One- and two-photon absorption spectra of organoboron complexes: Vibronic and environmental effects

SUPPORTING INFORMATION

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Table S1: Vibrational reorganization energies of the studied compounds in chloroform. Unsigned relative errors were calculated with respect to the EOM-CCSD reference values.

	vibrational reorganization energies, cm^{-1}				unsigned relative error, %				MAPE, %
	1	**2**	**3**	**4**	**1**	**2**	**3**	**4**	
B3LYP	1788.45	1367.46	1756.52	2199.26	30.43	26.30	11.90	43.90	28.13
BH&HLYP	2256.67	1743.56	2383.81	2574.51	12.22	6.03	19.55	34.33	18.03
BLYP	2904.51	1456.64	1432.15	2015.88	12.97	21.49	28.17	48.58	27.80
CAM-B3LYP	2132.44	1579.18	2113.33	2384.41	17.05	14.89	5.99	39.18	19.28
LC-BLYP	2592.81	2201.66	2674.41	2707.15	0.85	18.65	34.13	30.95	21.14
M06-2X	2407.94	1673.00	2218.73	2473.94	6.33	9.83	11.28	36.89	16.08
M06-HF	3170.19	2486.97	2975.31	2891.81	23.31	34.03	49.22	26.24	33.20
MN15	2142.16	1463.06	2013.57	2390.40	16.67	21.15	0.99	39.03	19.46
PBE0	1894.97	1356.41	1811.61	2243.19	26.29	26.89	9.13	42.78	26.27
ωB97X	2299.44	1818.14	2294.04	2483.09	10.55	2.01	15.05	36.66	16.07
ωB97X-D	2066.11	1540.42	2033.87	2334.40	19.63	16.98	2.00	40.45	19.77
EOM-CCSD	2570.87	1855.50	1993.82	3920.63					

Table S2: Photophysical properties calculated at the IEF-PCM(CHCl$_3$)/LC-BLYP/cc-pVDZ level of theory using the vertical approximation. Absorption wavelength λ_{abs}, excitation energy E_{abs}, and oscillator strength f are listed. Values given in brackets correspond to experimental measurements.

	$S_0 \rightarrow S_1$		
	λ_{abs}, nm	E_{abs}, cm^{-1}	f
1	262 (307)	38170 (32570)	0.39
2	283 (339)	35340 (29500)	0.54
3	284 (343)	35210 (29150)	0.37
4	301 (368)	33220 (27170)	0.21

	$S_0 \rightarrow S_2$		
	λ_{abs}, nm	E_{abs}, cm^{-1}	f
F-1	224	44640	<0.01
F-2	248	40320	0.06
F-3	241	41490	0.18
F-4	260	38460	0.49

Table S3: Linear regression equations and the corresponding determination coefficient, R^2, obtained with the machine learning approach (Fig. 6).

	equation	R^2
1	$y = 1.002x - 69.0$	0.94
2	$y = 0.918x + 2623.9$	0.79
3	$y = 0.858x + 4539.1$	0.86
4	$y = 1.018x - 521.6$	0.97

- Molecule **1**: (Z)-[1-(Difluoroboryloxy)ethylidene]-2-pyridylamine, ^{1}H NMR (700MHz, CDCl$_3$) δ: 8.30 (m, 1H), 8.07 (ddd, 1H, J=8.4, 7.4, 1.8 Hz, 1H), 7.39 (ddd, 1H, J=7.4, 6.0, 1.3), 7.36 (d, 1H, J=8.4), 2.33 (s, 3H). ^{13}C NMR (CDCl$_3$) δ:171.6, 153.9, 144.0, 138.5, 122.7, 120.8, 23.6, ^{11}B NMR (CDCl$_3$) δ: 0.41 (t, J=13.7 Hz), ^{15}N NMR (CDCl$_3$) δ: -175.4, -169.4. Mp.=137.7-139.0 $^\circ$C.

- Molecule **2**: (Z)-[1-(Difluoroboryloxy)ethylidene]-2-quinolylamine, ^{1}H NMR (700MHz, CDCl$_3$) δ: 8.58 (dtt, 1H, J=8.8, 2.9, 0.8), 8.38 (dd, 1H, J=8.8, 0.4), 7.84 (m, 2H), 7.62 (ddd, 1H, J=8.1, 7.1, 0.9), 7.34 (d, 1H, J=8.8 Hz), 2.41 (s, 3H). ^{13}C NMR (CDCl$_3$) δ: 173.4, 155.2, 144.5, 137.9, 137.9, 132.8, 128.6, 127.4, 126.6, 123.0, 120.9, 23.5. ^{11}B NMR δ: 1.16 (t, J=16.2 Hz). ^{15}N NMR δ: -173.0. Mp = 208-209.5 $^\circ$C.

- Molecule **3**: (Z)-[1-(Difluoroboryloxy)ethylidene]-1-isoquinolylamine, ^{1}H NMR (700MHz, CDCl$_3$) δ: 8.94 (ddt, 1H, J=8.4, 1.4, 0.8 Hz), 8.03 (dd, 1H, J=6.7, 2.4 Hz), 7.93 (ddd, 1H, J=8.2, 6.9, 1.3 Hz), 7.86 (dt, 1H, J=8.1Hz, 0.8 Hz), 7.77 (ddd, 1H, J=8.3, 6.9, 1.3Hz), 7.62 (dd, 1H, J=6.8, 0.8 Hz), 2.47 (s, 3H). ^{13}C NMR (CDCl$_3$) δ: 173.4, 154.3, 138.2, 134.5, 129.5, 129.1, 128.1, 126.5, 124.1, 119.1, 24.2. ^{13}B NMR δ: 0.72 (J=14.2 Hz). ^{15}N NMR (CDCl$_3$) δ: -191.1, -175.5. Mp.= 194-194 $^\circ$C.

