

## Supplementary Information

### Experimental and computational characterisation of an artificial light harvesting complex

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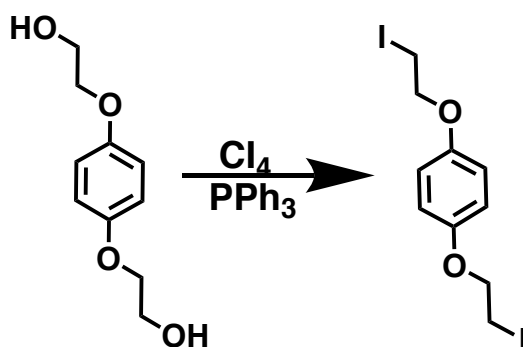
### Table of Contents

<b>S1.</b>	<b>Synthesis of materials</b> .....	<b>2</b>
S1.1.	The synthesis of 1,4-bis(2-iodoethoxy)benzene .....	2
S1.2.	The synthesis of ten iodides bearing pillar .....	3
S1.3.	The synthesis of pillar .....	4
S1.4.	The synthesis of 8-{4-(chloromethyl)phenyl}-2,6-diethyl-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene.....	5
S1.5.	The synthesis of 8-{4-(azidomethyl)phenyl}-2,6-diethyl-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene.....	6
S1.6.	The synthesis of 8-{4-(aminomethyl)phenyl}-2,6-diethyl-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (chromophore) .....	7
S1.7.	The synthesis of LHC .....	8
<b>S2.</b>	<b>Additional experimental data</b> .....	<b>9</b>
S2.1.	Infrared spectroscopy .....	9
S2.2.	UV-visible spectroscopy .....	22
S2.3.	Time-resolved photoluminescence spectroscopy .....	24
S2.4.	Transient absorption spectroscopy.....	26
S2.4.1.	Spectral evolution .....	26
S2.4.2.	Spectra of chromophore vs LHC.....	26
S2.5.	Broadband pump-probe spectroscopy .....	27
S2.5.1.	Pulse characterization .....	27
S2.5.2.	Chromophore .....	28
S2.5.3.	LHC.....	29
S2.5.4.	Acetone (solvent) .....	30
S2.6.	Harmonic frequencies of chromophore-T in 600 cm <sup>-1</sup> range .....	31
	<b>References</b> .....	<b>32</b>

## S1. Synthesis of materials

All  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra of the compounds were carried out on a Varian 400 instrument (standard Trimethylsilane) at 298 K in  $\text{CDCl}_3$ . The FT-IR spectra of the compounds were collected by a Bruker Fourier Transform Infrared (attenuated total reflection). The elemental analysis and the melting points were measured with Leco CHNS 932 and the Gallenkamp instruments, respectively. Target compounds were synthesized under an argon atmosphere, prepared with a known literature procedure.<sup>1</sup> In the synthesis of the chromophore, dichloromethane dried with  $\text{CaH}_2$  was performed. The completing processes of the reactions were tracked with Merck TLC plates (silica gel 60 on aluminum plate). Triethylamine, lithium bromide, carbon tetraiodide, boron trifluoride ethyl etherate, paraformaldehyde, triphenylphosphine, sodium azide, 4-hydroxybenzaldehyde, and other solvents-reagents were purchased from Sigma-Aldrich, Acros, TCI Chemicals, Merck, and used without further purification.

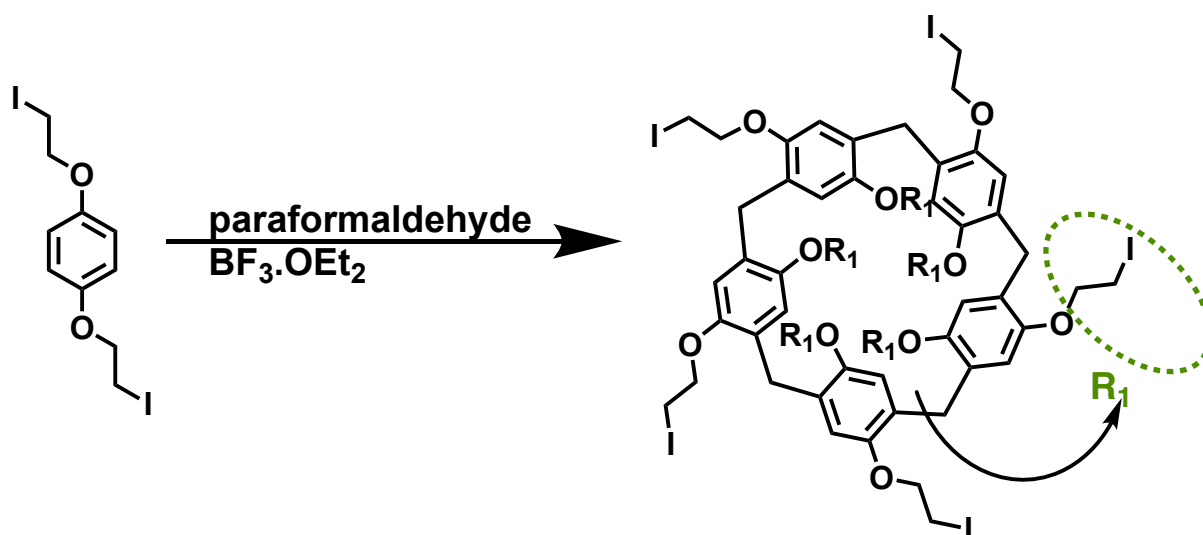
### S1.1. The synthesis of 1,4-bis(2-iodoethoxy)benzene



Carbon tetraiodide (12.24 g, 24 mmol) was slowly added in small portions to a solution of 1,4-bis(2-hydroxyethoxy)benzene (1) (2.38 g, 12 mmol) and triphenylphosphine (6.30 g, 12 mmol) in 100 mL of dry acetonitrile at 0 °C. Then, the reaction mixture was stirred at room temperature, and the resulting clear solution was stirred for another 3 h under Ar. 100 g of ice was added to the reaction mixture, where 1,4-bis(2-iodoethoxy)benzene slowly precipitated as a white solid. The product was collected by vacuum filtration, thoroughly washed with cold

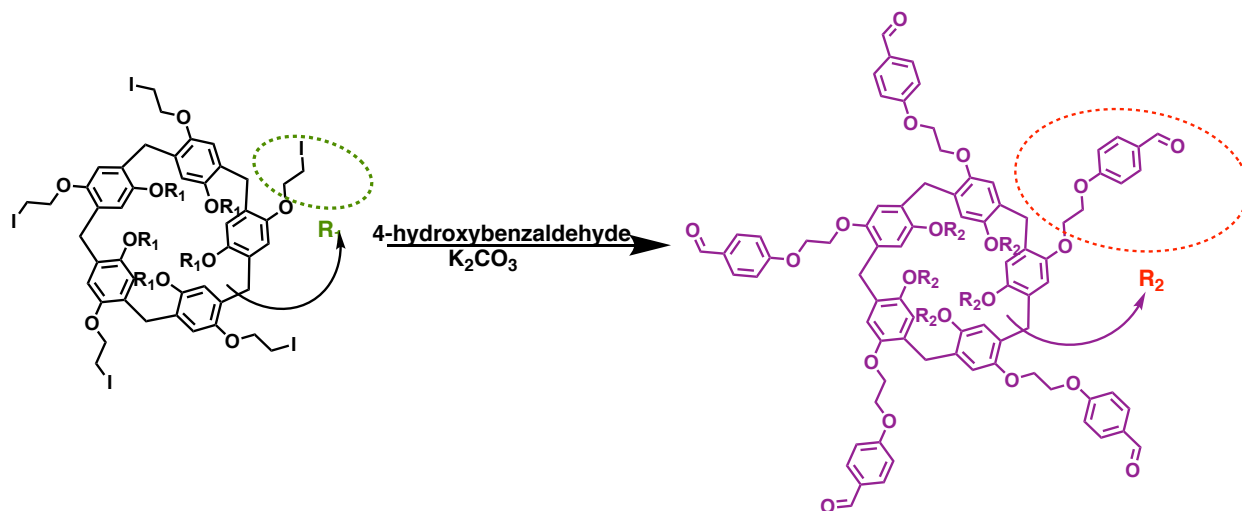
methanol/water, 60:40. The white flake-like crystals were dried in desiccator (4.37 g, 87%). M.P.: 92 °C. <sup>1</sup>H-NMR (400 MHz, chloroform-d, room temperature) δ (ppm): 6.92 (s, 4H), 4.33 (t, J = 5.2 Hz, 4H), 3.52 (t, J = 5.7 Hz, 4H). <sup>13</sup>C-NMR (100 MHz) δ (ppm): 150.38, 116.10, 75.18, 4.32.

### S1.2. The synthesis of ten iodides bearing pillar



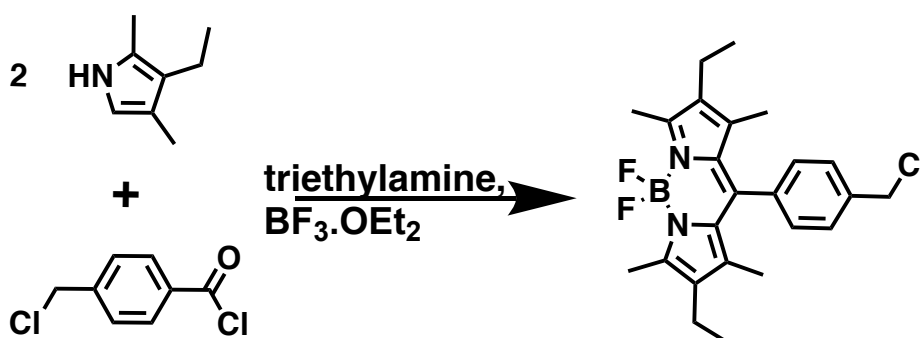
**Ten iodides bearing pillar** was prepared with a known literature procedure.<sup>1</sup>  $\text{BF}_3 \cdot \text{OEt}_2$  (0.8 g, 6.75 mmol) was added to a solution of 1,4-bis(2-iodoethoxy)benzene (2.82 g, 6.75 mmol) and paraformaldehyde (0.51 g, 18 mmol) in 1,2-dichloroethane (100 mL) at room temperature. The reaction mixture was stirred for 3 h under  $\text{N}_2$  atmosphere. Column chromatography ( $\text{SiO}_2$ ; petroleum ether/ $\text{CH}_2\text{Cl}_2$ , 1:1) gave **ten iodides bearing pillar** compound (0.99 g, 36%). M.P.: 275 °C <sup>1</sup>H-NMR (400 MHz, chloroform-d, room temperature) δ (ppm): 6.92 (s, 10H), 4.33 (t, J = 5.4 Hz, 20H), 3.85 (s, 10H), 3.52 (t, J = 5.4 Hz, 20H). <sup>13</sup>C-NMR (100 MHz) δ (ppm): 149.88, 125.87, 116.30, 67.38, 29.65, and 3.92. Elemental Analysis calcd.:  $\text{C}_{55}\text{H}_{60}\text{I}_{10}\text{O}_{10}$  : C, 30.72; H, 2.81; found: C, 30.55; H, 3.07.

### S1.3. The synthesis of pillar



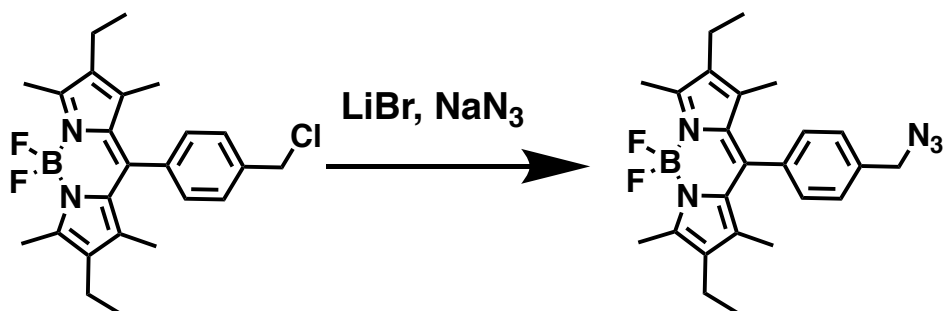
K<sub>2</sub>CO<sub>3</sub> (2.76 g, 20 mmol) was added to a solution of **ten iodides bearing pillar** compound (2.15 g, 1 mmol) and 4-hydroxybenzaldehyde (2.44 g, 20 mmol) in acetone/DMF (50 mL/3 mL) and the mixture was refluxed for 96 h. Column chromatography (SiO<sub>2</sub>; petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>, 1:1) obtained pillar as a pale yellow solid (1.6 g, 80%). M.P.: 132 °C. <sup>1</sup>H-NMR (400 MHz, chloroform-d, room temperature) δ (ppm): 9.81 (bs, 10H), (s, 10H), 7.77 (s, 10H), 7.42-7.28 (m, 10H), 7.03- 6.94 (m, 30H), 4.17 (s, 30H), 3.93-3.82 (m, 20H). <sup>13</sup>C-NMR (100 MHz) δ (ppm): 191.81, 163.93, 152.15, 132.77, 131.11, 116.57, 115.21, 67.76, 30.95 Elemental Analysis calcd. C<sub>125</sub>H<sub>110</sub>O<sub>30</sub>: C, 71.76; H, 5.30; found: C, 71.48; H, 5.45.

**S1.4. The synthesis of 8-{4-(chloromethyl)phenyl}-2,6-diethyl-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene**



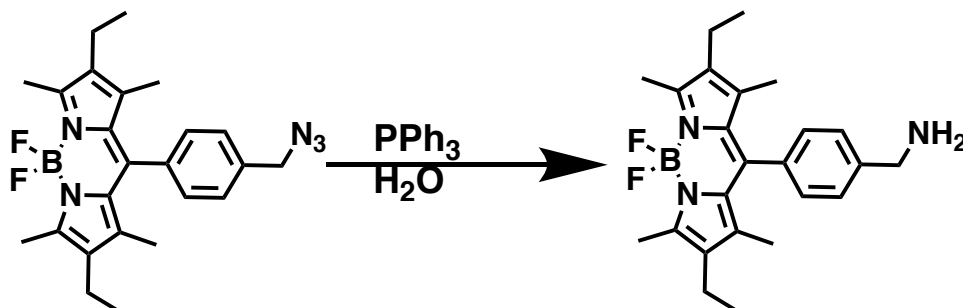
**8-{4-(chloromethyl)phenyl}-2,6-diethyl-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene** was synthesized with known literature procedures. 4-(chloromethyl)benzoyl chloride (1.875 g, 10 mmol) was dropwise added to a solution of 2,4-dimethyl-3-ethylpyrrole (2.7 mL, 20 mmol) in dry dichloromethane (100 mL) at room temperature and under  $\text{N}_2$ . The solution was heated to  $60^\circ\text{C}$  for 2 h while stirring. After cooling of the solution, triethylamine (TEA) (5 equiv.) was added to the residual solid, the mixture was stirred at room temperature for 30 min under  $\text{N}_2$  and then boron trifluoride diethyl etherate (7 equiv.) was added. The solution was stirred at  $60^\circ\text{C}$  for 2 h and the final residue was purified by column chromatography (petroleum ether-EtOAc; in 8:1 ratio) and obtained to a red solid (1.75 g, Yield 41%). M.P.:  $189^\circ\text{C}$ .  $^1\text{H}$  NMR [400 MHz,  $\text{CDCl}_3$ ]: 7.41 (d, 2H, ArH), 7.18 (d, 2H, ArH) 4.63 (s, 2H,  $\text{CH}_2$ ), 2.44 (s, 6H  $\text{CH}_3$ ) 2.21 (q, 4H,  $\text{CH}_2$ ) 1.27 (s, 6H,  $\text{CH}_3$ ) 0.89 (t, 6H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR [100 MHz,  $\text{CDCl}_3$ ]:  $\delta$  (ppm); 153.81, 139.42, 138.42, 136.12, 135.81, 132.83, 130.62, 129.02, 128.78, 45.59, 17.07, 14.43, 12.43, 11.62. Anal.Calc. for (%)  $\text{C}_{24}\text{H}_{28}\text{N}_2\text{F}_2\text{ClB}$ : C, 67.23; H, 6.58; N, 6.53; Found: C, 66.97; H, 6.98; N, 6.12. MS for  $\text{C}_{24}\text{H}_{28}\text{N}_2\text{F}_2\text{ClB}$  m/z: 428.2  $[\text{M}+\text{H}]^+$ .

**S1.5. The synthesis of 8-{4-(azidomethyl)phenyl}-2,6-diethyl-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene**



A mixture of **5** (0.22 mmol) **8-{4-(chloromethyl)phenyl}-2,6-diethyl-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene** and NaN<sub>3</sub> (172 mg, 2.64 mmol) in DMF (10 mL) was stirred for 24 h at room temperature under Ar., then H<sub>2</sub>O (45 mL) was added. The aqueous layer was extracted with ethylacetate. The combined organic layers were washed with water, dried with MgSO<sub>4</sub>, filtered, and concentrated. Column chromatography (SiO<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>) gave **8-{4-(azidomethyl)phenyl}-2,6-diethyl-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene** (278 mg, 97%) as a colourless solid that was used as received in the next step. Caution: Owing to its high number of azide residues, this compound must be handled with special care. Furthermore, this compound has always been prepared on a small scale. M.P.:140 °C. <sup>1</sup>H-NMR [400 MHz, CDCl<sub>3</sub>]: <sup>1</sup>H NMR [400 MHz, CDCl<sub>3</sub>]: 7.43 (d, 2H, ArH), 7.31 (d, 2H, ArH) 4.46 (s, 2H, CH<sub>2</sub>), 2.55 (s, 6H CH<sub>3</sub>) 2.30 (q, 4H, CH<sub>2</sub>) 1.26 (s, 6H, CH<sub>3</sub>) 1.02 (t, 6H, CH<sub>3</sub>). <sup>13</sup>C NMR [100 MHz, CDCl<sub>3</sub>]: δ (ppm); 153.22, 139.33, 138.12, 136.17, 135.53, 132.81, 130.62, 128.32, 128.18, 55.19, 17.44, 15.14, 12.32, 11.99.

