

Supporting Information

Four-Coordinate monoboron complexes with 8-hydroxyquinolin-5-sulfonate: synthesis, crystal structures, theoretical studies, and luminescence properties

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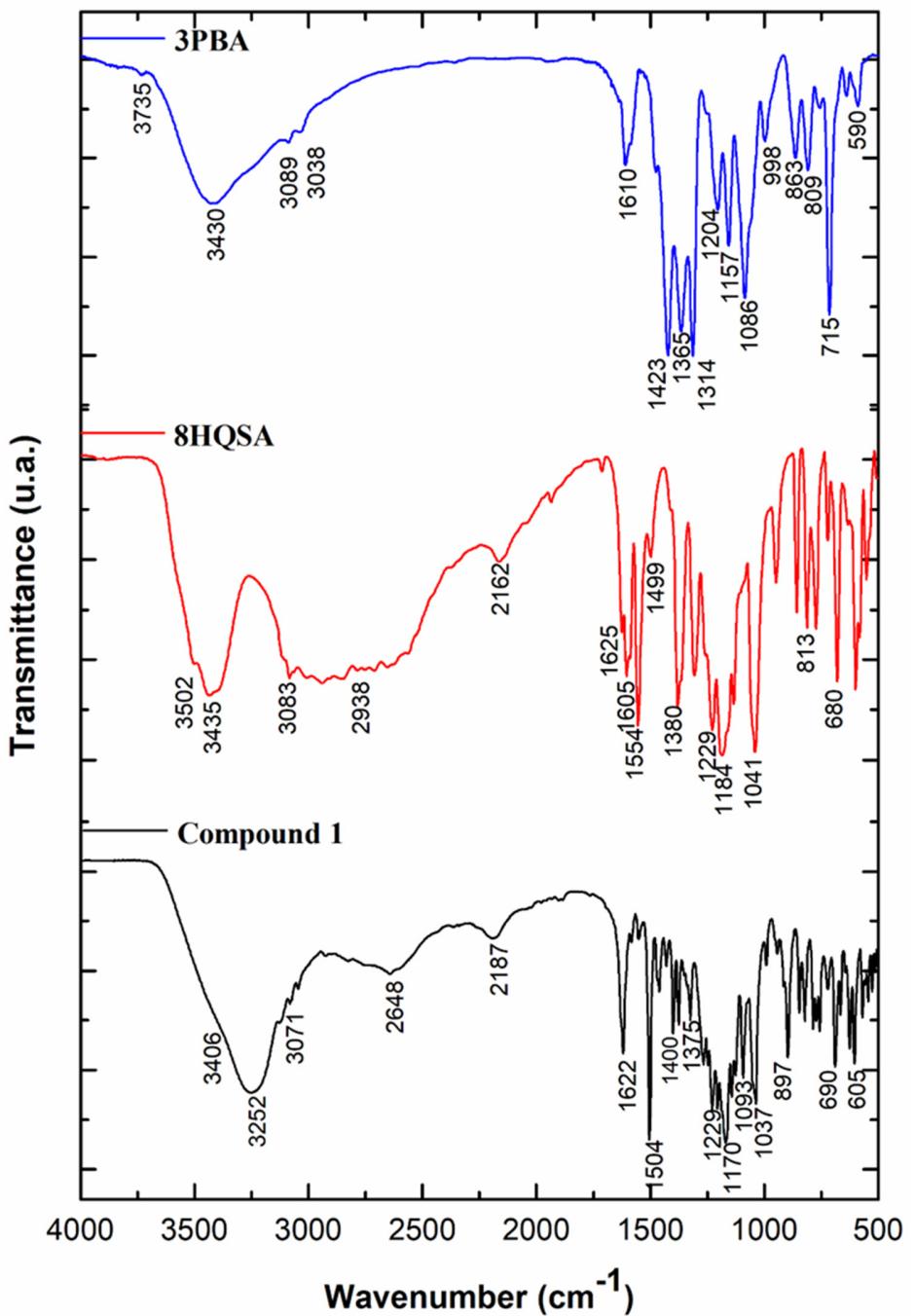


Figure S1. Infrared spectra of complex **1** and the corresponding starting materials.

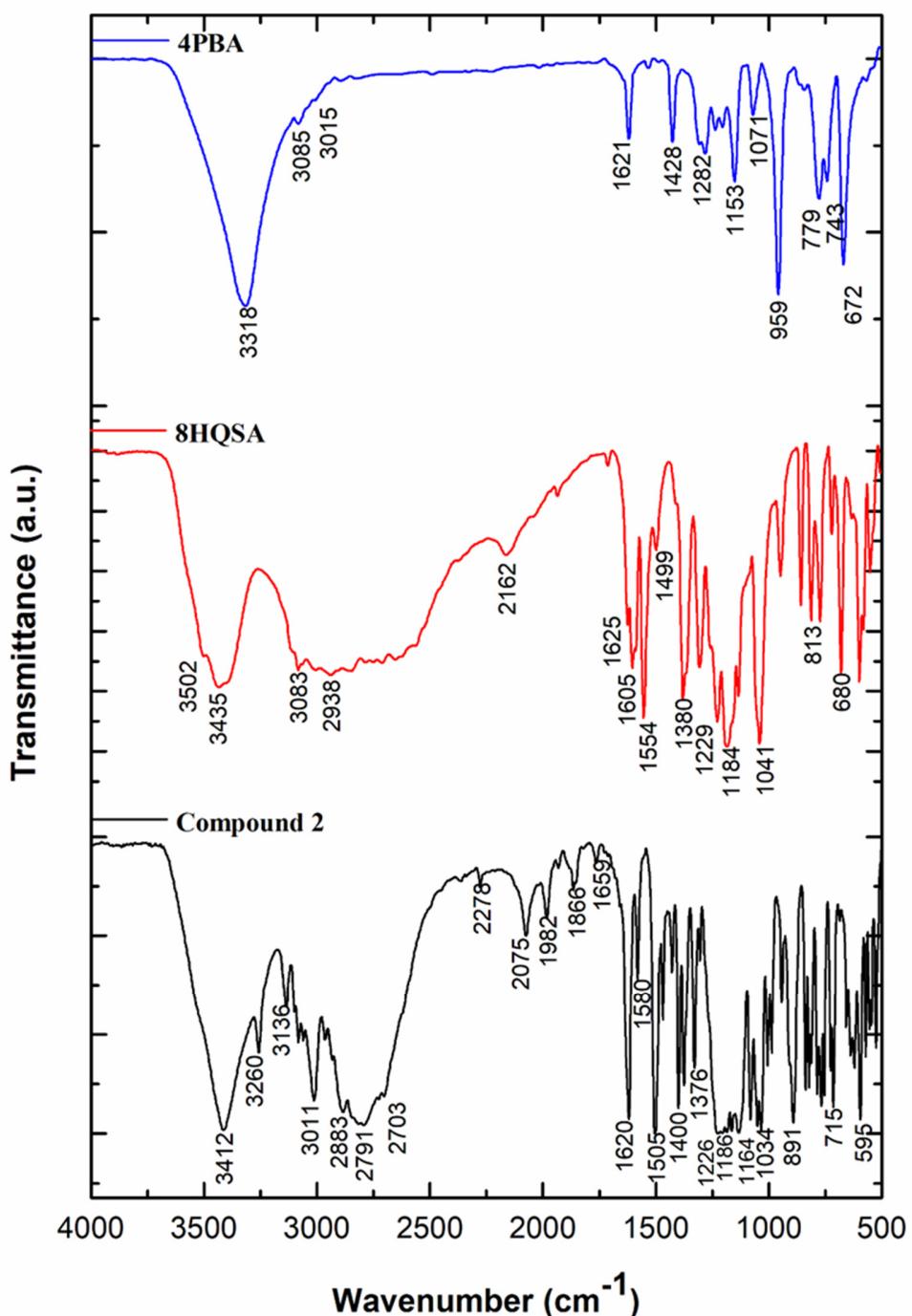


Figure S2. Infrared spectra of complex **2** and the corresponding starting materials.

