

# SUPPORTING INFORMATION

## *“Synthesis and properties of nitrogen-bridged dimers of boron subphthalocyanines”*

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### CONTENTS

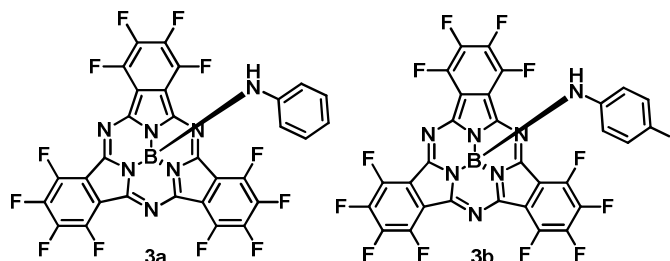
1. Experimental Section. General Information.	S2
2. Synthesis and characterization of compounds	S3
3. Copies of <sup>1</sup> H and <sup>13</sup> C NMR spectra	S6
4. Copies of MS and HRMS spectra	S9
5. <sup>19</sup> F NMR spectra ( <b>Figure S1</b> )	S15
6. Absorption and Emission Spectra in different solvents ( <b>Figure S2</b> )	S16
7. Quantum yield calculation	S17

## 1. Experimental Section

**General Information.** Chemicals were purchased from commercial suppliers and used without further purification. Solid, hygroscopic reagents were dried in a vacuum oven before use. Reaction solvents were thoroughly dried before use using standard methods. Column chromatography was carried out on silica gel *Merck-60* (230-400 mesh, 60 Å), and TLC on aluminium sheets precoated with silica gel 60 F254 (Merck). UV/Vis spectra were recorded with a *JASCO V-660* at room temperature. Emission spectra were obtained with a *JASCO-V8600* at room temperature. MALDI-TOF-MS spectra were obtained from a *BRUKER ULTRAFLEX III* instrument equipped with a nitrogen laser operating at 337 nm. NMR spectra were recorded with a *BRUKER AC-300* (300 MHz) instrument. The temperature was actively controlled at 298 K. Chemical shifts are measured in ppm using the signals of the deuterated solvent as the internal standard [ $\text{CHCl}_3$ , calibrated at 7.26 ppm ( $^1\text{H}$ ) and 77.0 ppm ( $^{13}\text{C}$ )]. Electrochemical measurements were performed on an Autolab PGStat 30 equipment using a three electrode configuration system. The measurements were carried out using THF solutions containing 0.1 M tetrabutylammonium hexafluorophosphate ( $\text{TBAPF}_6$ ). A platinum electrode was used as the working electrode, a platinum wire was employed as the counter electrode and an  $\text{Ag}/\text{AgNO}_3$  (in  $\text{CH}_3\text{CN}$ ) was used as the reference electrode. Ferrocene (Fc) was added as an internal reference and all the potentials are given relative to the  $\text{Fc}/\text{Fc}^+$  couple. The synthesis and characterization of the subphthalocyanines and (dodecafluoro)SubPcBCl,<sup>1</sup> hexa(dodecylthio)SubPcBCl,<sup>2</sup> and (triiodo)SubPcBCl<sup>3</sup> have been previously reported.

## 2. Synthesis and characterization of compounds

### SubPc 3 (a-b)



In a 25-mL round-bottomed flask, equipped with a magnetic stirrer, **(F)<sub>12</sub>-SubPcBCl** (50 mg, 0.077 mmol, 1 equiv.) and silver trifluoromethanesulfonate (26 mg, 0.100 mmol, 1.3 equiv.) were placed. Dry toluene (2 mL) was added and the mixture was stirred for 24 h under argon atmosphere until the starting subphthalocyanine is consumed. After that time aniline (**3a**) or 4-iodoaniline (**3b**) (0.154 mmol, 2 equiv.) and *N,N*-Diisopropylethylamine (0.096 mmol, 1.25 equiv) were added. The mixture was stirred at 100 °C until the reaction is completed (the reaction is monitored by TLC). The solvent was removed by evaporation under reduced pressure and the product was purified by chromatography on silica gel using as eluent toluene. It was recrystallized from DCM/methanol to afford compound **3a** and **3b** as a magenta solids in 74 and 80 % yield, respectively.

#### (3a)

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) = 6.79 (t, *J*<sub>o</sub> = 7.9 Hz, 2H), 6.43 (t, *J*<sub>o</sub> = 7.4 Hz, 1H), 5.04 (d, *J*<sub>o</sub>' = 7.6 Hz, 2H).

<sup>13</sup>C-NMR (75.5 MHz, CDCl<sub>3</sub>): δ (ppm) = 149.0, 143.3, 142.8, 142.7, 142.6, 129.4, 118.1, 115.1, 114.9, 114.6, 114.2.

**MS (MALDI-TOF, DCTB):** *m/z* = 703.1 [M]<sup>+</sup> (100%).

**HR-MS** (C<sub>30</sub>H<sub>6</sub>BF<sub>12</sub>N<sub>6</sub>) [M]<sup>+</sup>: Calculated: 703.0586; Found: 703.0614.

#### (3b)

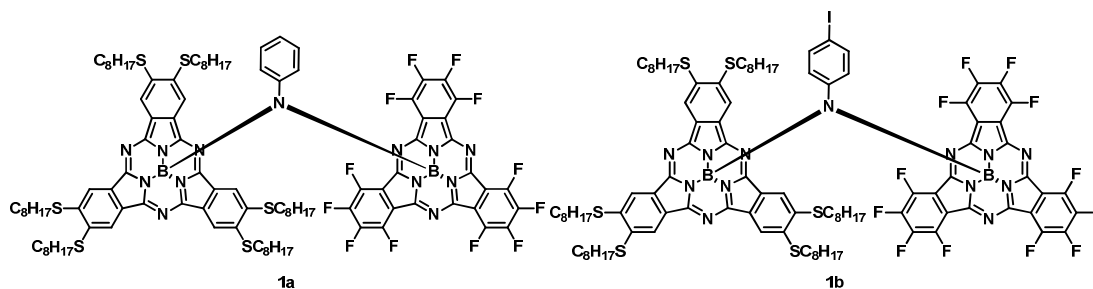
<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) = 7.03 (d, *J*<sub>o</sub> = 8.7 Hz, 2H), 4.81 (d, *J*<sub>o</sub> = 8.7 Hz, 2H).

<sup>13</sup>C-NMR (75.5 MHz, CDCl<sub>3</sub>): δ (ppm) = 149.0, 144.5, 144.4, 144.3, 144.2, 142.4, 141.1, 140.8, 140.8, 137.9, 116.5, 115.1, 114.9, 114.9.

**MS (MALDI-TOF, DCTB):** *m/z* = 829.0 [M]<sup>+</sup> (100%).

**HR-MS** (C<sub>30</sub>H<sub>5</sub>BF<sub>12</sub>IN<sub>6</sub>) [M]<sup>+</sup>: Calculated: 828.9553; Found: 828.9534.

## Dimers 1 (a-b)



In a 25-mL round-bottomed flask, equipped with a magnetic stirrer, **(SC<sub>8</sub>H<sub>17</sub>)<sub>6</sub>-SubPcBCl** (50 mg, 0.032 mmol, 1 equiv.) and silver trifluoromethanesulfonate (10.8 mg, 0.042 mmol, 1.3 equiv.) were placed. Dry toluene (2 mL) was added and the mixture was stirred for 45 minutes under argon atmosphere until the starting subphthalocyanine **5** is consumed and the triflate analogue is formed. After that time **3a** or **3b** (0.042 mmol, 1 equiv.) and *N,N*-Diisopropylethylamine (0.052 mmol, 1.25 equiv) were added. The mixture was stirred at 90 °C until the reaction is completed (the reaction is monitored by TLC). The solvent was removed by evaporation under reduced pressure and the product was purified by chromatography on silica gel using as eluent toluene/hexane (5:4). It was recrystallized from DCM/methanol to afford compound **1a** and **1b** as a magenta solids in 40 and 53 % yield, respectively.

### (1a)

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.39 (s, 6H), 6.85 (t, *J*<sub>o</sub> = 7.3 Hz, 1H), 6.53 (t, *J*<sub>o</sub>' = 7.6 Hz, 2H), 4.25 (d, *J*<sub>o</sub>' = 7.5 Hz, 2H), 3.49-3.02 (m, 12H), 2.03-1.72 (m, 12H), 1.60 (m, 12H), 1.50-1.15 (m, 48H), 0.88 (m, 18H).