- Molecule **4**: (Z)-[1-(Difluoroboryloxy)ethylidene]-3-isoquinolylamine, ^{1}H NMR (700MHz, CDCl$_3$) δ: 9.17 (s, 1H), 8.10 (dd, 1H, J=8.4 Hz, 0.8 Hz),7.93 (dd, 1H, J=8.5, 0.5 Hz), 7.88 (ddd, 1H, J=8.5, 6.7 Hz, 1.2 Hz), 7.75 (s, 1H), 7.68 (ddd, 1H, J=8.4, 6.7, 1.2 Hz), 2.36 (s, 3H), ^{13}C NMR (CDCl$_3$) δ: 168.1, 146.5, 143.7, 140.7, 134.9, 129.3, 128.5, 126.9, 125.7, 117.4, 23.5. ^{11}B NMR δ: 0.65 (t, J=14.1 Hz). ^{15}N NMR δ: -179.1, -173.0. Mp.= 185.5 - 187 $^\circ$C.
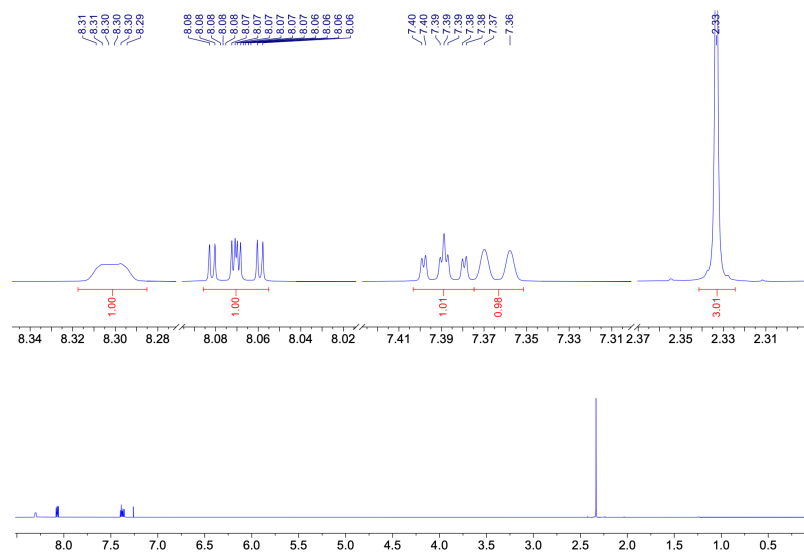
Figure S1: ^{1}H NMR spectrum for compound **1**.

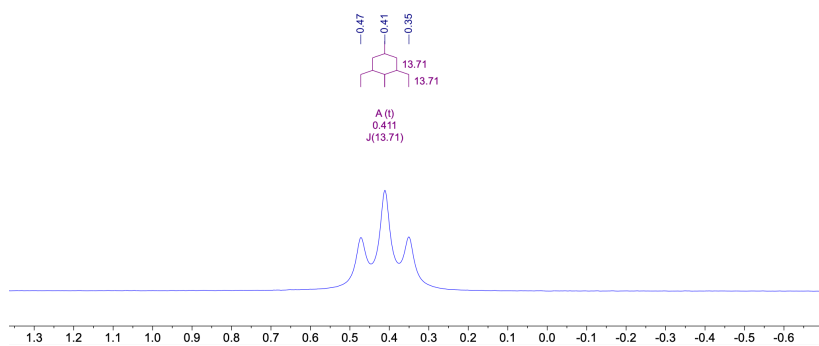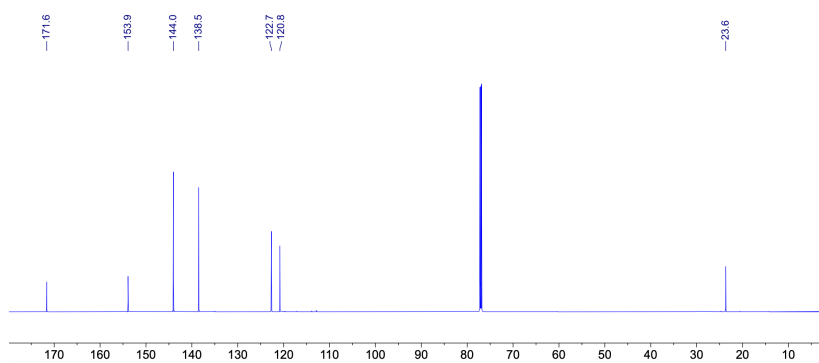Figure S2: ^{11}B NMR spectrum for compound **1**.

Figure S3: ^{13}C NMR spectrum for compound **1**.

Figure S4: ^{1}H, ^{15}N HMBC NMR spectrum for compound **1**.

Figure S5: ^{1}H NMR spectrum for compound **2**.

Figure S6: ^{11}B NMR spectrum for compound **2**.

Figure S7: ^{13}C NMR spectrum for compound **2**.

