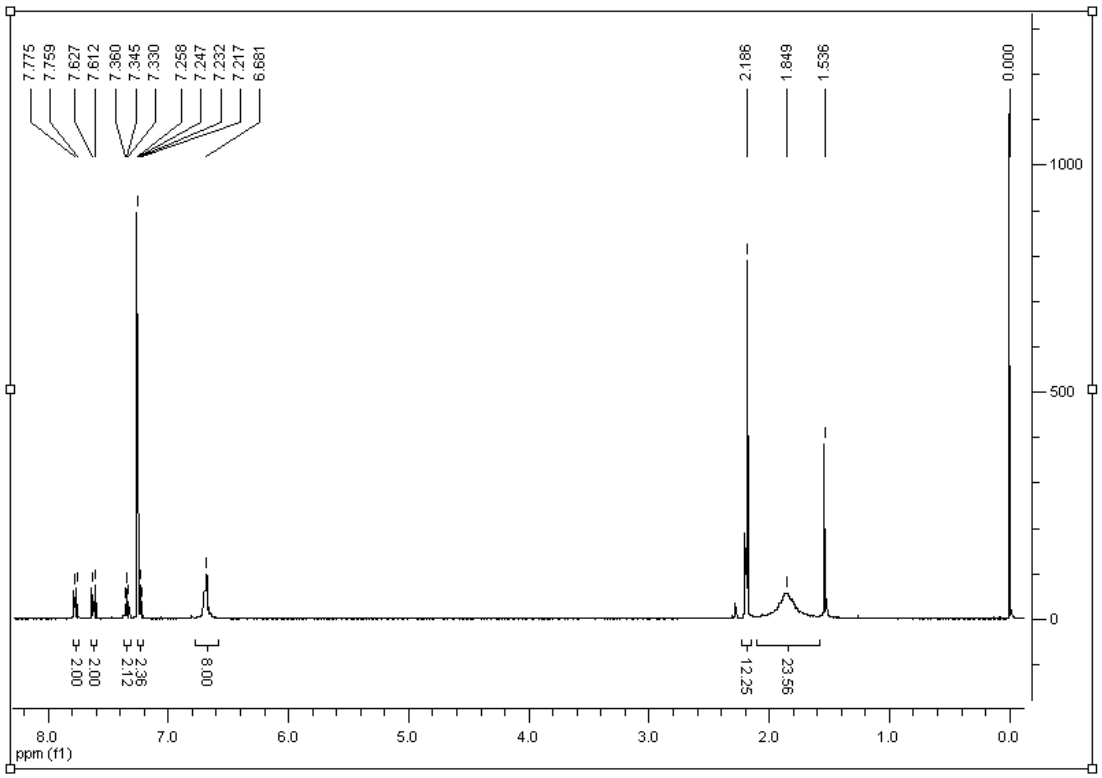


Fig. S3 ^{1}H NMR spectrum of compound **3**.

