

Supplementary Information (SI) for:

**Self-Assembling Figure-of-Eight and Pseudoplectoneme Aromatic  
Oligoamide Ribbons**

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# 1. Methods

## Nuclear Magnetic Resonance

NMR spectra were recorded on 2 different NMR spectrometers: (1) an Avance II NMR spectrometer (Bruker Biospin) with a vertical 7.05 T narrow-bore/ultrashield magnet operating at 300 MHz for  $^1\text{H}$  observation and 75 MHz for  $^{13}\text{C}$  observation by means of a 5-mm direct BBO H/X probe with Z gradient capabilities; (2) a DPX-400 NMR spectrometer (Bruker Biospin) with a vertical 9.4 T narrow-bore/ultrashield magnet operating at 400 MHz for  $^1\text{H}$  observation by means of a 5-mm direct QNP  $^1\text{H}/^{13}\text{C}/^{31}\text{P}/^{19}\text{F}$  probe with gradient capabilities; Chemical shifts are reported in parts per million (ppm,  $\delta$ ) relative to the  $^1\text{H}$  residual signal of the deuterated solvent used.  $^1\text{H}$  NMR splitting patterns with observed first-order coupling are designated as singlet (s), doublet (d), triplet (t), or quartet (q). Coupling constants ( $J$ ) are reported in hertz. Samples were not degassed. Data processing was performed with Topspin 3.6 software.

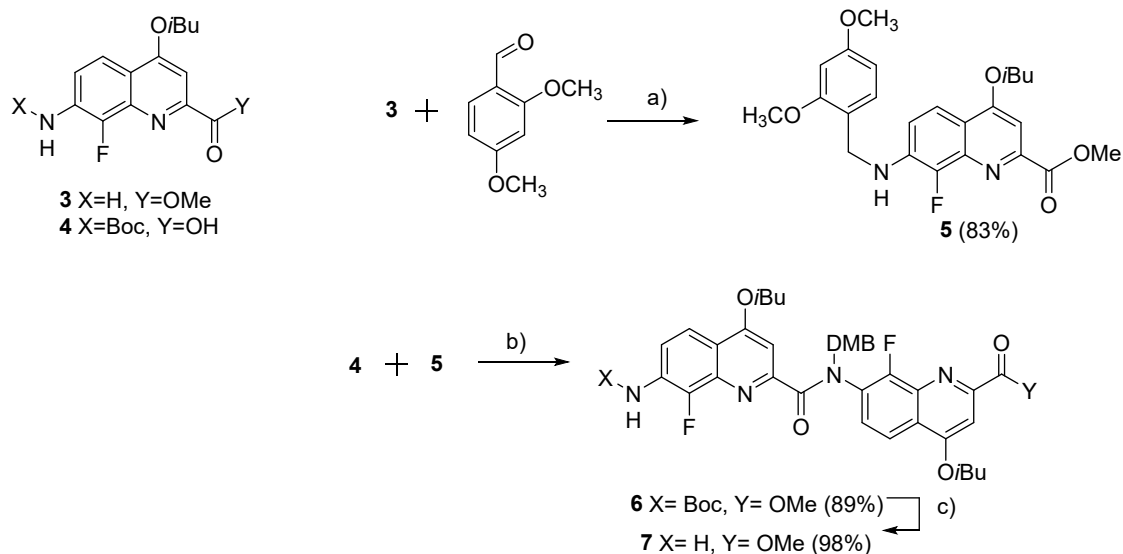
## Crystallography

The diffraction data for compounds **1b** and **2b** were collected at the IECB X-ray facility (CNRS UAR 3033 – INSERM US001, University of Bordeaux) with a Rigaku FRX rotating anode (2.9 kW) diffractometer using  $\text{CuK}\alpha$  wavelength with a partial chi goniometer (AFC11). The X-ray source is equipped with high flux Osmic Varimax mirrors and a Pixel Hybrid Dectris Eiger1M detector. Data were processed with the Rigaku Oxford Diffraction CrysAlisPro software (version 1.171.41.118a).<sup>[1]</sup> The crystal structure of compound **1b** was solved with the dual-space algorithm implemented into Shelxt<sup>[2]</sup> while the structure of **2b** with Shelxd<sup>[2]</sup>. Both structures were refined by full-matrix least-squares method on F<sup>2</sup> with Shelxl-2014<sup>[2]</sup> within Olex2.<sup>[3]</sup> Only non-H atoms of the backbones and side chains observable in the electron density maps were refined with anisotropic displacement parameters. H-atoms were refined in the riding-model approximation, with Uiso(H)=1.2Ueq (CH, CH<sub>2</sub>, NH). DFIX, AFIX, RIGU and SIMU restraints were applied to model geometry of the molecules and thermal motion parameters. Some residual electron density peaks observed in the difference Fourier maps could not be modelled. The PLATON/SQUEEZE<sup>[4]</sup> procedure was applied on both datasets. Highly disordered Chlorobenzene, methanol and water solvent molecules were squeezed in structures **1b** and **2b** corresponding to contributions of some 2279 and 1602 electrons respectively.