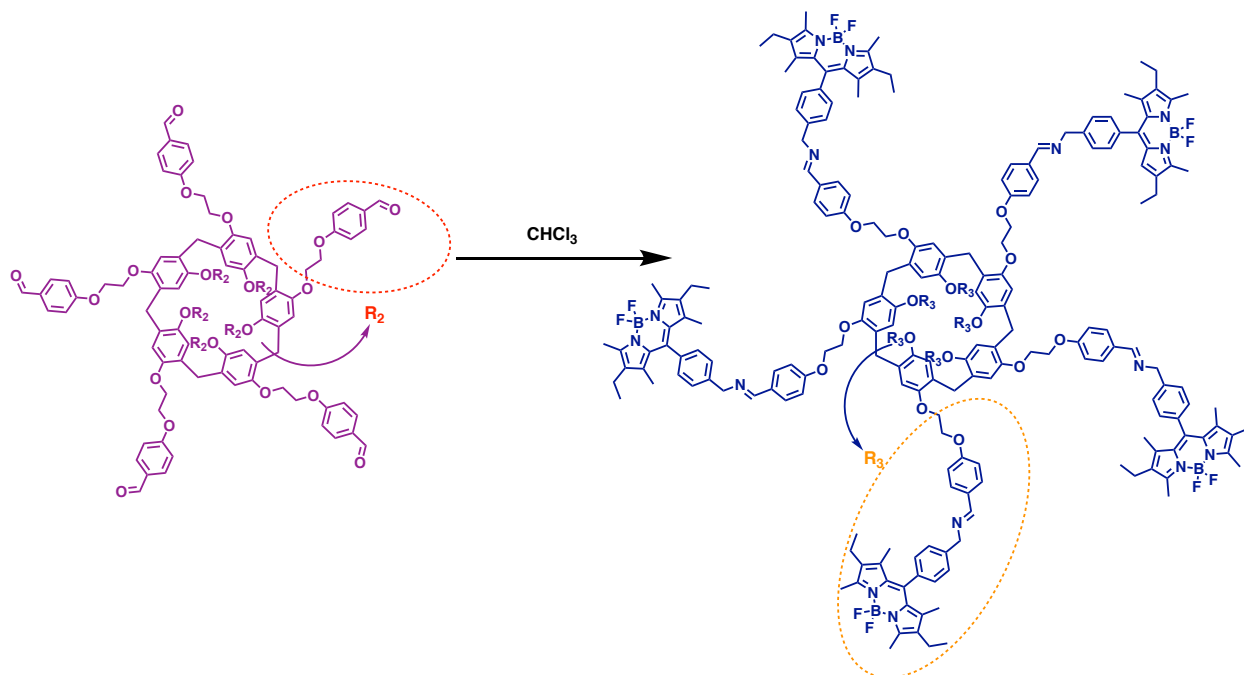
**S1.6. The synthesis of 8-{4-(aminomethyl)phenyl}-2,6-diethyl-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (chromophore)**



A mixture of **8-{4-(azidomethyl)phenyl}-2,6-diethyl-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene** (435 mg, 1 mmol,) and PPh<sub>3</sub> (1 mmol, 262 mg) in dry THF (20 mL) was stirred for 5 h at room temperature under Ar., then H<sub>2</sub>O (2 drops) was added. This mixture was stirred for overnight and evaporated to solvent. Column chromatography (SiO<sub>2</sub>; DCM/MeOH: 10/1) gave the chromophore (298 mg, 73%) as a red solid. M.P.≈170 °C.

<sup>1</sup>H-NMR [400 MHz, CDCl<sub>3</sub>]: <sup>1</sup>H NMR [400 MHz, CDCl<sub>3</sub>]: 7.43 (d, 2H, ArH), 7.25 (d, 2H, ArH) 4.02 (s, 2H, CH<sub>2</sub>), 2.55 (s, 6H CH<sub>3</sub>) 2.35 (q, 4H, CH<sub>2</sub>) 1.22 (s, 6H, CH<sub>3</sub>) 1.0 (t, 6H, CH<sub>3</sub>). <sup>13</sup>C NMR [100 MHz, CDCl<sub>3</sub>]: δ (ppm); 154.22, 142.33, 139.82, 137.17, 134.83, 132.99, 130.76, 128.32, 128.00, 46.22, 17.34, 14.84, 12.42, 12.02.

## S1.7. The synthesis of LHC



**Chromophore** (0.409 g, 1 mmol) was solved in 20 mL chloroform and added dropwise a solution of **pillar** (0.2092 g, 0.1 mmol) in 20 mL chloroform. The mixture was refluxed for 72 h. After the evaporation of solvent, raw product was purified on column. A red solid. (Yield 72%). M.P.: 238 °C. <sup>1</sup>H-NMR [400 MHz, CDCl<sub>3</sub>]: 8.55 (s, 10H, N=CH) 7.65 (m, 60H, ArH), 7.18 (m, 30, ArH), 4.97 (s, 20H, CH<sub>2</sub>), 4.77-4.67 (m, 50H, CH<sub>2</sub> and CH<sub>2</sub>), 2.98 (s, 60H, CH<sub>3</sub>) 2.55-2.40 (q, 40H, CH<sub>2</sub>), 1.20 (s, 60H, CH<sub>3</sub>) 0.90 (t, 60H, CH<sub>3</sub>). <sup>13</sup>C NMR [100 MHz, CDCl<sub>3</sub>]: δ (ppm); 161.11, 149.45, 137.67, 134.78, 132.21, 131.11, 129.32, 127.41, 124.33, 122.81, 118.63, 115.21, 111.46, 109.21, 63.33, 61.53, 17.99, 15.17, 14.32, 11.67. Anal.Calc. for (%), C<sub>365</sub>H<sub>390</sub>B<sub>10</sub>F<sub>20</sub>N<sub>30</sub>O<sub>20</sub>: C, 73.00; H, 6.55; N, 7.00; Found: C, 73.37; H, 6.78; N, 7.33. MS for C<sub>365</sub>H<sub>390</sub>B<sub>10</sub>F<sub>20</sub>N<sub>30</sub>O<sub>20</sub> m/z: 6005.2 [M+H]<sup>+</sup>.



## S2. Additional experimental data

### S2.1. Infrared spectroscopy

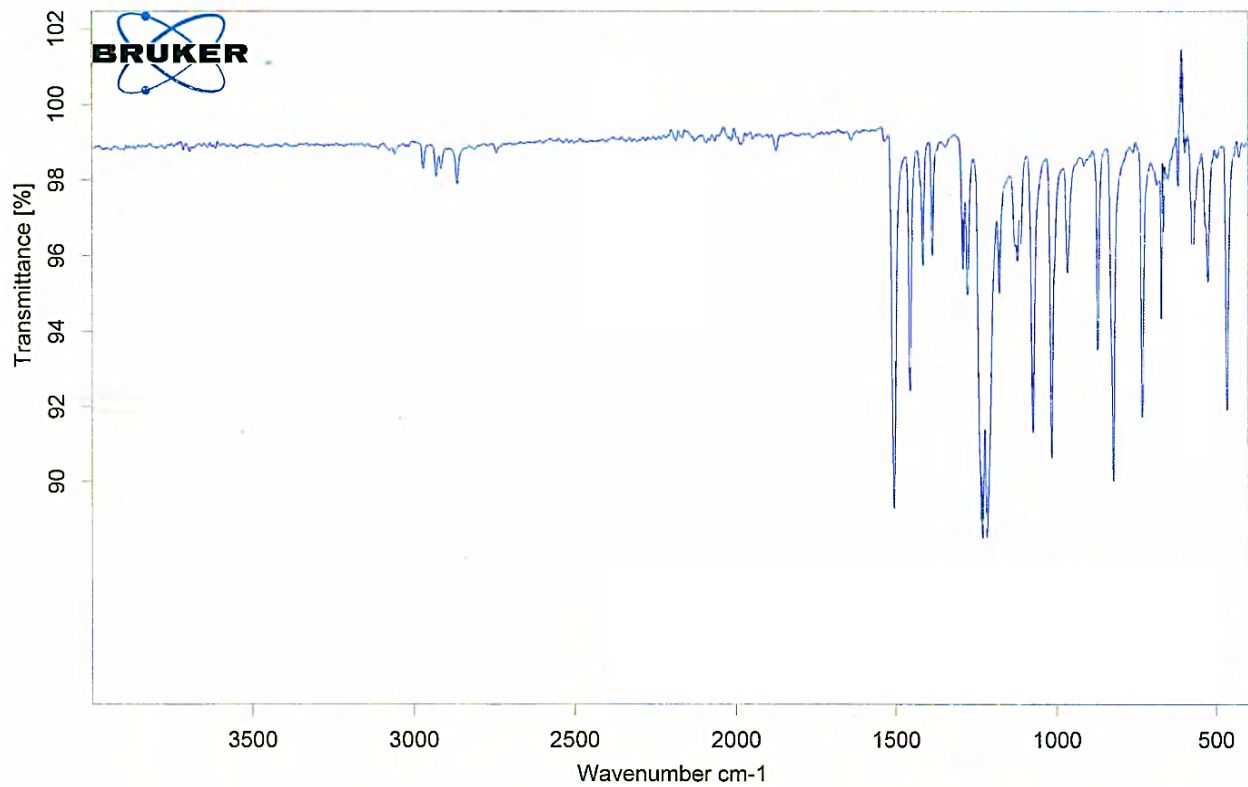


Figure S2.1 FT-IR spectrum of ten iodide bearing pillar.

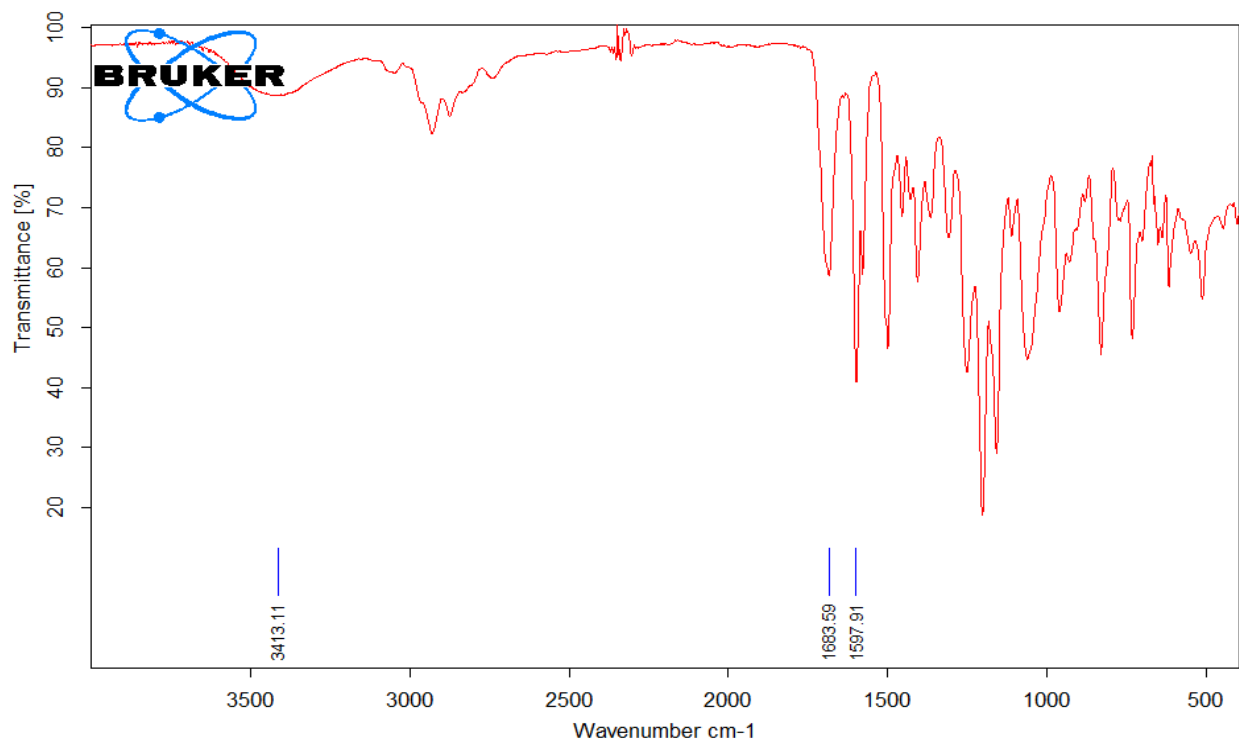
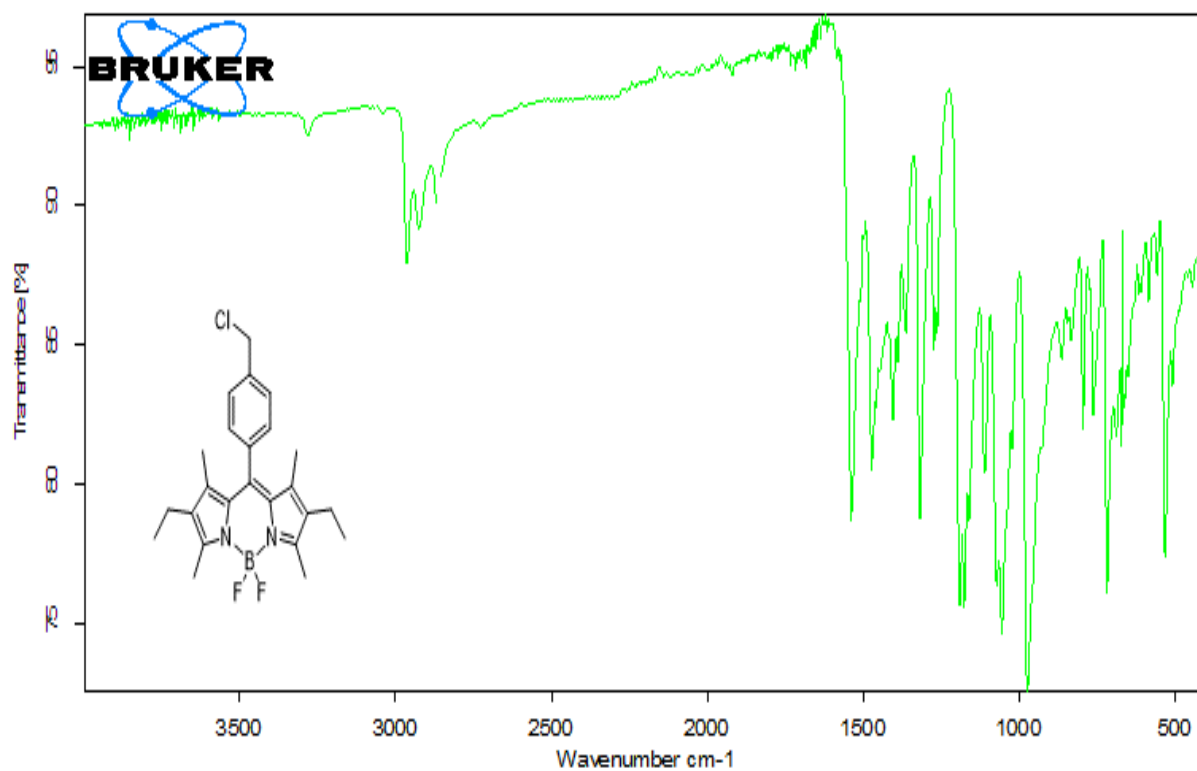
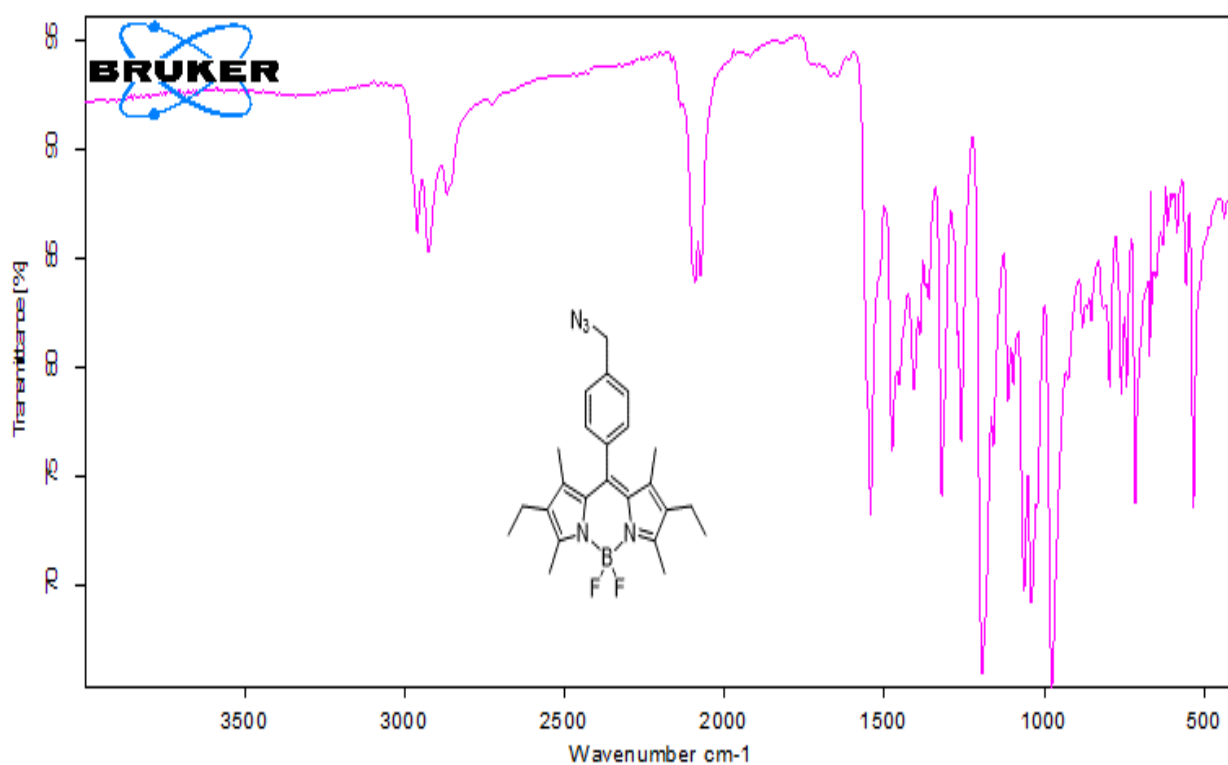


Figure S2.2 FT-IR spectrum of pillar.