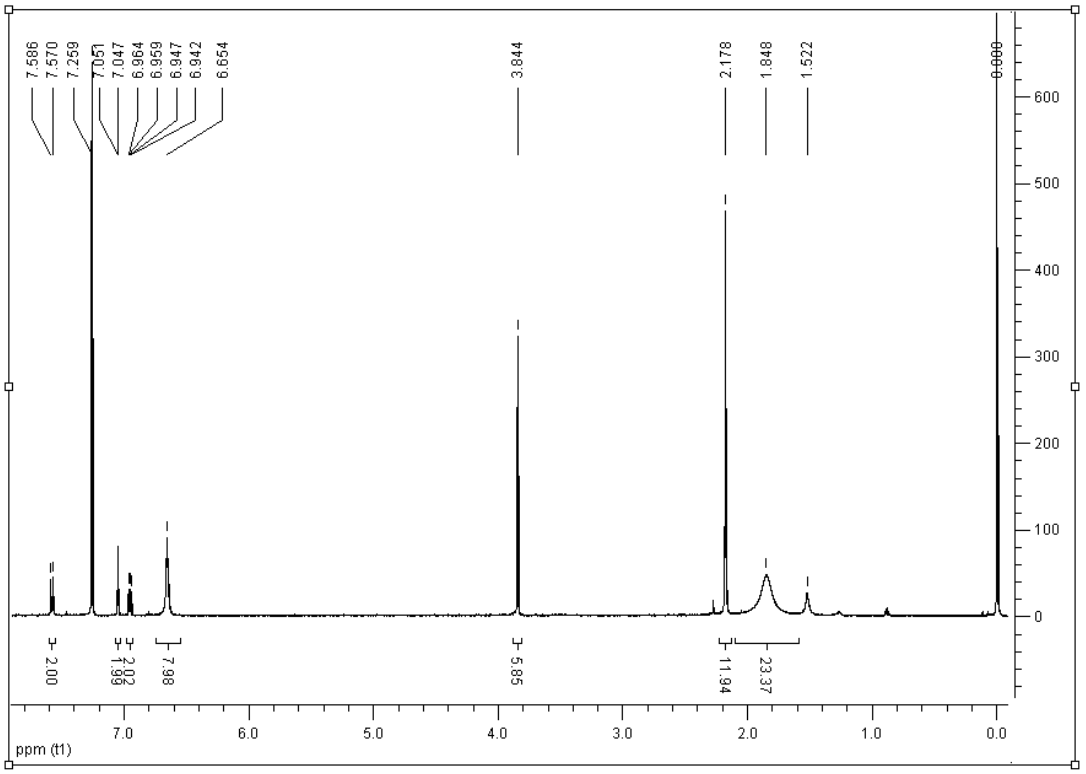


Fig. S4 ^{1}H NMR spectrum of compound **4**.