## 2. Materials and Methods for chemical synthesis

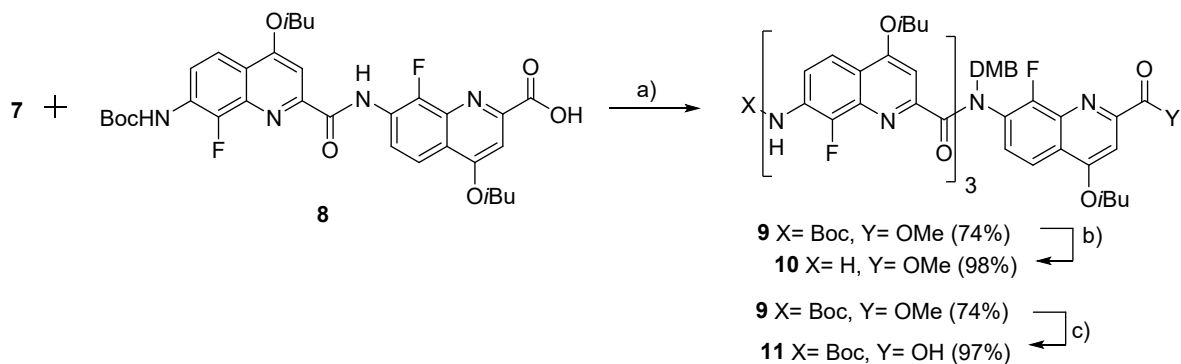
All reactions were carried out under a dry nitrogen atmosphere. Commercial reagents were purchased from SigmaAldrich, TCI Chemicals or Alfa-Aesar and were used without further purification. Tetrahydrofuran (THF) and dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) were dried over alumina columns (MBRAUN SPS-800 solvent purification system); chloroform ( $\text{CHCl}_3$ ) and diisopropylethylamine (DIEA) were distilled over calcium hydride ( $\text{CaH}_2$ ) prior to use. Reactions were monitored by thin layer chromatography (TLC) on Merck silica gel 60-F254 plates and observed under UV light. Column chromatography purifications were carried out on Merck GEDURAN Si60 (40-63  $\mu\text{m}$ ). Radial centrifugally accelerated chromatography purifications were carried out on Chromatotron® with silica gel, Merck grade 7749, TLC grade with binder and fluorescent indicator. Preparative recycling GPC (gel permeation chromatography) were performed on JAIGEL 20\*600 mm columns (Japan Analytical Industry) at a flow rate of  $10 \text{ mL min}^{-1}$  with a mobile phase composed of 1% (vol/vol)  $\text{Et}_3\text{N}$  in chloroform. Monitoring by UV detection was carried out at 254 nm, 280 nm, 300 nm and 360 nm. ESI mass spectra were obtained from the Mass Spectrometry Laboratory at the European Institute of Chemistry and Biology (UMS 3033 & US01 - IECB), Pessac, France

## 2.1 Synthesis of dimers



**Scheme S1.** Synthesis of DMB protected  $Q^F$  dimer **6** and **7**: a) sodium triacetoxyborohydride, 1,2-dichloroethane, room temperature, 16h; b) i) 1-chloro-N,N,2-trimethyl-1-propenylamine,  $CHCl_3$ , room temperature, 3 h ; ii) DIEA,  $CHCl_3$ , room temperature, 12 h; c) HCl 4N in dioxane, room temperature, 4h.

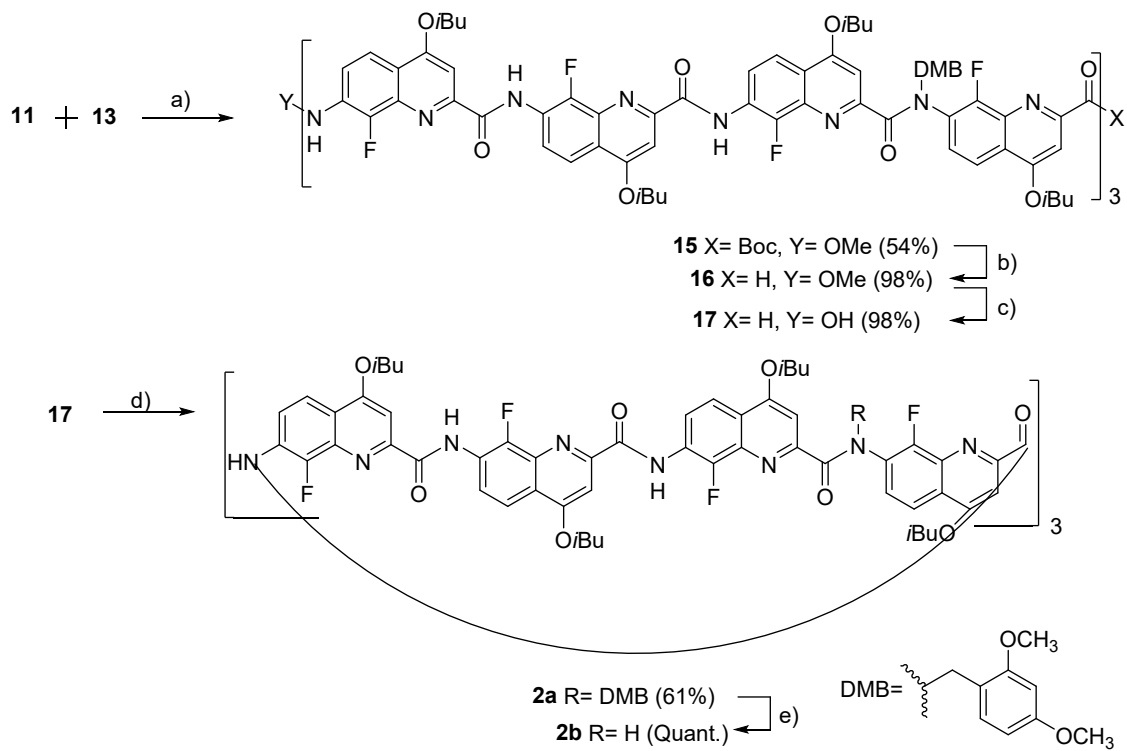
## 2.2 Synthesis of tetramers



**Scheme S2.** Synthesis of  $Q^F$  tetramer **10** and **11**: a) i)1-chloro-N,N,2-trimethyl-1-propenylamine,  $CHCl_3$ , room temperature, 3 h ; ii) DIEA,  $CHCl_3$ , room temperature, 12 h; b) HCl 4N in dioxane, room temperature, 4 h. c) LiOH, THF,  $H_2O$ , room temperature, 4 h.