**Figure S2.3** FT-IR spectrum of 8-{4-(chloromethyl)phenyl}-2,6-diethyl-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene.



**Figure S2.4** FT-IR spectrum of 8-{4-(azidomethyl)phenyl}-2,6-diethyl-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene.

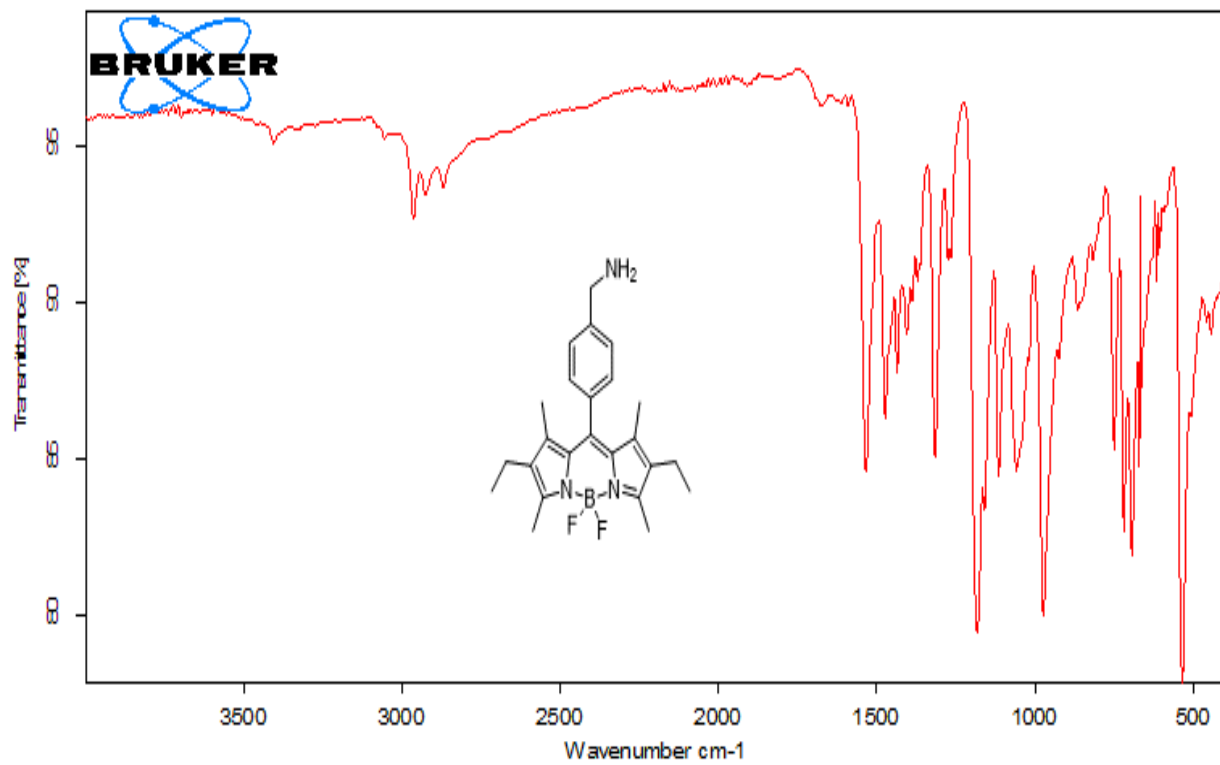


Figure S2.5 FT-IR spectrum of **chromophore**.

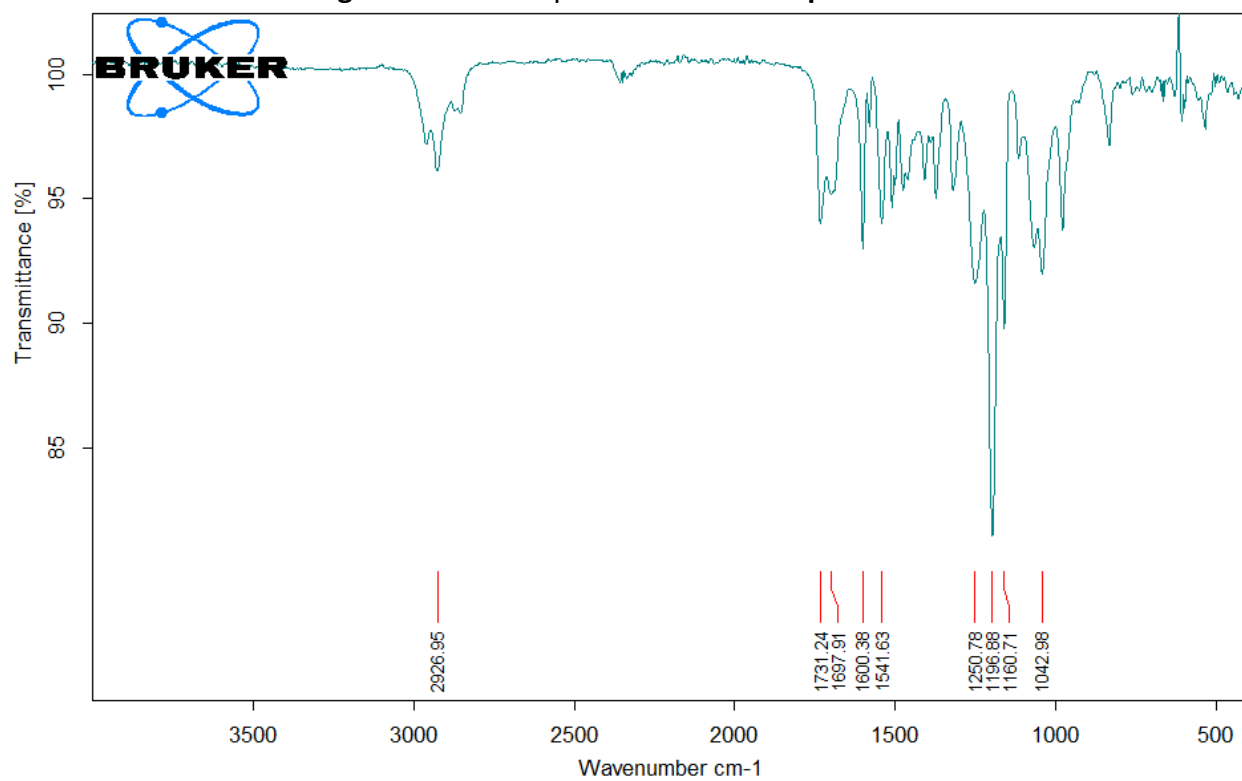
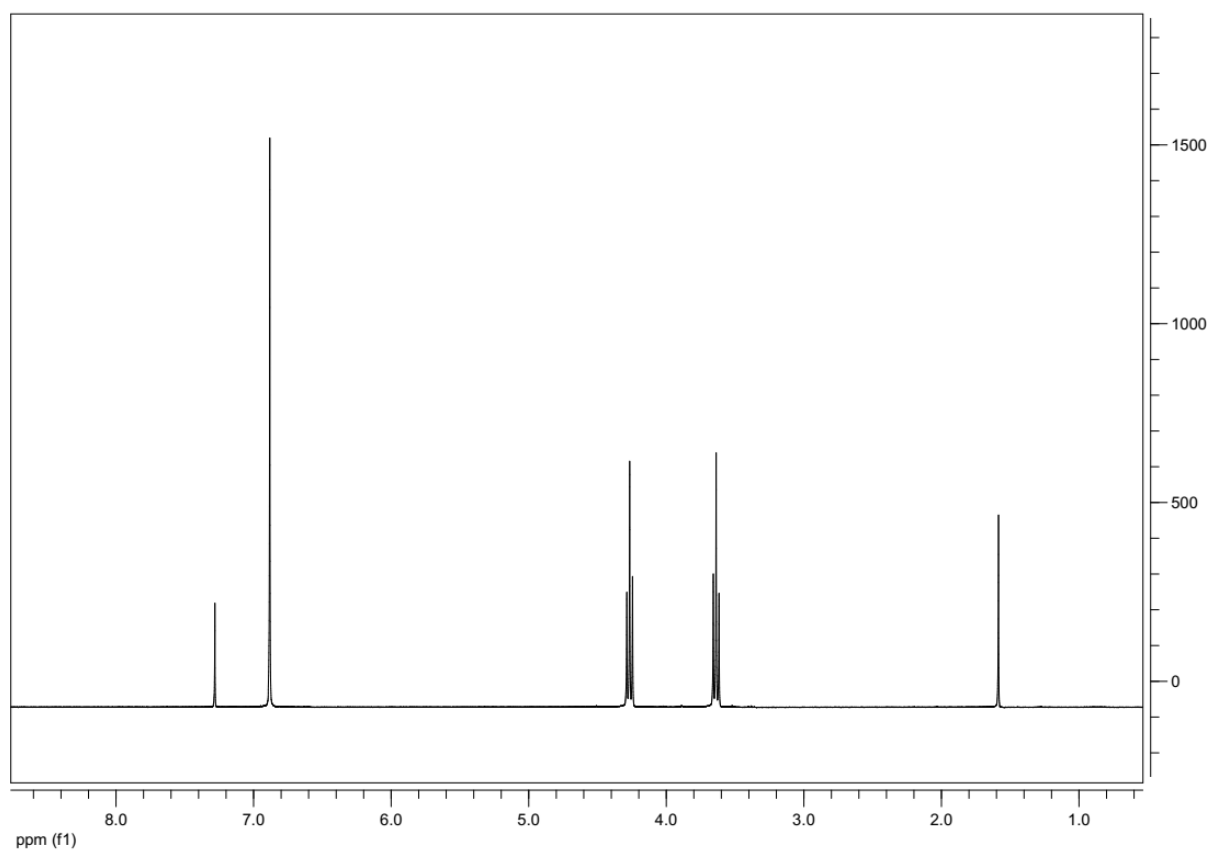
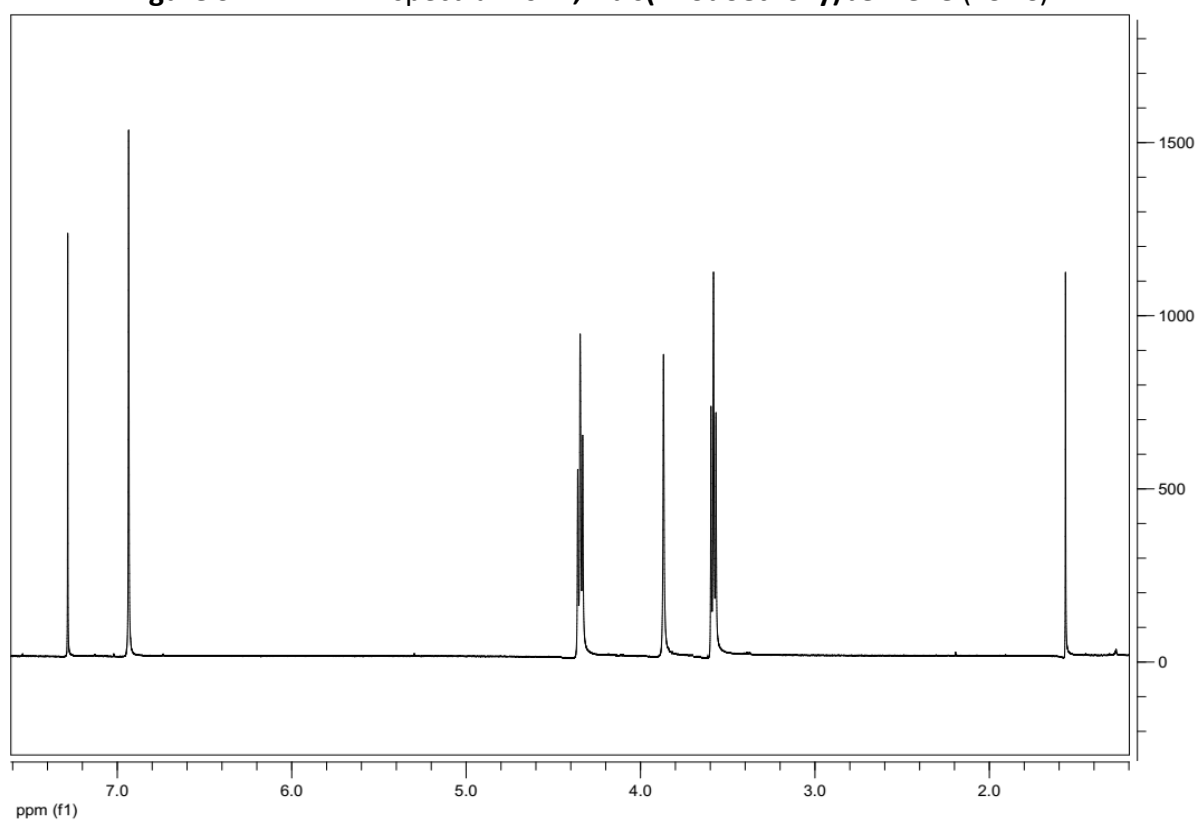


Figure S2.6 FT-IR spectrum of **LHC**.



**Figure S2.7**  $^1\text{H-NMR}$  spectrum of 1,4-bis(2-iodoethoxy)benzene (25 °C).



**Figure S2.8**  $^1\text{H-NMR}$  spectrum of ten iodide bearing pillar (25 °C).

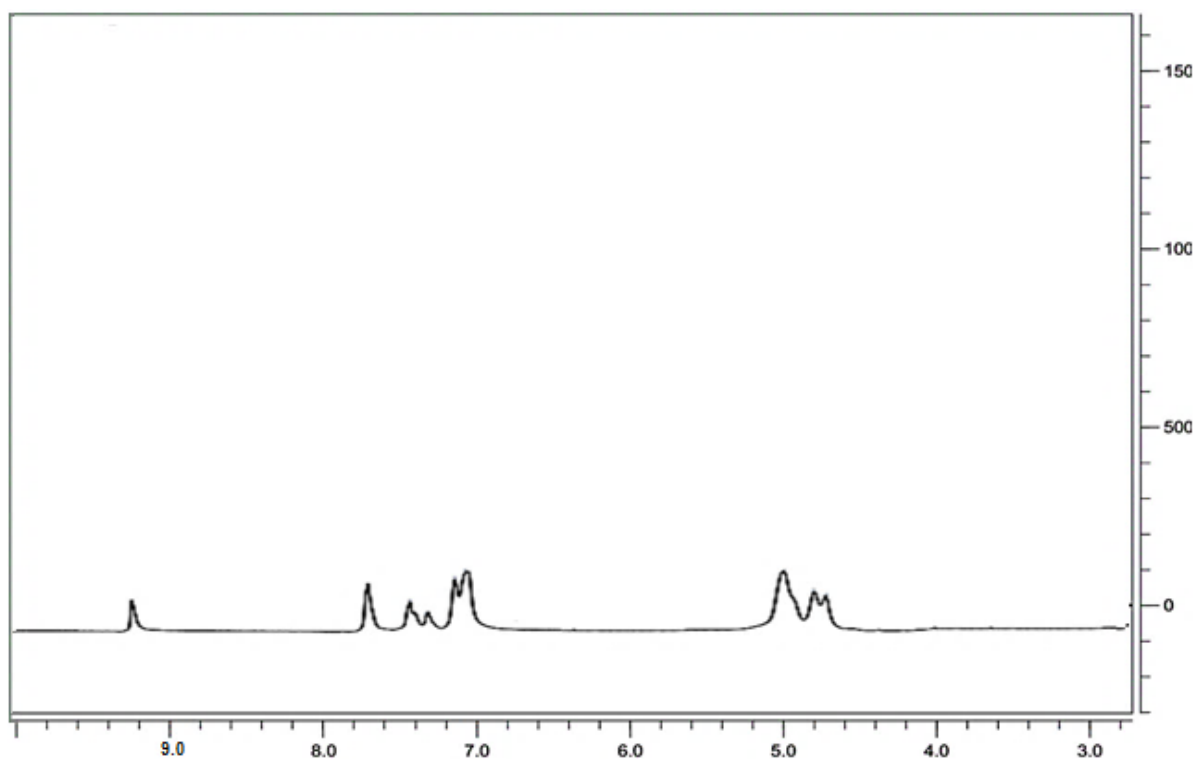


Figure S2.9  $^1\text{H}$ -NMR spectrum of **pillar** (25 °C).