<sup>13</sup>C-NMR (75.5 MHz, CDCl<sub>3</sub>): δ (ppm) = 150.2, 147.8, 144.0, 143.8, 143.6, 143.4, 140.2, 138.9, 138.9, 134.3, 128.9, 128.4, 127.8, 125.9, 118.5, 114.8, 114.5, 114.2, 33.7, 32.0, 29.3, 29.3, 28.5, 22.8, 14.3.

**MS (MALDI-TOF, DCTB):** *m/z* = 1962.7 [M]<sup>+</sup> (100%).

**HR-MS** (C<sub>102</sub>H<sub>113</sub>B<sub>2</sub>F<sub>12</sub>N<sub>13</sub>S<sub>6</sub>) [M]<sup>+</sup>: Calculated: 1962.7598; Found: 1962.7569

### (1b)

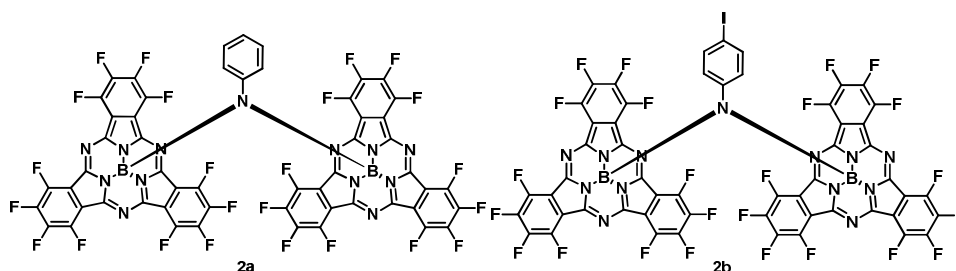
<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.37 (s, 6H), 6.81 (d, *J*<sub>o</sub> = 8.0 Hz, 2H), 4.03 (d, *J*<sub>o</sub> = 8.3 Hz, 2H), 3.42-3.03 (m, 12H), 1.87 (m, 12H), 1.77-1.09 (m, 60H), 0.88 (m, 18H).

<sup>13</sup>C-NMR (75.5 MHz, CDCl<sub>3</sub>): δ (ppm) = 150.3, 140.5, 127.8, 77.2, 77.1, 33.7, 32.2, 32.0, 29.4, 28.6, 26.9, 22.8, 14.3.

**MS (MALDI-TOF, DCTB):** *m/z* = 2088.6 [M]<sup>+</sup> (100%).

**HR-MS** (C<sub>102</sub>H<sub>112</sub>B<sub>2</sub>F<sub>12</sub>IN<sub>13</sub>S<sub>6</sub>) [M]<sup>+</sup>: Calculated: 2087.6549; Found: 2087.6557.

## Dimers 2 (a-b)



In a 25-mL round-bottomed flask, equipped with a magnetic stirrer, **F<sub>12</sub>-SubPc-Cl** (50 mg, 0.077 mmol, 1 equiv.) and silver trifluoromethanesulfonate (26 mg, 0.100 mmol, 1.3 equiv.) were placed. Dry toluene (2 mL) was added and the mixture was stirred for 24 hours under argon atmosphere until the starting subphthalocyanine is consumed. After that time **3a** or **3b** (0.042 mmol, 1 equiv.) and *N,N*-Diisopropylethylamine (0.052 mmol, 1.25 equiv) were added. The mixture was stirred at 90 °C until the reaction is completed (the reaction is monitored by TLC). The solvent was removed by evaporation under reduced pressure and the product was purified by chromatography on silica gel using as eluent DCM/hexane (3:1). It was recrystallized from DCM/methanol to afford compound **2a** and **2b** as a magenta solids in 15 and 30 % yield, respectively. Big amount of  $\mu$ -oxo dimer was formed during this reaction.

### (2a)

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 6.74 (t,  $J_o = 7.4$  Hz, 1H), 6.52 (t,  $J_o' = 7.7$  Hz, 2H), 4.31 (d,  $J_o = 7.3$  Hz, 2H).

<sup>13</sup>C-NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 147.9, 135.3, 134.9, 134.5, 128.9, 127.6, 120.8, 116.6, 116.3, 113.6, 112.8, 77.2.

MS (MALDI-TOF, DCTB):  $m/z = 1313.1$  [M]<sup>+</sup> (100%).

HR-MS (C<sub>54</sub>H<sub>5</sub>B<sub>2</sub>F<sub>24</sub>N<sub>13</sub>) [M]<sup>+</sup>: Calculated: 1313.0594; Found: 1313.0599.

### (2b)

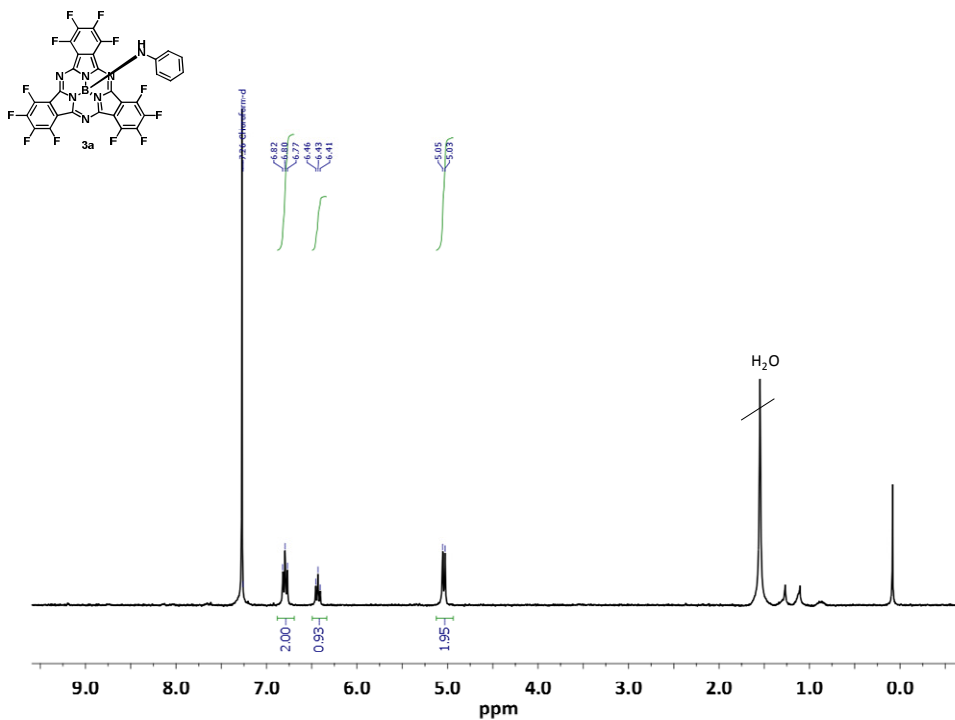
<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 6.83 (d,  $J_o = 8.3$  Hz, 2H), 4.09 (d,  $J_o = 8.3$  Hz, 2H).

<sup>13</sup>C-NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 147.7, 144.3, 144.0, 140.7, 140.5, 139.6, 139.3, 138.0, 129.5, 124.9, 114.2.