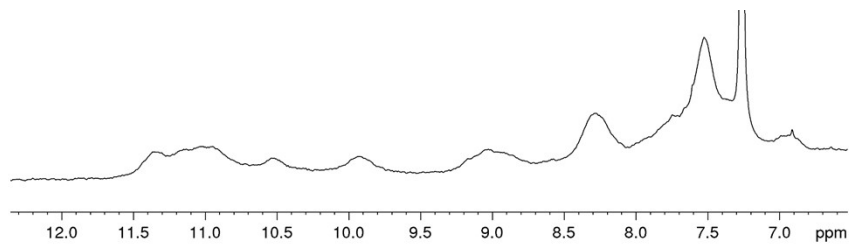
## 2.4 Synthesis of cyclco-dodecamers



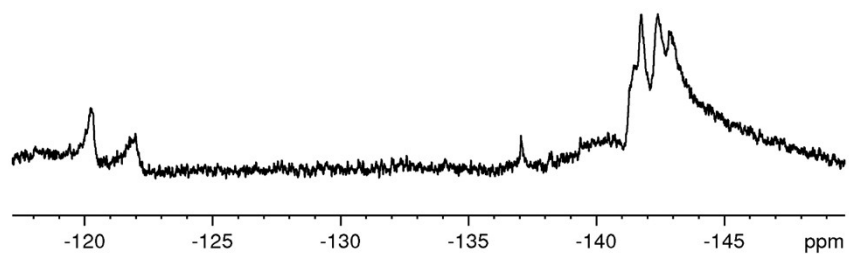
**Scheme S4.** Synthesis of  $Q^F$  dodecamer macrocycle **2b**: a) i) 1-chloro-N,N,2-trimethyl-1-propenylamine,  $CHCl_3$ , room temperature, 3 h ; ii) DIEA,  $CHCl_3$ , room temperature, 12 h; b) HCl 4N in dioxane, room temperature, 4 h; c) sodium hydroxide, THF,  $H_2O$ , room temperature, 4 h; d) triphenylphosphine, trichloroacetonitrile, DIPEA,  $CHCl_3$ , room temperature, 48 h; e) trifluoroacetic acid,  $CHCl_3$ ,  $60^\circ C$ , 2 h.

### 3. Solution studies

#### 3.1 NMR spectra of **1b**



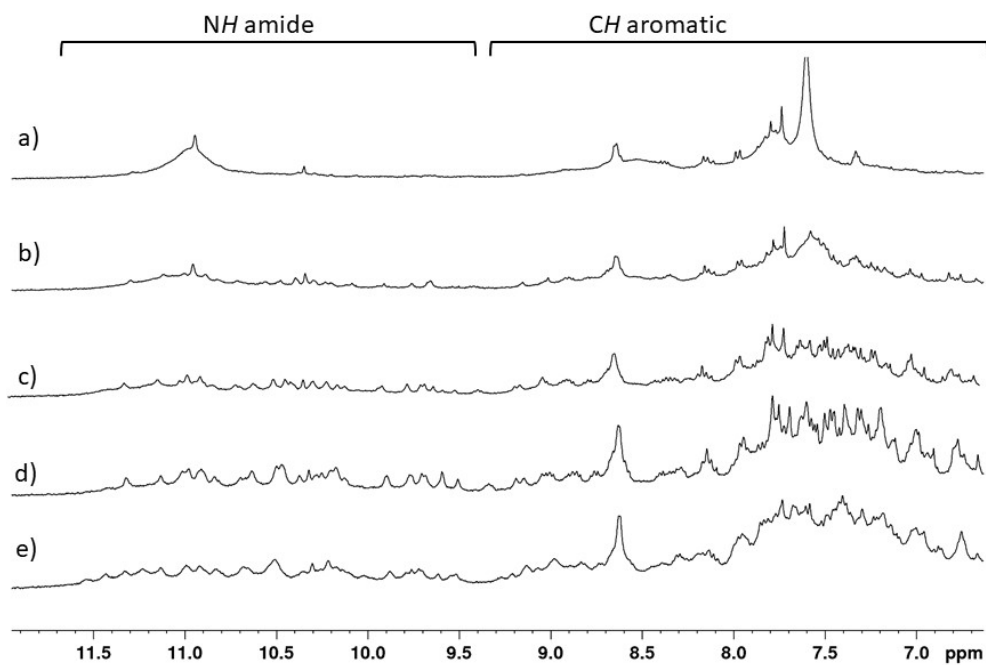
**Figure S1.** Part of <sup>1</sup>H NMR spectrum (400 MHz, 0.5mM, CDCl<sub>3</sub>) of octamer macrocycle **1b**.



**Figure S2.** <sup>19</sup>F NMR spectrum (400 MHz, 0.5mM, CDCl<sub>3</sub>) of octamer macrocycle **1b**.



### 3.2 Variable temperature experiment of **1b**



**Figure S3.** Part of <sup>1</sup>H NMR spectra (400 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>) for octamer macrocycle **1b** at variable temperature, a) 353 K, b) 333 K, c) 313 K, d) 298 K, e) 278 K.

### 3.3 NMR spectra of 2b

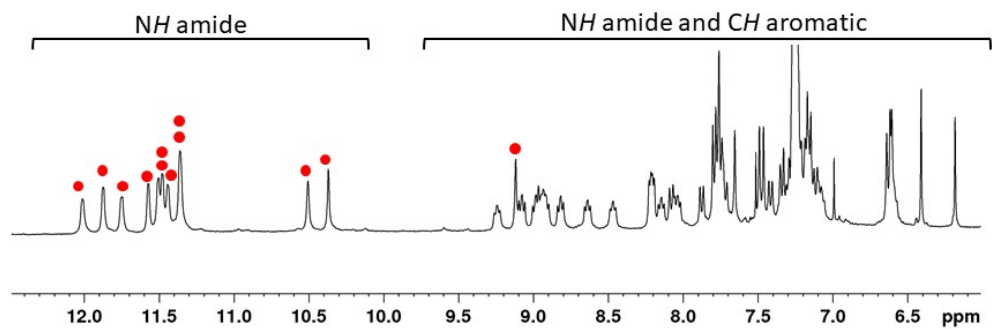


Figure S4. Part of  $^1\text{H}$  NMR spectrum (400 MHz, 0.7mM,  $\text{CDCl}_3$ ) of dodecamer macrocycle **2b**.

