Asymmetric boron-complexes containing keto-isoindolinyl and pyridyl groups: solvatochromic fluorescence, efficient solid-state emission and DFT calculation

Yanping Wu,[a] Hua Lu,[a*] Sisi Wang,[a] Yuan Deng,[a] Zhen Shen [b*]

I Materials and instrumentations

All reagents were obtained from commercial suppliers and used without further purification unless otherwise indicated.   All air and moisture-sensitive reactions were carried out under nitrogen atmosphere in oven-dried glassware.   Glassware was dried in an oven at 120 °C and cooled under a stream of inert gas before use.   Both dichloromethane and triethylamine were distilled over calcium hydride. ^{1}H NMR spectra were recorded on a Bruker DRX400 spectrometer and referenced to the residual proton signals of the solvent.   HR-MS were recorded on a Bruker Daltonics microTOF-Q II spectrometer.   All the solvents employed for the spectroscopic measurements were of UV spectroscopic grade (Aldrich).

II. Supplementary Figure

Fig. S1. Absorption and emission spectra of **1a** in a range of different solvents. λ_{ex} = 330 nm.
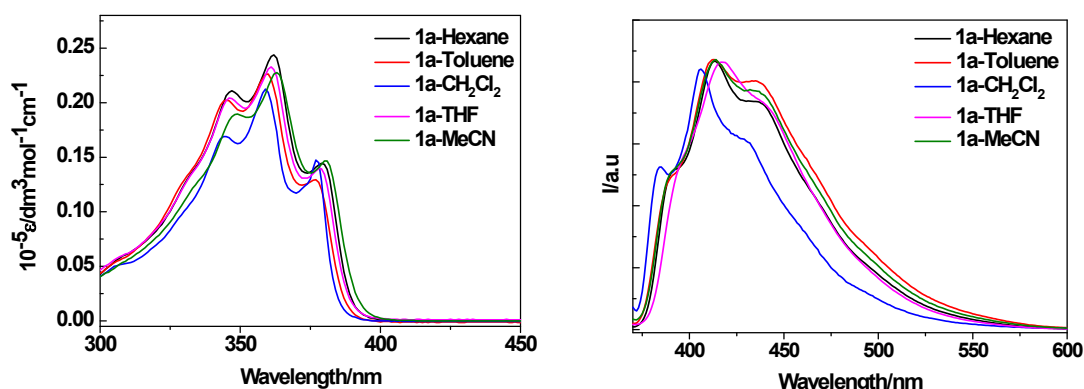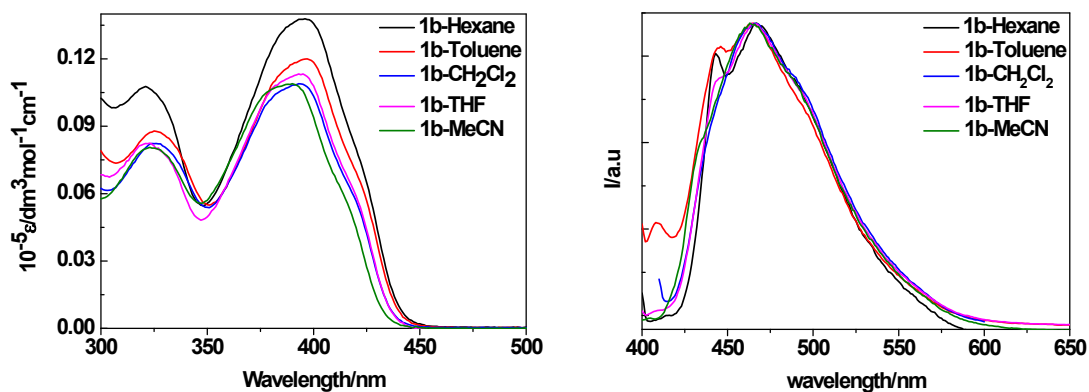