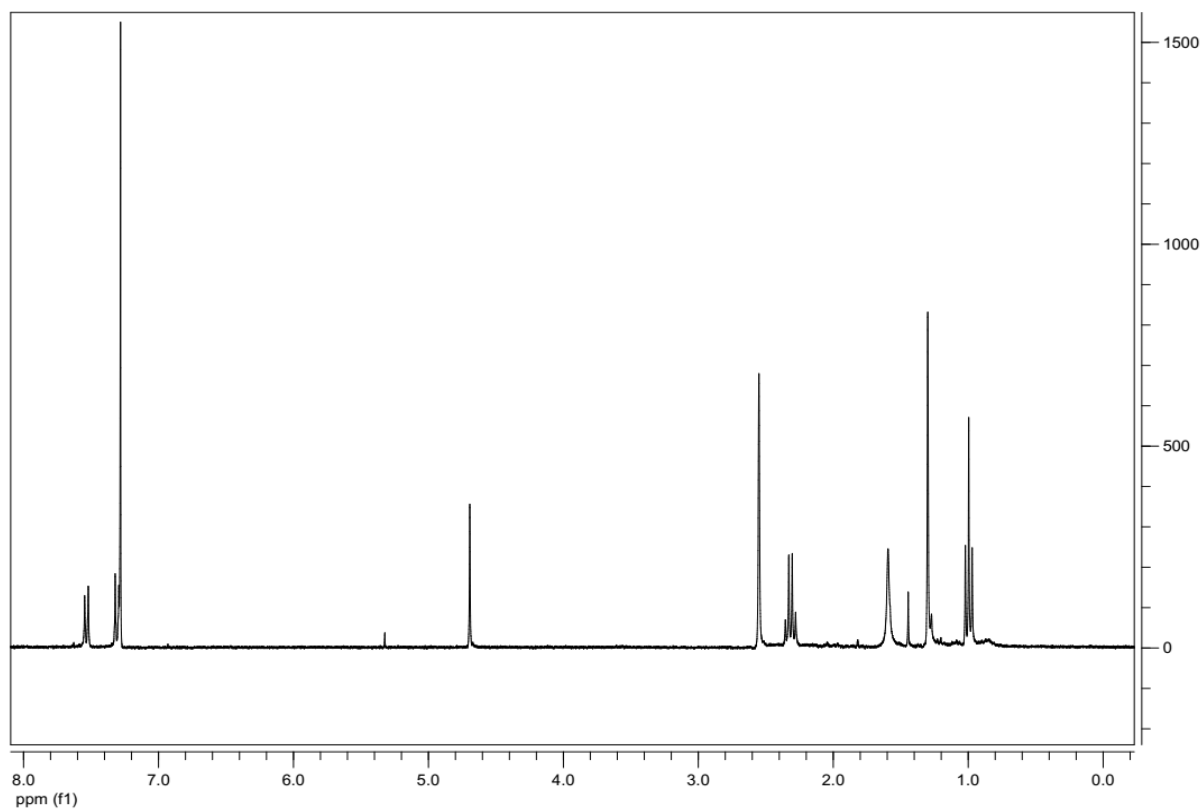
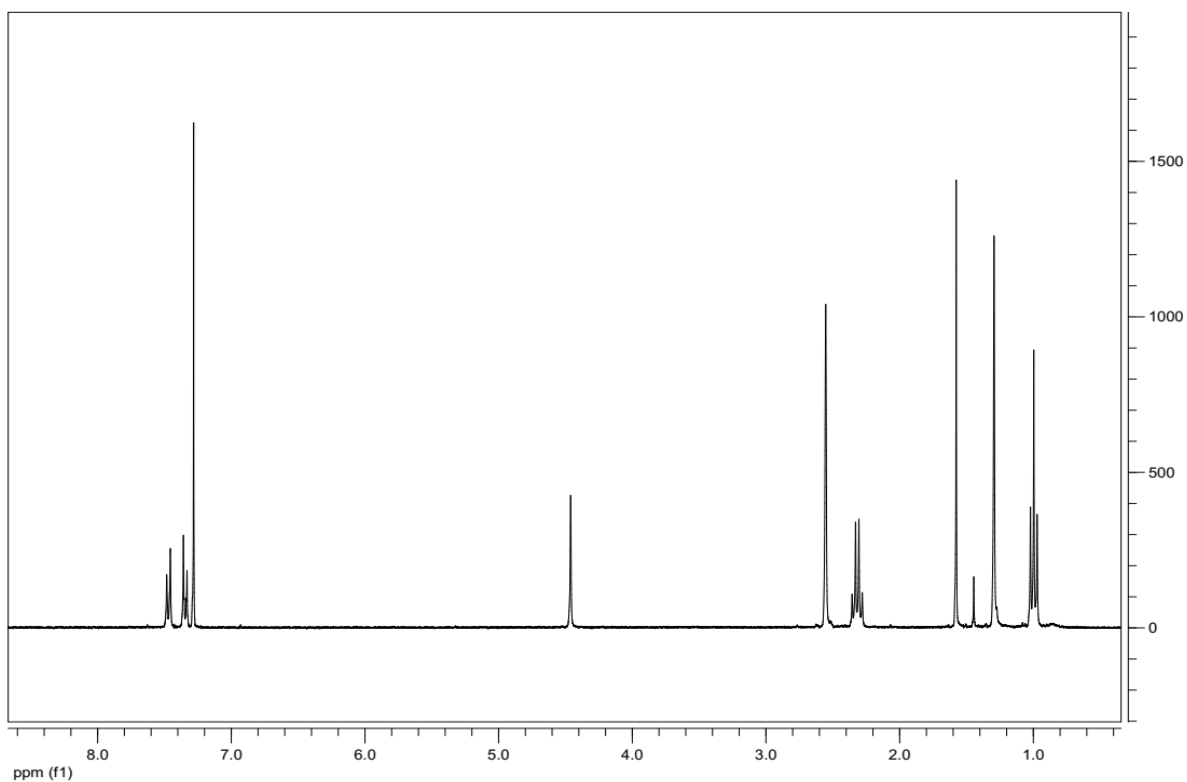
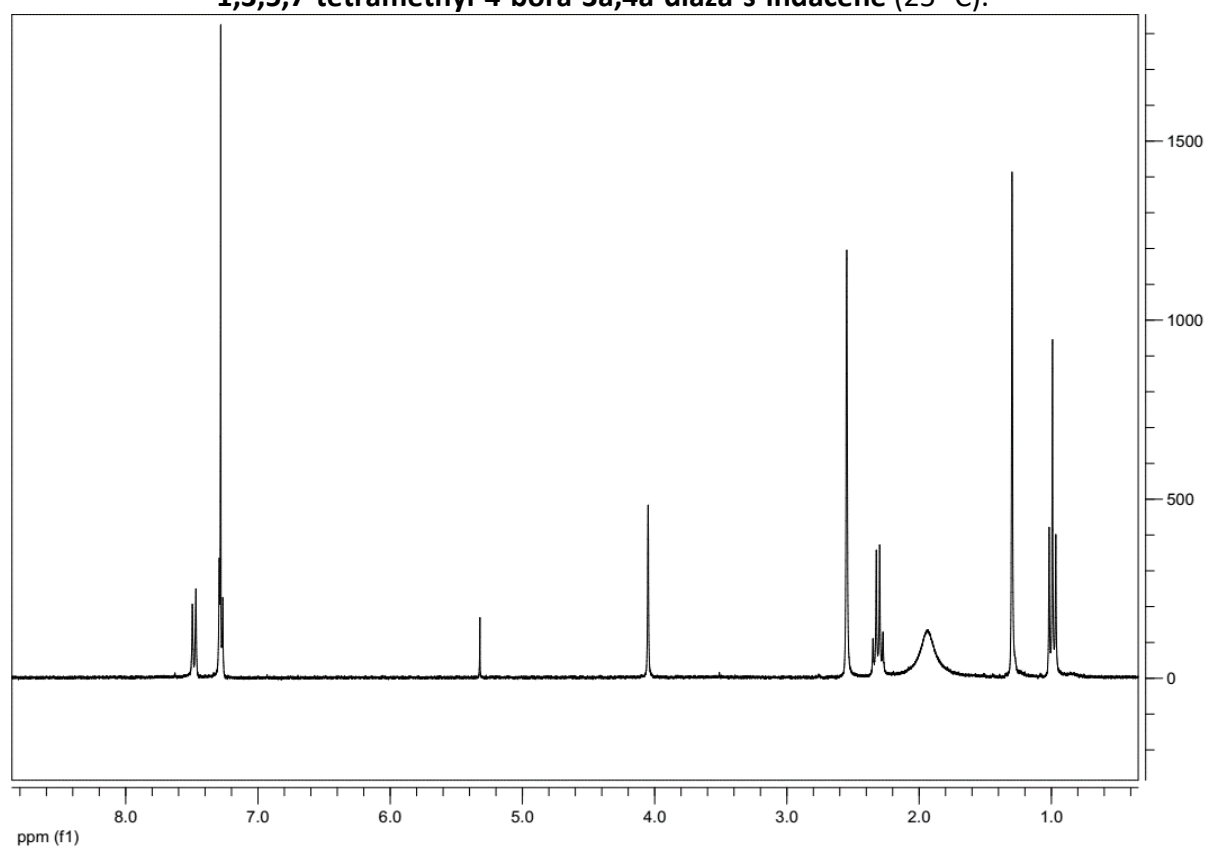


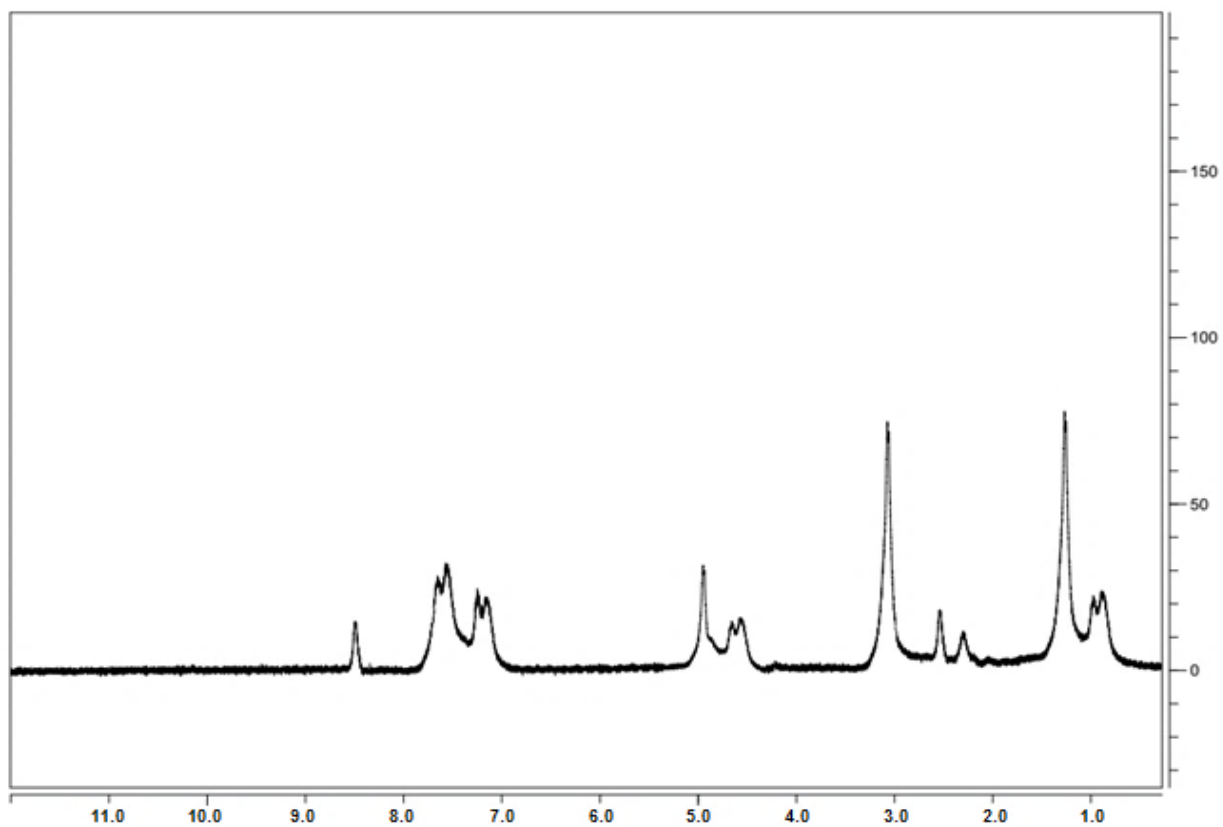
Figure S2.10  $^1\text{H}$ -NMR spectrum of **8-{4-(chloromethyl)phenyl}-2,6-diethyl-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene**.



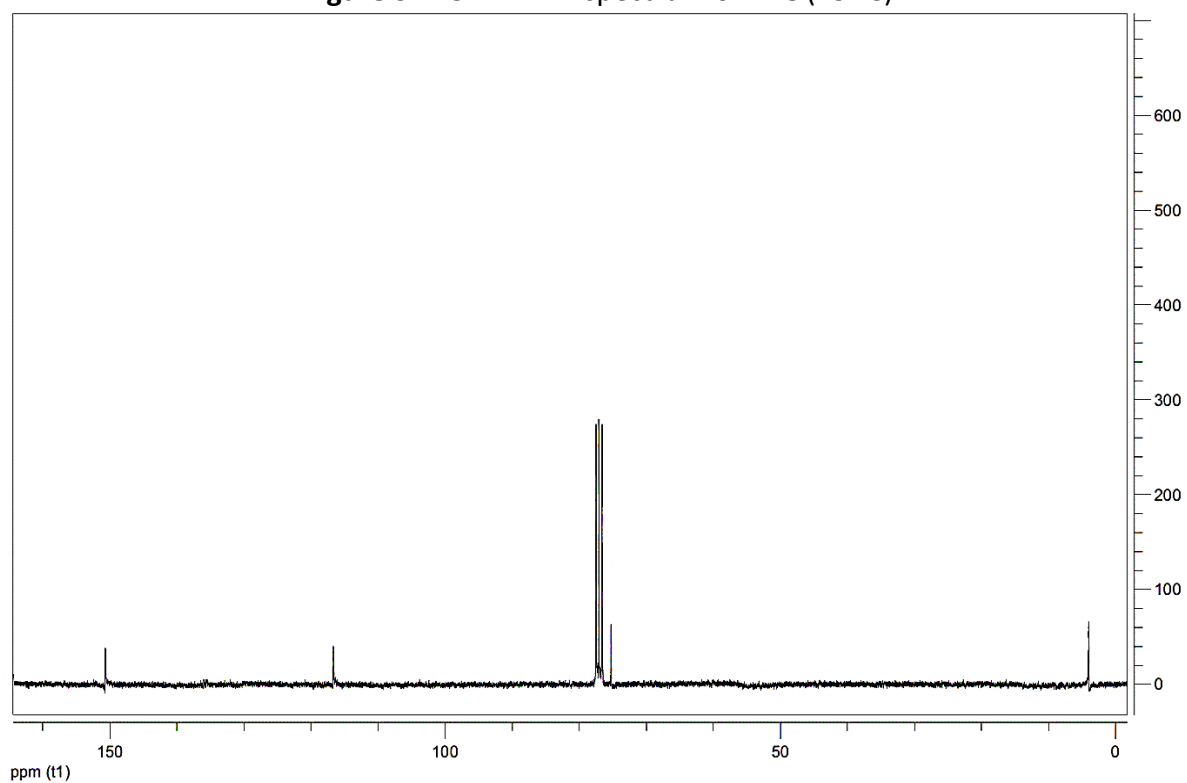
**Figure S2.11** <sup>1</sup>H-NMR spectrum of **8-{4-(azidomethyl)phenyl}-2,6-diethyl-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene** (25 °C).



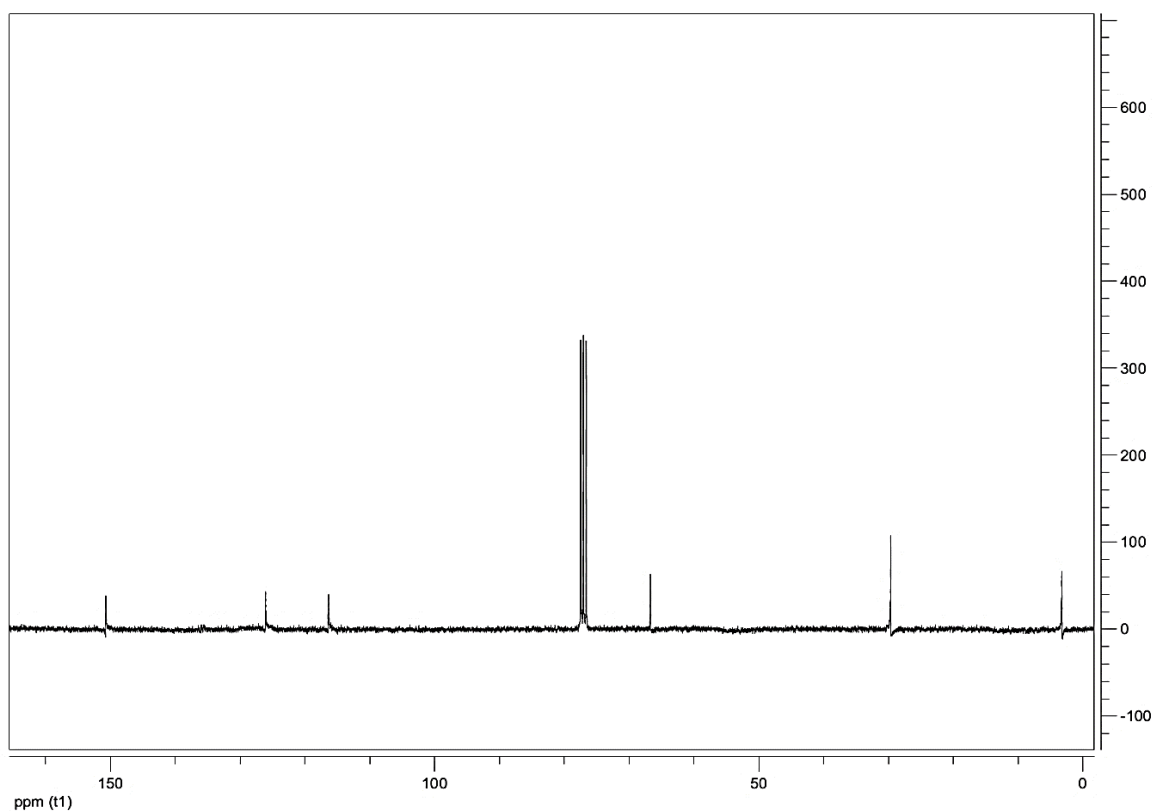
**Figure S2.12** <sup>1</sup>H-NMR spectrum of **chromophore** (25 °C).