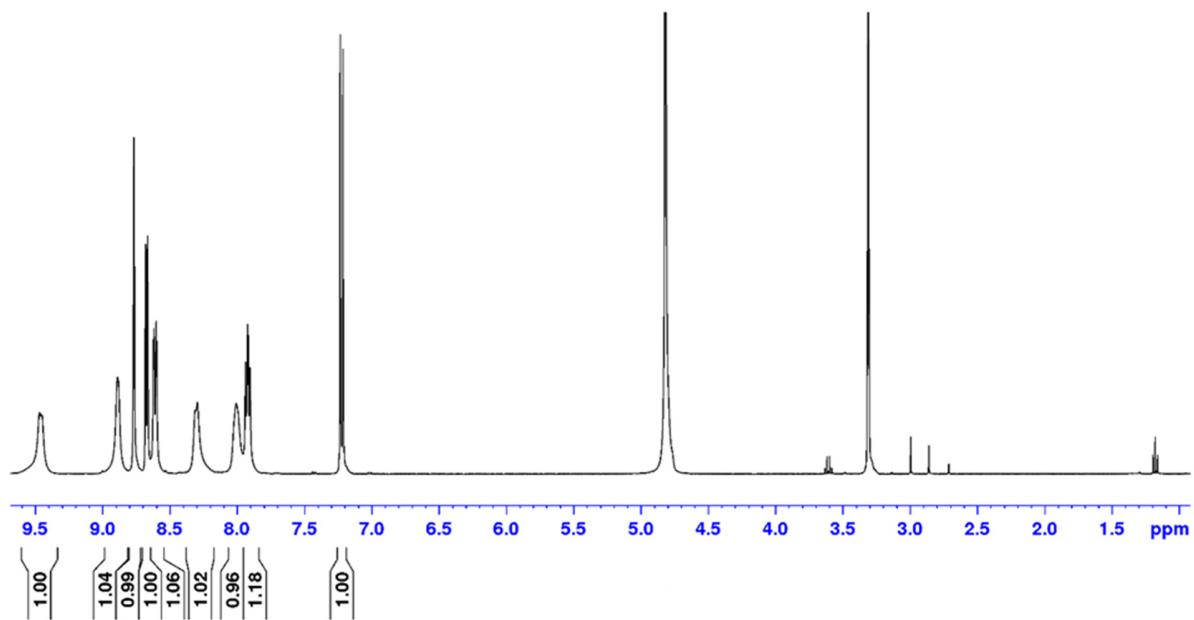


Figure S3. ¹H NMR spectrum of compound **1** in CD_3OD ($C = 5.3 \times 10^{-3} \text{ M}$).

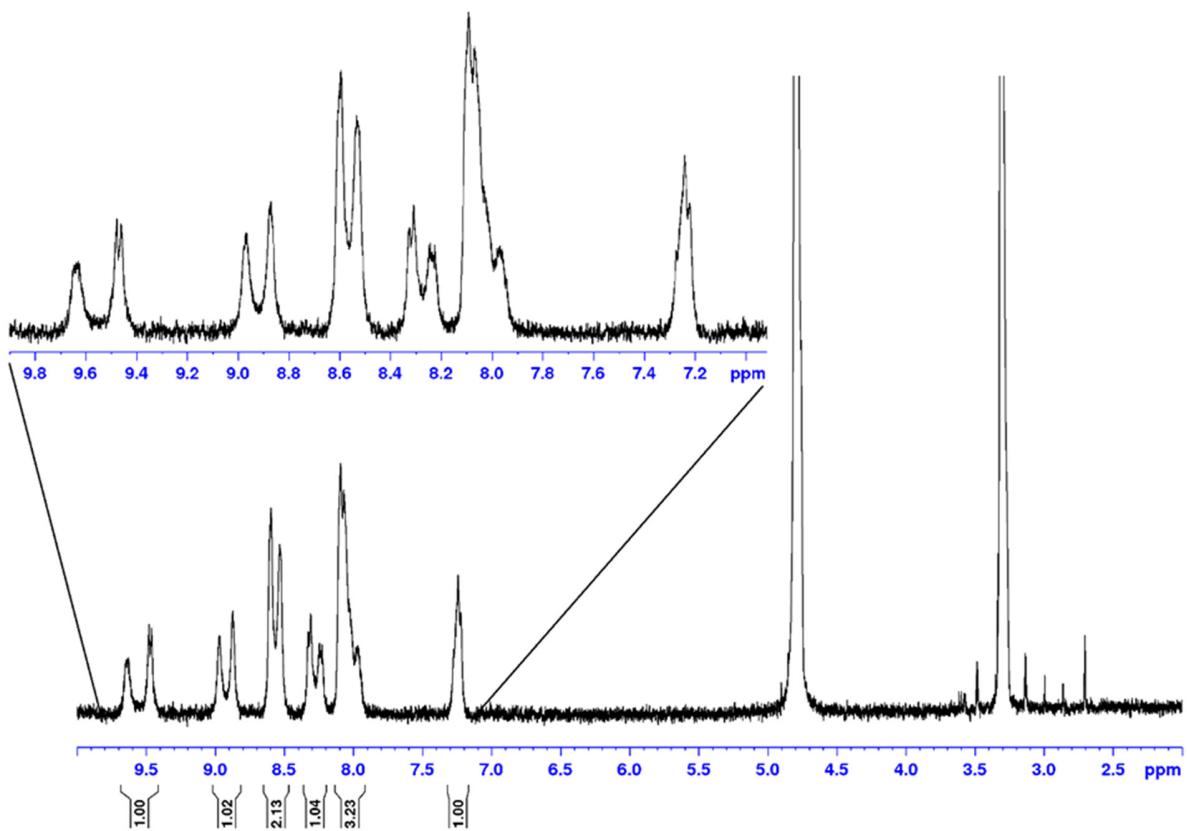


Figure S4. ^1H NMR spectrum of compound **2** in CD_3OD ($\text{C} = 5.0 \times 10^{-3}$ M).