Fig. S2. Absorption and emission spectra of **1b** in a range of different solvents. λ_{ex} = 360 nm.
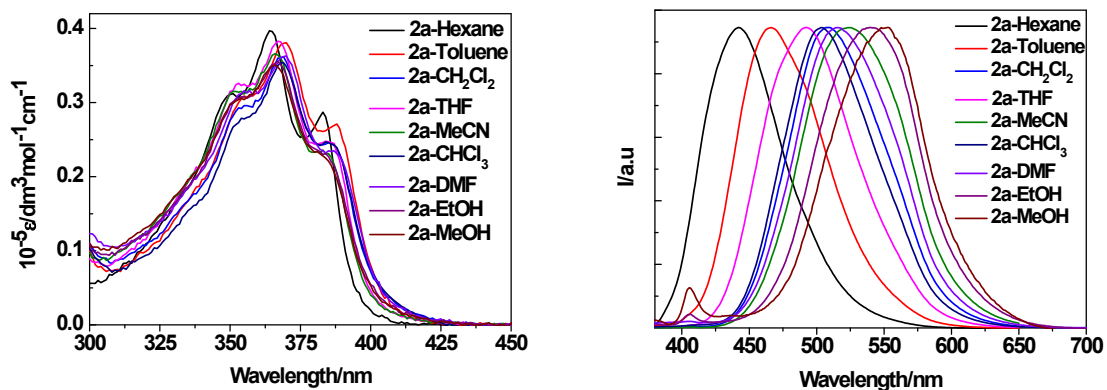
Fig. S3. Absorption and emission spectra of **2a** in a range of different solvents. λ_{ex} = 360 nm.
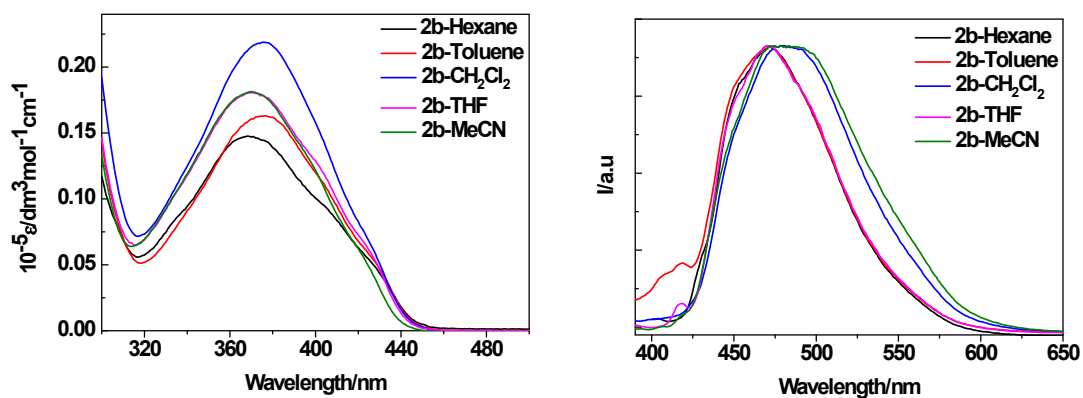

Fig. S4. Absorption and emission spectra of **2b** in a range of different solvents. λ_{ex} = 360 nm.

Table S1. Spectroscopic properties of **1a**, **1b**, **2a** and **2b** in various solvents at 298 K

	Solvent	λ_{abs}[a] [nm]	ε_{abs}[b] M^{-1} cm^{-1}	λ_{em} [nm]	$\Delta\upsilon_{em\text{-}abs}$[c] $[cm^{-1}]$	Φ_F	τ_f [ns]	k_r $[10^8 s^{-1}]$	k_{nr} $[10^8 s^{-1}]$
1a	hexane	359	21300	406	3224	0.05	<0.20	nd	nd
	Toluene	363	22800	417	3567	0.32	0.90	3.55	7.55
	CH$_2$Cl$_2$	361	24400	413	3488	0.33	1.01	3.27	6.63
	THF	361	23300	414	3546	0.18	0.64	2.81	12.8
	CH$_3$CN	360	22600	413	3565	0.15	0.58	2.59	14.65
1b	Hexane	396	12800	467	3839	0.002	0.13	0.15	76.77
	Toluene	397	12000	465	3684	0.01	0.25	0.40	39.60
	CH$_2$Cl$_2$	393	10900	466	3986	0.005	0.20	0.25	49.75
	THF	395	11300	464	3765	0.007	0.20	0.35	49.65
	MeCN	388	10800	463	4175	0.004	0.11	0.36	90.55
2a	Hexane	365,383(sh)	39600	442	3485	0.16	2.13	0.75	3.94
	Toluene	370,388(sh)	38100	466	4314	0.32	5.54	0.58	1.23
	CH$_2$Cl$_2$	368,386(sh)	36000	509	6260	0.30	17.0	0.17	0.41
	THF	367,385(sh)	38300	492	5949	0.40	11.31	0.35	0.53
	CHCl$_3$	368,385(sh)	35400	504	6133	0.30	15.04	0.20	0.47
	MeCN	366,383(sh)	36600	524	7026	0.17	15.97	0.11	0.52
	DMF	369,386(sh)	36400	516	6527	0.19	15.05	0.13	0.54
	EtOH	367,384(sh)	35500	538	7454	0.03	5.30	0.06	1.83
	MeOH	366,383(sh)	35000	549	7895	0.01	2.43	0.04	4.07
2b	Hexane	368	14700	472	5987	0.007	0.31	0.23	32.03
	Toluene	377	16400	470	5249	0.02	0.57	0.35	17.19
	CH$_2$Cl$_2$	376	21900	480	5762	0.015	0.80	0.19	12.31
	THF	371	18100	470	5678	0.013	0.41	0.32	24.07
	MeCN	370	18100	474	5930	0.013	0.79	0.16	12.49

[a] sh = shoulder. [b] The molar absorption coefficient was measured in solution containing 1% CH$_2$Cl$_2$ as a co-solvent. [c] DFT calculation predict that the shoulder around 385 nm in the absorption spectra of **2a** can be assigned to the S$_0$-S$_1$ transtion, therefore, Stokes shifts are calculated using these values.   In case of **1a**, **1b** and **2b**, λ_{abs} values are the most intense absorption wavelength.