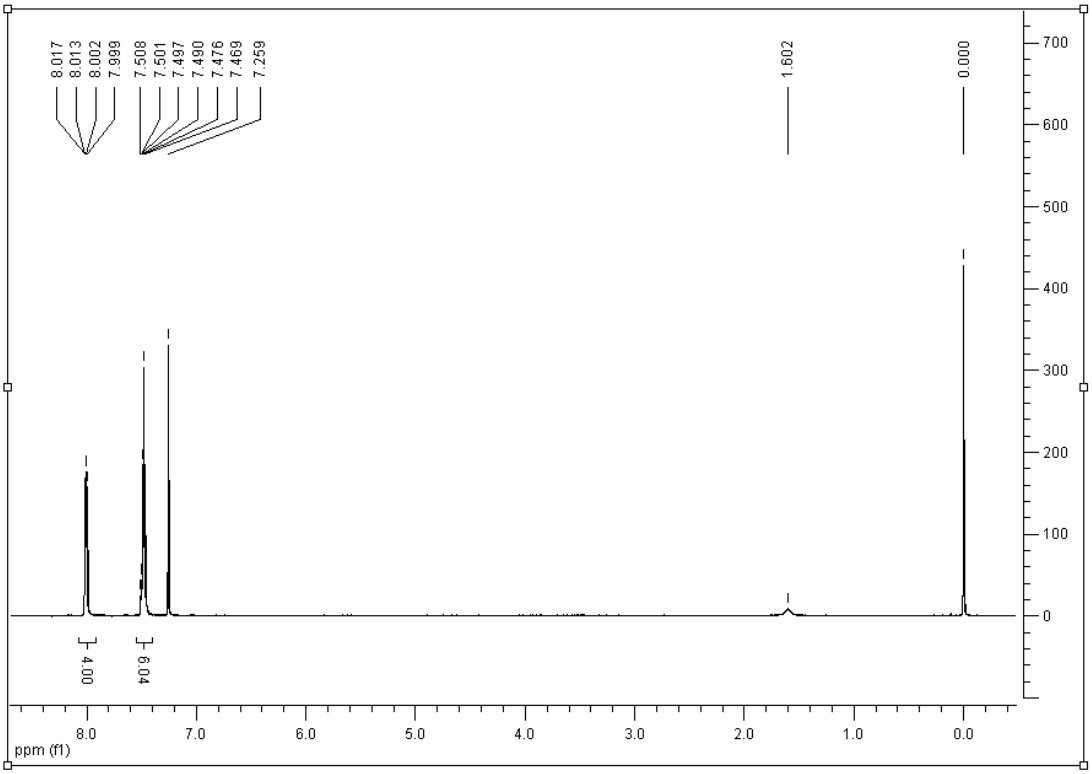


Fig. S5 ^{1}H NMR spectrum of compound **5**.

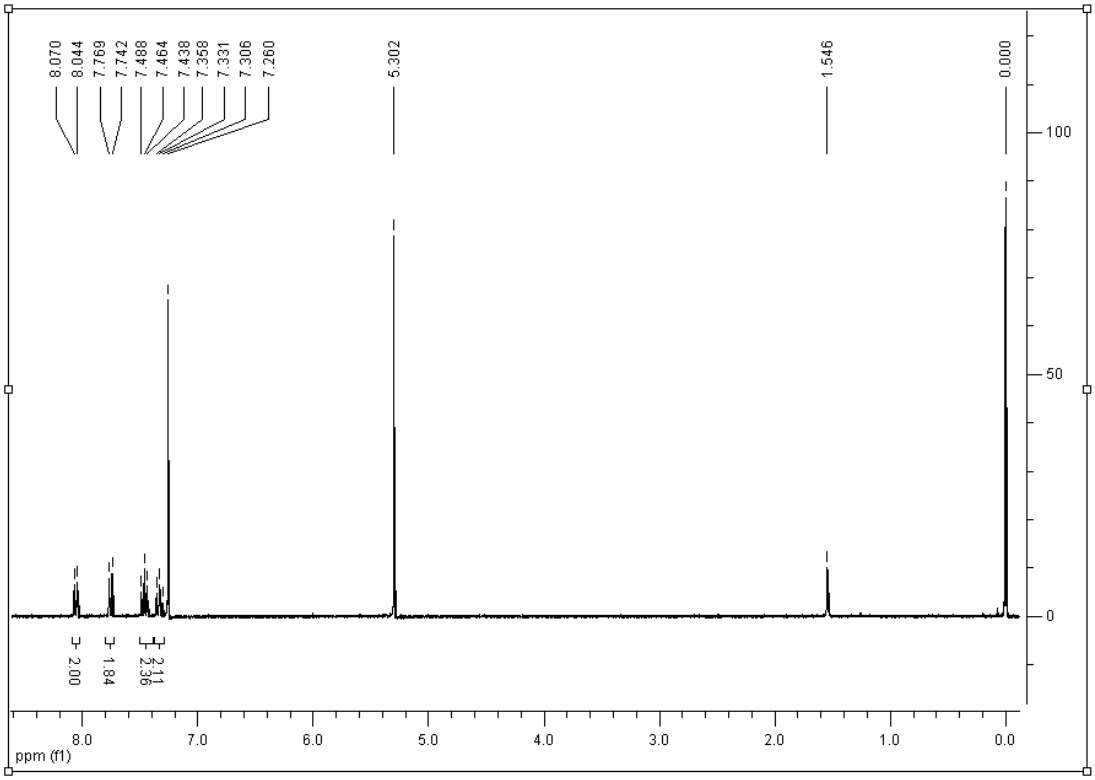


Fig. S6 ^{1}H NMR spectrum of compound **L1Br$_2$**.