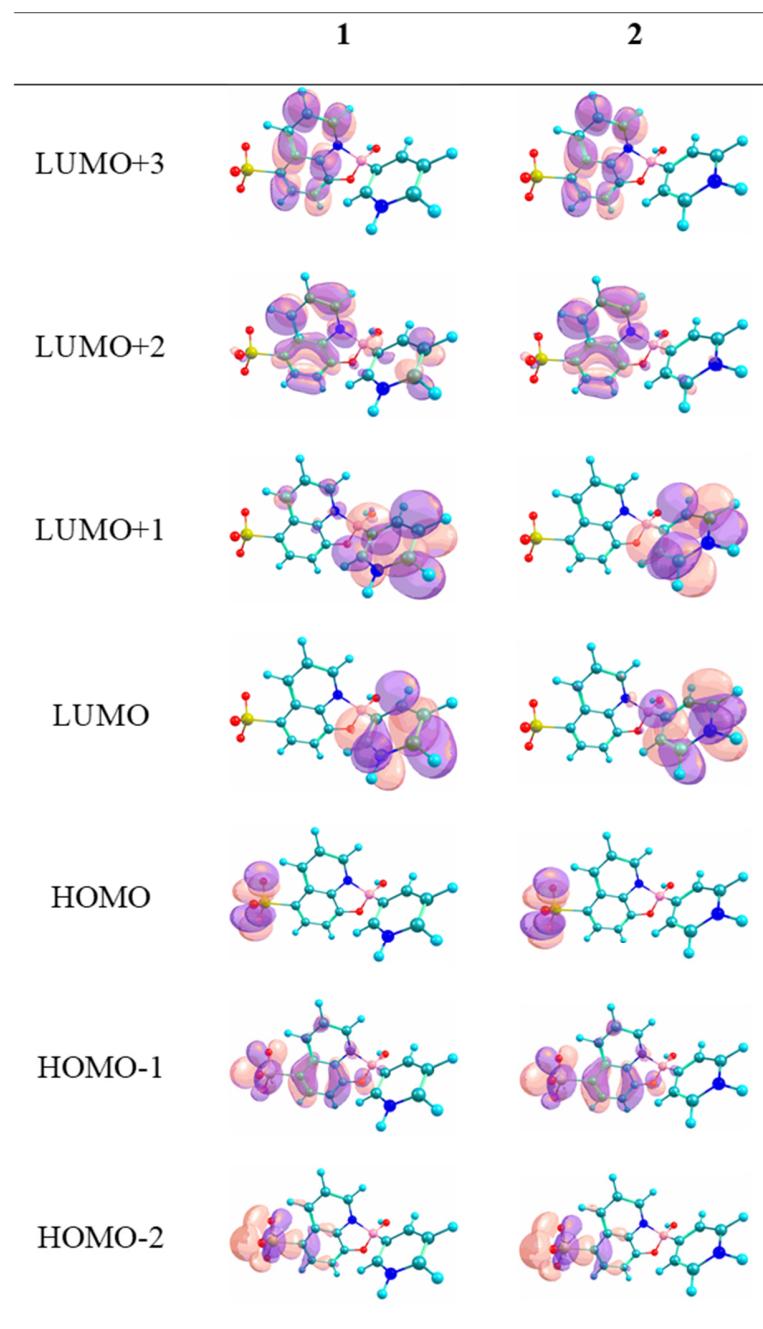


Figure S5. HOMOs and LUMOs frontier orbital plots of the compounds **1** and **2** based on TD-DFT calculation.

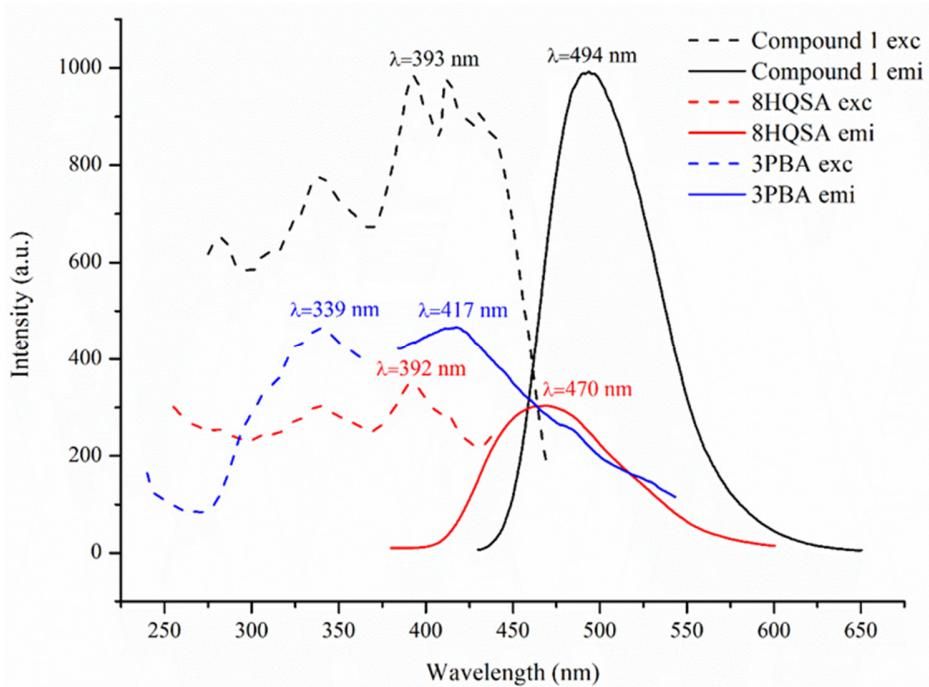


Figure S6. Solid-state emission spectra of **3PBA**, **8HQSA** and **1** at room temperature.

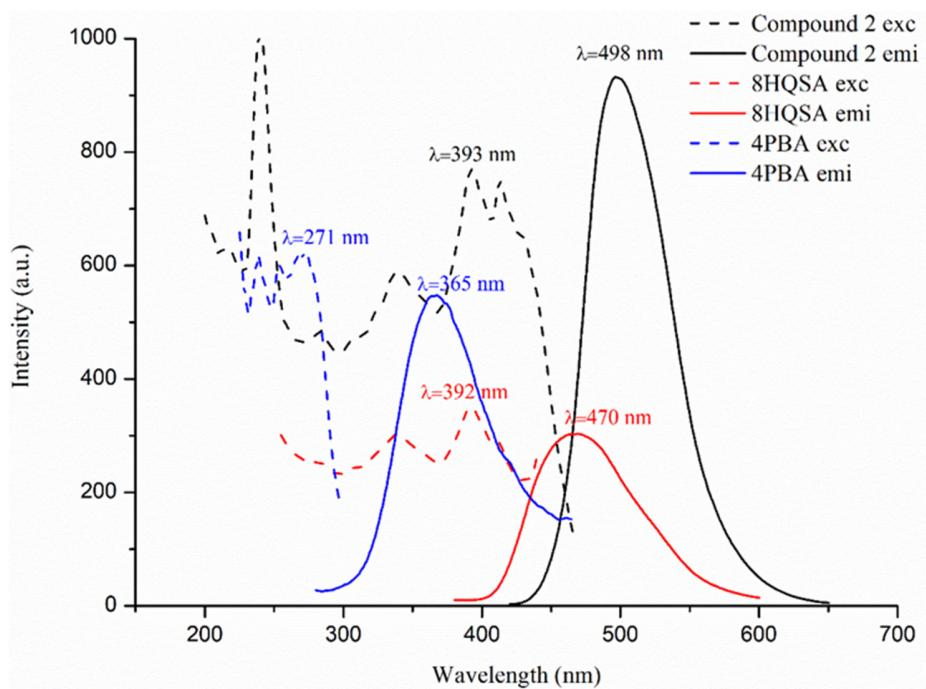


Figure S7. Solid-state emission spectra of **4PBA**, **8HQSA** and **2** at room temperature.