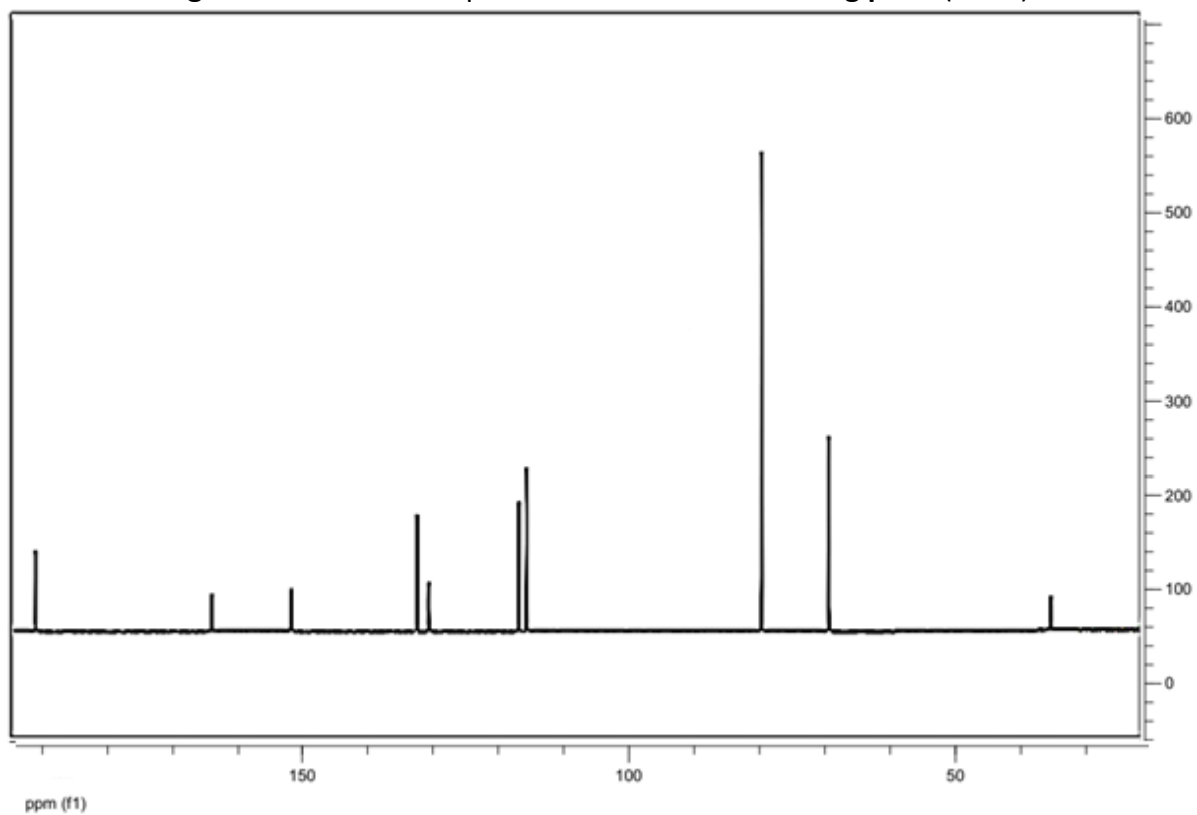
**Figure S2.13**  $^1\text{H}$ -NMR spectrum of LHC (25 °C).



**Figure S2.14**  $^{13}\text{C}$ -NMR spectrum of 1,4-bis(2-iodoethoxy)benzene (25 °C).

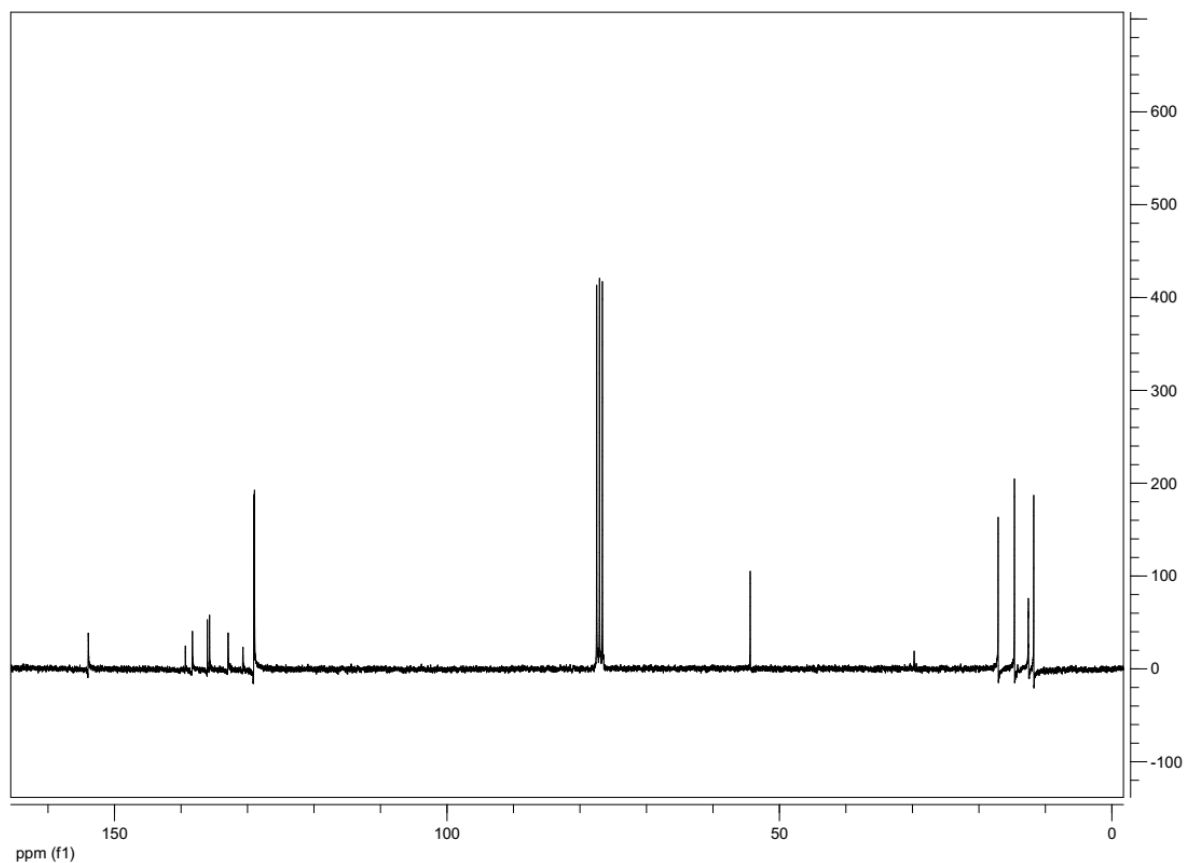


**Figure S2.15**  $^{13}\text{C}$ -NMR spectrum of ten iodide bearing pillar (25 °C).

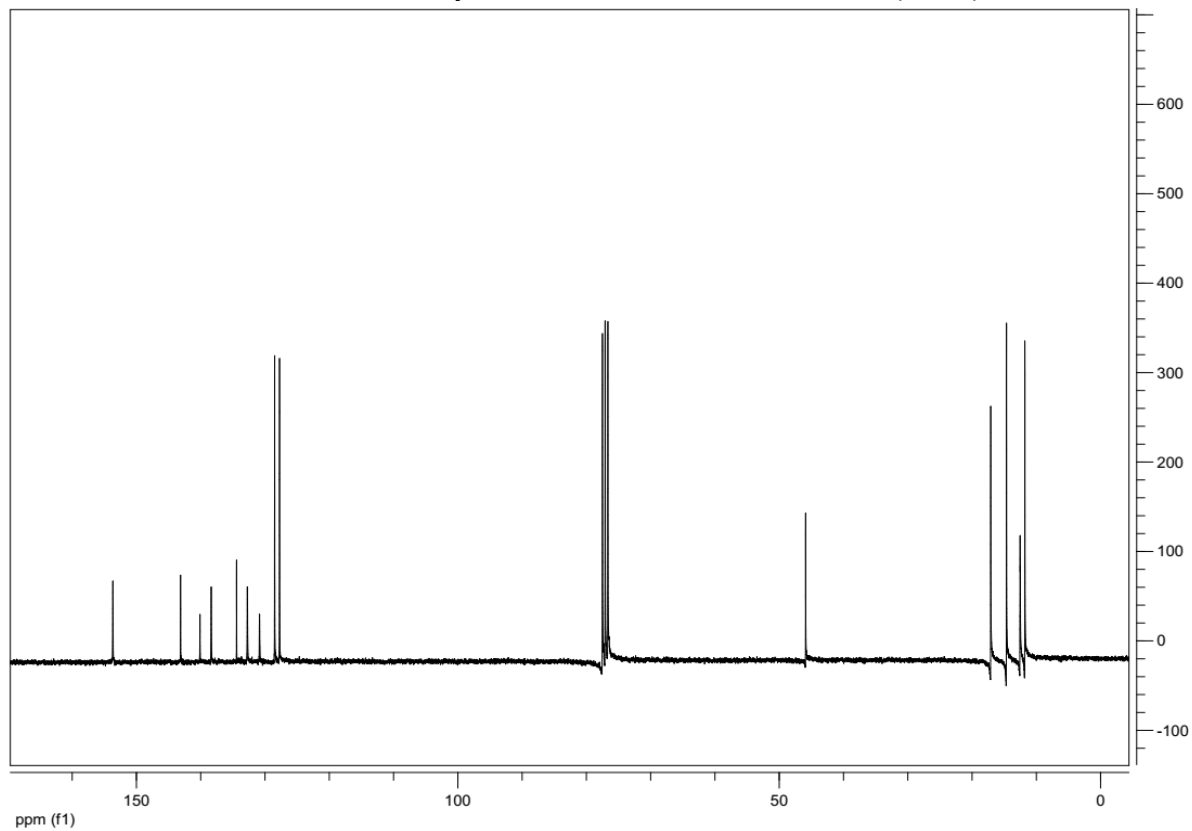


**Figure S2.16**  $^{13}\text{C}$ -NMR spectrum of pillar (25 °C).





**Figure S2.17**  $^{13}\text{C}$ -NMR spectrum of **8-{4-(azidomethyl)phenyl}-2,6-diethyl-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene** (25 °C).



**Figure S2.18**  $^{13}\text{C}$ -NMR spectrum of **chromophore**(25 °C).

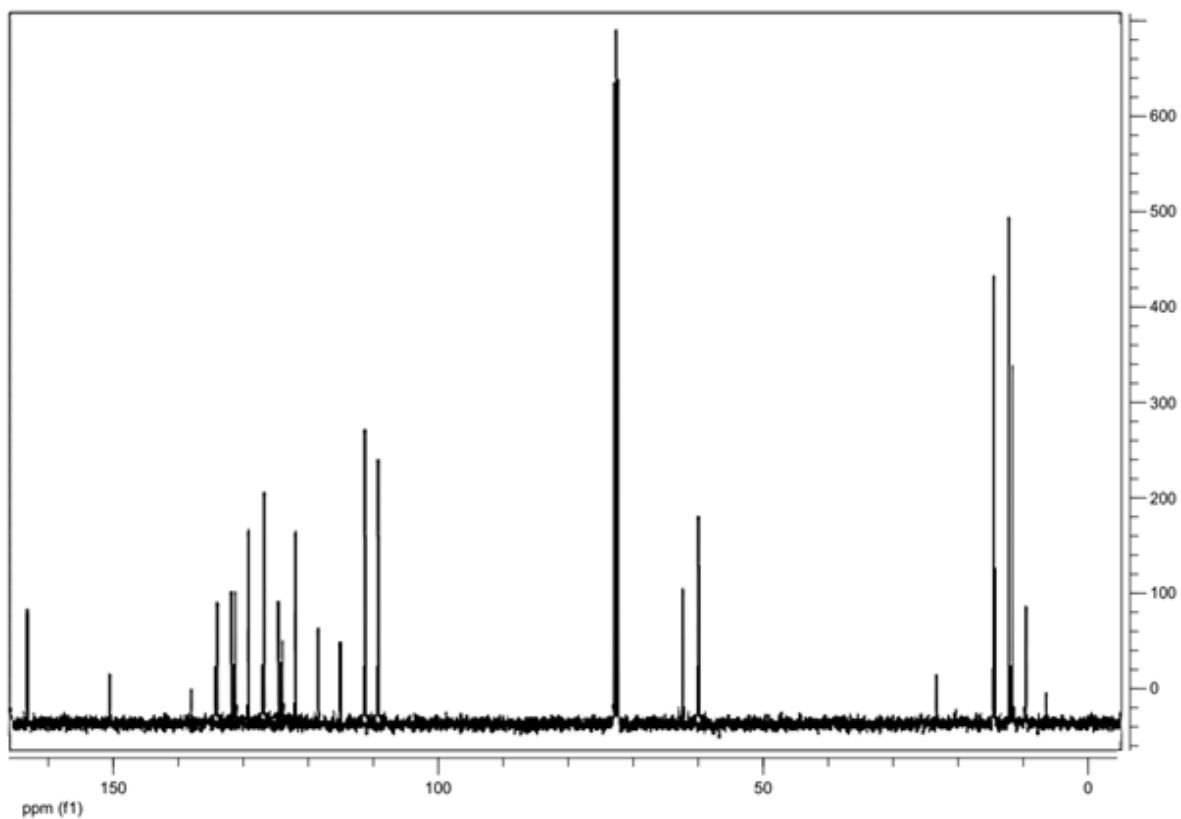


Figure S2.19  $^{13}\text{C}$ -NMR spectrum of LHC (25 °C).