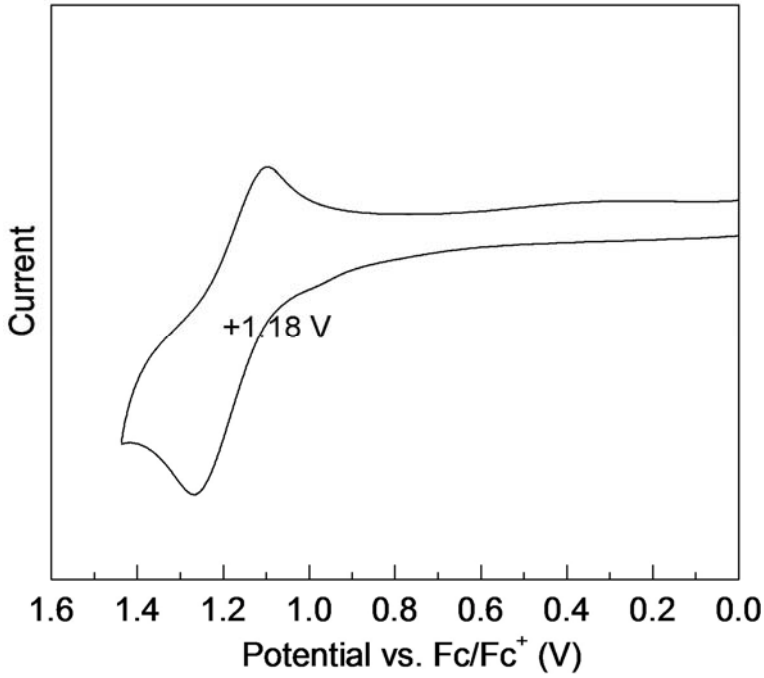


Fig. S7 Cyclic voltammogram for oxidation measurement of **5** in CH_2Cl_2 (1 mM), measured with TBAP (0.1 M) as a supporting electrolyte at a scan rate of 100 mV s^{-1}.

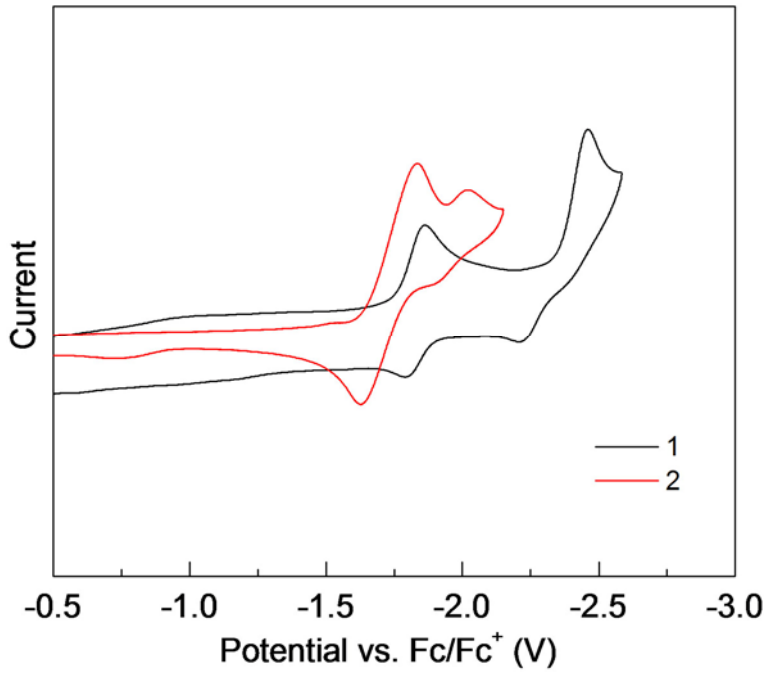


Fig. S8 Cyclic voltammograms of **3** and **5** with two sequential reduction peaks in THF (1 mM), measured with TBAP (0.1 M) as a supporting electrolyte at a scan rate of 100 mV s^{-1}.