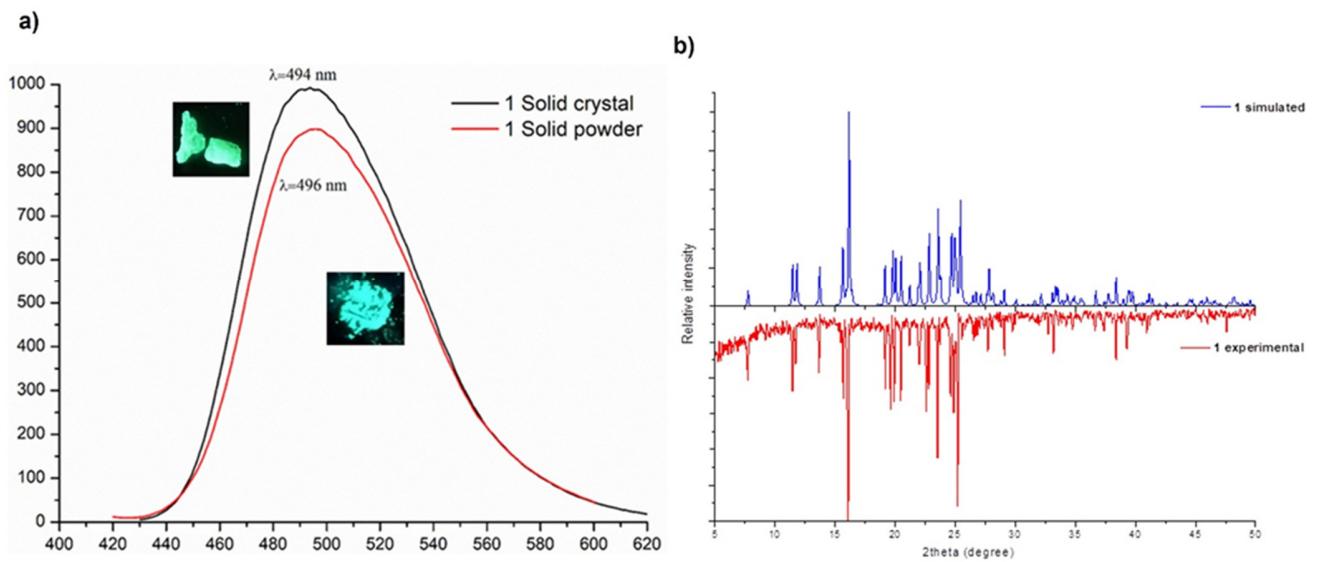


Figure S8. a) Solid-state emission spectra of crystals and powder of **1** at room temperature upon excitation at $\lambda = 340$ nm. Inset: photos of solid crystals and powder under 365 nm UV-light. b) Experimental PXRD pattern for compound **1** in comparison with the pattern simulated from the SCXRD analysis. Note: Contrary to the experimental PXRD pattern, which was measured at $T = 293$ K, the SCXRD data were acquired at low temperature ($T = 100$ K), causing slight shifts of the peaks due to the change of the unit cell parameters.

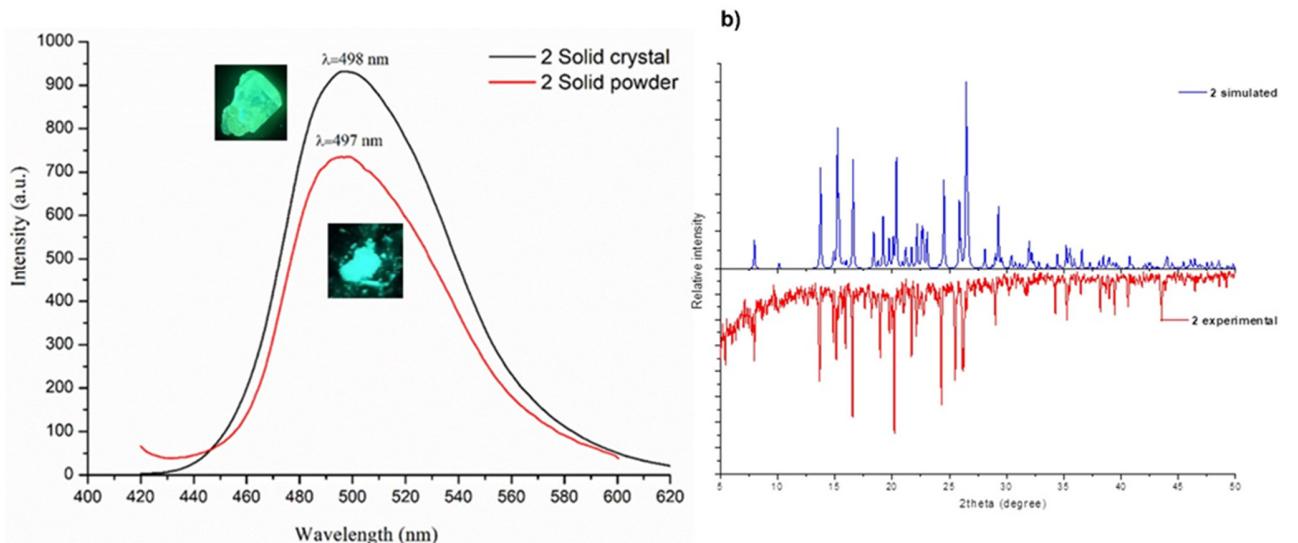


Figure S9. a) Solid-state emission spectra of crystals and powder of **2** at room temperature upon excitation at $\lambda = 340$ nm. Inset: photos of solid crystals and powder under 365 nm UV-light. b) Experimental PXRD pattern for compound **2** in comparison with the pattern simulated from the SCXRD analysis. Note: Contrary to the experimental PXRD pattern, which was measured at $T = 293$ K, the SCXRD data were acquired at low temperature ($T = 100$ K), causing slight shifts of the peaks due to the change of the unit cell parameters.

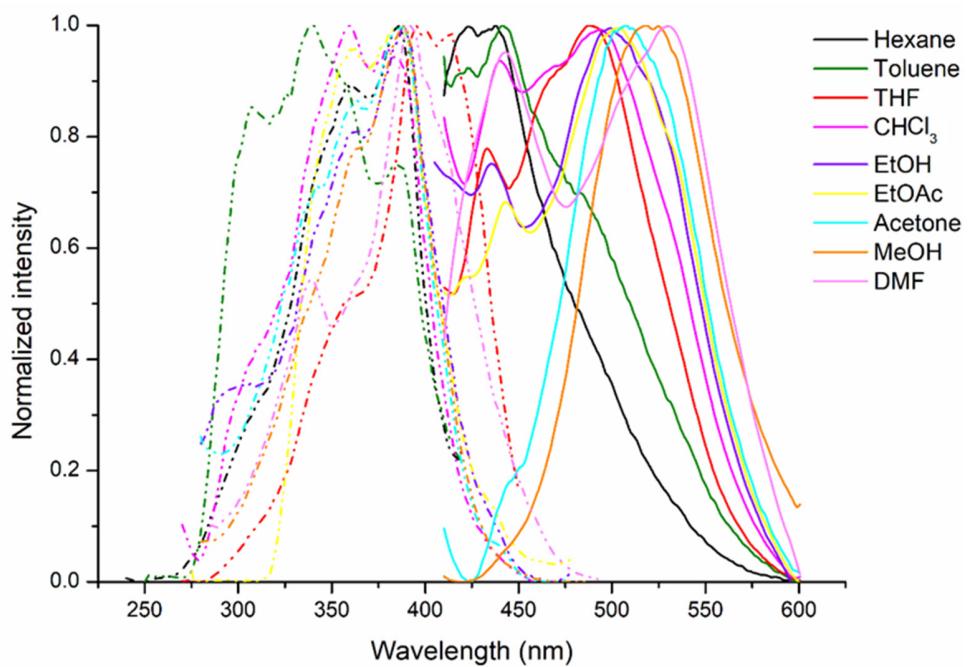


Figure S10. Normalized absorption (dashed lines) and emission (solid lines) spectra of solutions of compound **1** in different solvents (1×10^{-5} M, $\lambda_{\text{ex}} = 365$ nm, slit: 10/6).