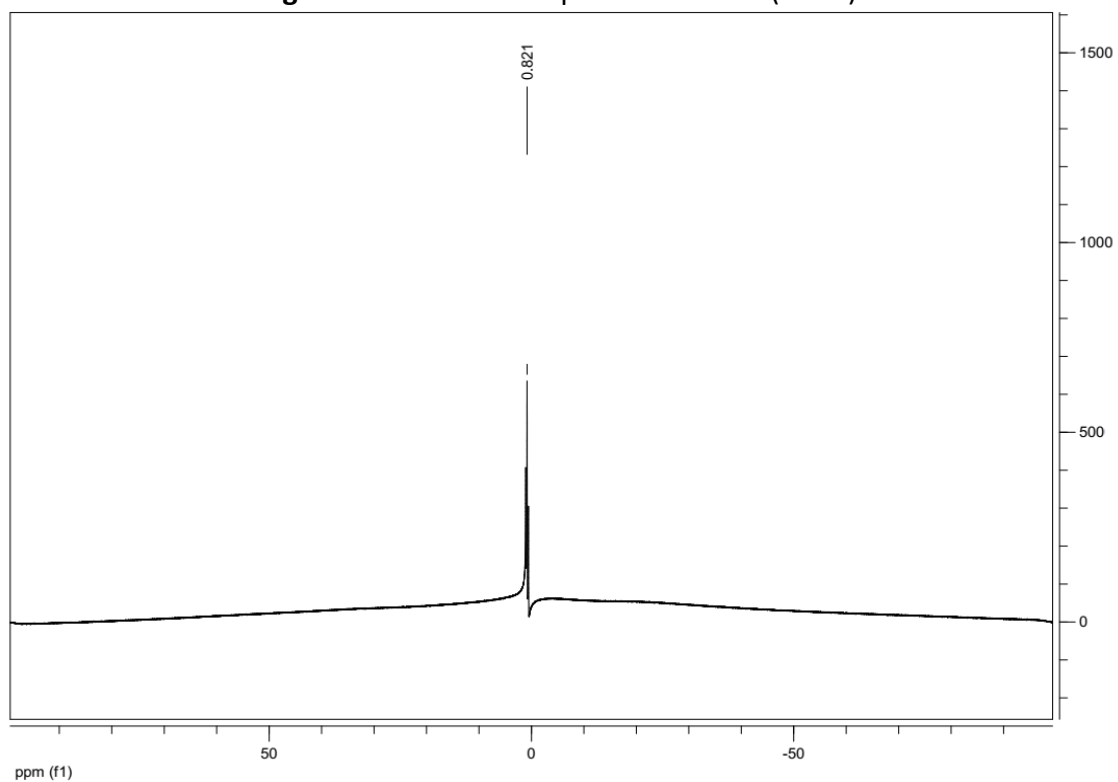
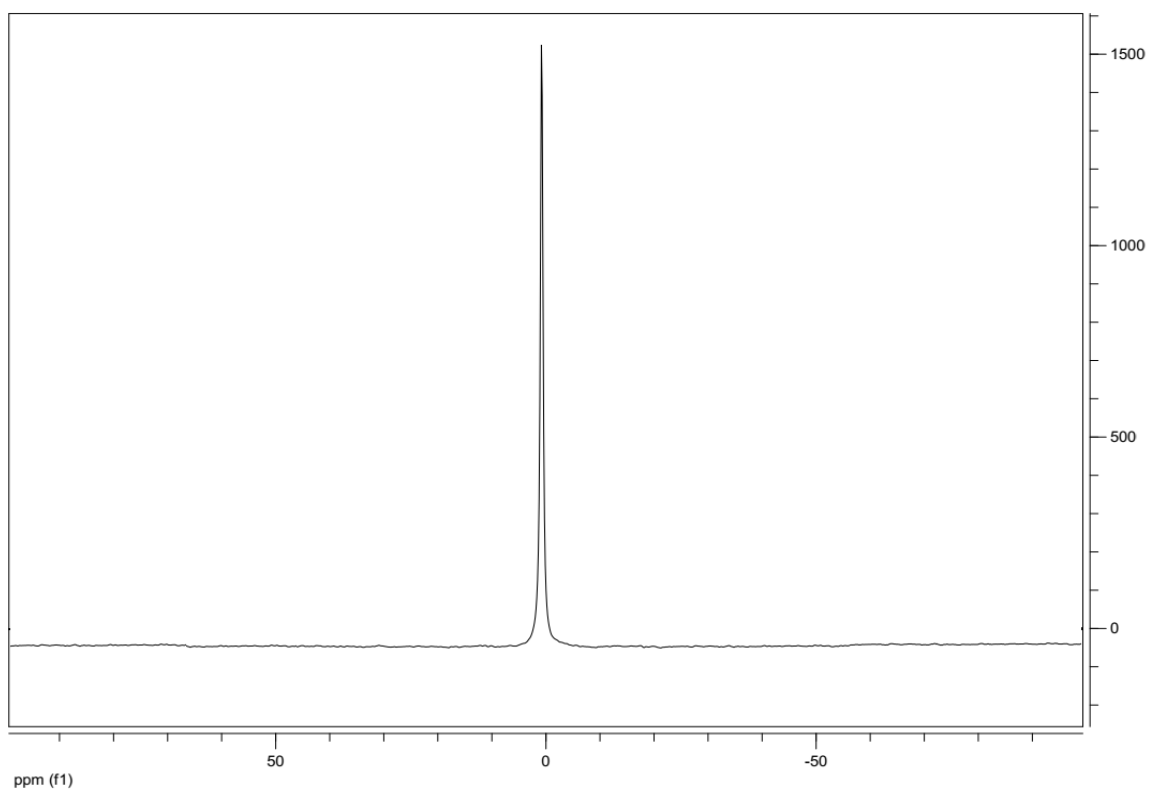
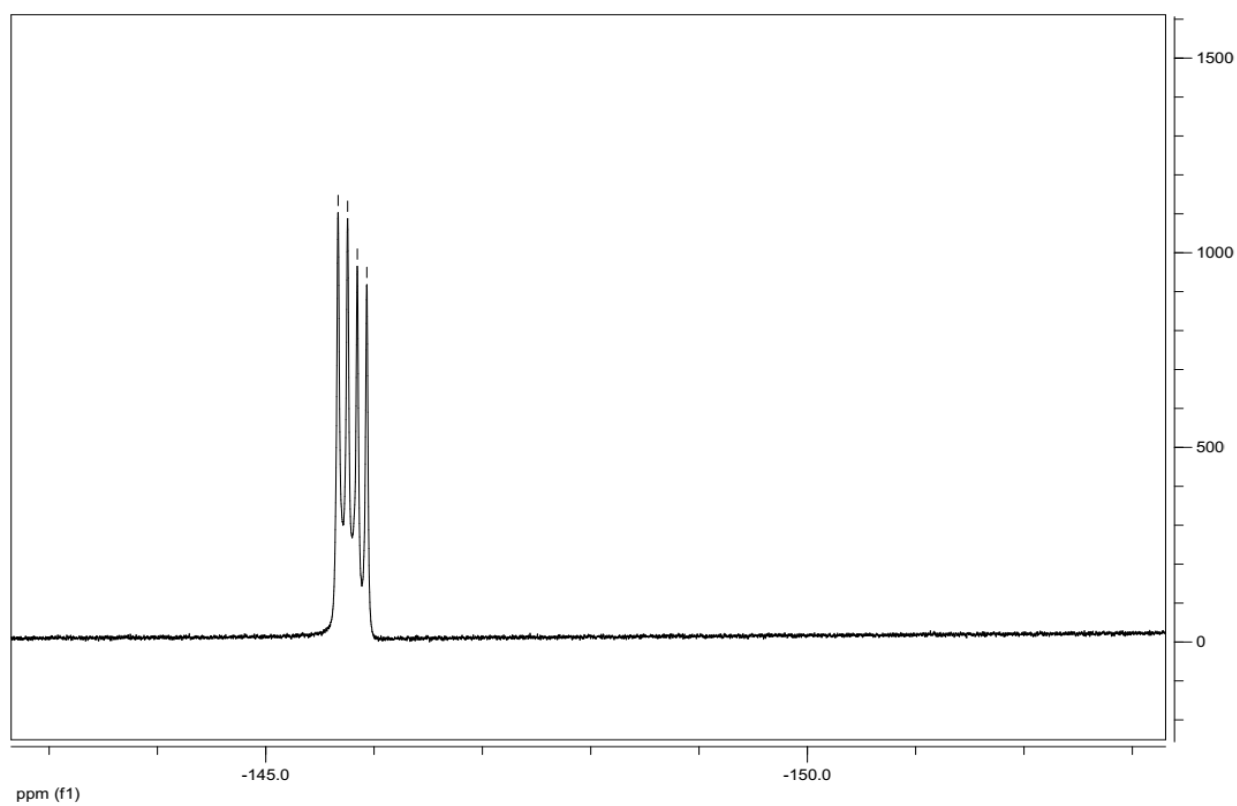


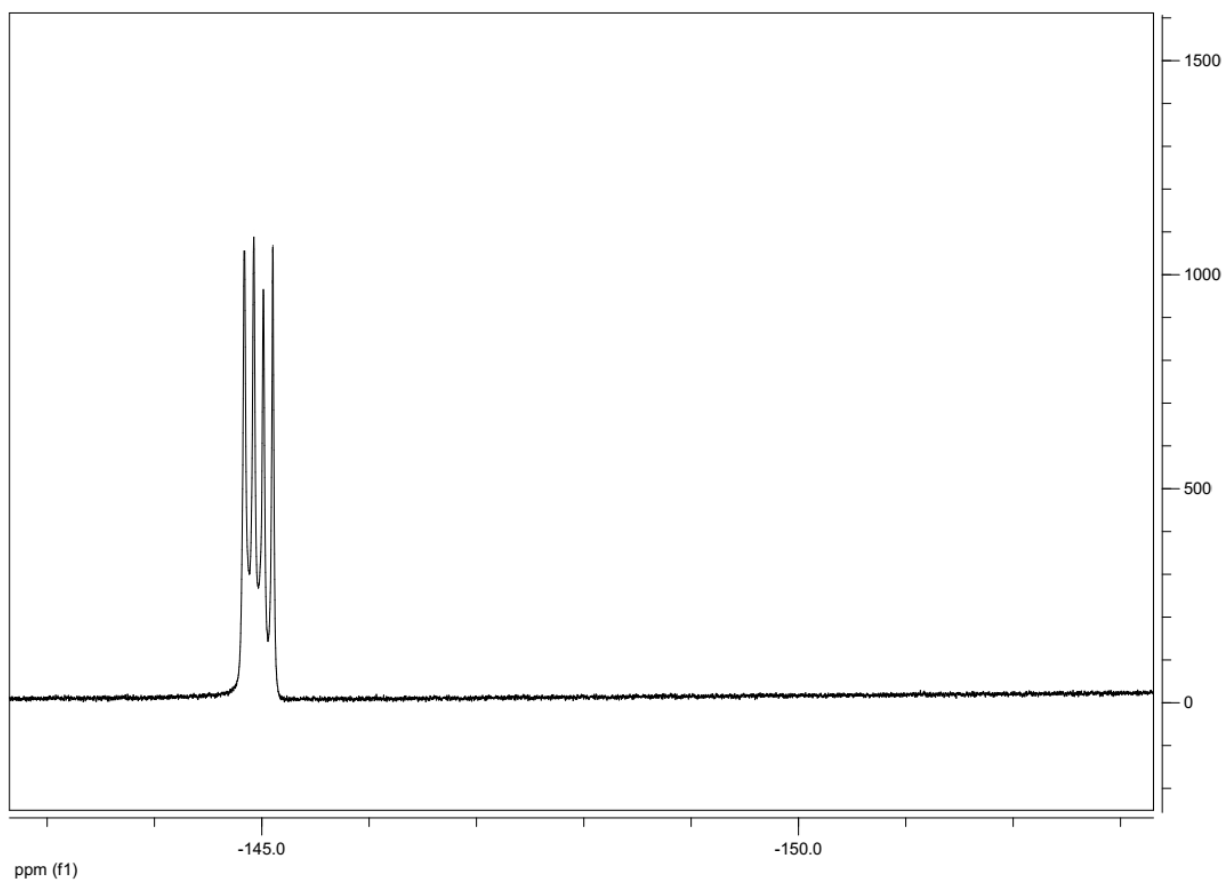
Figure S2.20  $^{11}\text{B}$ -NMR spectrum of 8-{4-(azidomethyl)phenyl}-2,6-diethyl-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (25 °C).



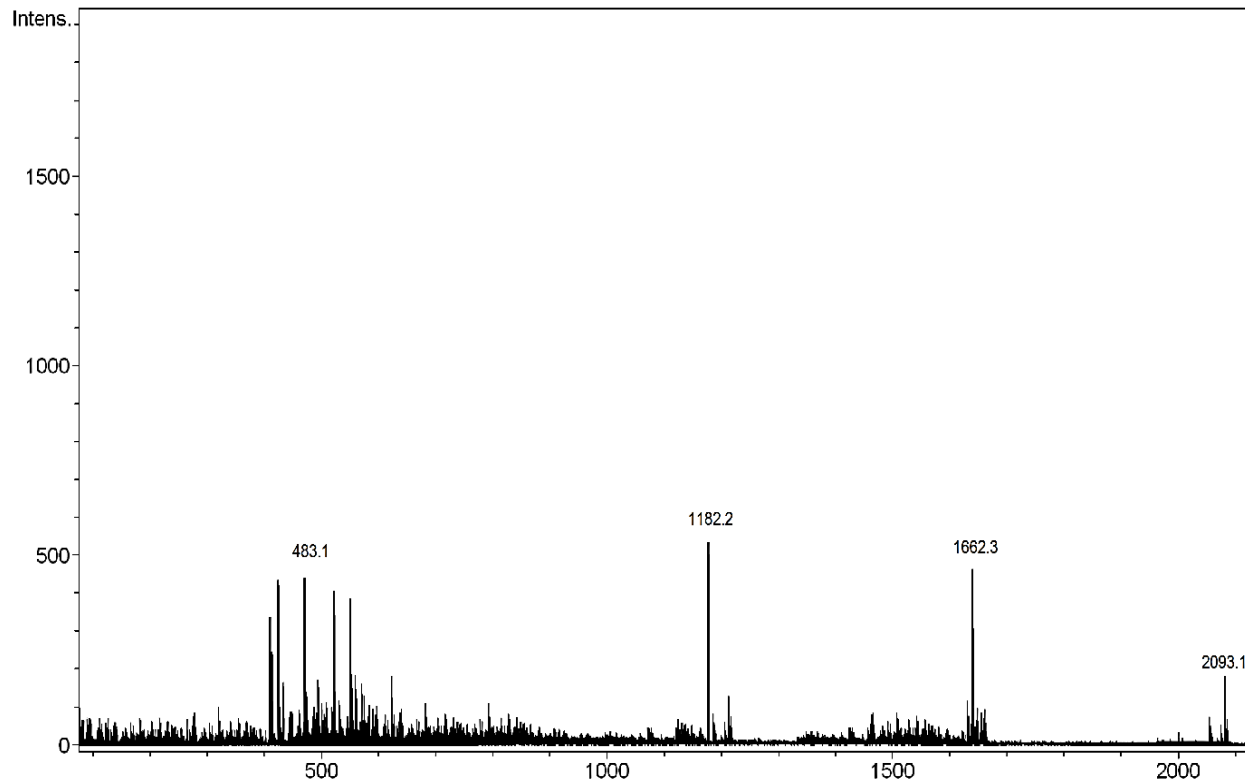
**Figure S2.21**  $^{11}\text{B}$ -NMR spectrum of **chromophore** (25 °C).



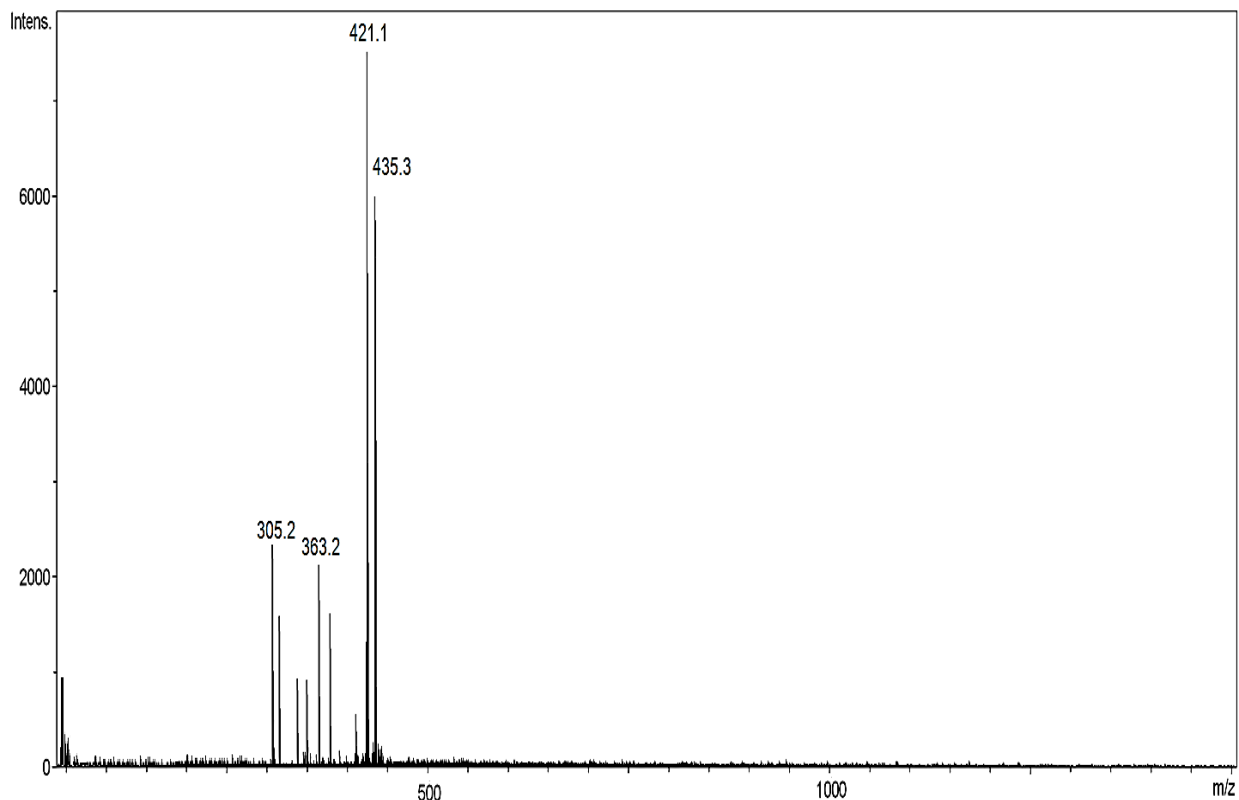
**Figure S2.22**  $^{19}\text{F}$ -NMR spectrum of **8-{4-(azidomethyl)phenyl}-2,6-diethyl-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene** (25 °C).



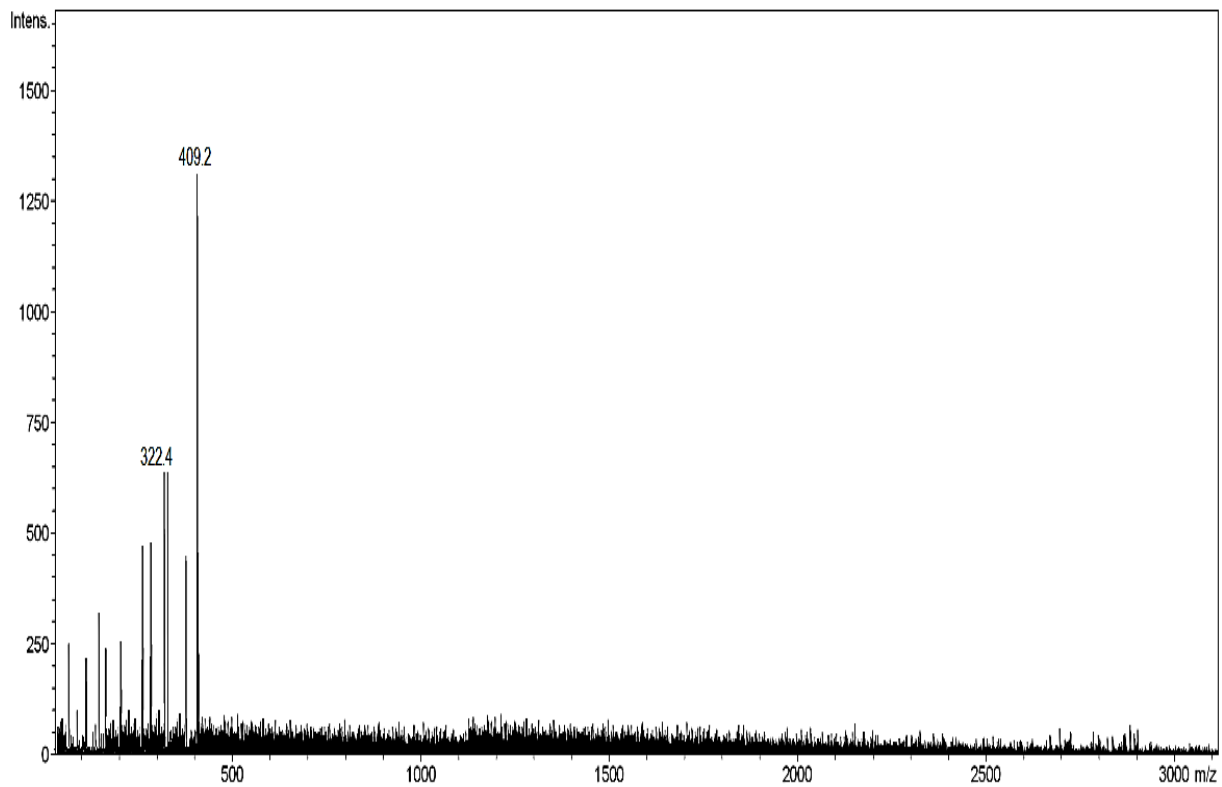
**Figure S2.23**  $^{19}\text{F}$ -NMR spectrum of **chromophore** (25 °C).