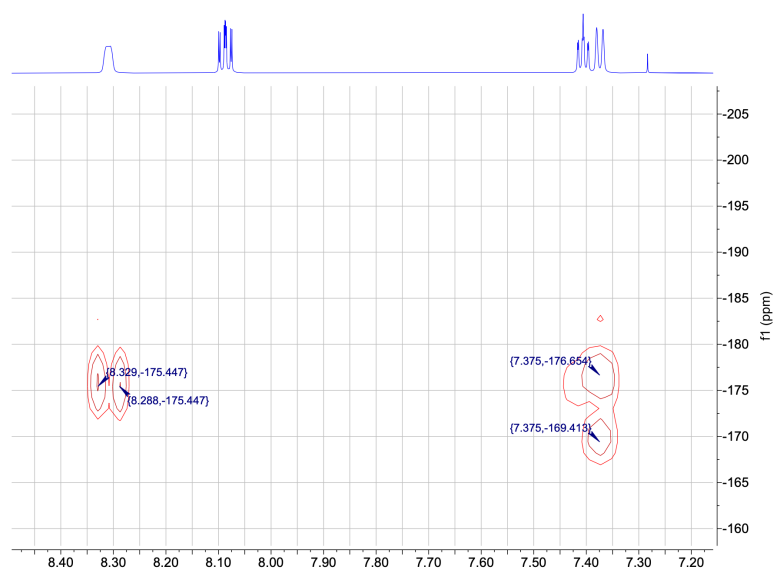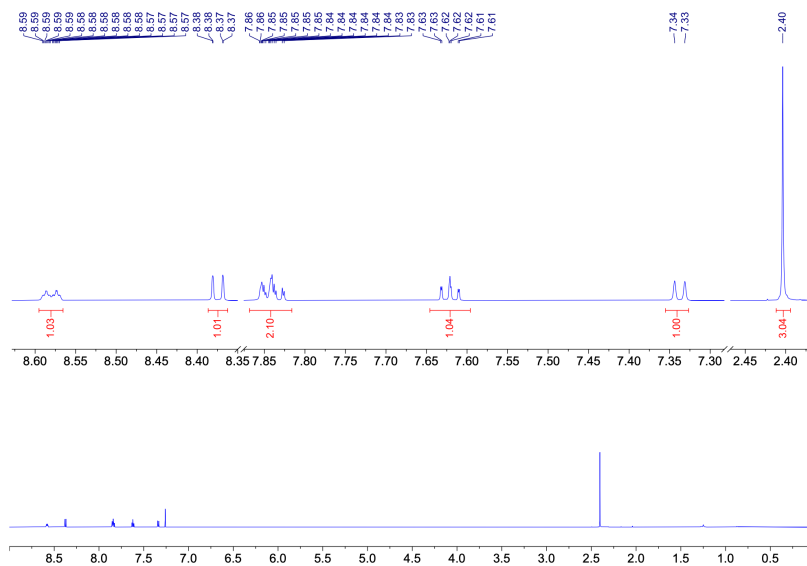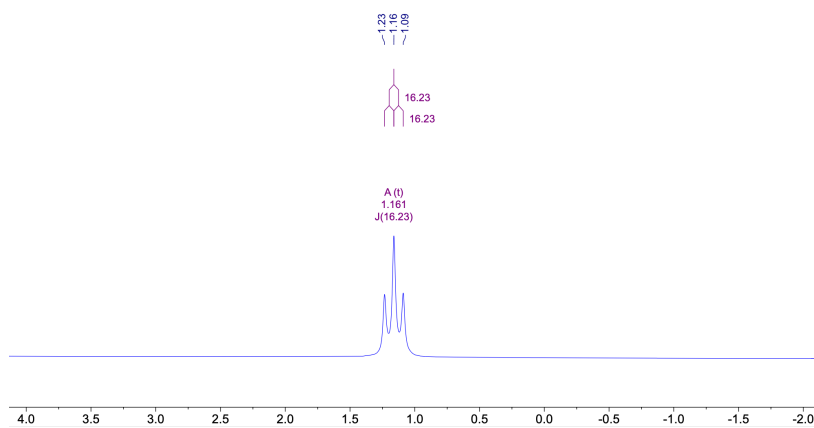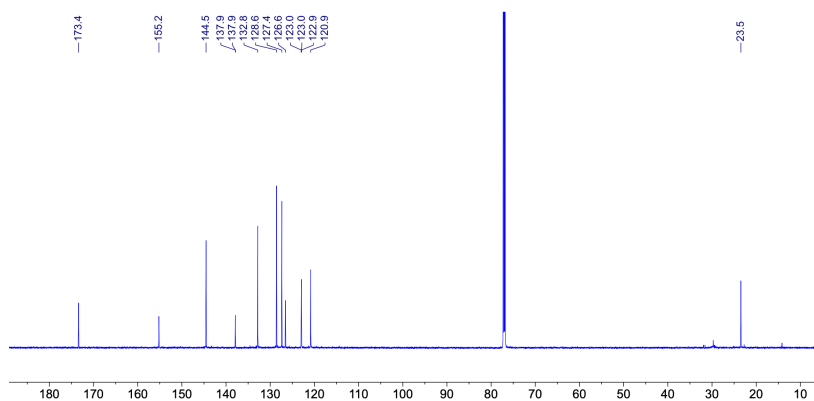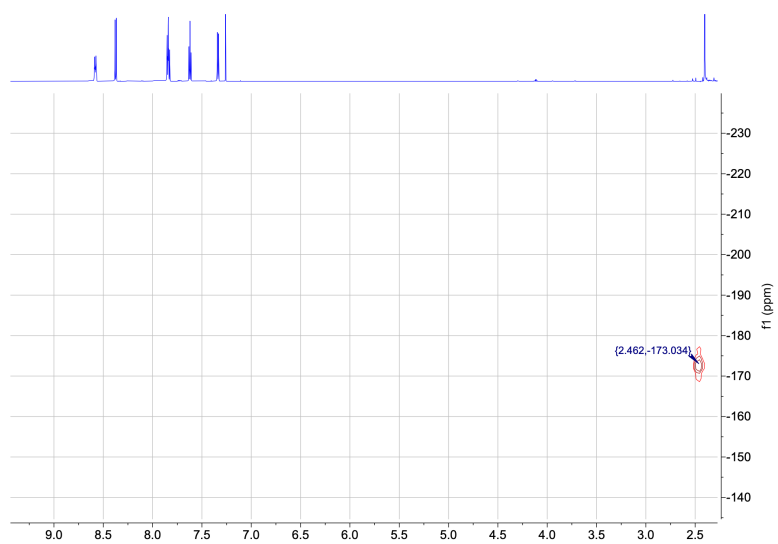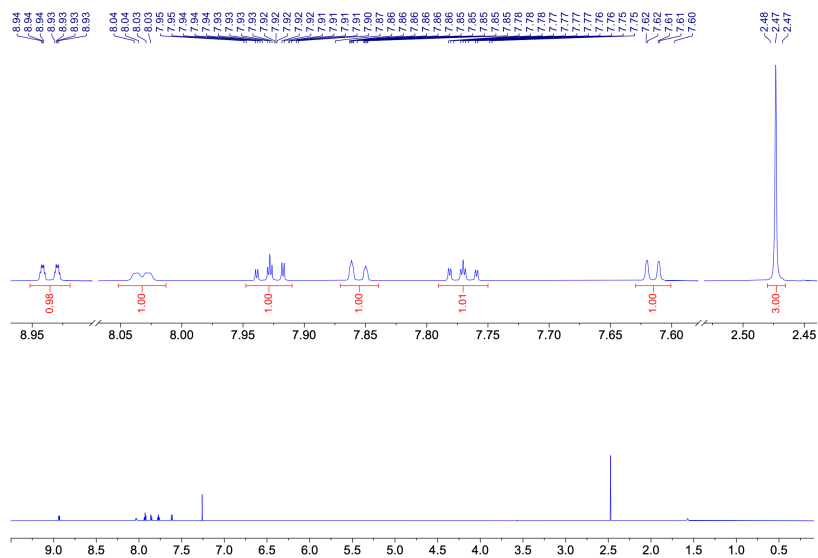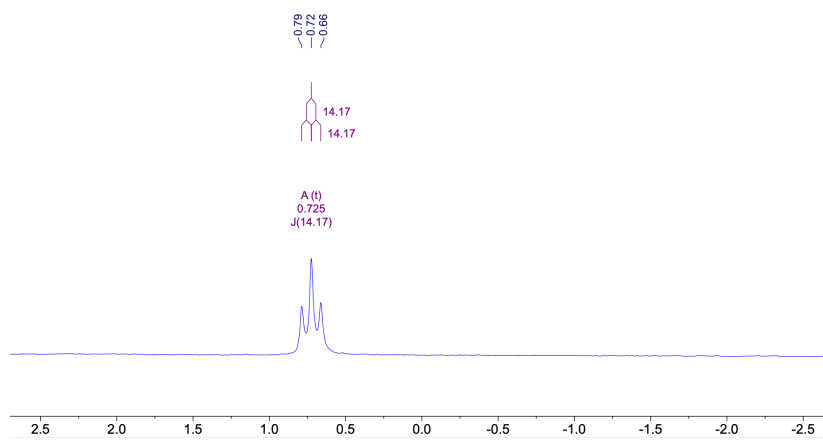