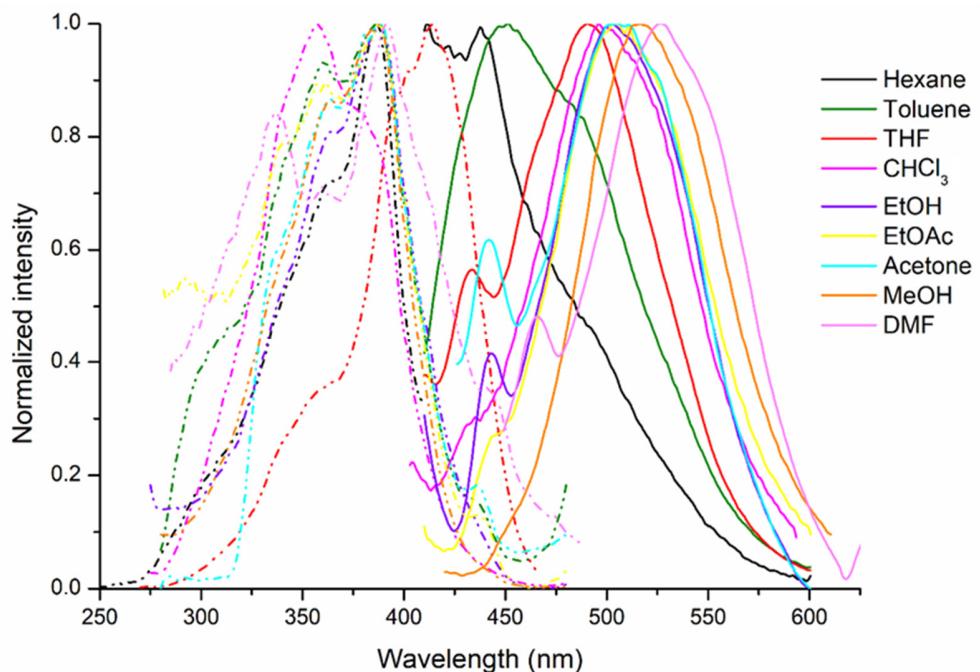


Figure S11. Normalized absorption (dashed lines) and emission (solid lines) spectra of solutions of compound **2** in different solvents (1×10^{-5} M, $\lambda_{\text{ex}} = 365$ nm, slit: 10/6).

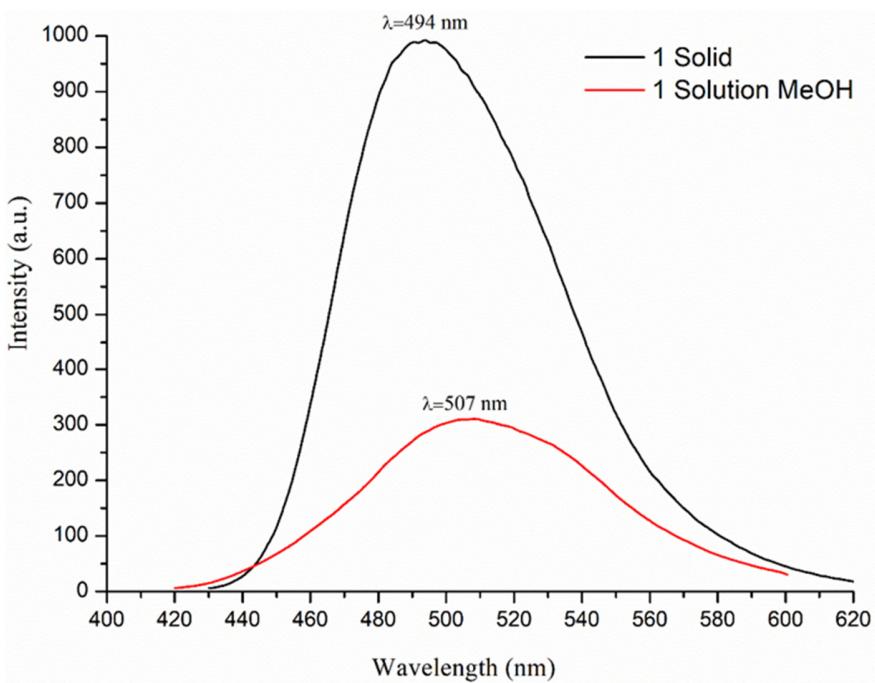


Figure S12. Emission spectra of **1** in the solid state (black) and in methanol solution [1.0 x 10⁻⁴ M] (red).

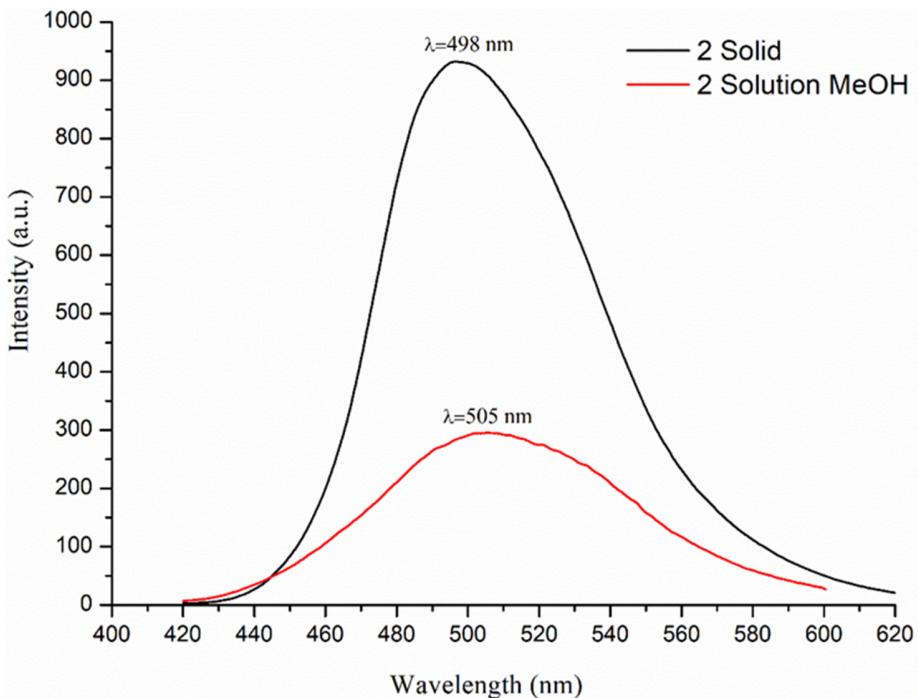


Figure S13. Emission spectra of **2** in the solid state (black) and in methanol solution [1.0 x 10⁻⁴ M] (red).