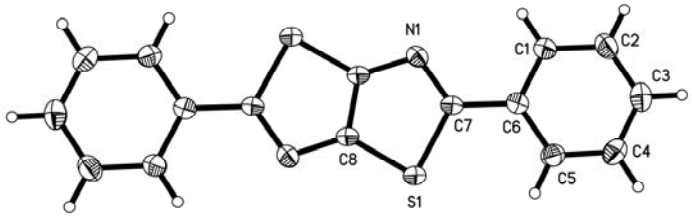


Fig. S9 ORTEP drawing of **5** with 30% thermal ellipsoids.

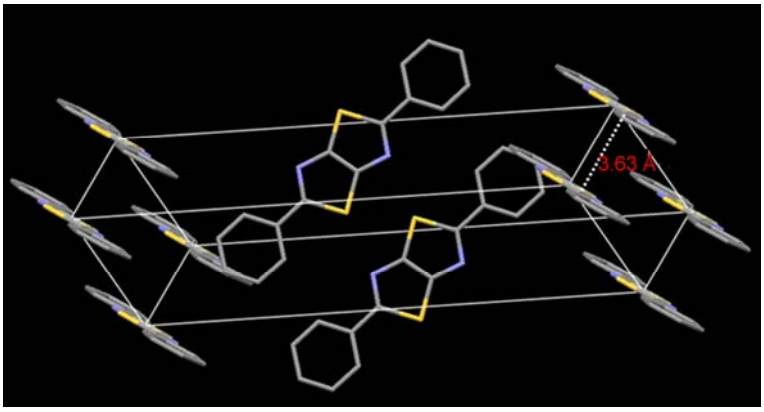


Fig. S10 Crystal packing structure of **5**.

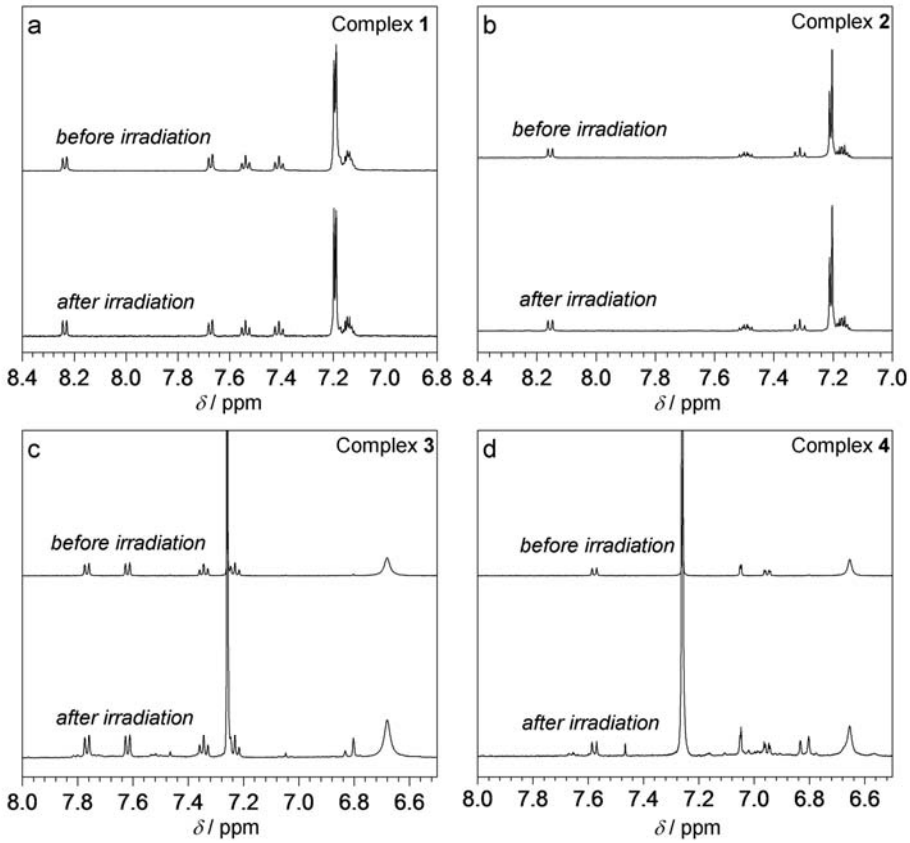


Fig. S11 Proton NMR spectra of boron complexes (**1** and **2** in d_6-DMSO; **3** and **4** in $CDCl_3$) before and after UV irradiation (365 nm) for 2 hours.