Table S2. Calculated electronic excitation energies, oscillator strengths and the related wave functions for **1a**, **1b**, **2a** and **2b** in kind of solvents calculated with the polarisable continuum model (PCM) by using the B3LYP functional with 6-31G(d) basis sets

Solvents		State [a]	E [eV]	Exp λ [nm]	Cal λ [nm]	f [b]	Orbitals (coefficient) [c]
Hexane	**1a**	S_1	3.62	359	343	0.5747	H > L (91%)
	1b	S_2	3.05	396	406	0.0378	H-1 > L (87%)
		S_4	3.28		379	0.1357	H-3 > L (89%)
	2a	S_1	2.94	368	422	0.0992	H > L (98%)
		S_2	3.40		365	0.6416	H-1 > L (95%)
	2b	S_3	3.14	368	396	0.2071	H-2 > L (57%), H-1 > L (28%)
		S_5	3.26		381	0.3608	H-4 > L (92%)
Toluene	**1a**	S_1	3.60	363	345	0.6151	H > L (92%)
	1b	S_1	3.02	397	410	0.0366	H > L (92%)
		S_4	3.30		376	0.1427	H-3 > L (90%)
	2a	S_1	2.92	368	424	0.1047	H > L (98%)
		S_2	3.38		367	0.6835	H-1 > L (96%)
	2b	S_2	3.04	377	408	0.0316	H-1 > L (54%), H-2 > L (39%)
		S_3	3.14		394	0.2709	H-2 > L (53%), H-1 > L (34%)
DCM	**1a**	S_1	3.60	361	345	0.6376	H > L (94%)
	1b	S_1	3.11	393	399	0.0881	H > L (93%)
		S_3	3.37		367	0.1256	H-3 > L (56%), H-2 > L (38%)
	2a	S_1	2.89	368	429	0.0981	H > L (98%)
		S_2	3.36		370	0.6669	H-1 > L (97%)
	2b	S_2	3.12	376	397	0.1362	H-1 > L (54%), H-2 > L (39%)
		S_3	3.18		389	0.2909	H-2 > L (55%), H-1 > L (35%)
		S_4	3.32		373	0.2306	H-3 > L (94%)
THF	**1a**	S_1	3.60	361	344	0.6296	H > L (93%)
	1b	S_1	3.10	395	392	0.0806	H > L (92%)
		S_4	3.37		368	0.1299	H-3 > L (50%), H-2 > L (44%)
	2a	S_1	2.89	368	429	0.0973	H > L (98%)
		S_2	3.36		369	0.6601	H-1 > L (97%)
	2b	S_2	3.12	371	398	0.1121	H-1 > L (51%), H-2 > L (43%)
		S_3	3.18		390	0.2980	H-2 > L (51%), H-1 > L (38%)
		S_4	3.32		374	0.2381	H-3 > L (92%)
MeCN	**1a**	S_1	3.61	360	344	0.6272	H > L (94%)
	1b	S_1	3.14	388	396	0.1016	H > L (92%)
		S_3	3.40		364	0.1204	H-3 > L (20%), H-2 > L (74%)
	2a	S_1	2.88	366	430	0.0926	H > L (98%)
		S_2	3.35		370	0.6473	H-1 > L (97%)
	2b	S_2	3.15	370	394	0.2125	H-1 > L (62%), H-2 > L (30%)
		S_3	3.21		387	0.2343	H-2 > L (64%), H-1 > L (26%)
		S_4	3.35		370	0.2092	H-3 > L (95%)
CHCl$_3$	**2a**	S_1	2.90	368	428	0.1003	H > L (98%)
		S_2	3.36		369	0.6705	H-1 > L (97%)
DMF	**2a**	S_1	2.88	369	430	0.0962	H > L (98%)
		S_2	3.35		371	0.6710	H-1 > L (97%)
EtOH	**2a**	S_1	2.88	367	430	0.0937	H > L (98%)
		S_2	3.35		370	0.6517	H-1 > L (97%)
MeOH	**2a**	S_1	2.89	366	430	0.0918	H > L (98%)
		S_2	3.36		370	0.6418	H-1 > L (97%)

[a] Excited state. [b] Oscillator strength (<0.035 are not included). [c] MOs involved in the transitions with H and L denoting

the HOMO and LUMO, respectively.