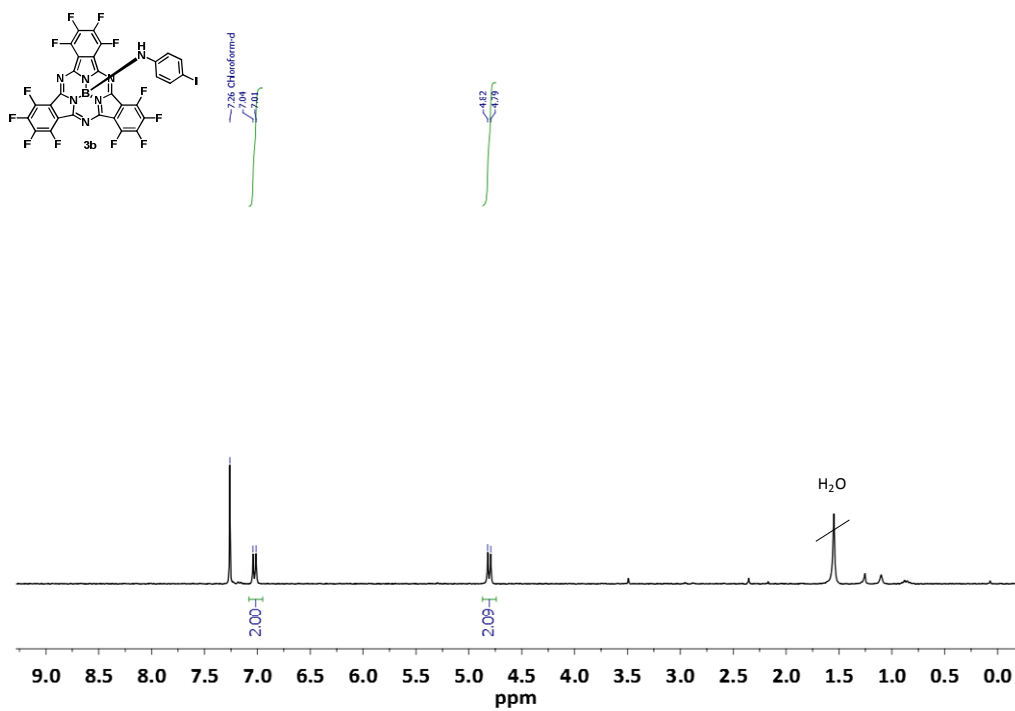
MS (MALDI-TOF, DCTB):  $m/z = 1439.0$  [M]<sup>+</sup> (100%).

HR-MS (C<sub>54</sub>H<sub>4</sub>B<sub>2</sub>F<sub>24</sub>I<sub>1</sub>N<sub>13</sub>) [M]<sup>+</sup>: Calculated: 1438.9571; Found: 1438.9587.

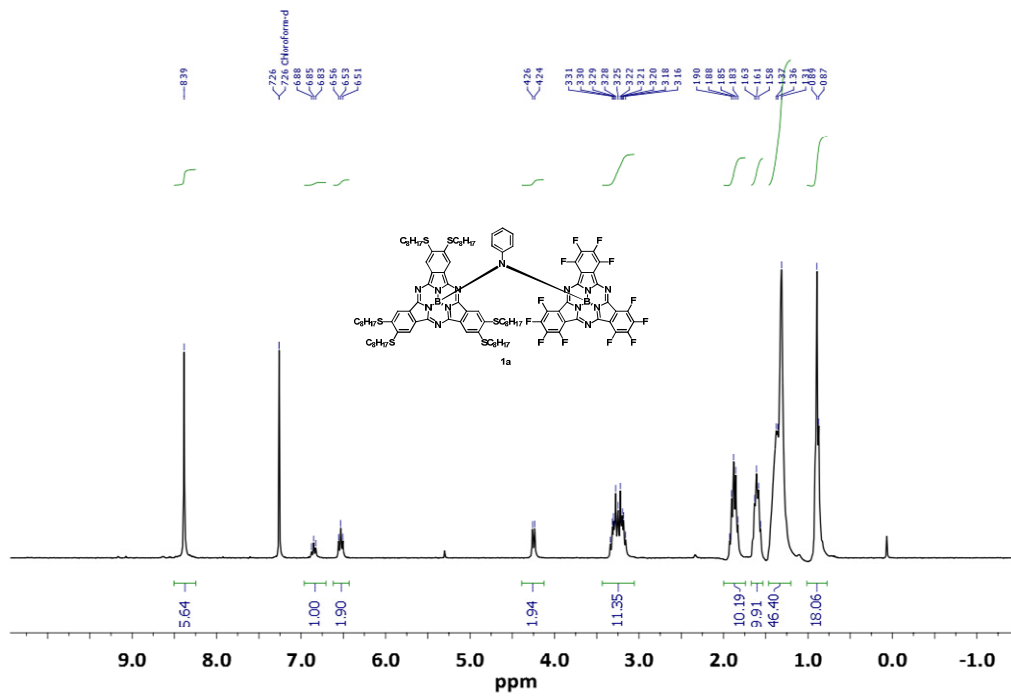
### 3. Copies of $^1\text{H}$ NMR spectra