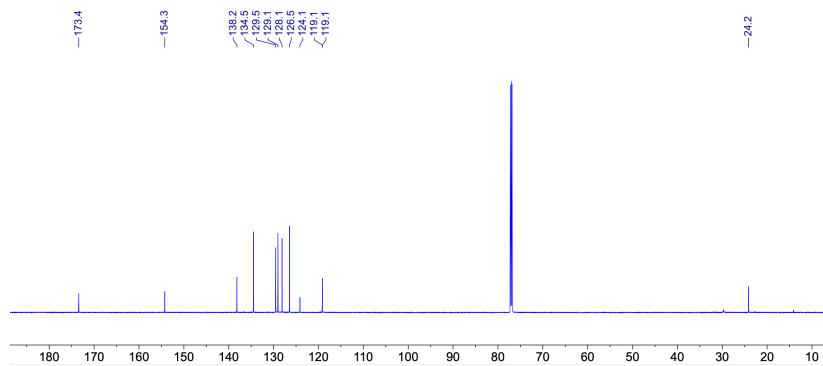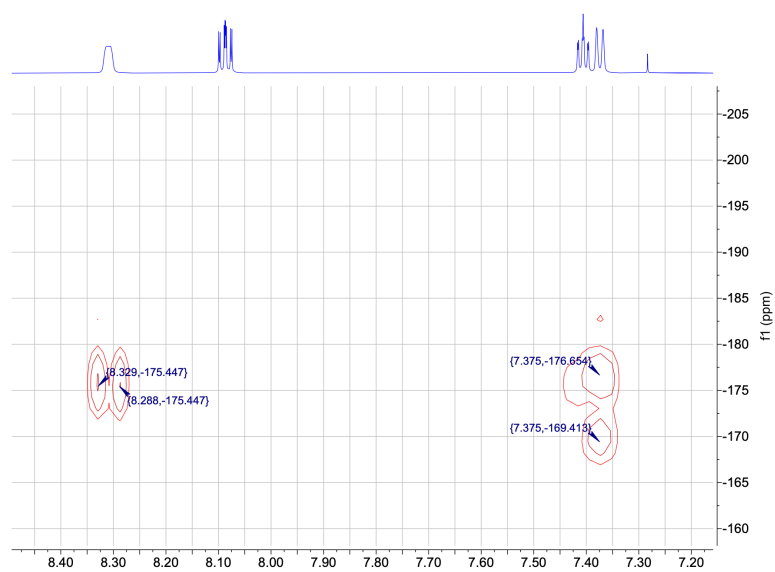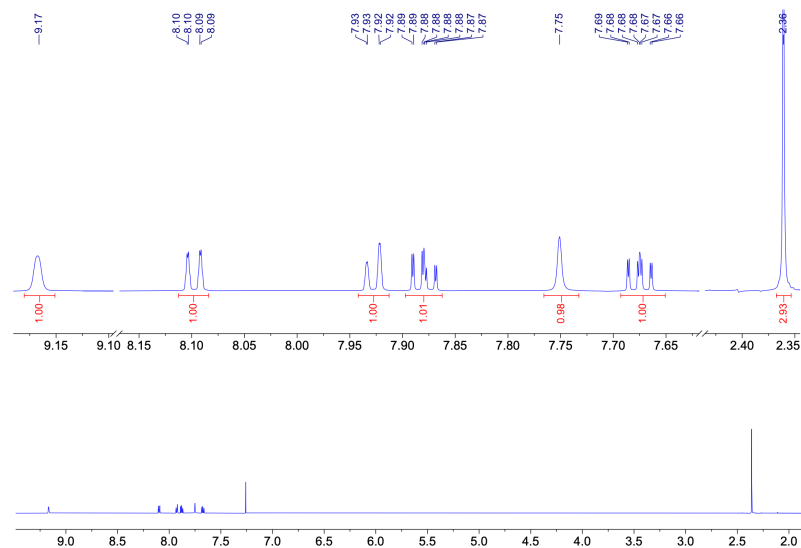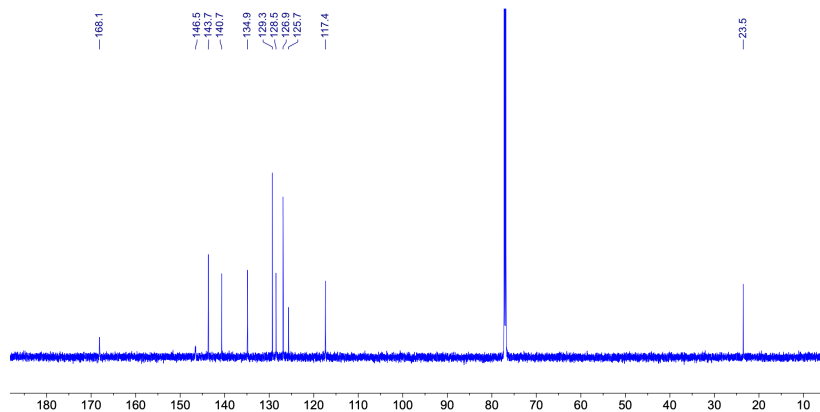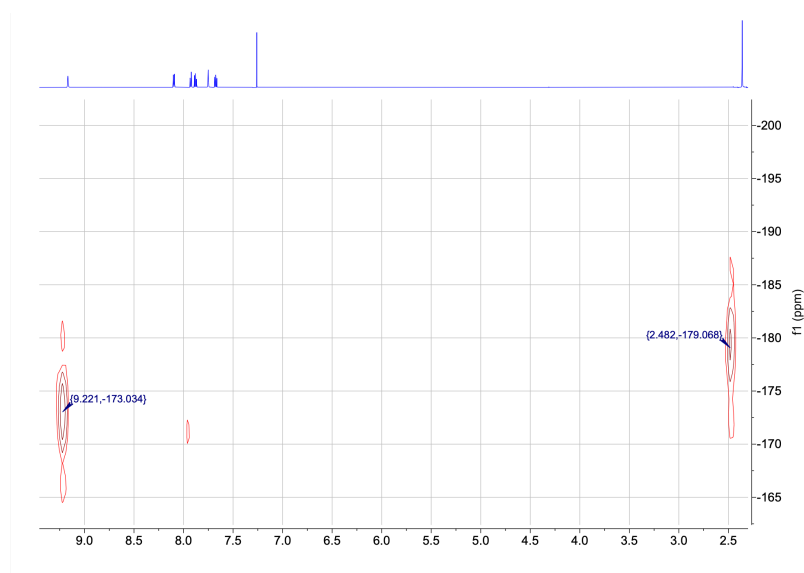Figure S8: ^{1}H, ^{15}N HMBC NMR spectrum for compound **2**.