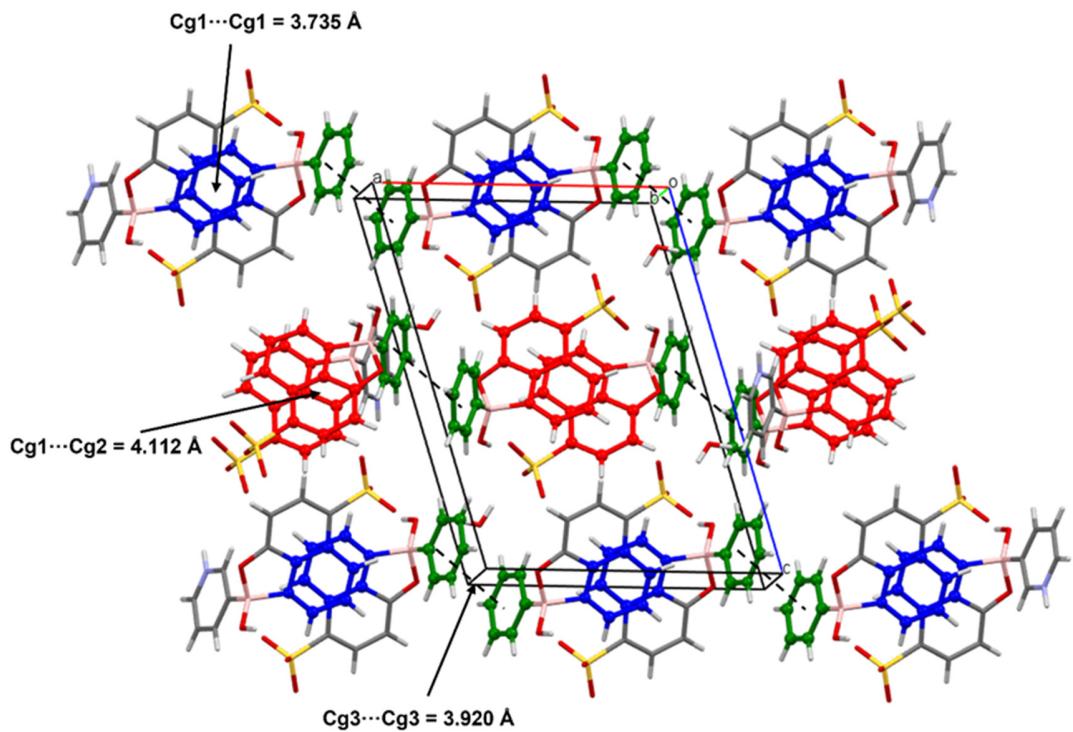


Figure S14. Packing diagram of the crystal structure of **1**, showing the π -stacking interactions between the quinoline and pyridinium rings of symmetry equivalent molecules.

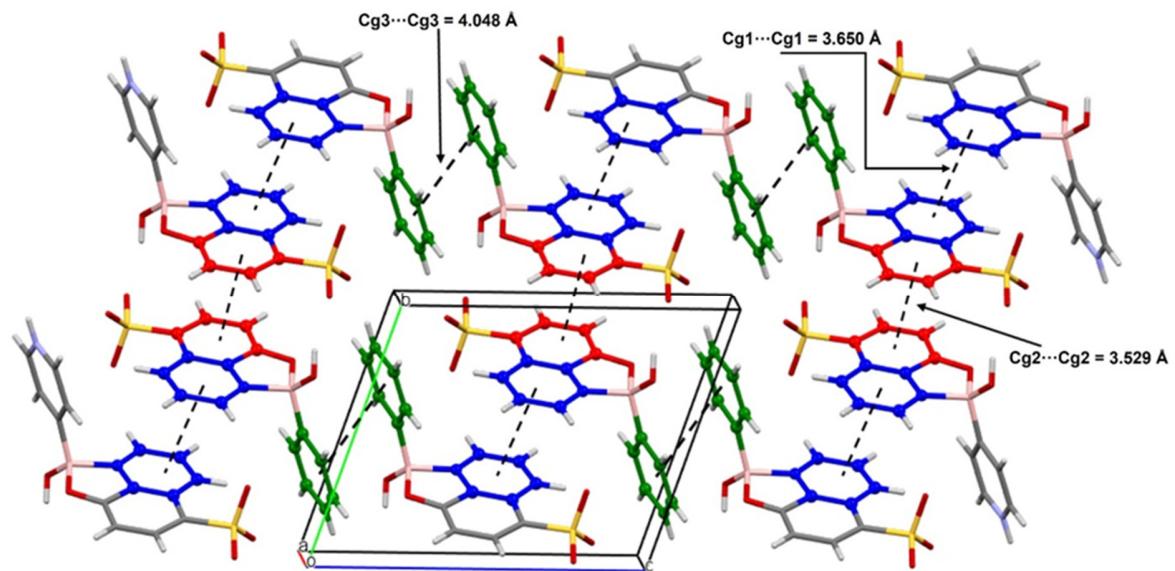


Figure S15. Packing diagram of the crystal structure of **2**, showing the π -stacking interactions between the quinoline and pyridinium rings of symmetry equivalent molecules.

Table S1. Bond distances (\AA) of complex **1**.

1			
S(1)-O(3)	1.4630(11)	C(2)-C(3)	1.379(2)
S(1)-O(4)	1.4585(10)	C(3)-C(4)	1.4215(19)
S(1)-O(5)	1.4469(11)	C(4)-C(5)	1.4299(19)
S(1)-C(5)	1.7689(14)	C(4)-C(9)	1.397(2)
O(1)-C(8)	1.3400(17)	C(5)-C(6)	1.378(2)
O(1)-B(1)	1.5176(18)	C(6)-C(7)	1.418(2)
O(2)-B(1)	1.4121(18)	C(7)-C(8)	1.369(2)
N(1)-C(1)	1.3272(18)	C(8)-C(9)	1.4119(19)
N(1)-C(9)	1.3559(17)	C(10)-C(11)	1.3867(19)
N(1)-B(1)	1.6422(19)	C(10)-C(14)	1.400(2)
N(2)-C(11)	1.3469(19)	C(10)-B(1)	1.614(2)
N(2)-C(12)	1.339(2)	C(12)-C(13)	1.375(2)
C(1)-C(2)	1.406(2)	C(13)-C(14)	1.386(2)

Table S2. Bond angles ($^{\circ}$) complex **1**.

1			
O(3)-S(1)-C(5)	104.29(6)	C(8)-C(7)-C(6)	117.87 (13)
O(4)-S(1)-O(3)	110.80(6)	O(1)-C(8)-C(7)	129.25 (13)
O(4)-S(1)-C(5)	105.64(6)	O(1)-C(8)-C(9)	112.12 (12)
O(5)-S(1)-O(3)	113.49(7)	C(7)-C(8)-C(9)	118.63 (13)
O(5)-S(1)-O(4)	114.49(7)	N(1)-C(9)-C(4)	124.55 (13)
O(5)-S(1)-C(5)	107.21(7)	N(1)-C(9)-C(8)	110.47 (12)
C(8)-O(1)-B(1)	111.23 (11)	C(4)-C(9)-C(8)	124.99 (13)
C(1)-N(1)-C(9)	119.65 (12)	C(11)-C(10)-C(14)	116.25 (13)
C(1)-N(1)-B(1)	132.73 (12)	C(11)-C(10)-B(1)	122.41 (12)
C(9)-N(1)-B(1)	107.61 (11)	C(14)-C(10)-B(1)	121.30 (12)
C(12)-N(2)-C(11)	122.64 (12)	N(2)-C(11)-C(10)	120.96 (13)
N(1)-C(1)-C(2)	119.82 (13)	N(2)-C(12)-C(13)	119.69 (13)
C(3)-C(2)-C(1)	121.06 (13)	C(12)-C(13)-C(14)	118.53 (14)
C(2)-C(3)-C(4)	119.54 (13)	C(13)-C(14)-C(10)	121.90 (13)
C(3)-C(4)-C(5)	129.57 (13)	O(1)-B(1)-N(1)	98.25 (10)
C(9)-C(4)-C(3)	115.24 (12)	O(1)-B(1)-C(10)	109.84 (11)
C(9)-C(4)-C(5)	115.18 (12)	O(2)-B(1)-O(1)	114.71 (12)
C(4)-C(5)-S(1)	119.78 (11)	O(2)-B(1)-N(1)	111.63 (11)
C(6)-C(5)-S(1)	120.36 (11)	O(2)-B(1)-C(10)	110.87 (12)
C(6)-C(5)-C(4)	119.70 (13)	C(10)-B(1)-N(1)	110.94 (11)
C(5)-C(6)-C(7)	123.47 (13)		

Table S3. Bond distances (Å) of complex **2**.