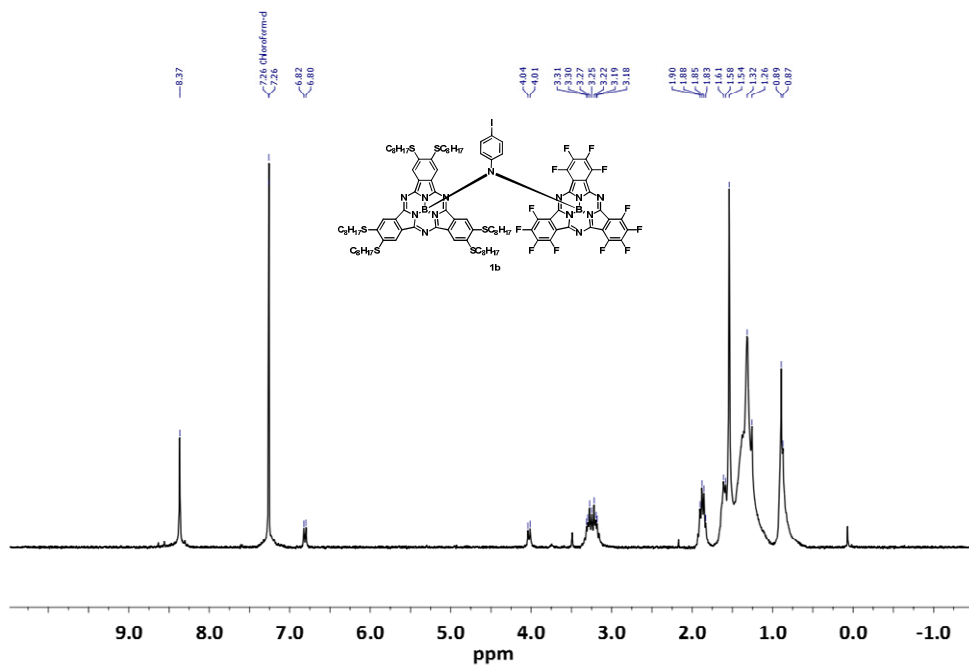
$^1\text{H}$  NMR spectra of 3a



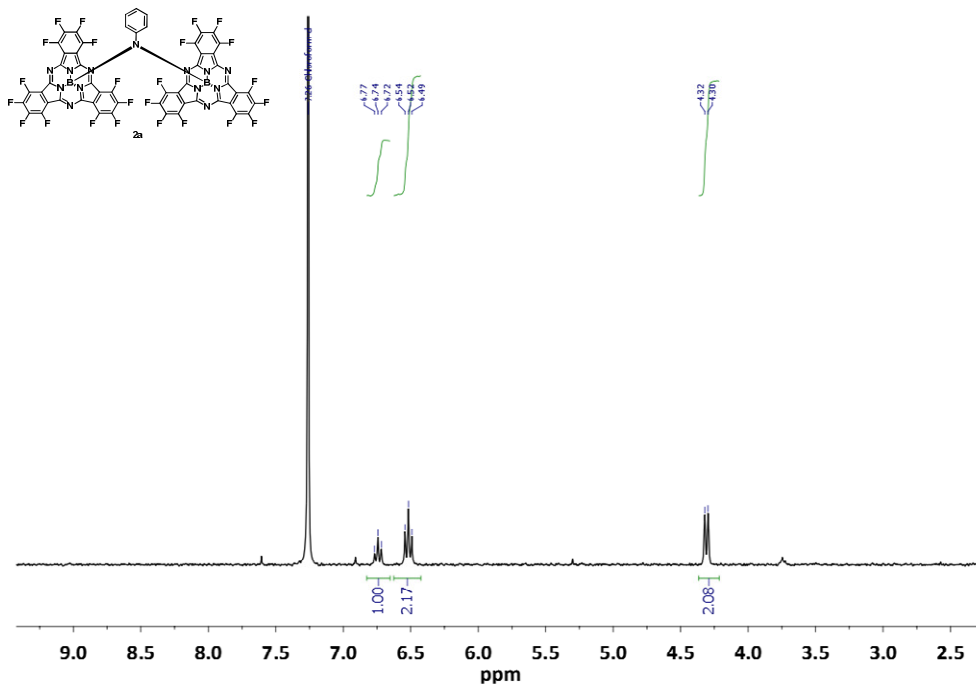
$^1\text{H}$  NMR spectra of 3b



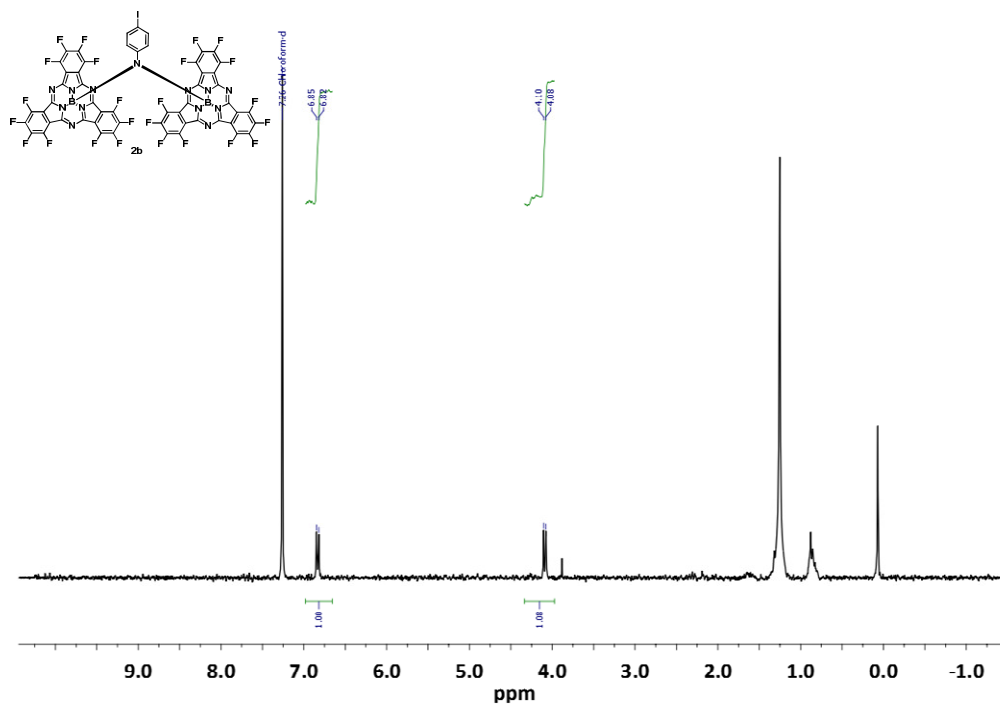
$^1\text{H}$  NMR spectra of **1a**



$^1\text{H}$  NMR spectra of **1b**



$^1\text{H}$  NMR spectra of **2a**

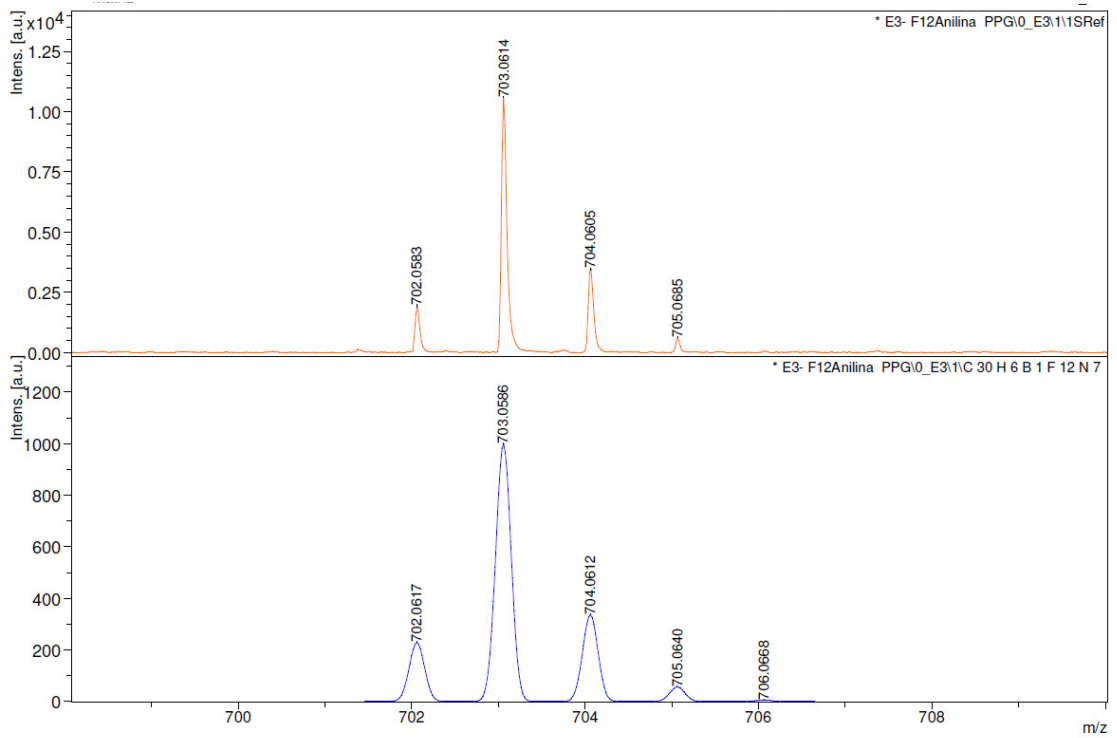
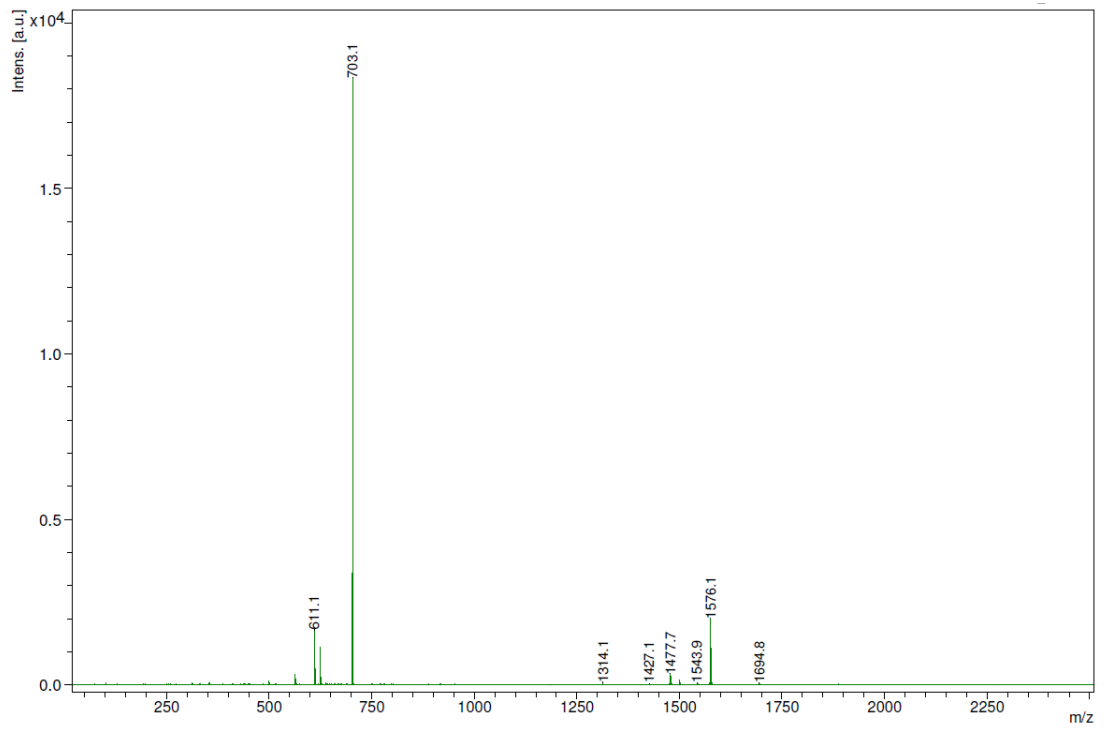