Figure S9: ^{1}H NMR spectrum for compound **3**.

Figure S10: ^{11}B NMR spectrum for compound **3**.

Figure S11: ^{13}C NMR spectrum for compound **3**.

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Figure S12: ^{1}H, ^{15}N HMBC NMR spectrum for compound **3**.

Figure S13: ^{1}H NMR spectrum for compound **4**.
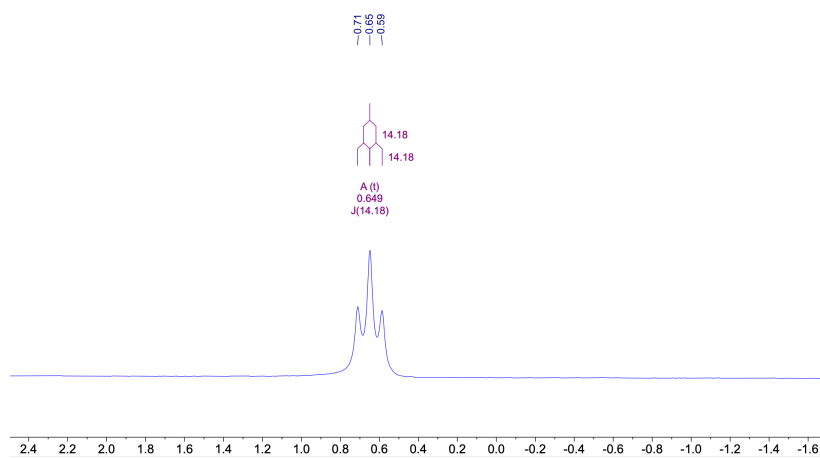
Figure S14: ^{11}B NMR spectrum for compound **4**.

Figure S15: ^{13}C NMR spectrum for compound **4**.

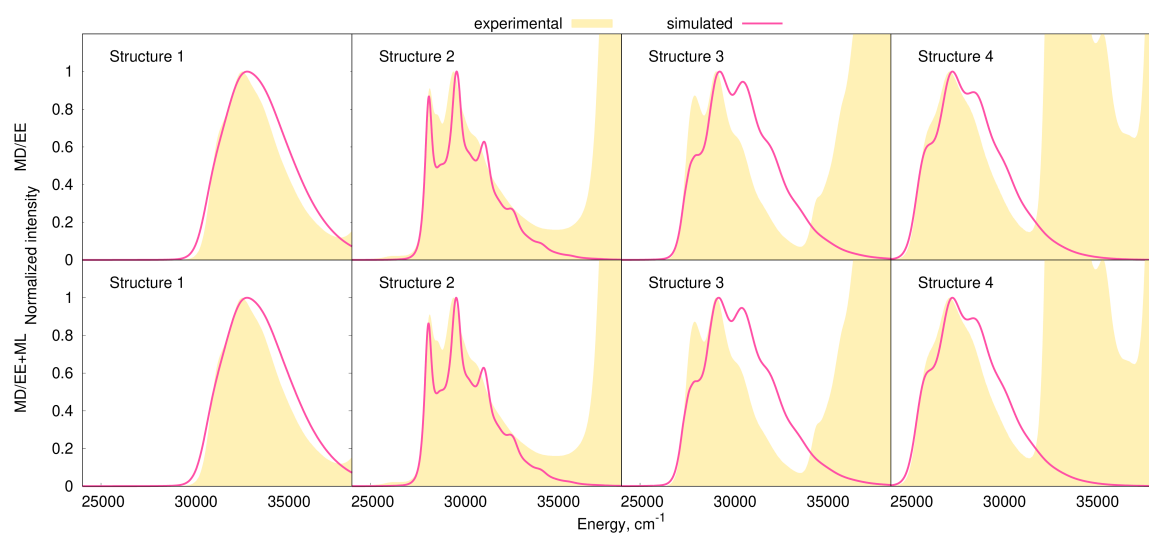Figure S16: ^{1}H, ^{15}N HMBC NMR spectrum for compound **4**.