Table S1. Crystal Data for Compounds **3** and **5**

	3	**5**
formula	$C_{52}H_{52}B_2N_2S_2$	$C_{16}H_{10}N_2S_2$
fw	790.72	294.40
crystal system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a (Å)	9.0889(18)	5.735(4)
b (Å)	14.676(3) A	5.124(3)
c (Å)	16.295(3)	23.1380(16)
α (deg)	90	90
β (deg)	94.18(3)	101.01(3)
γ (deg)	90	90
V (Å^3)	2167.8(7)	667.5(7)
Z	2	2
D_c (g cm^{-3})	1.211	1.465
θ_{max} (deg)	27.48	27.45
no. of reflns meads	20384	6138
no. of reflns used	4954	1529
no. of parameters	268	91
R_{int}	0.1747	0.0174
final *R* [I > 2σ(I)]		
R1	0.1086	0.0395
wR	0.2000	0.1135
R (all data)		
R1	0.2464	0.0439
wR2	0.2605	0.1176
GOF on F^2	1.064	1.069

Table S2. Selected Bond Lengths (Å) and Angles (deg) for **3**[a] and **5**[b]

Complex **3**			
B(1)-C(18)	1.628(8)	C(6)#1-B(1)-N(3)	93.8(3)
B(1)-C(9)	1.630(8)	C(1)-C(6)-B(1)#1	131.8(4)
B(1)-C(6)#1	1.630(7)	C(5)-C(6)-B(1)#1	112.8(4)
B(1)-N(3)	1.704(6)	N(3)#1-C(7)-C(5)	113.2(4)
C(5)-C(7)	1.450(6)	N(3)#1-C(7)-S(1)	115.8(3)
C(6)-B(1)#1	1.630(7)	C(5)-C(7)-S(1)	131.0(3)
C(7)-N(3)#1	1.335(5)	C(8)#1-C(8)-N(3)	114.8(5)
C(7)-S(1)	1.712(4)	C(8)#1-C(8)-S(1)	110.8(4)
C(8)-C(8)#1	1.371(8)	N(3)-C(8)-S(1)	134.3(3)
C(8)-N(3)	1.378(5)	C(10)-C(9)-C(14)	116.1(5)
C(8)-S(1)	1.725(4)	C(10)-C(9)-B(1)	120.6(5)
C(18)-B(1)-C(9)	116.5(4)	C(14)-C(9)-B(1)	123.2(5)
C(18)-B(1)-C(6)#1	102.9(4)	C(7)#1-N(3)-C(8)	109.7(4)
C(9)-B(1)-C(6)#1	124.7(5)	C(7)#1-N(3)-B(1)	110.9(3)
C(18)-B(1)-N(3)	117.6(4)	C(8)-N(3)-B(1)	138.6(3)
C(9)-B(1)-N(3)	100.0(4)	C(7)-S(1)-C(8)	88.8(2)
Complex **5**			
S(1)-C(8)	1.7105(19)	C(8)-S(1)-C(7)	88.46(8)
S(1)-C(7)	1.7593(17)	C(7)-N(1)-C(8)#1	107.10(14)
N(1)-C(7)	1.330(2)	N(1)-C(7)-C(6)	123.44(14)
N(1)-C(8)#1	1.376(2)	N(1)-C(7)-S(1)	116.30(13)
C(8)-C(8)#1	1.372(3)	C(6)-C(7)-S(1)	120.26(12)
C(6)-C(7)	1.471(2)	C(8)#1-C(8)-S(1)	109.71(16)

Symmetry codes: [a] #1, -x+1,-y,-z ; [b] #1, $-x + 2, -y + 2, -z + 2$.