$^1\text{H}$  NMR spectra of **2b**

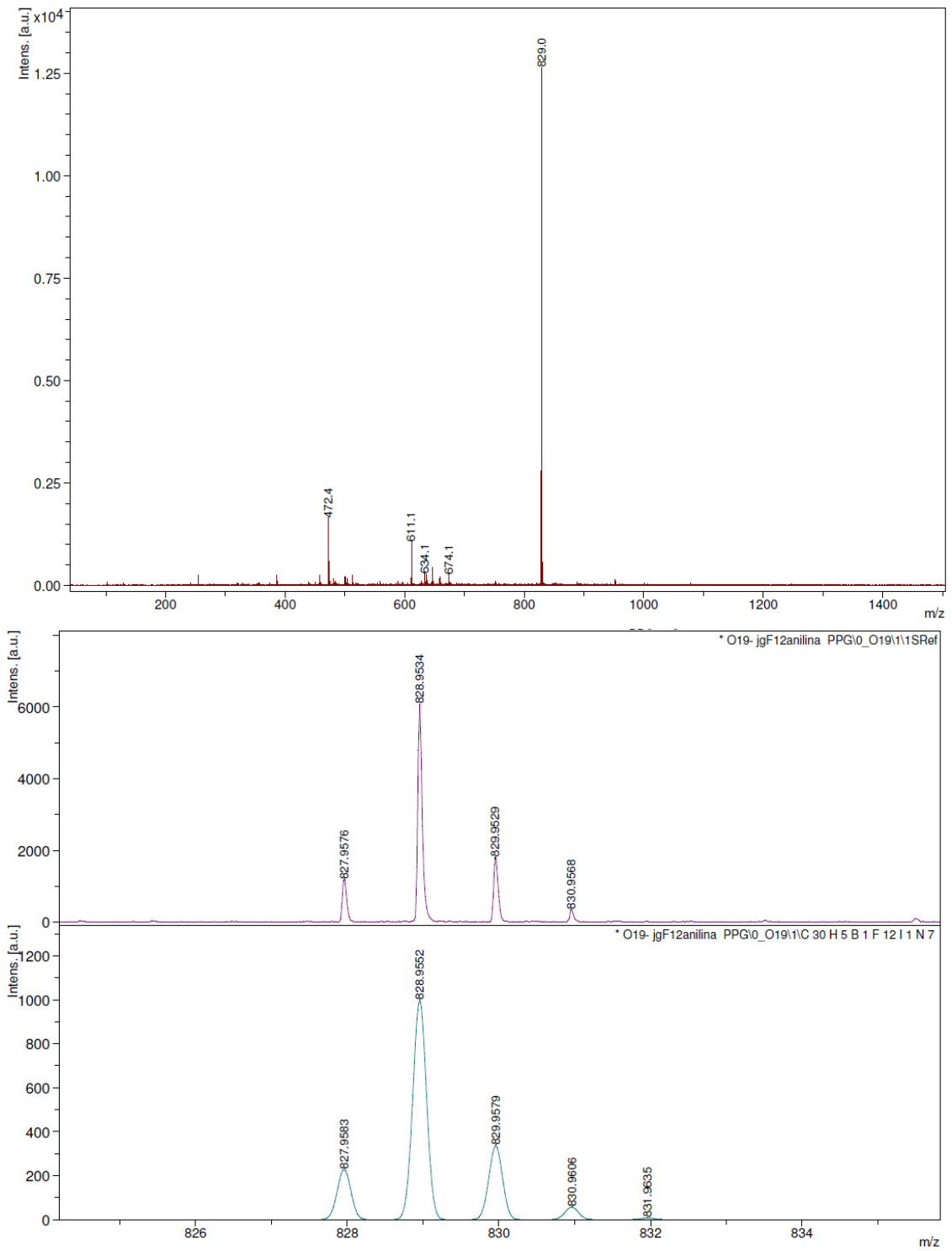


#### 4. Copies of MS and HRMS

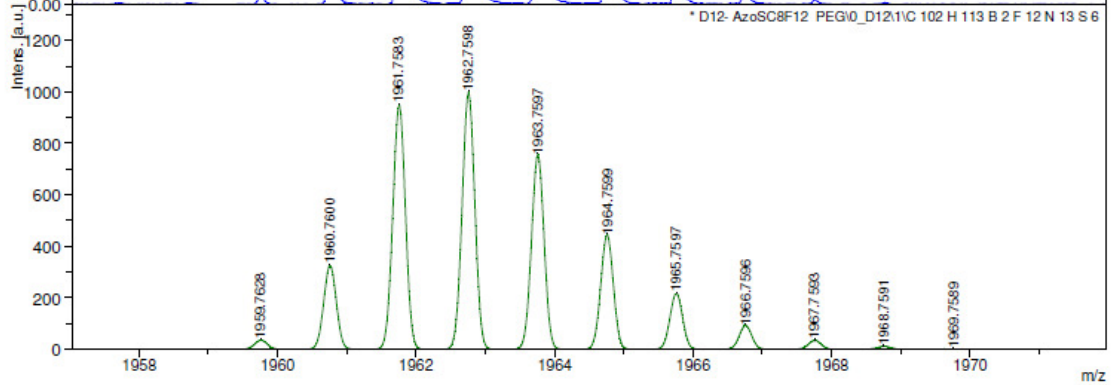
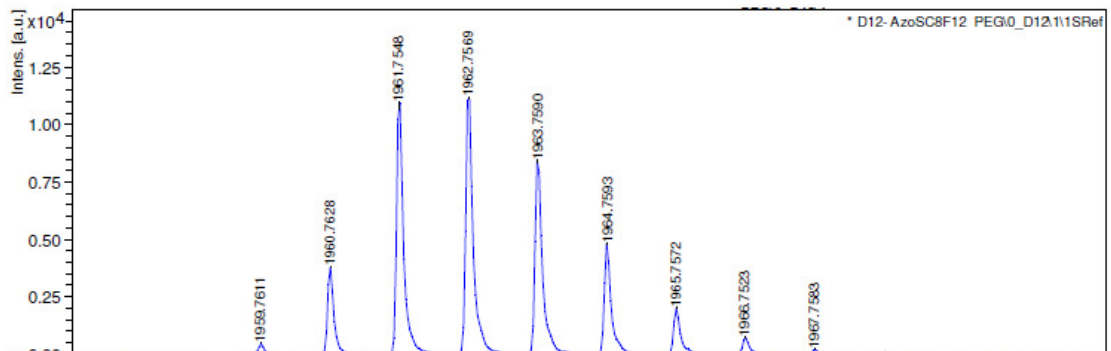
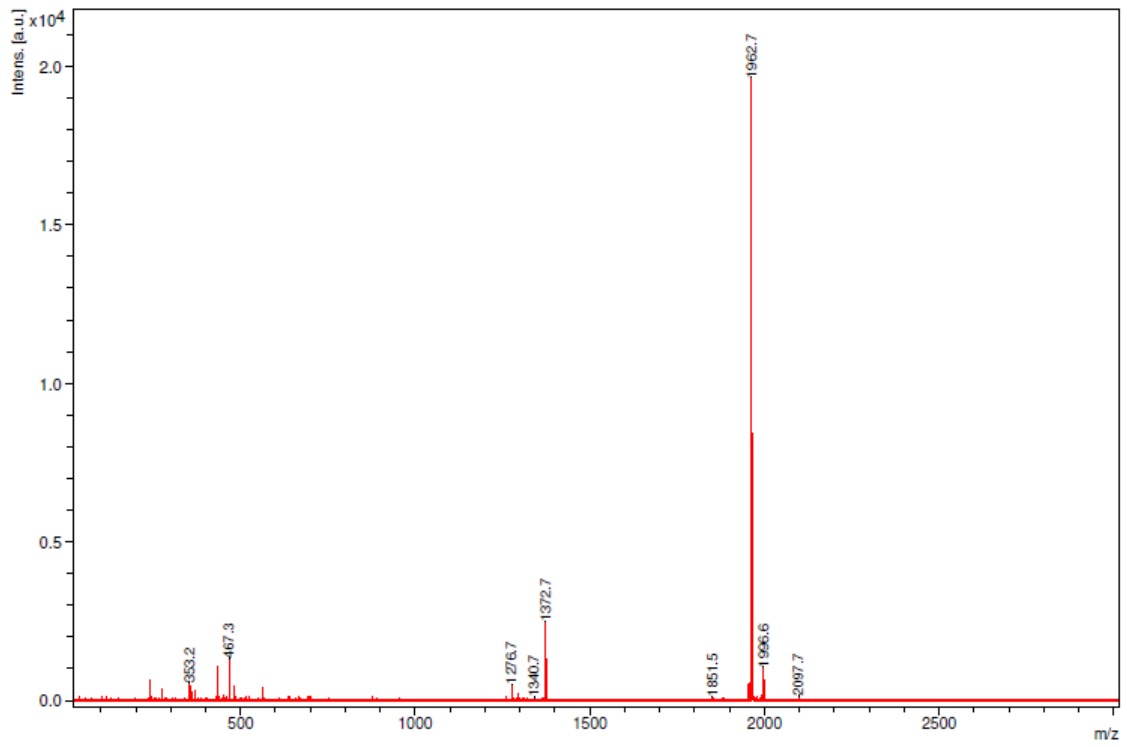
##### MS and HR-MS spectra of **3a**