Figure S17: Vibronic absorption spectra of the investigated dyes in chloroform, at 298 K, computed using FC theory in the TD formalism combined with the AH vibrational space, and convoluted with an inhomogeneous broadening computed by EE (first row) and ML (second row) approaches.
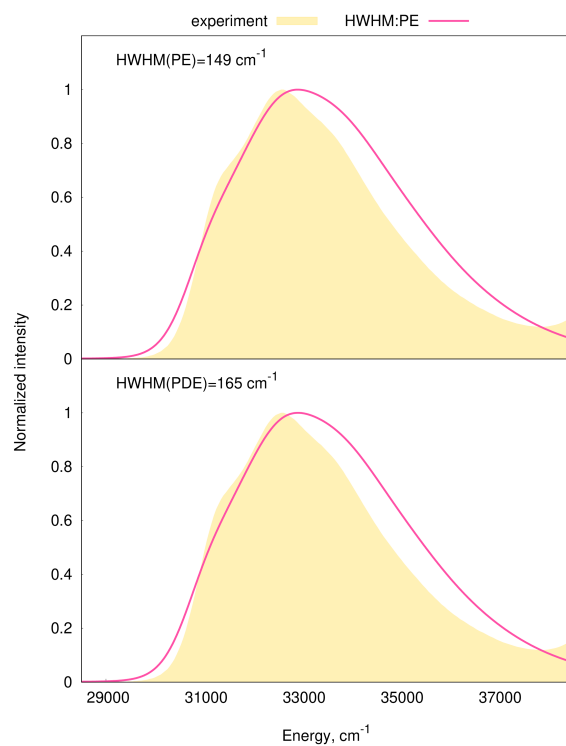
Figure S18: Comparison between the spectra simulated with PE and PDE&PE inhomogeneous broadenings for compound **1**. LC-BLYP electronic structure calculations in chloroform (IEF-PCM), AH vibrational space, TD formalism, 298 K.
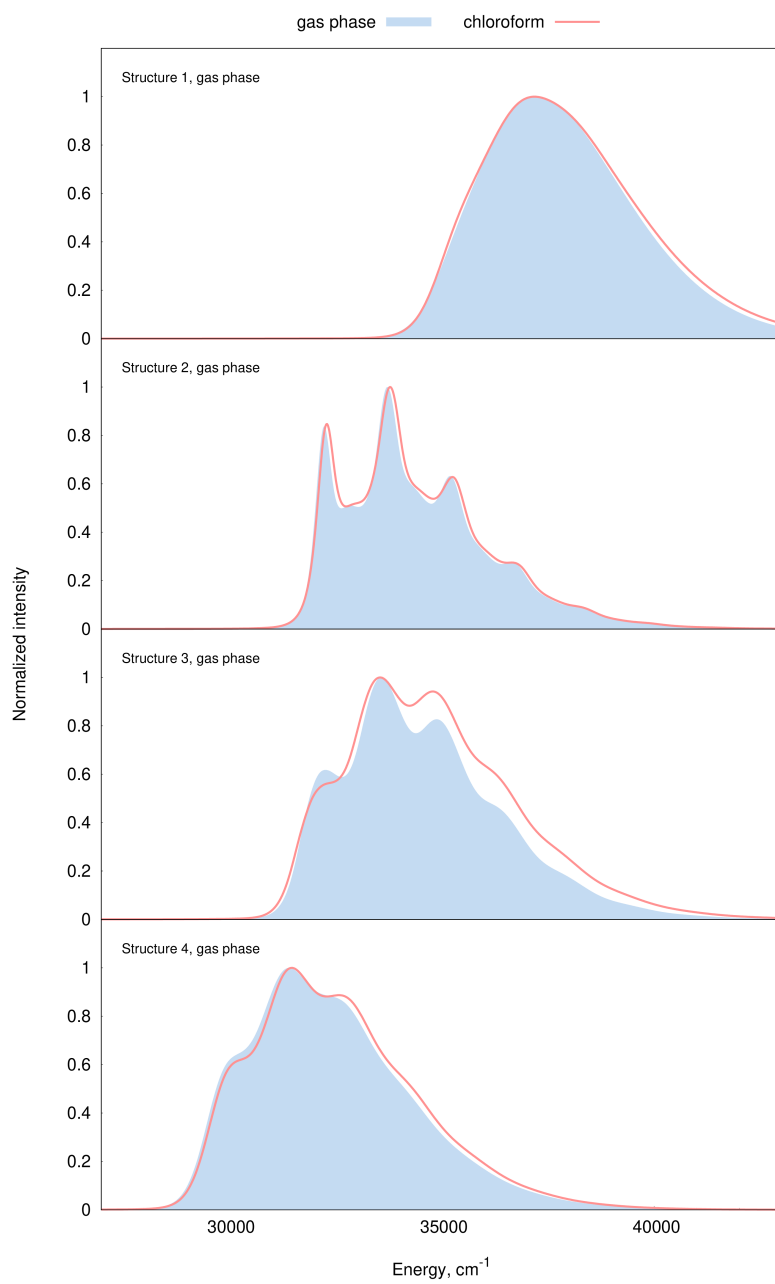
Figure S19: Comparison between the vibronic spectra in gas phase and chloroform (IEF-PCM) at 298 K. LC-BLYP electronic structure calculations, AH model using internal coordinates, HWHM was estimated using the PE model (see text for details).