2			
S(1)-O(3)	1.4512(13)	C(2)-C(3)	1.381(3)
S(1)-O(4)	1.4628(15)	C(3)-C(4)	1.415(3)
S(1)-O(5)	1.4595(15)	C(4)-C(5)	1.429(3)
S(1)-C(5)	1.7778(19)	C(4)-C(9)	1.401(3)
O(1)-C(8)	1.333(2)	C(5)-C(6)	1.378(3)
O(1)-B(1)	1.516(2)	C(6)-C(7)	1.419(3)
O(2)-B(1)	1.400(2)	C(7)-C(8)	1.375(3)
N(1)-C(1)	1.326(2)	C(8)-C(9)	1.413(3)
N(1)-C(9)	1.356(2)	C(10)-C(11)	1.400(3)
N(1)-B(1)	1.665(3)	C(10)-C(14)	1.401(3)
N(2)-C(11)	1.340(3)	C(10)-B(1)	1.621(3)
N(2)-C(12)	1.341(3)	C(12)-C(13)	1.377(3)
C(1)-C(2)	1.408(3)	C(13)-C(14)	1.375(3)

Table S4. Bond angles (°) complex **2**.

2			
O(3)-S(1)-C(5)	111.94(8)	C(8)-C(7)-C(6)	117.58(17)
O(4)-S(1)-O(3)	113.34(8)	O(1)-C(8)-C(7)	128.66(18)
O(4)-S(1)-C(5)	105.58(8)	O(1)-C(8)-C(9)	112.74(16)
O(5)-S(1)-O(3)	105.87(8)	C(7)-C(8)-C(9)	118.60(17)
O(5)-S(1)-O(4)	113.30(8)	N(1)-C(9)-C(4)	124.64(17)
O(5)-S(1)-C(5)	106.01(9)	N(1)-C(9)-C(8)	110.21(16)
C(8)-O(1)-B(1)	111.62(14)	C(4)-C(9)-C(8)	125.14(17)
C(1)-N(1)-C(9)	119.43(16)	C(11)-C(10)-C(14)	117.06(17)
C(1)-N(1)-B(1)	133.10(16)	C(11)-C(10)-B(1)	121.63(17)
C(9)-N(1)-B(1)	107.47(15)	C(14)-C(10)-B(1)	121.26(16)
C(12)-N(2)-C(11)	122.36(17)	C(12)-C(11)-C(10)	120.56(18)
N(1)-C(1)-C(2)	120.04(17)	N(2)-C(12)-C(11)	119.72(17)
C(3)-C(2)-C(1)	120.92(18)	N(2)-C(13)-C(14)	119.60(18)
C(2)-C(3)-C(4)	119.62(17)	C(13)-C(14)-C(10)	120.68(18)
C(3)-C(4)-C(5)	129.71(17)	O(1)-B(1)-N(1)	97.69(13)
C(9)-C(4)-C(3)	115.29(17)	O(1)-B(1)-C(10)	110.26(15)
C(9)-C(4)-C(5)	114.99(17)	O(2)-B(1)-O(1)	114.78(16)
C(4)-C(5)-S(1)	120.30(14)	O(2)-B(1)-N(1)	113.14(16)
C(6)-C(5)-S(1)	119.67(15)	O(2)-B(1)-C(10)	112.00(16)
C(6)-C(5)-C(4)	119.84(17)	C(10)-B(1)-N(1)	107.99(14)
C(5)-C(6)-C(7)	123.78(18)		

Table S5. Geometries of intermolecular hydrogen bonds and $\pi \cdots \pi$ contacts in compounds **1** and **2**.

Compound	H-bond	D-H [Å]	H…A [Å]	D…A [Å]	\angle DHA [°]	Symmetry code
1	O2-H2…O4	0.84	1.82	2.646(1)	169	1-x,1-y,1-z
	O6-H6A…O3	0.85	1.88	2.719(1)	169	1-x,0.5+y,0.5-z
	O6-H6B…O2	0.85	1.87	2.722(1)	170	2-x,1-y,1-z
	N2-H2A…O6	0.88	1.84	2.676(2)	159	x,-1+y,z
	C1-H1…O3	0.95	2.48	3.244(2)	138	1-x,-y,1-z
	C2-H2B…O5	0.95	2.66	3.608(2)	173	x,0.5-y,0.5+z
	C7-H7…O6	0.95	2.51	3.378(2)	153	x,y,z
	C7-H7…O3	0.95	2.60	3.340(2)	134	1-x,0.5+y,0.5-z
	C11-H11…O5	0.95	2.50	3.308(2)	144	1-x,-0.5+y,0.5-z
	C12-H12…O1	0.95	2.76	3.082(2)	101	2-x,-y,1-z
	C12-H12…O6	0.95	2.50	3.284(2)	140	2-x,-y,1-z
	C13-H13…O2	0.95	2.43	3.234(2)	142	2-x,-0.5+y,1.5-z
	Cg1…Cg1 ^a			3.735		1-x,-y,1-z
	Cg1…Cg2 ^a			4.112		1-x,1-y,1-z
	Cg3…Cg3 ^a			3.920		2-x,-y,1-z
2	O2-H2…O5	0.84	1.97	2.785(2)	165	1-x,2-y,1-z
	N2-H2A…O4	0.88	1.82	2.695(2)	175	x,-1+y,1+z
	C1-H1…O3	0.95	2.41	3.176(2)	138	1-x,1-y,1-z
	C2-H2B…O3	0.95	2.51	3.285(3)	138	-1+x,y,z
	C12-H12…O3	0.95	2.56	3.162(2)	121	2-x,1-y,1-z
	C13-H13…O2	0.95	2.63	3.281(1)	127	-x,1-y,2-z
	Cg1…Cg1 ^a			3.650		1-x,1-y,1-z
	Cg2…Cg2 ^a			3.529		1-x,2-y,1-z
	Cg3…Cg3 ^a			4.048		1-x,1-y,2-z

[a] Cg1 = N1, C1-C4, C9; Cg2 = C4-C9; Cg3 = N2, C10-14.

Table S6. Calculation of τ_4 for complexes **1** and **2**.

Complex 1	Complex 2
Angles (°)	Angles (°)
O1 B1 N1 98.25(10)	O1 B1 N1 97.69(13)
O1 B1 C10 109.84(11)	O1 B1 C10 110.26(15)
O2 B1 O1 114.71(12)	O2 B1 O1 114.78(16)
O2 B1 N1 111.63(11)	O2 B1 N1 113.14(16)
O2 B1 C10 110.87(12)	O2 B1 C10 112.00(16)
C10 B1 N1 110.94(11)	C10 B1 N1 107.99(14)
$\tau_4 = \frac{360 - (\alpha + \beta)}{141}$	$\tau_4 = \frac{360 - (\alpha + \beta)}{141}$
$\tau_4 = \frac{360 - (114.71 + 111.63)}{141}$	$\tau_4 = \frac{360 - (114.78 + 113.14)}{141}$
$\tau_4 = \frac{360 - (226.34)}{141}$	$\tau_4 = \frac{360 - (227.92)}{141}$
$\tau_4(\text{complex } \mathbf{1}) = 0.9479$ (distorted tetrahedral)	$\tau_4(\text{complex } \mathbf{2}) = 0.936$ (distorted tetrahedral)

Table S7. Calculation of THC for complexes **1** and **2**.