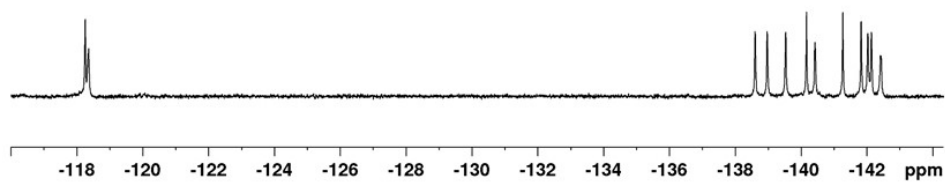
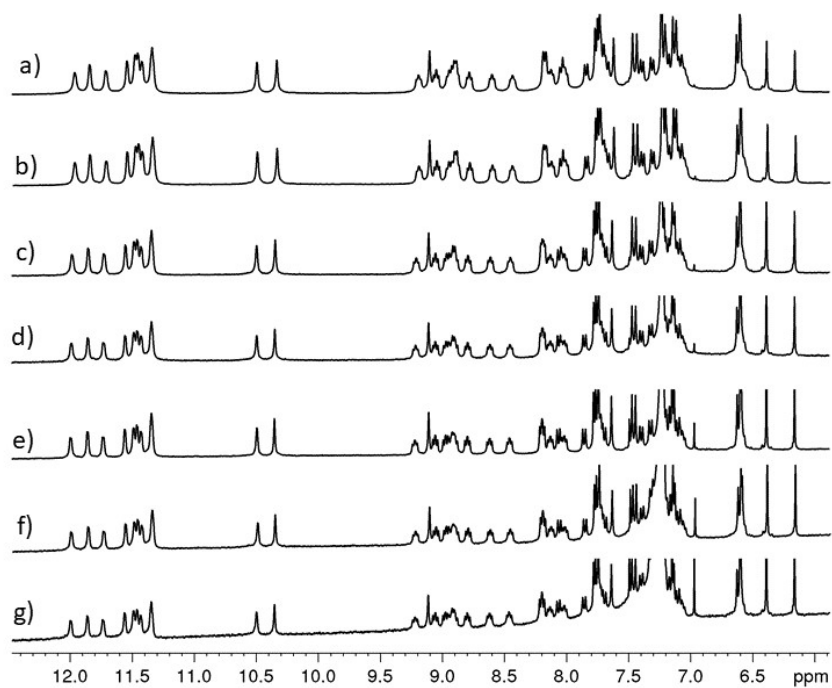


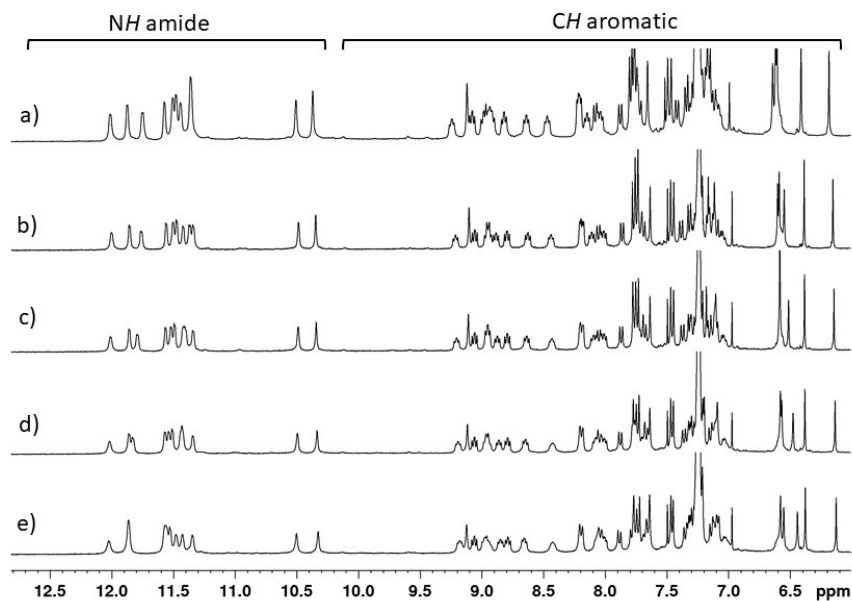
Figure S5.  $^{19}\text{F}$  NMR spectrum (400 MHz, 0.7mM,  $\text{CDCl}_3$ ) of dodecamer macrocycle **2b**.

### 3.4 Variable concentration experiment for 2b

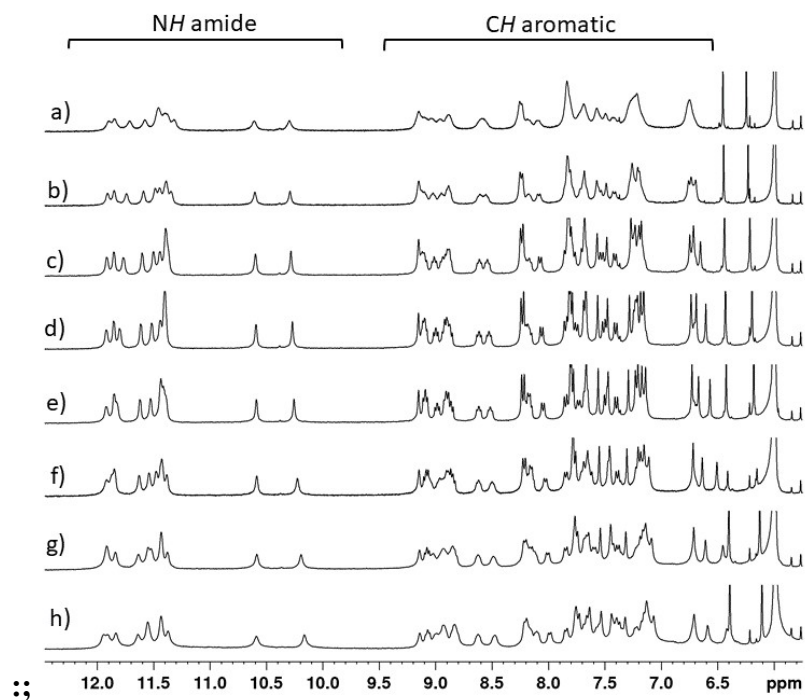


**Figure S6.** Part of <sup>1</sup>H NMR spectra (400 MHz, CDCl<sub>3</sub>, 298 K) of dodecamer **2b** at different concentrations, a) 3.20 mM, b) 2.37 mM, c) 1.57 mM, d) 0.98 mM, e) 0.49 mM, f) 0.24 mM, g) 0.1 mM.