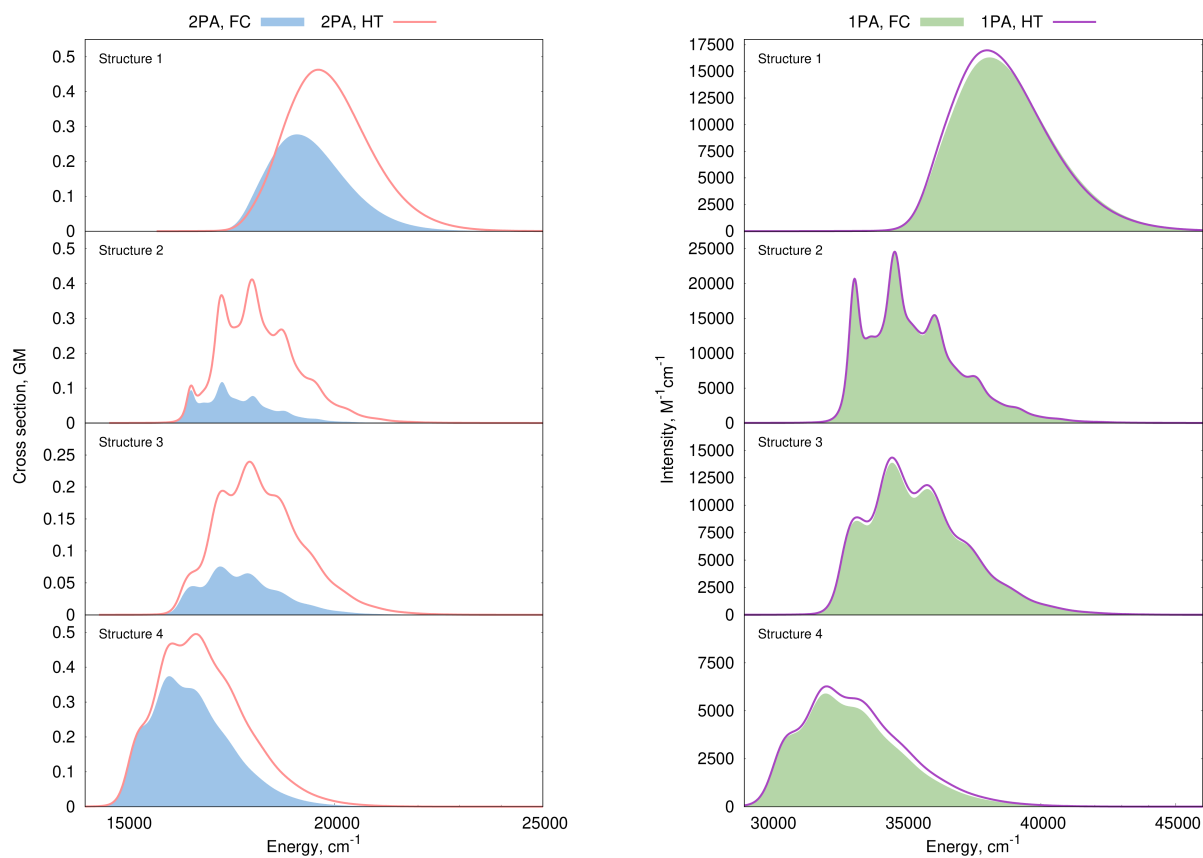
Figure S20: Comparison between FC and FC/HT models in simulating the vibrationally-resolved 1PA and 2PA $S_0 \rightarrow S_1$ transitions based on LC-BLYP electronic structure calculations. The vibronic simulations use the AH PES model and rely on internal coordinates. Simulations were performed in the gas phase at 298 K using broadening estimated with the PE model. Spectra are shown in absolute values, not normalized
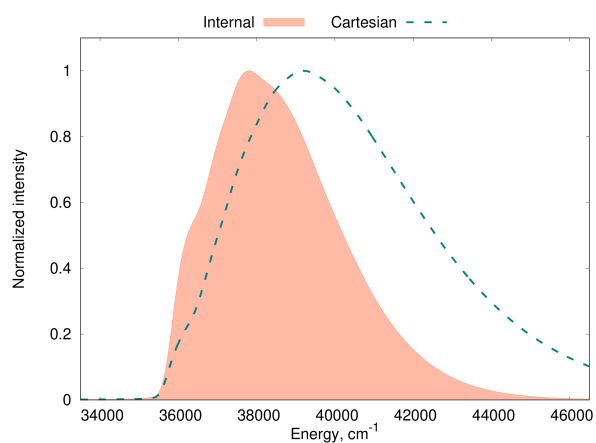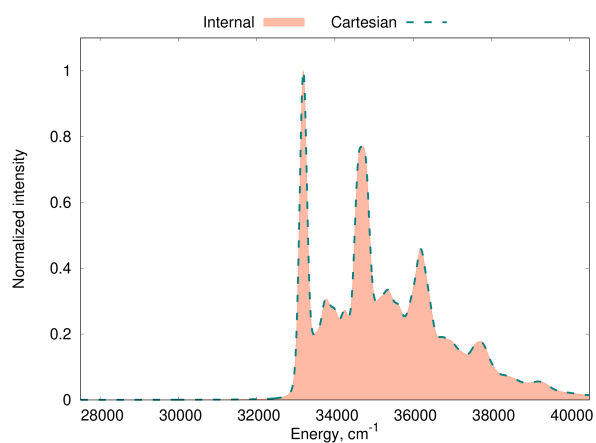
(a) Absorption spectra simulated using the AH vibrational space in the TD formalism, convoluted with Gaussian broadening (HWHM=100 cm^{-1}).
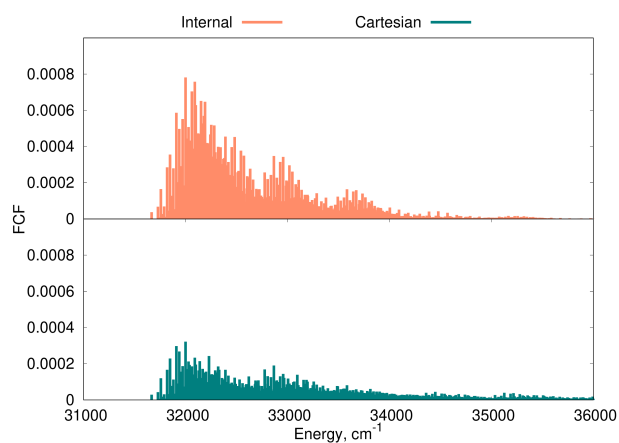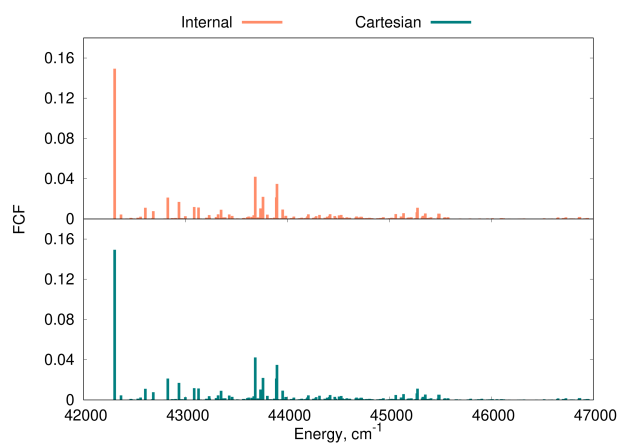
(b) Franck-Condon factor stick spectra simulated using the AH vibrational space in the TI formalism.