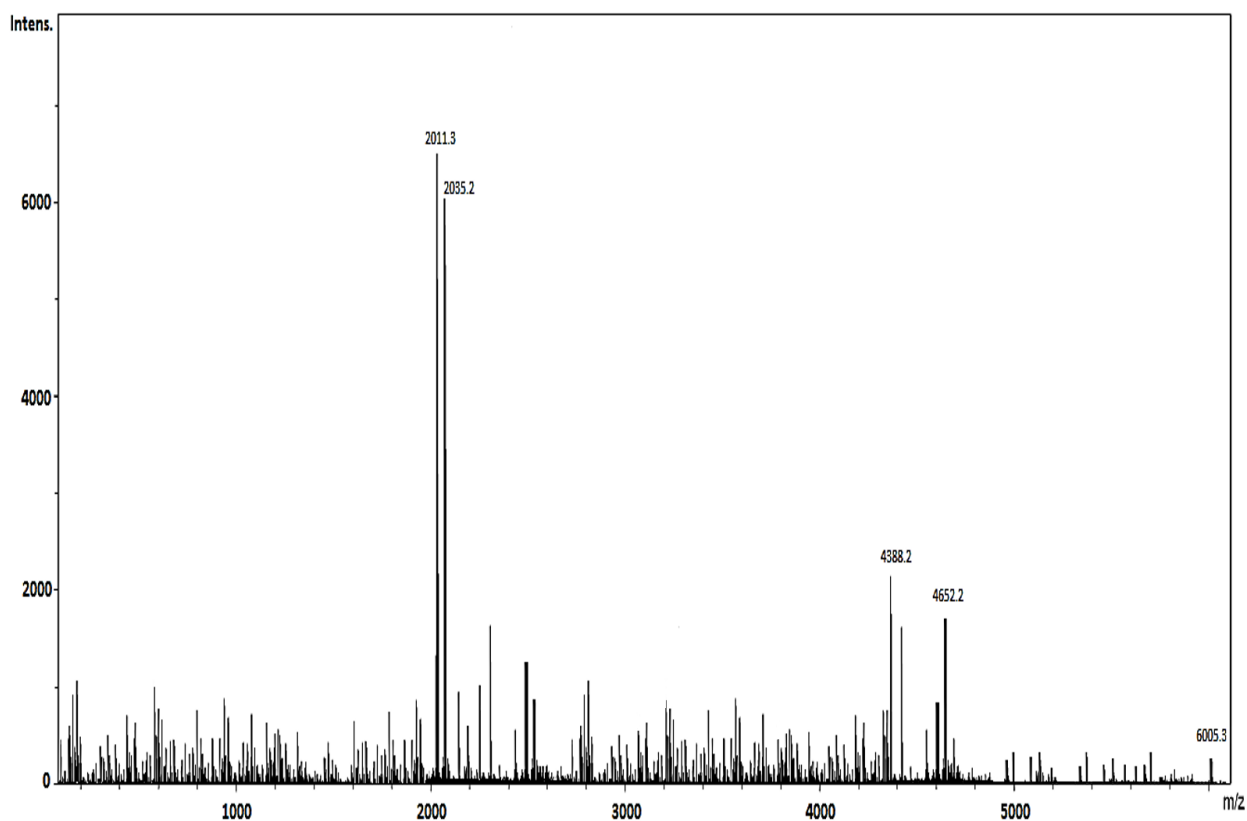
**Figure S2.24** Mass spectrum of **pillar**.



**Figure S2.25** Mass spectrum of **8-{4-(azidomethyl)phenyl}-2,6-diethyl-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene**.



**Figure S2.26** Mass spectrum of **chromophore**.



**Figure S2.27** Mass spectrum of LHC.

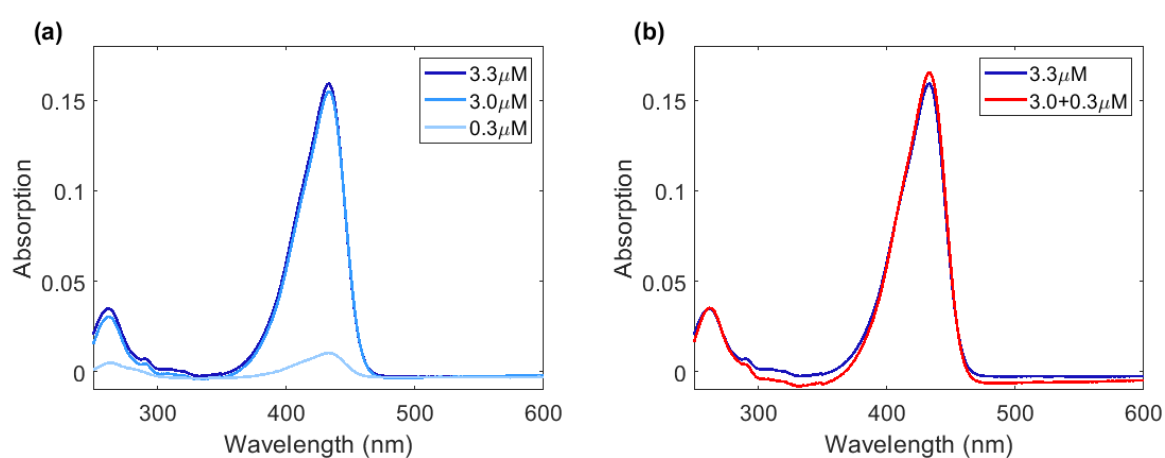
## S2.2. UV-visible spectroscopy

To compare the absorption spectra of the LHC to chromophores at molar equivalent concentrations, we conducted a control experiment using coumarin dissolved in dichloromethane (DCM) to determine whether the absorption of different concentrations of coumarin can be totalled to give the absorption spectrum of a solution at the summed concentration. Using the Beer-Lambert Law this can be shown to be true for two different concentrations denoted  $c_1$  and  $c_2$  of a compound with absorptions  $A_1$  and  $A_2$  respectively:

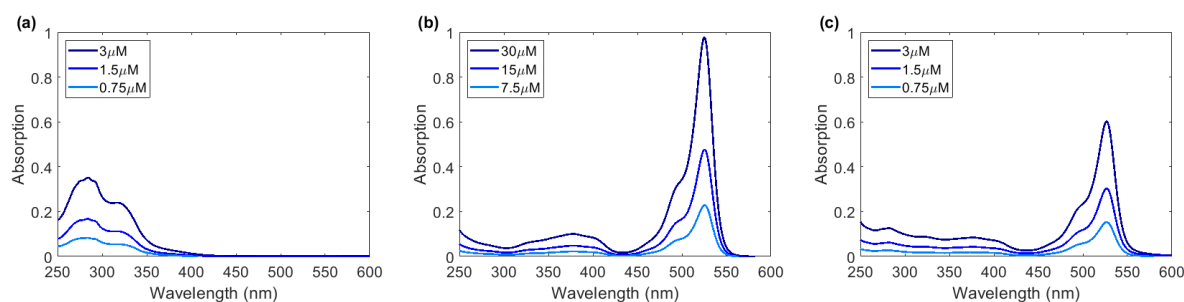
$$\begin{aligned}
 A_3 &= A_1 + A_2 & \mathbf{S2.1} \\
 &= \epsilon c_1 l + \epsilon c_2 l \\
 &= \epsilon c_3 l
 \end{aligned}$$

In **Equation S2.1**  $c_3$  is equivalent to adding the concentrations of Samples 1 and 2. The concentrations of coumarin solution analysed were 0.3  $\mu\text{M}$ , 3.0  $\mu\text{M}$ , and 3.3  $\mu\text{M}$ .

The choice of such concentrations allowed for us to ascertain whether the sum of the 0.3  $\mu\text{M}$  and 3.0  $\mu\text{M}$  absorption data results in the same absorption spectrum as that obtained from measuring the absorption of the 3.3  $\mu\text{M}$  solution directly. Absorption spectroscopy was performed using the Cary 5000 UV-Vis-NIR spectrophotometer in the UV-visible spectrum. The absorption spectra for the three concentrations of coumarin analysed show that the absorption of the 0.3  $\mu\text{M}$  and 3.0  $\mu\text{M}$  can be summed to give the absorption spectrum of the 3.3  $\mu\text{M}$  (**Figure S2.28**) as shown theoretically in **Equation S2.1**.

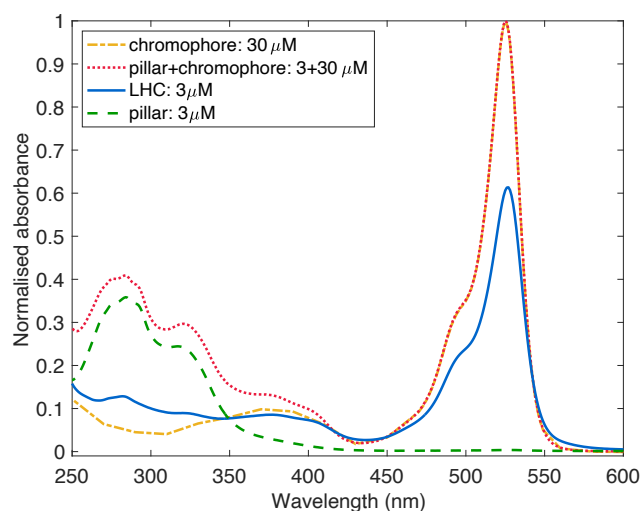


**Figure S2.28** Absorption peak for three concentrations of coumarin. The absorption peak for coumarin is evident at 433 nm. (b) The summed absorption for the 0.3  $\mu\text{M}$  and 3.0  $\mu\text{M}$  coumarin solutions.



**Figure S2.29** Absorption spectra for (a) pillar, (b) chromophore, and (c) LHC.

**Figure S2.30** illustrates the absorption spectra of the chromophore, pillar+chromophore, LHC and pillar. A 40 % reduction in absorption at 532 nm is observed for the LHC compared to the pillar+chromophore spectrum.

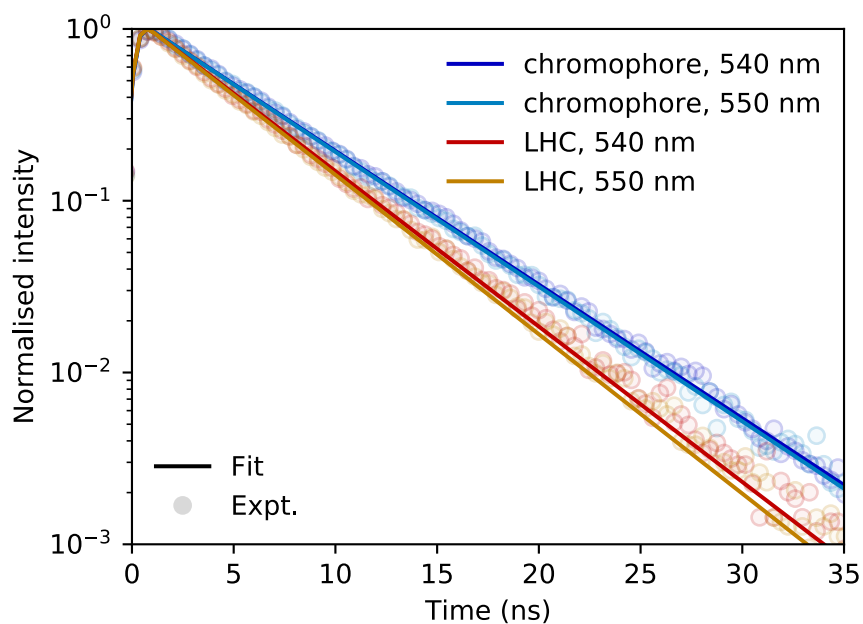


**Figure S2.30** Absorption spectra of LHC, pillar and chromophore. The pillar+chromophore spectrum (red) is the summation of the chromophore spectrum (yellow) and pillar spectrum (green). Each spectrum is normalised to the pillar+chromophore spectrum.

### S2.3. Time-resolved photoluminescence spectroscopy

Fluorescence lifetime data was obtained on a commercial spectrometer (Halcyone, Ultrafast Systems) configured in time-correlated single photon counting (TCSPC) mode. The 400 nm excitation light was generated by frequency doubling the 800 nm fundamental output from a Ti-sapphire oscillator (Tsunami, Spectra Physics) using a  $\beta$ -barium borate (BBO) crystal. The laser pulses had a duration of  $\sim 150$  fs and the repetition rate was reduced to 4 MHz using a pulse-picker. Samples were held in a 2-mm path-length quartz cuvette (21-Q-2, Starna Cells), diluted in acetone until the maximum absorbance was  $\sim 0.1$ , and stirred continuously during measurements. The excitation power was sufficiently low that the data did not exhibit dependence on pulse energy, nor was any photodegradation of the sample observed.





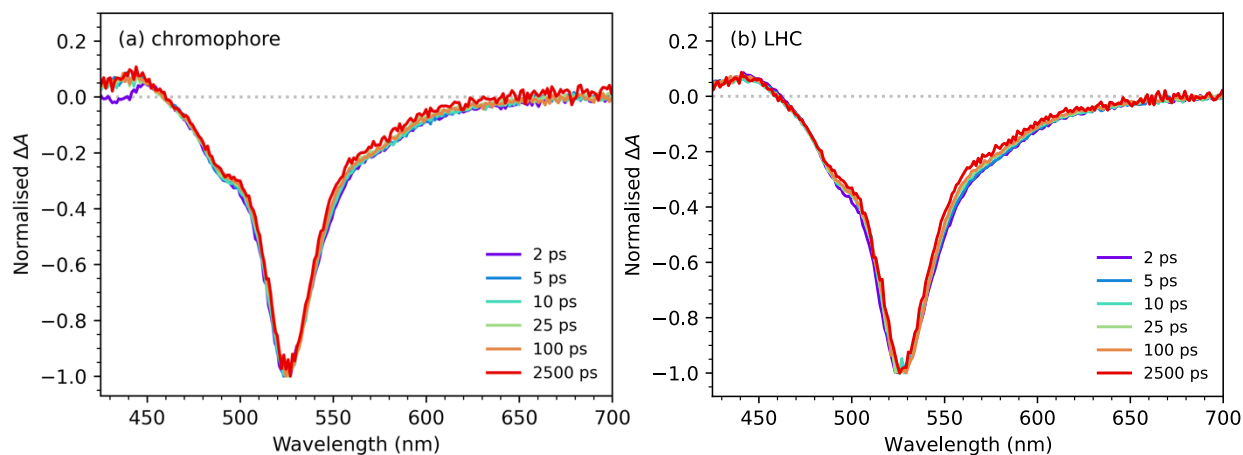
**Figure S2.31** Time-resolved fluorescence data for the chromophore and LHC at two different detection wavelengths. Data were collected using a time-correlated single photon counting (TCSPC) technique with a 400 nm excitation. Both samples fit to a single-exponential decay model (**Table S2.1**), with the LHC exhibiting a slightly shorter lifetime of the excited state. The effectively identical decay kinetics at each detection wavelength indicates there is minimal evolution (red-shifting) of the emission peaks during the experimental time window.

**Table S2.1** Fitting parameters for the TCSPC data shown in **Figure S2.31**. The monoexponential decay is modelled by fitting the fluorescence intensity as convoluted with an experimentally determined Gaussian instrument response function of 0.65 ns.

Sample	$\lambda$ (nm)	$\tau$ (ns)
Chromophore	540	5.6
Chromophore	550	5.5
LHC	540	4.8
LHC	550	4.7

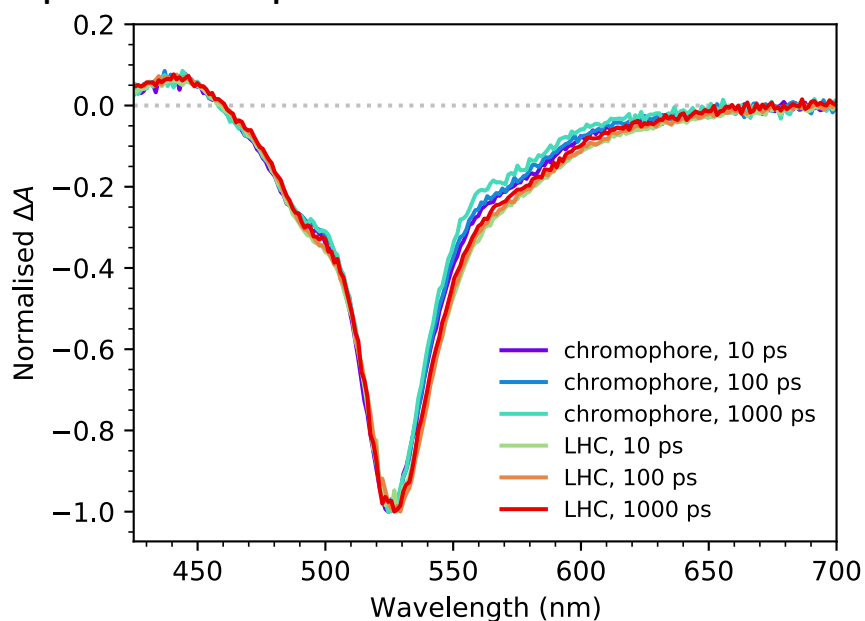
## S2.4. Transient absorption spectroscopy

### S2.4.1. Spectral evolution



**Figure S2.32** Transient absorption spectra for the (a) chromophore and (b) LHC at selected pump-probe delay times. Spectra are normalised to their minima at  $\sim 525$  nm corresponding to the ground-state bleach band. Negligible spectral evolution is observed for either sample in the time and spectral windows of the experiment.