### 3.5 Variable temperature experiment for 2b

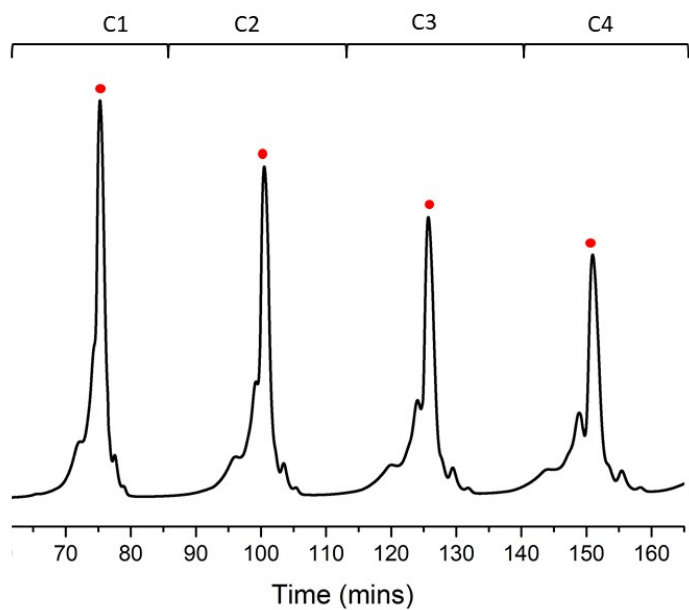


**Figure S7.** Part of <sup>1</sup>H NMR spectra (400 MHz, 0.5 mM, CDCl<sub>3</sub>) of dodecamer **2b** in variable temperature, a) 298 K, b) 288 K, c) 278 K, d) 268 K, e) 258 K.

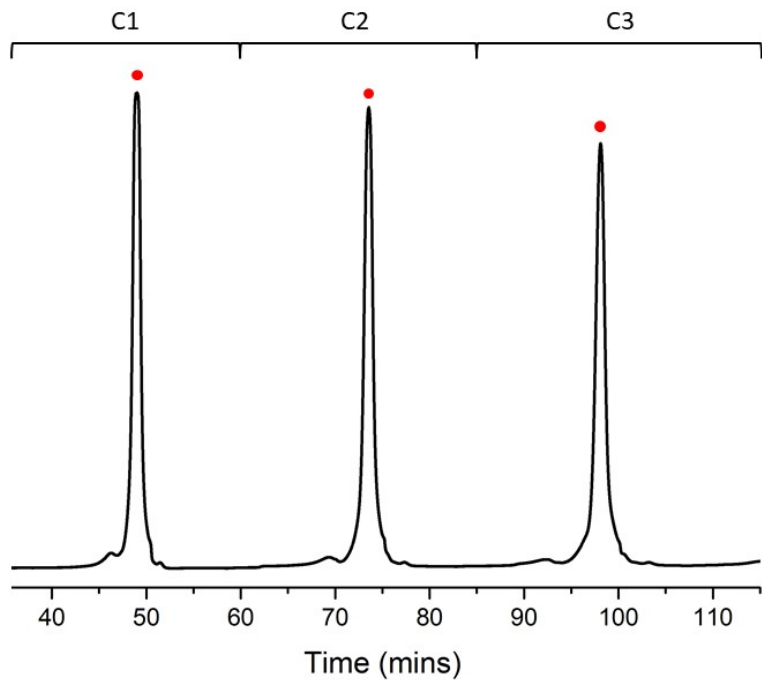


**Figure S8.** Part of <sup>1</sup>H NMR spectra (400 MHz, 0.5 mM, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>) of dodecamer **2b** in variable temperature, a) 353 K, b) 343 K, c) 333 K, d) 323 K, e) 313 K, f) 298 K, g) 283 K, h) 273 K.

### 3.6 Gel permeation chromatography (GPC)

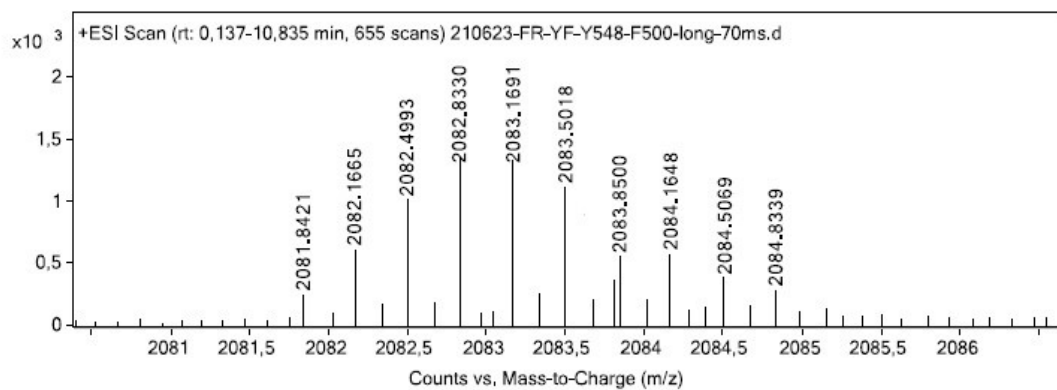
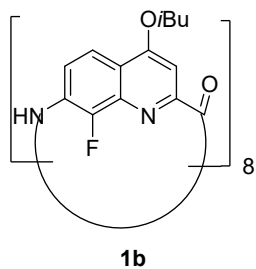


**Figure S9.** Chromatogram of recycling GPC of **1a** purification. The peaks marked with red circle stand for the DMB functionalized macrocycle **1a**.