Figure S21: Comparison between Cartesian and internal coordinates for the computed vibronic structure for compound **1** in vacuum, 0 K.
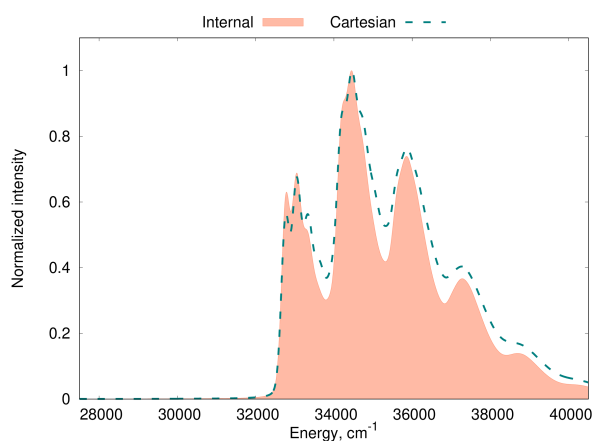

(a) Absorption spectra simulated using the AH vibrational space in the TD formalism, convoluted with Gaussian broadening (HWHM=100 cm^{-1}).
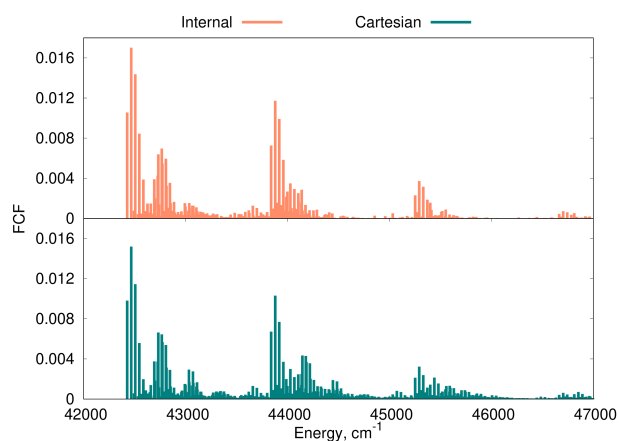
(b) Franck-Condon factor stick spectra simulated using the AH vibrational space in the TI formalism.

Figure S22: Comparison between Cartesian and internal coordinates for the computed vibronic structure for compound **2** in vacuum, 0 K.

(a) Absorption spectra simulated using the AH vibrational space in the TD formalism, convoluted with Gaussian broadening (HWHM=100 cm^{-1}).

(b) Franck-Condon factor stick spectra simulated using the AH vibrational space in the TI formalism.

Figure S23: Comparison between Cartesian and internal coordinates for the computed vibronic structure for compound **3** in vacuum, 0 K.
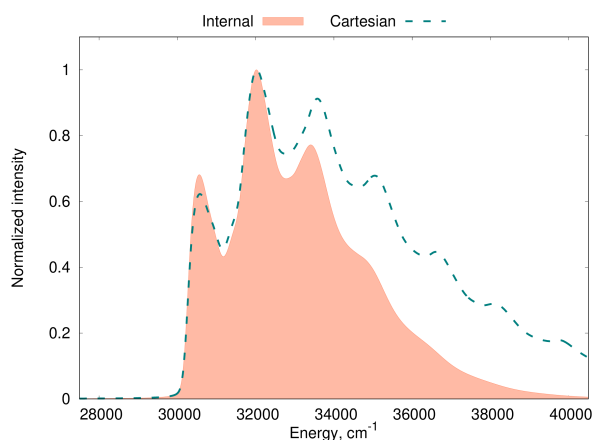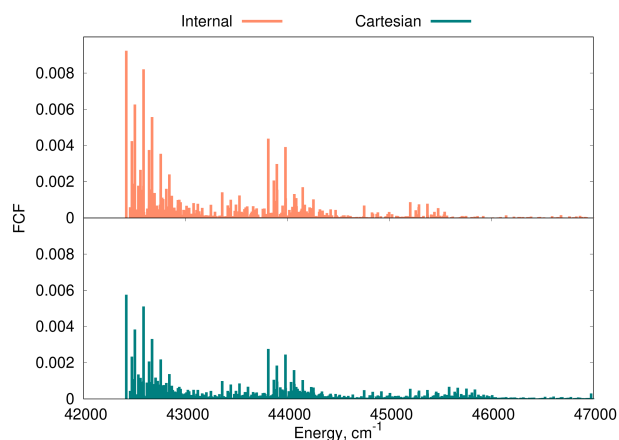

(a) Absorption spectra simulated using the AH vibrational space in the TD formalism, convoluted with Gaussian broadening (HWHM=100 cm^{-1}).

(b) Franck-Condon factor stick spectra simulated using the AH vibrational space in the TI formalism.

Figure S24: Comparison between Cartesian and internal coordinates for the computed vibronic structure for compound **4** in vacuum, 0 K.