Table S3. Calculated electronic excitation energies, oscillator strengths and the related wave functions for **1a**, **1b**, **2a** and **2b** in CH_2Cl_2 calculated with the polarisable continuum model (PCM) by using the B3LYP and CAM-B3LYP functionals with 6-31G(d) basis sets

Cal Functuonals		State [a]	E [eV]	Exp λ [nm]	Cal λ [nm]	f [b]	Orbitals (coefficient) [c]
CAM-B3LYP	**1a**	S_1	3.92	361	316	0.6959	H > L (89%)
	1b	S_1	3.59	393	345	0.3099	H > L (78%)
		S_3	4.20		296	0.2466	H-5 > L (53%) H-2 > L (29%)
	2a	S_1	3.72	368	333	0.3059	H > L (80%)
		S_2	3.84		323	0.8548	H-1 > L (70%)
	2b	S_1	3.52	376	352	0.2442	H-1 > L (65%)
		S_2	3.76		330	0.5870	H > L (65%)
B3LYP	**1a**	S_1	3.60	361	345	0.6376	H > L (94%)
	1b	S_1	3.11	393	399	0.0881	H > L (93%)
		S_3	3.37		367	0.1256	H-3 > L (56%), H-2 > L (38%)
	2a	S_1	2.89	368	429	0.0981	H > L (98%)
		S_2	3.36		370	0.6669	H-1 > L (97%)
	2b	S_2	3.12	376	397	0.1362	H-1 > L (54%), H-2 > L (39%)
		S_3	3.18		389	0.2909	H-2 > L (55%), H-1 > L (35%)
		S_4	3.32		373	0.2306	H-3 > L (94%)

[a] Excited state. [b] Oscillator strength (<0.035 are not included). [c] MOs involved in the transitions with H and L denoting the HOMO and LUMO, respectively.
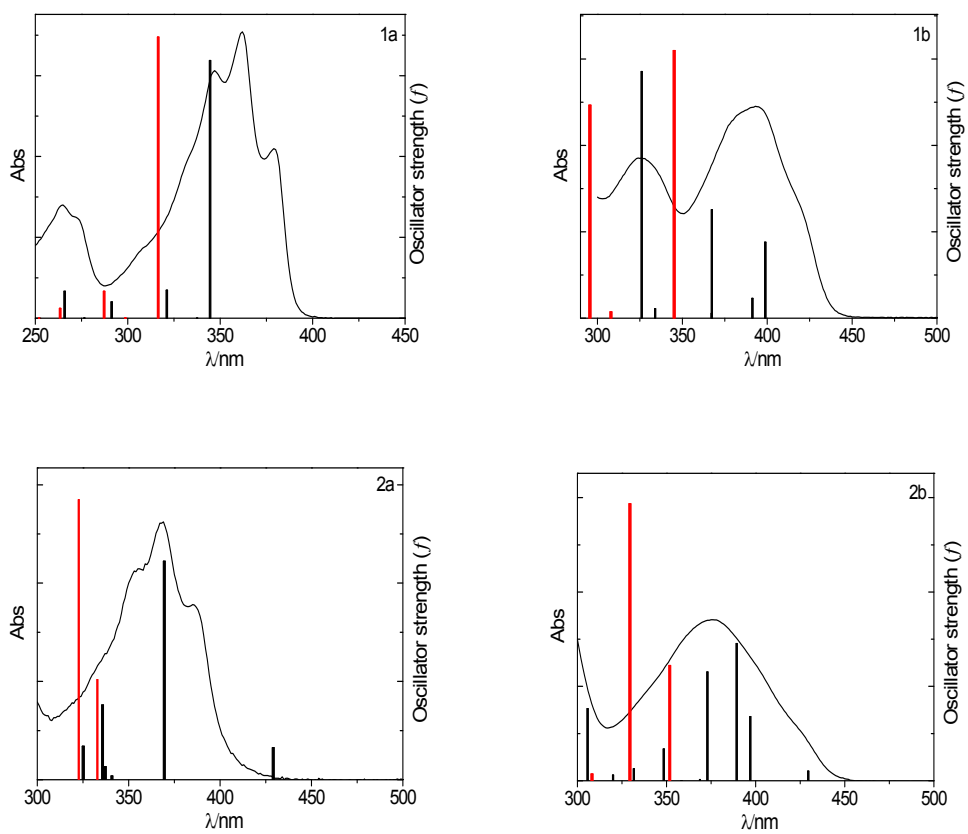
Fig. S5. Observed spectra in CH_2Cl_2 (black line) and calculated TD-DFT oscillator strength in CH_2Cl_2 based on geometry optimizations using the B3LYP functional (black bar) and CAM-B3LYP functional (red bar) with 6-31G(d) basis sets.

II ^{1}H NMR