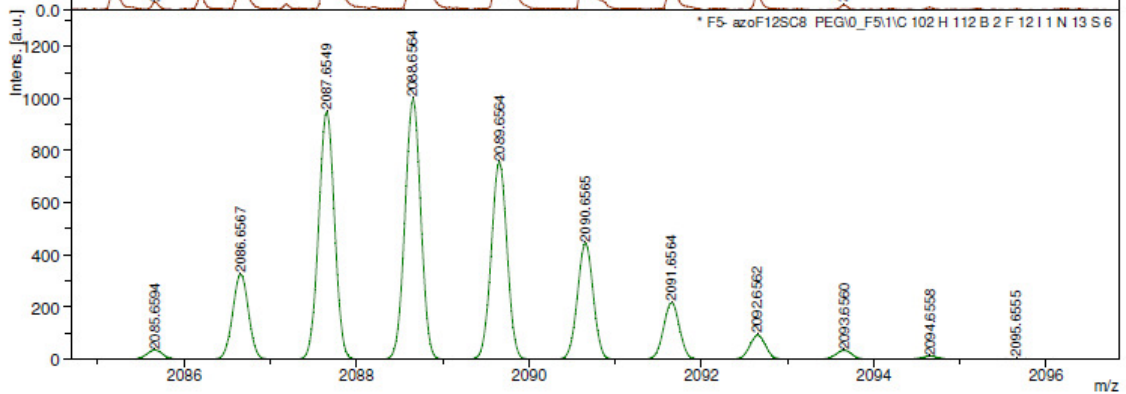
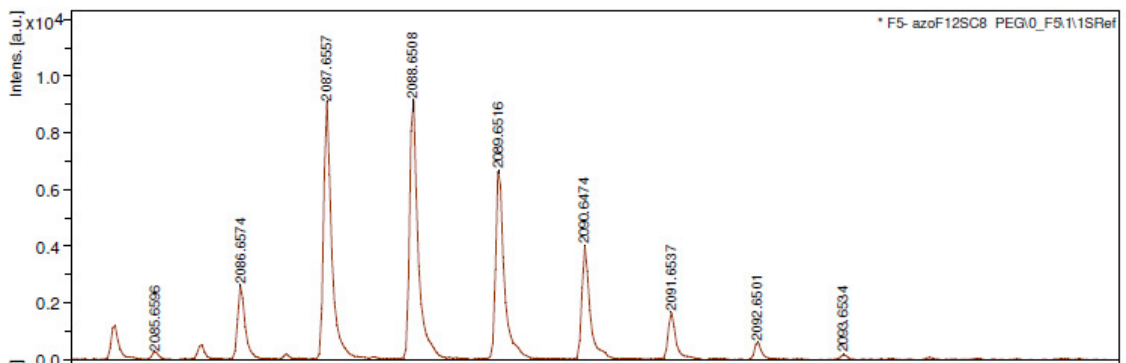
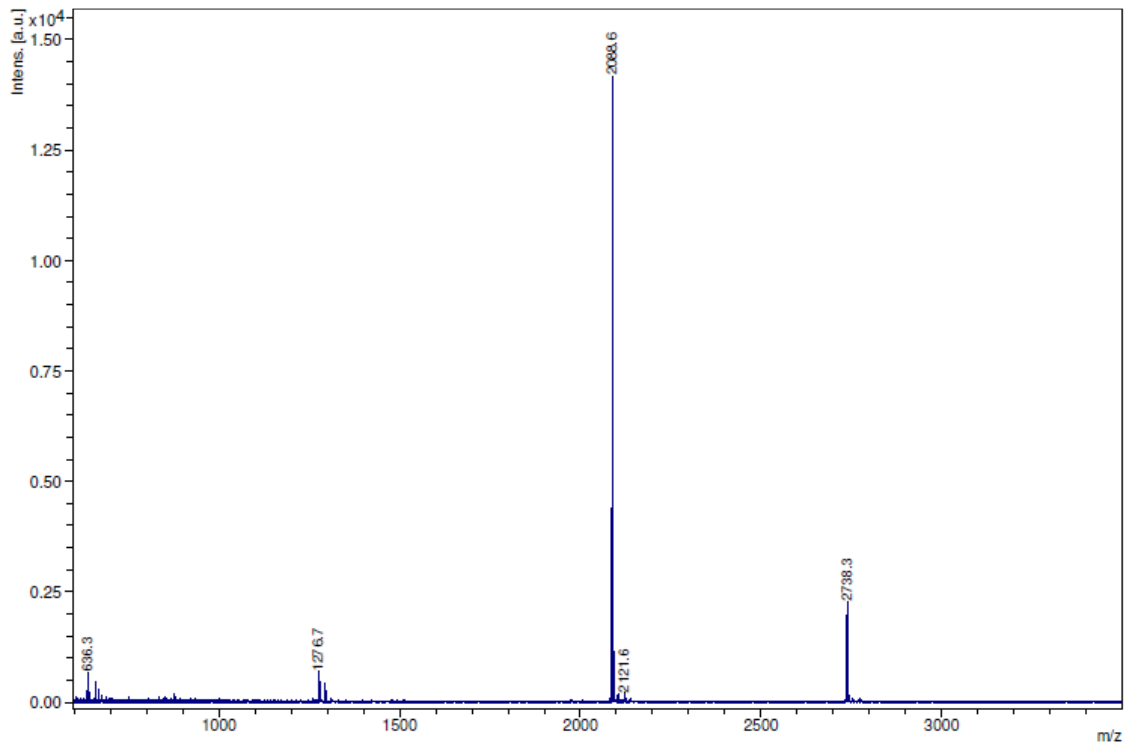
### MS and HR-MS spectra of **3b**



