Electronic Supplementary Material (ESI) for New Journal of Chemistry. This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2020

## Artificial Light–harvesting Systems (LHSs) Based on Boron-difluoride (BF<sub>2</sub>) Hydrazone Complexes (BODIHYs)

Vishwa Deepak Singh, Bhupendra Kumar Dwivedi, Yogesh Kumar and Daya Shankar Pandey\*

Department of Chemistry, Institute of Science, Banaras Hindu University, Varanasi – 221 005 (U. P.) India

Contents:	Page
1. <sup>1</sup> H and <sup>13</sup> C NMR spectra of L1	<b>S</b> 3
2. <sup>1</sup> H and <sup>13</sup> C NMR spectra of L2	S4
3. $^{1}$ H, $^{13}$ C, $^{11}$ B and $^{19}$ F NMR spectra of <b>B1</b>	S5-S6
4. <sup>1</sup> H, <sup>13</sup> C, <sup>11</sup> B and <sup>19</sup> F NMR spectra of <b>B1</b>	<b>S7-S8</b>
5. ESI-MS of Ligands and complexes	<b>S9</b>
6. Absorption and Emission of Ligands	S10
7. Emission spectra of L1–L2 in solvents of varying polarities	<b>S10</b>
8. Emission spectra of <b>B1–B2</b> in solvents of varying polarities	<b>S10</b>
9. Absorption spectra of L1–L2 in THF/water	<b>S11</b>
10. Emission spectra of L1–L2 in THF/water	<b>S</b> 11
11. Absorption spectra of <b>B1–B2</b> in THF/water	S11
12. SEM images of aggregates	S12
13. Absorption spectra of <b>B1–B2</b> in CH <sub>3</sub> OH/glycerol	S12
14. Plot of average fluorescence lifetimes and fluorescence contrast $(I/I_0)$ vs. v	viscosity S13
15. Plot between radiative $(k_r)$ and non-radiative $(k_{nr})$ rate constants vs. viscos	sity <b>S13</b>
16. Fluorescence spectra of <b>B1</b> with RhB	S14
17. UV-vis spectra of <b>B1</b> and <b>B2</b> obtained from TD-DFT calculations	<b>S14</b>
18. Table	S15



Fig. S1.  $^{1}$ H (a) and  $^{13}$ C (b) NMR spectra of L1.



Fig. S2.  $^{1}$ H (a) and  $^{13}$ C (b) NMR spectra of L2.



Fig. S3.  $^{1}$ H (a) and  $^{13}$ C (b) NMR spectra of B1.



Fig. S4.  $^{11}B$  (c) and  $^{19}F$  (d) NMR spectra of B1.



**Fig. S5.**  $^{1}$ H (a) and  $^{13}$ C (b) NMR spectra of **B2**.



Fig. S6.  $^{11}B$  (c) and  $^{19}F$  (d) NMR spectra of **B2**.







Fig. S7. Mass spectra of L1 (a), L2 (b), B1 (c) and B2 (d).



Fig. S8. Normalized UV–Visible (a) and normalized emission (b) spectra of L1 and L2 (c, 50  $\mu$ M).



Fig. S9. Emission spectra of L1 (a) and L2 (b) in various solvent polarities (c,  $50 \mu$ M).



Fig. S10. Emission spectra of B1 (a) and B2 (b) in various solvent polarities (c,  $50 \mu$ M).



Fig. S11. Absorption spectra of L1 (a) and L2 (b) in THF/water fraction (c,  $50 \mu$ M).



Fig. S12. Emission spectra of L1 (a) and L2 (b) in THF/water fraction (c,  $50 \ \mu M$ ).



Fig. S13. Absorption spectra of B1 (a) and B2 (b) in THF/water fraction (c,  $50 \mu$ M).



Fig. S14. SEM images of aggregates of B1 (a) and B2 (b) formed in mixture of THF/water (c,  $50 \mu$ M).



Fig. S15. Absorption spectra of B1 (a) and B2 (b) in CH<sub>3</sub>OH/glycerol fraction (c,  $50 \mu$ M).



Fig. S16. (a) Average fluorescence lifetimes of B1 and B2 as function of viscosity; (b) Fluorescence contrast  $(I/I_0)$  of B1 and B2 as function of viscosity.



Fig. S17. Plot between radiative  $(k_r)$  and non-radiative  $(k_{nr})$  rate constants vs. viscosity for B1 (a) and B2 (b).



Fig. S18. UV–Vis spectra of B1 (a) and B2 (b) obtained from TD-DFT calculations.



Fig. S19. (a) Fluorescence spectra of B1 with gradual addition of RhB ( $\lambda_{ex} = 540$  nm) in THF/water ( $f_w$  70%) ([B1] = 50 µM and [RhB] = 0.0, 0.2 × 10<sup>-6</sup>, 0.4 × 10<sup>-6</sup>, 0.6 × 10<sup>-6</sup>, 0.8 × 10<sup>-6</sup>, 1.0 × 10<sup>-6</sup>, 1.2 × 10<sup>-6</sup>, 1.4 × 10<sup>-6</sup>, 1.6 × 10<sup>-6</sup>, 1.8 × 10<sup>-6</sup>, 2.0 × 10<sup>-6</sup> M); (b) emission spectra of B1 (50 µM), RhB+B1 ([B1] = 50 µM, [RhB] = 1 µM) and RhB (0.25 µM); (c) and (d) Change in the fluorescence decay profiles of B1 in the presence of RhB in THF/water (70%; v/v).

	Experimental	Calculated	Oscillator	Energy	%	Assignments
	Wavelength	Wavelength	Strength	(eV)	Contribution	
	(nm)	(nm)	(f)			
<b>B1</b>	436	387	1.455	3.20	16	$HOMO-1 \rightarrow LUMO$
					72	$HOMO \rightarrow LUMO$
		255	0.381	4.86	36	$HOMO-1 \rightarrow LUMO$
					32	$HOMO \rightarrow LUMO+1$
<b>B2</b>	440	393	1.520	3.15	75	$HOMO \rightarrow LUMO$
					7	HOMO-1 $\rightarrow$ LUMO
		262	0.380	4.73	42	$HOMO \rightarrow LUMO+1$
					18	$HOMO-2 \rightarrow LUMO$

Table S1. Experimental/theoretical absorption wavelength, energy, oscillation strength (f) and assignments