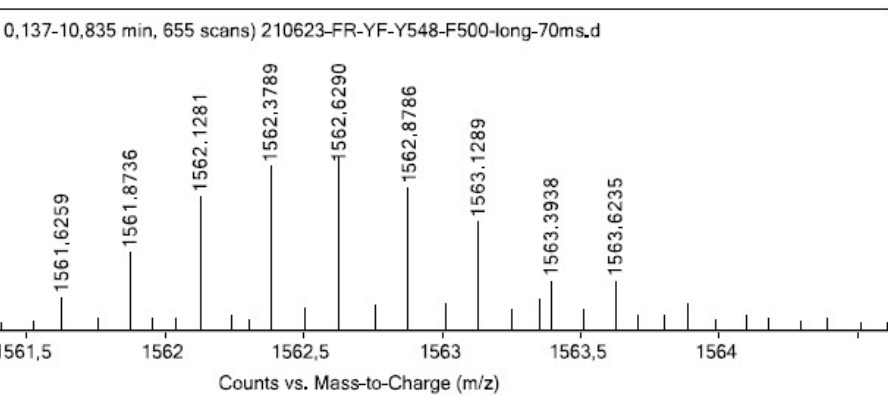


**Figure S10.** GPC Chromatogram of **2a** purification. The peaks marked with red circle stand for **2a**. The residual time can be calculated by the time between two cycles of same peaks.

### 3.7 Mass spectrometry of cyclo-octamer 1b



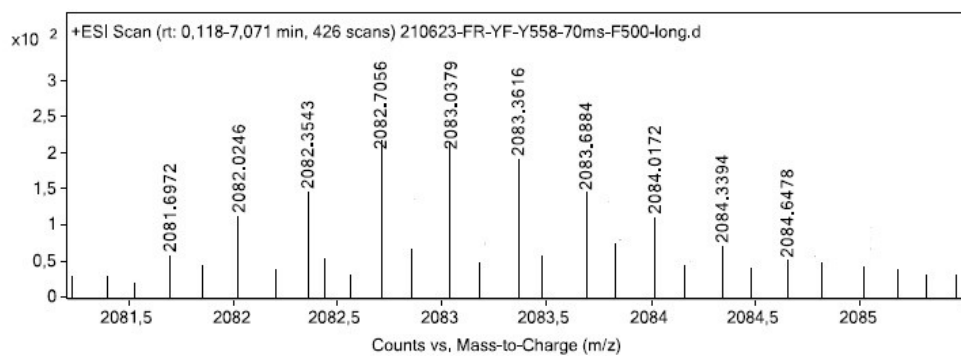
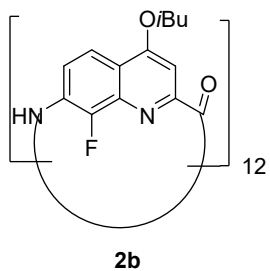
MS (ESI): m/z calcd for C<sub>336</sub>H<sub>316</sub>F<sub>24</sub>N<sub>48</sub>O<sub>48</sub> [3M+3H]<sup>3+</sup> 2082.4450 ; found 2082.4993



MS (ESI): m/z calcd for  $C_{336}H_{316}F_{24}N_{48}O_{48} [3M+4H]^{4+}$  1562.3364 ; found 1562.3789

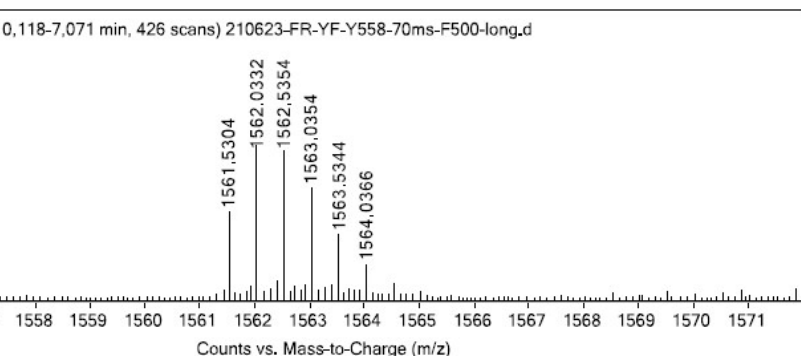
**Figure S11:** Zoom of the Electrospray mass spectrometry (ESI-MS) spectra of **1b**

### 3.8 Mass spectrometry of cyclo-dodecamer 2b



MS (ESI): m/z calcd for  $C_{336}H_{316}F_{24}N_{48}O_{48}$   $[2M+3H]^{3+}$  2082.7795 ; found 2082.7056