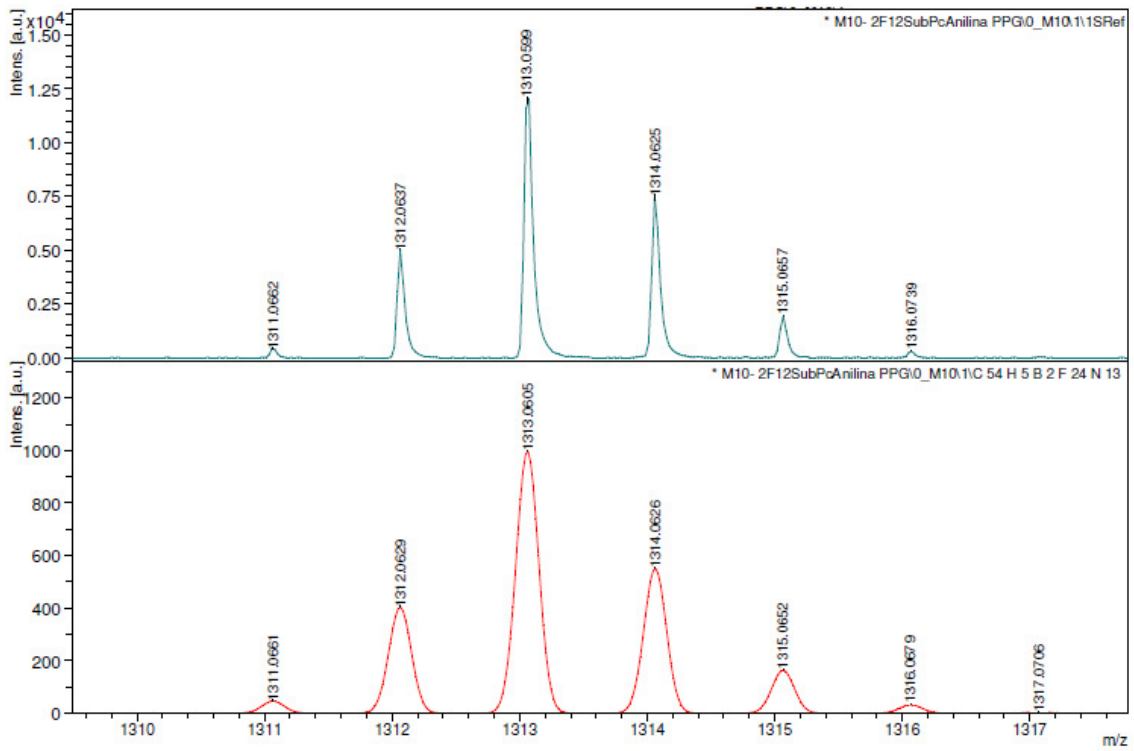
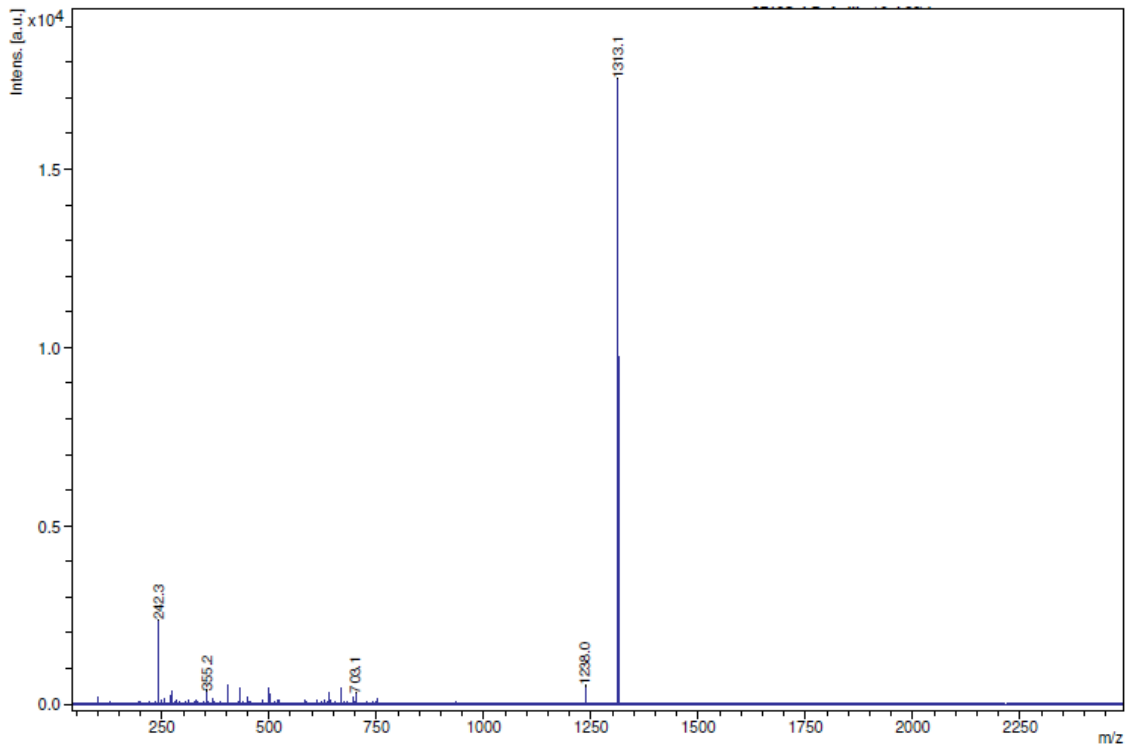
# MS and HR-MS spectra of **1a**



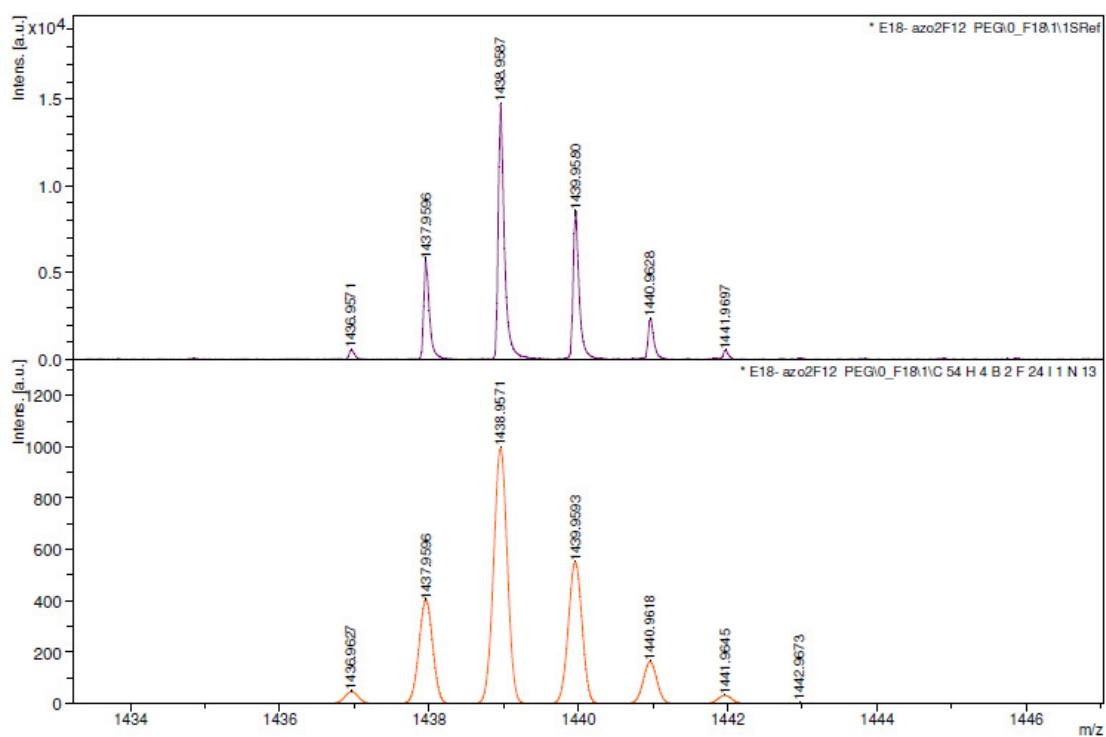
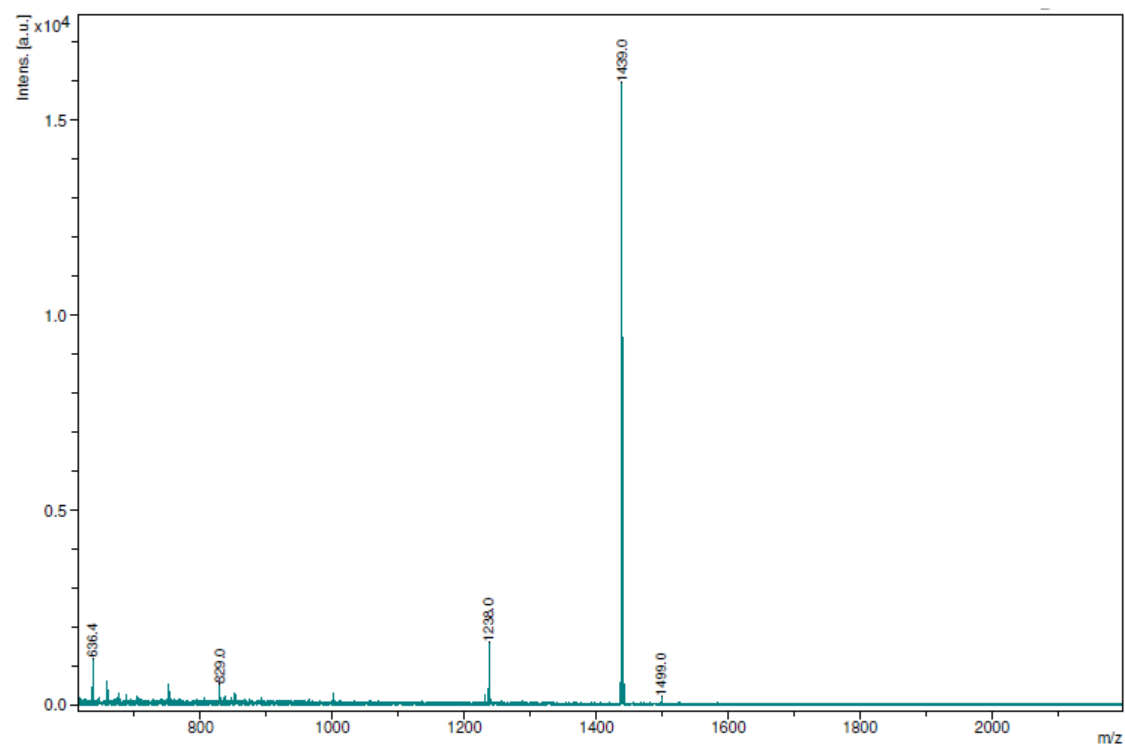
### MS and HR-MS spectra of **1b**