### S2.4.2. Spectra of chromophore vs LHC

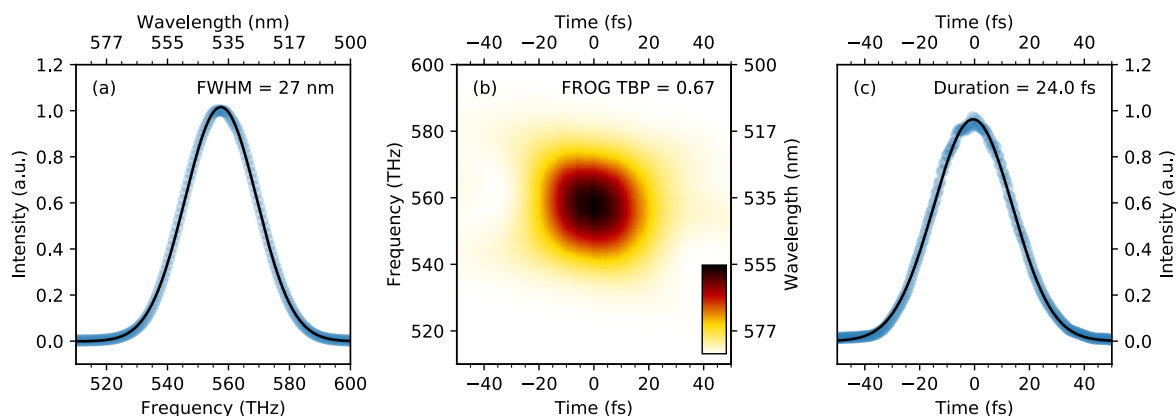


**Figure S2.33** Comparison of the transient absorption spectra for the chromophore and LHC at selected pump-probe delay times. Spectra are normalised to their minima at  $\sim 525$  nm corresponding to the ground-state bleach band.

## S2.5. Broadband pump-probe spectroscopy

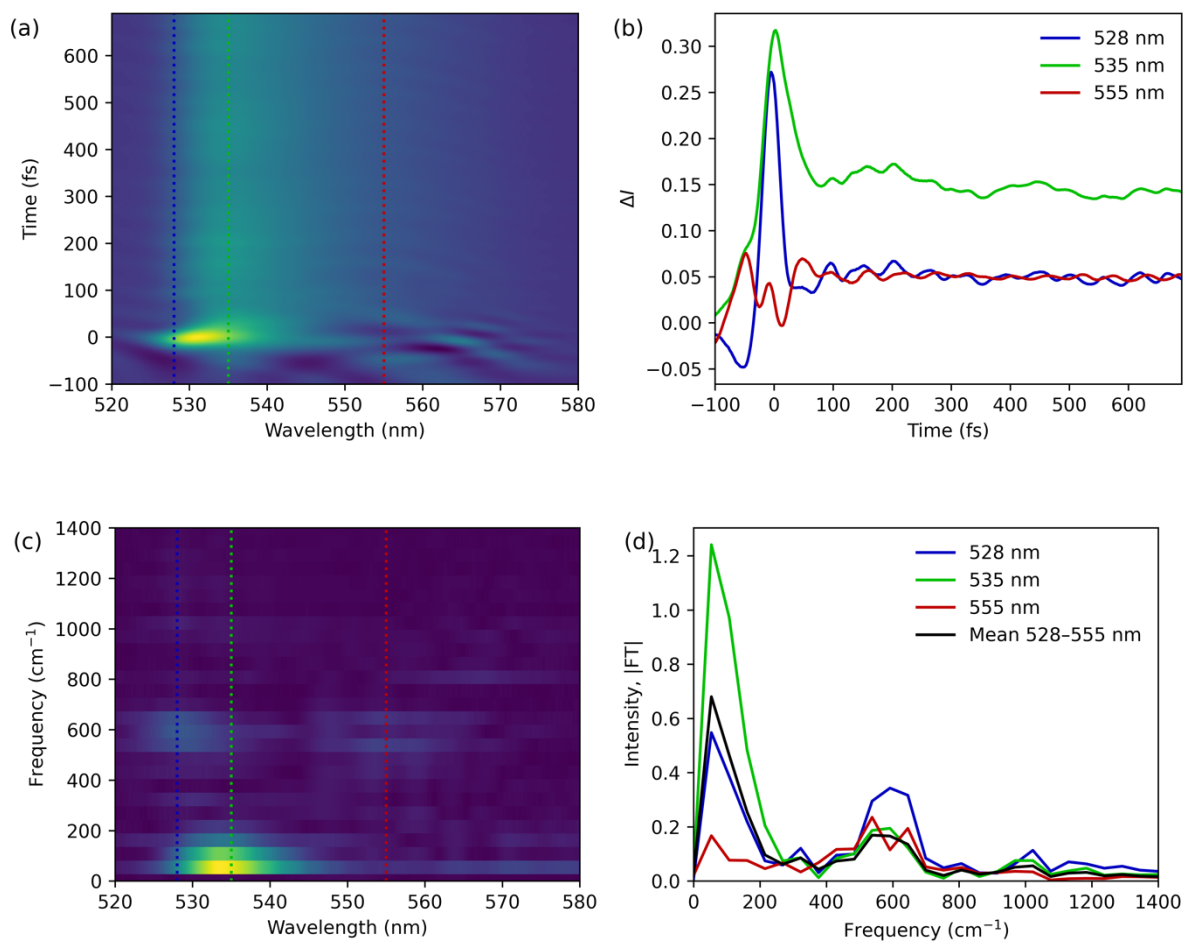
BBPP data for a solvent blank was taken to ensure any detected oscillation frequencies in the sample experiments were not due to the solvent. As shown in **Figures S2.35 to S2.37**, there is a distinct solvent signal present at  $800\text{ cm}^{-1}$ . **Figure 5** of the main text shows a comparison of the frequencies detected in the sample and solvent.

### S2.5.1. Pulse characterization



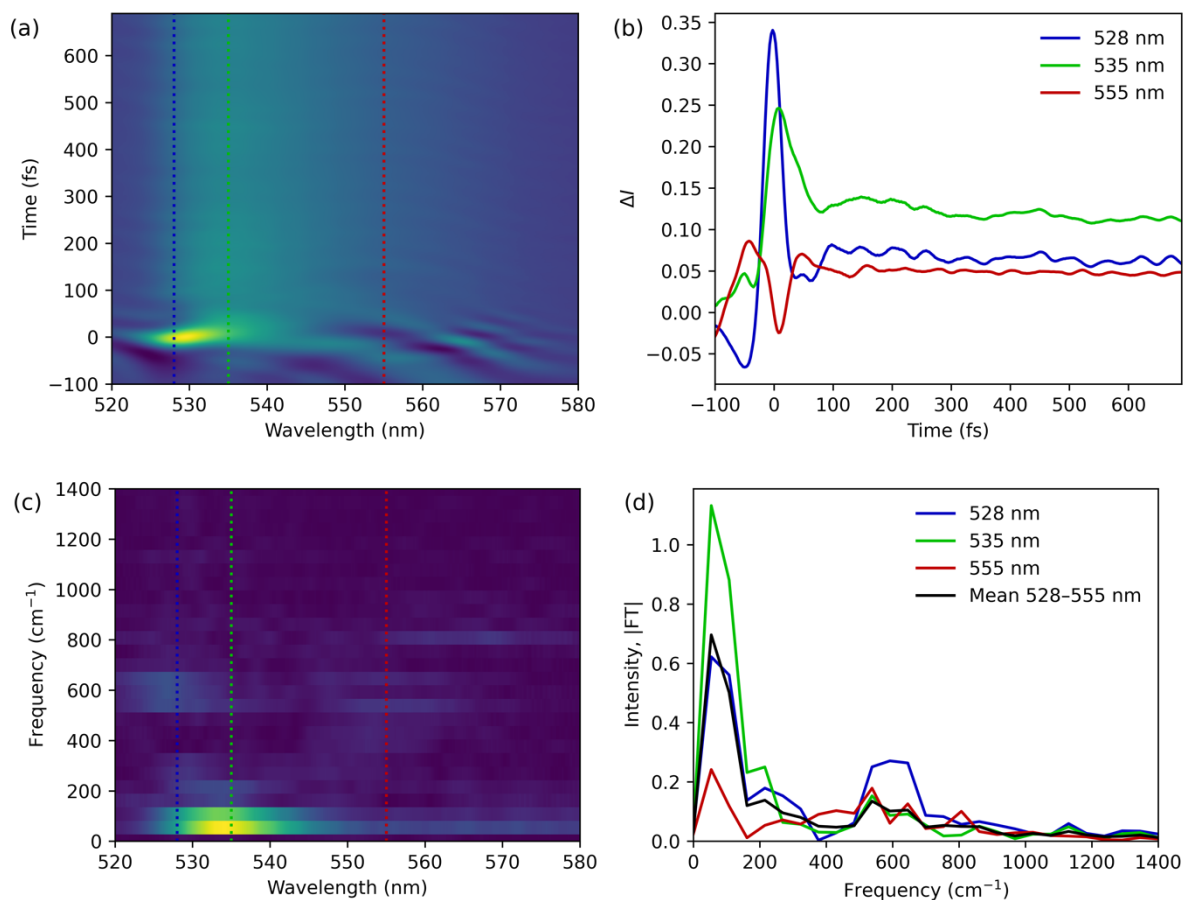
**Figure S2.34** Compressed laser pulse output from the non-collinear optical parametric amplifier (NOPA) used for the BBPP and 2DES experiments, characterised using frequency-resolved optical gating (FROG). The spectral bandwidth is 27 nm full-width at half-maximum (FWHM) with a pulse duration of 24 fs. TBP is time-bandwidth-product, where a theoretical minimum value of 0.44 is obtained for perfectly compressed (transform limited) Gaussian-shaped pulses.

## S2.5.2. Chromophore



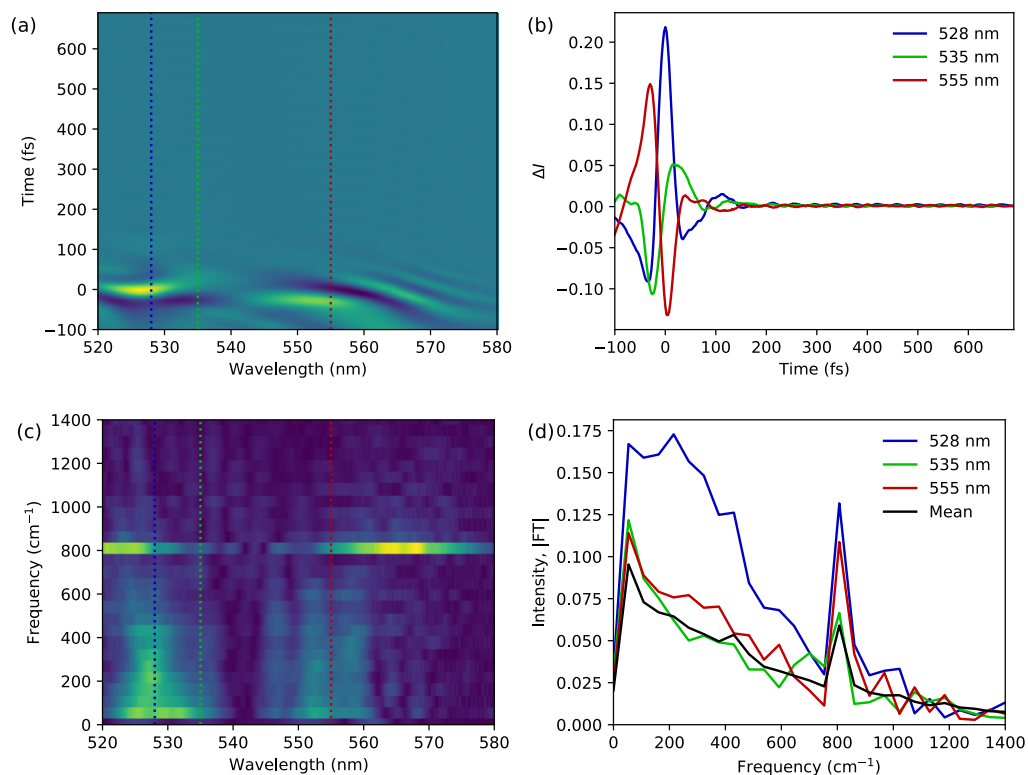
**Figure S2.35** (a) BBPP data for the chromophore shown in (a) and (b). The vertical dotted lines in (a) correspond to the kinetic slices at selected detection wavelengths shown in (b). Frequency analysis performed using Fourier transform is given in (c) and (d). Oscillations for the chromophore are observed at  $\sim 100 \text{ cm}^{-1}$  and  $600 \text{ cm}^{-1}$ . The black curve is the mean of all probe wavelengths between 528 nm and 555 nm.

### S2.5.3. LHC



**Figure S2.36** (a) BBPP data for the LHC shown in (a) and (b). The vertical dotted lines in (a) correspond to the kinetic slices at selected detection wavelengths shown in (b). Frequency analysis performed using Fourier transform is given in (c) and (d). Oscillations observed at  $\sim 100 \text{ cm}^{-1}$  and  $600 \text{ cm}^{-1}$  are attributed to the chromophore as shown in **Figure S2.35**. A low-intensity oscillation is observed at  $\sim 800 \text{ cm}^{-1}$  which corresponds to a known Raman mode of acetone.<sup>2</sup>

### S2.5.4. Acetone (solvent)



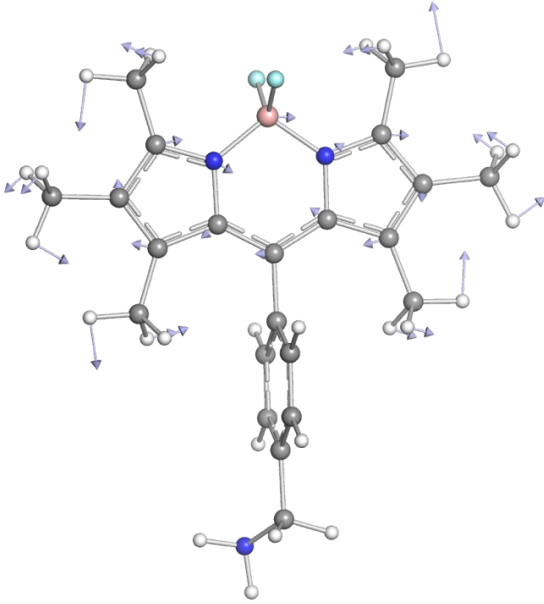
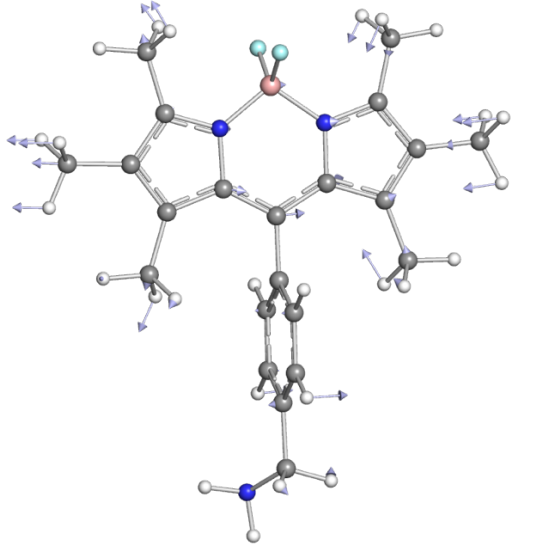
**Figure S2.37** BBPP data for the neat solvent (acetone) shown in (a) and (b). Kinetic slices are taken at selected wavelengths indicated by the vertical dotted lines and shown in (b). Frequency analysis performed using Fourier transform is given in (c) and (d). A distinct but low-intensity oscillation is observed at  $\sim 800 \text{ cm}^{-1}$  which corresponds to a known Raman mode of acetone.<sup>2</sup>

## S2.6. Harmonic frequencies of chromophore-T in 600 cm<sup>-1</sup> range

From the harmonic frequency analysis of the equilibrium structure of chromophore-T, vibrational frequencies with corresponding IR intensities are given in **Table S2.2**. The two vibrational modes with highest computed IR frequencies within the 500 cm<sup>-1</sup> to 700 cm<sup>-1</sup> range are shown in **Figure S2.38**.

**Table S2.2.** Harmonic frequencies of chromophore-T at 500 cm<sup>-1</sup> to 700cm<sup>-1</sup> range, and calculated IR intensities in arbitrary units

Frequency / cm <sup>-1</sup>	IR intensities / arbitrary units
526.8	1.6
540.9	2.8
556.9	32.6
565.4	4.4
567.5	3.3
599.5	2.1
627.1	0.2
649.9	2.4
665.0	0.2
688.8	0.8
695.1	0.8
698.9	17.8

	<p>Freq: 556.9 IR intensity: 32.6</p>
	<p>Freq: 698.9 IR intensity: 17.8</p>

**Figure S2.38.** Vibration modes of chromophore-T for frequencies 556.9 and 698.9  $\text{cm}^{-1}$ .

## References

1. A. N. Kursunlu and C. Baslak, *Tetrahedron Letters*, 2018, **59**, 1958-1962.
2. L. Jensen, P. M. Mortensen, R. Trane, P. Harris and R. W. Berg, *Applied Spectroscopy*, 2009, **63**, 92-97.