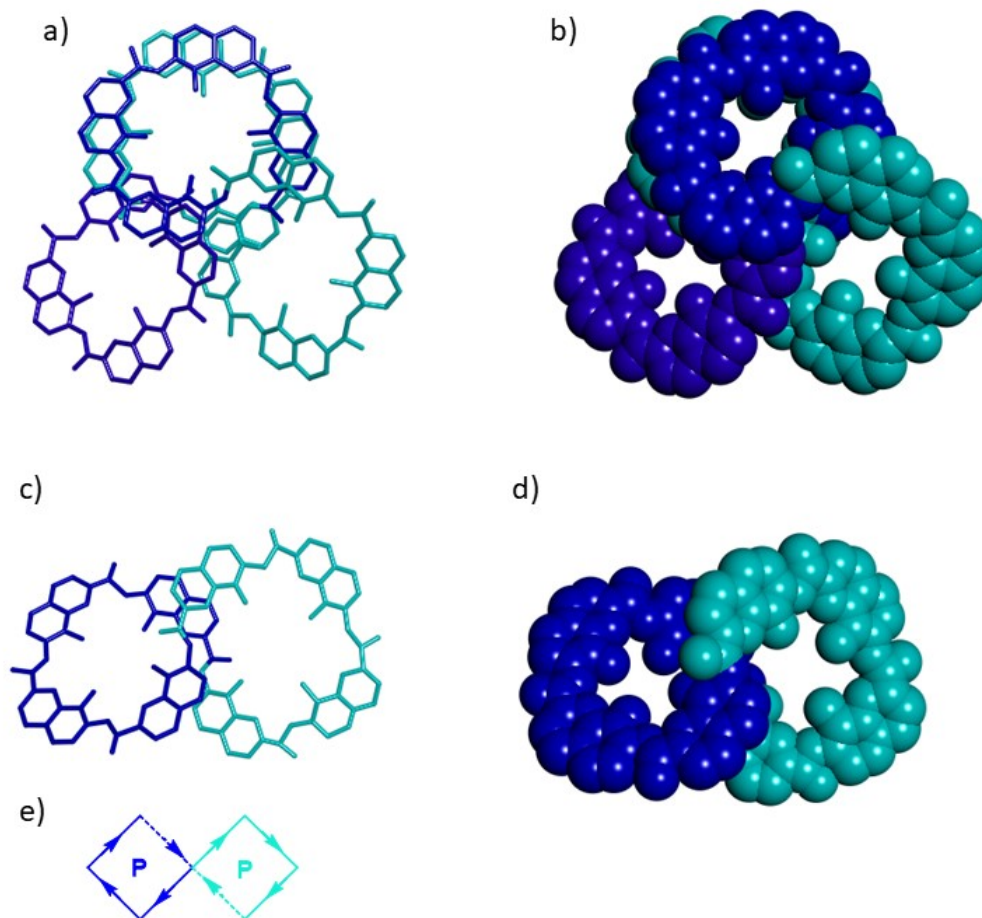


MS (ESI): m/z calcd for  $C_{168}H_{158}F_{12}N_{24}O_{24} [M+2H]^{2+}$  1562.0856 ; found 1562.0332

**Figure S12:** Zoom of the Electrospray mass spectrometry (ESI-MS) of **2b**

## 4. Solid state studies: X-ray crystallography

### 4.1 Crystal structure and X-ray data for **1b**

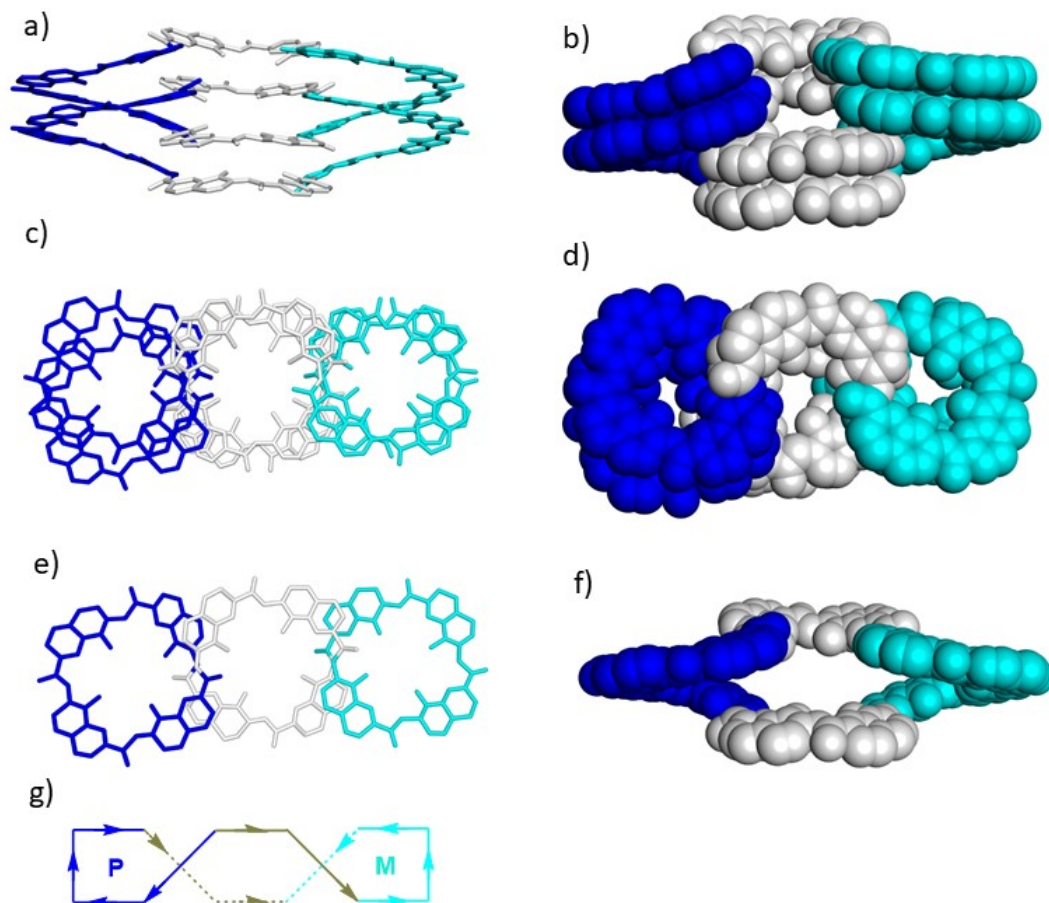


**Figure S13.** X-ray structure of octamer macrocycle **1b**, a, b) top view of crystal packing showing a dimeric architecture (**1b**)<sub>2</sub>; c, d) Top view of monomeric **1b** which is one strand from (**1b**)<sub>2</sub>, both cycles have P helicity; e) Schematic representations of monomeric **1b**, straight line represent a Q<sup>F</sup> unit, the solid line is in the front and dot line is in the back. Arrows represent handedness P or M. Side chains (O*i*Bu groups) and hydrogen atoms have been removed for clarity.