Complex 1		Complex 2	
Angles (°)		Angles (°)	
O1B1C10	$\Theta_1=109.84(11)$	O1B1C10	$\Theta_1=110.26(15)$
O2B1O1	$\Theta_2=114.71(12)$	O2B1O1	$\Theta_2=114.78(16)$
O2B1C10	$\Theta_3=110.87(12)$	O2B1C10	$\Theta_3=112.00(16)$
C10B1N1	$\Theta_4=110.94(11)$	O1B1N1	$\Theta_4=97.69(13)$
O1B1N1	$\Theta_5=98.25(10)$	C10B1N1	$\Theta_5=107.99(14)$
O2B1N1	$\Theta_6=111.63(11)$	O2B1N1	$\Theta_6=113.14(16)$
$THC_{OKI}[\%] = \frac{120^\circ - \frac{(\theta_1 + \theta_2 + \theta_3)^\circ}{3}}{120^\circ - 109.5^\circ} \times 100$		$THC_{OKI}[\%] = \frac{120^\circ - \frac{(\theta_1 + \theta_2 + \theta_3)^\circ}{3}}{120^\circ - 109.5^\circ} \times 100$	
$THC_{OKI}[\%] = 78.03\%$		$THC_{OKI}[\%] = 72.88\%$	
$THC_{DA}[\%] = \left[1 - \frac{\sum_{n=1-6} 109.5 - \theta_n ^\circ}{90^\circ} \right] \times 100$		$THC_{DA}[\%] = \left[1 - \frac{\sum_{n=1-6} 109.5 - \theta_n ^\circ}{90^\circ} \right] \times 100$	
$THC_{DA \text{ complex 1}} = 75.85\%$		$THC_{DA \text{ complex 2}} = 71.66\%$	

Table S8. Percentages of intermolecular interactions for complexes **1** and **2**.

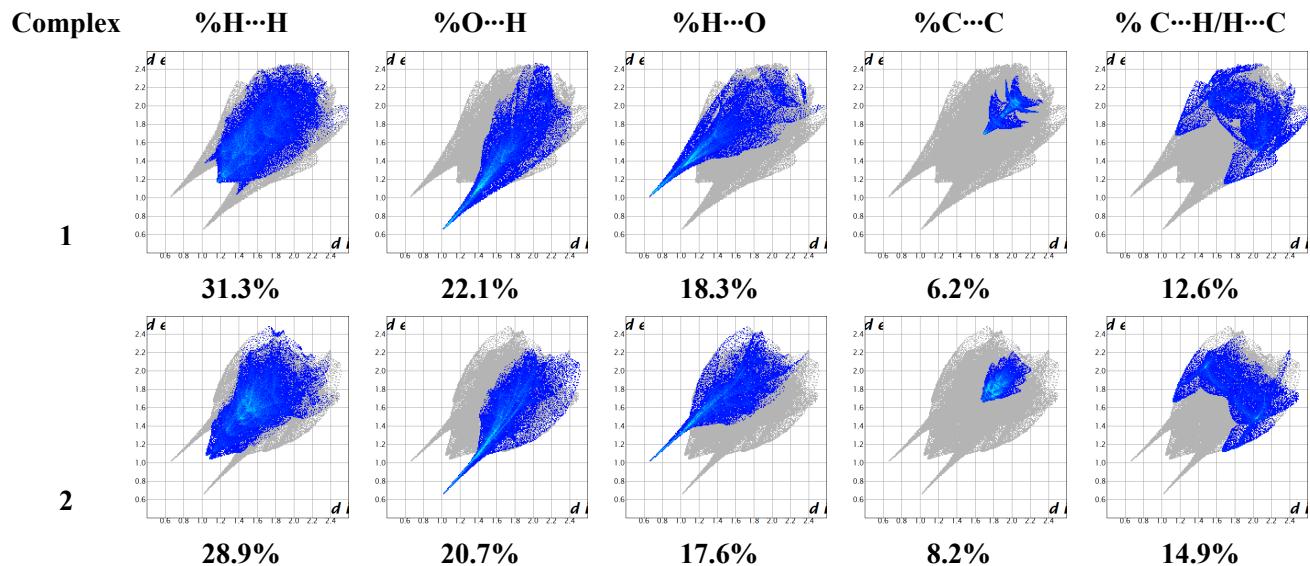


Table S9. Selected IR spectroscopic data (in cm^{-1}) for **1** and **2** in comparison to the corresponding starting materials.

	$\nu(\text{O}-\text{H})$	$\nu(\text{N}^+-\text{H})$	$\nu(\text{C}=\text{N})/\nu(\text{C}=\text{N}^+-\text{H})$	$\nu(\text{B}-\text{O})$	$\nu(\text{B}-\text{C})$	$\nu(\text{S}-\text{O})$
Starting reagents						
3PBA	3430	—	1610/—	1314	1086	—
4PBA	3318	—	1621/—	1282	1071	—
8HQSA	3502–3435	—	1605/—	—	—	1184/1041
Boron complexes						
1	3406	3252	1622/1504	1375	1093	1170/1037
2	3412	3260	1620/1505	1376	1081	1186/1034

Table S10. Electronic excited states calculated through Time-dependent Density Functional Theory (TD-DFT) with the calculation level M06-2X/6-31G(d) for compounds **1** and **2**.

Table

Compound	λ [nm] (E, eV)	Oscillator force	Transition (CI coeff.)
1	336 (3.69)	0.0831	HOMO→LUMO (0.86)
	278 (4.46)	0.0077	HOMO→LUMO+1 (0.79)
	234 (5.29)	0.0508	HOMO→LUMO+2 (0.63)
	226 (5.48)	0.1886	HOMO→LUMO+3 (0.43) HOMO-2→LUMO (0.35)
2	339 (3.66)	0.0802	HOMO→LUMO (0.78)
			HOMO→LUMO+1 (0.20)
	287 (4.32)	0.0039	HOMO→LUMO+1 (0.71) HOMO→LUMO (0.18)
	230 (5.40)	0.1888	HOMO→LUMO+2 (0.67) HOMO-2→LUMO (0.20)
	227 (5.45)	0.2139	HOMO→LUMO+3 (0.44) HOMO-2→LUMO (0.24)

S11.

Table S11. Photophysical properties of the solutions of complexes **1** and **2** in different solvents, 1.0×10^{-5} M, $\lambda_{\text{ex}} = 365$ nm.

Complex	Solvent	$\lambda_{\text{ex,max}}$ (nm) ^[a]	$\lambda_{\text{em,max}}$ (nm) ^[b]	Stokes shifts		
				$\Delta\lambda$ (nm) ^[c]	$\Delta\nu$ (cm^{-1}) ^[d]	$\Delta\nu$ (eV)
1	Hexane	359, 387	422, 438	51	3009	0.37
	Toluene	340	441	101	6763	0.83
	THF	394	489	95	4931	0.61
	CHCl ₃	390	493	103	5357	0.66
	EtOH	386	498	112	5827	0.72
	EtOAc	388	503	115	5892	0.73
	Acetone	387	507	120	6116	0.75
	MeOH	389	524	135	6623	0.82
	DMF	390	529	139	6737	0.83
2	Hexane	387	437	50	2957	0.36
	Toluene	385	451	66	3801	0.47
	THF	413	491	78	3846	0.48
	CHCl ₃	357	496	139	7850	0.97
	EtOH	358	495	137	7731	0.96
	EtOAc	387	509	122	6194	0.77
	Acetone	385	510	129	6498	0.80
	MeOH	387	517	125	6498	0.80
	DMF	388	527	139	6798	0.84

[a] Absorption maximum. [b] Emission maximum. [c,d] Stokes shift.