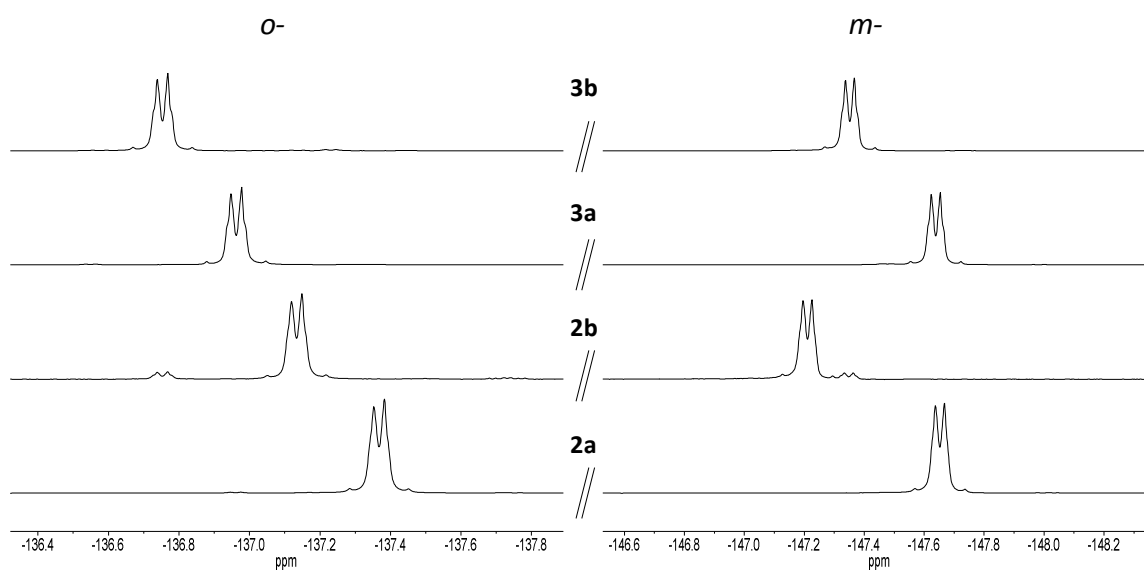
### MS and HR-MS spectra of **2a**



## MS and HR-MS spectra of **2b**

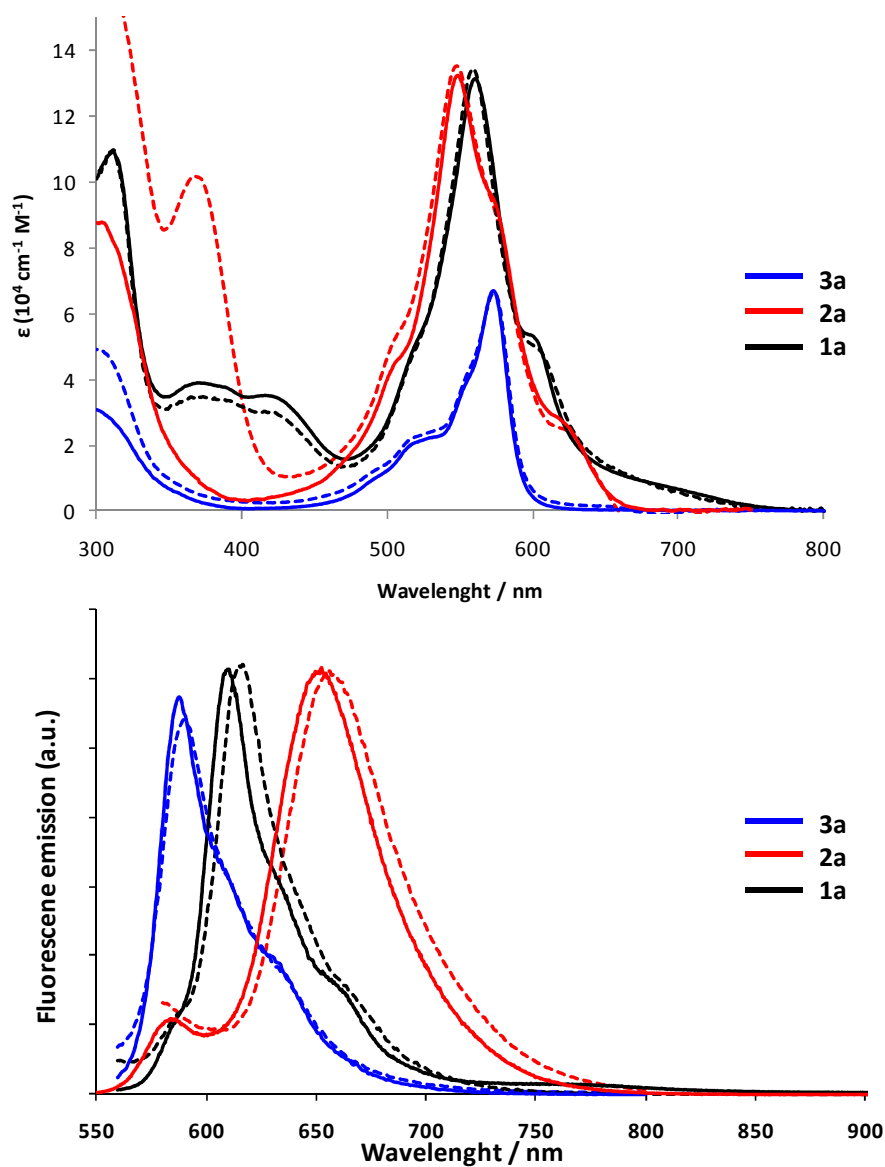


## 5. $^{19}\text{F}$ NMR spectra



**Figure S1.** Selected regions of the  $^{19}\text{F}$  NMR spectra of compounds **3b**, **3a**, **2b** and **2a** (from top to bottom) showing the two types of fluorine atoms in *o*- and *m*-positions with respect to the macrocycle. The presence of the iodine substituent at the aniline ring shifts both signals upfield, whereas the stacked structure in the  $\mu$ -azo dimers affects only the *o*-fluorine atoms, which further shift upfield.

## 6. Absorption and Emission Spectra in different solvents



**Figure S2.** a) Uv-vis spectra of **1a** (black), **2a** (red), and **3a** (blue) in toluene (solid line) and benzonitrile (dashed line); b) Emission spectra ( $\lambda_{\text{exc}} = 530 \text{ nm}$ ) of **1a** (black), **2a** (red) and **3a** (blue) in toluene (solid line) and benzonitrile (dashed line).



## 7. Quantum yield calculations

The fluorescence quantum yields were calculated according to the equation below:

$$\varphi = \varphi_{ST} \left( \frac{Grad_x}{Grad_{ST}} \right) \left( \frac{n_x^2}{n_{ST}^2} \right)$$

Where the scripts ST and X denote standard and test, respectively,  $\varphi$  is the fluorescence quantum yield, *Grad* the gradient from the plot of integrated fluorescence intensity vs absorbance, and  $n$  the refractive index of the solvent.<sup>4</sup>

## References

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<sup>1</sup> C. G. Claessens, D. González-Rodríguez, B. del Rey, T. Torres, G. Mark, H-P. Schuchmann, C. Von Sonntag, J. G. MacDonald, R. S. Nohr, *Eur. J. Org. Chem.* **2003**, 2547-2551.

<sup>2</sup> a) B. del Rey, U. Keller, T. Torres, G. Rojo, F. Agulló-López, S. Nonell, C. Martí, S. Brasselet, I. Ledoux, J. Zyss, *J. Am. Chem. Soc.* **1998**, *120*, 12808; b) J. Guilleme, D. González-Rodríguez, T. Torres, *Angew. Chem Int. Ed.* **2011**, *50*, 3506.

<sup>3</sup> D. González-Rodríguez, T. Torres, D. M. Guldi, J. Rivera, M. A. Herranz, L. Echegoyen, *J. Am. Chem. Soc.*, **2004**, *126*, 6301-6313

<sup>4</sup> "A guide to recording fluorescence quantum yields", Horiba.

<http://www.horiba.com/fileadmin/uploads/Scientific/Documents/Fluorescence/quantumyieldstrad.pdf>