<i>CCDC code</i>	<b>2160708</b>
<i>Empirical formula</i>	$C_{232}H_{190}Cl_{3.5}F_{16}N_{32}O_{32}$
<i>Formula weight</i>	4366.22
<i>Temperature/K</i>	130
<i>Crystal system</i>	monoclinic
<i>Space group</i>	$P2_1/c$
<i>a/Å</i>	36.4661(5)
<i>b/Å</i>	42.5825(5)
<i>c/Å</i>	20.4587(3)
<i>α/°</i>	90.0
<i>β/°</i>	99.8128(14)
<i>γ/°</i>	90.0
<i>Volume/Å<sup>3</sup></i>	31303.9(8)
<i>Z</i>	4
<i>ρ<sub>calc</sub>/cm<sup>3</sup></i>	0.926
<i>μ/mm<sup>-1</sup></i>	0.844
<i>F(000)</i>	9062.0
<i>Crystal size/mm<sup>3</sup></i>	0.1 × 0.01 × 0.01
<i>Radiation</i>	Cu Kα (λ = 1.54178)
<i>2θ range for data collection/°</i>	4.15 to 88.588
<i>Index ranges</i>	-31 ≤ h ≤ 32, -37 ≤ k ≤ 38, -18 ≤ l ≤ 18
<i>Reflections collected</i>	126576
<i>Independent reflections</i>	23865 [R <sub>int</sub> = 0.1958, R <sub>sigma</sub> = 0.0964]
<i>Data/restraints/parameters</i>	23865/22844/2864
<i>Goodness-of-fit on F<sup>2</sup></i>	1.389
<i>Final R indexes [I ≥ 2σ (I)]</i>	R <sub>1</sub> = 0.1390, wR <sub>2</sub> = 0.3808
<i>Final R indexes [all data]</i>	R <sub>1</sub> = 0.1979, wR <sub>2</sub> = 0.4304

**Table**  
**S1.** Crystal data  
and structure  
refinement for  
**1b.**

## 4.2 Crystal structure and X-ray data for **2b**

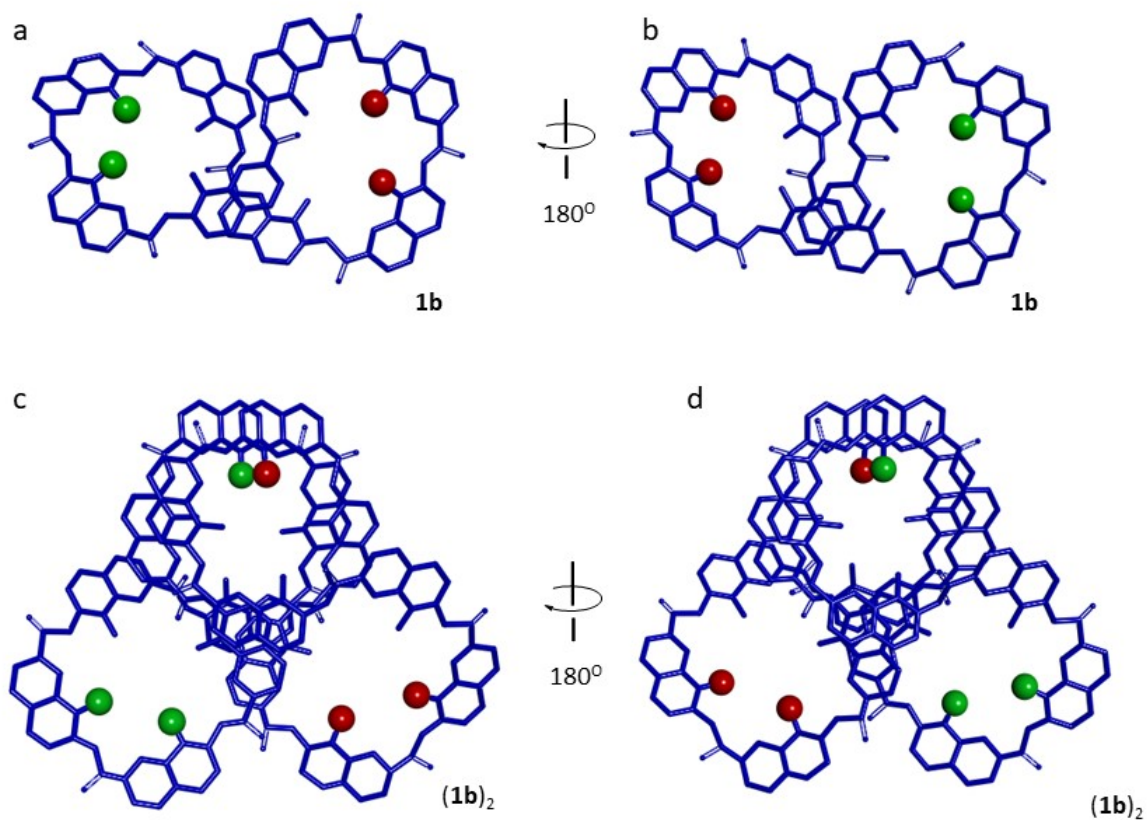


**Figure S14.** X-ray structure of dodecamer macrocycles (**2b**)<sub>2</sub>, a) Front view of (**2b**)<sub>2</sub>, opposite handedness cycles were marked as blue (P) and light blue (M), middle cycle was marked as white; b) front view of (**2b**)<sub>2</sub> in CPK style; c) top view of (**2b**)<sub>2</sub>; d) top view of (**2b**)<sub>2</sub> in CPK style; e) top view of monomeric **2b** which is one strand from crystal packing (**2b**)<sub>2</sub>; f) front view of monomeric **2b** in CPK style; g) schematic representation of **2b**, straight line represent a Q<sup>F</sup> unit, the solid line is in the front layer and dot line is in the back. Arrows denote the P or M handedness; side chains (O*i*Bu groups) and hydrogen atoms have been removed for clarity.

**Table S2.** Crystal data and structure refinement for **2b**

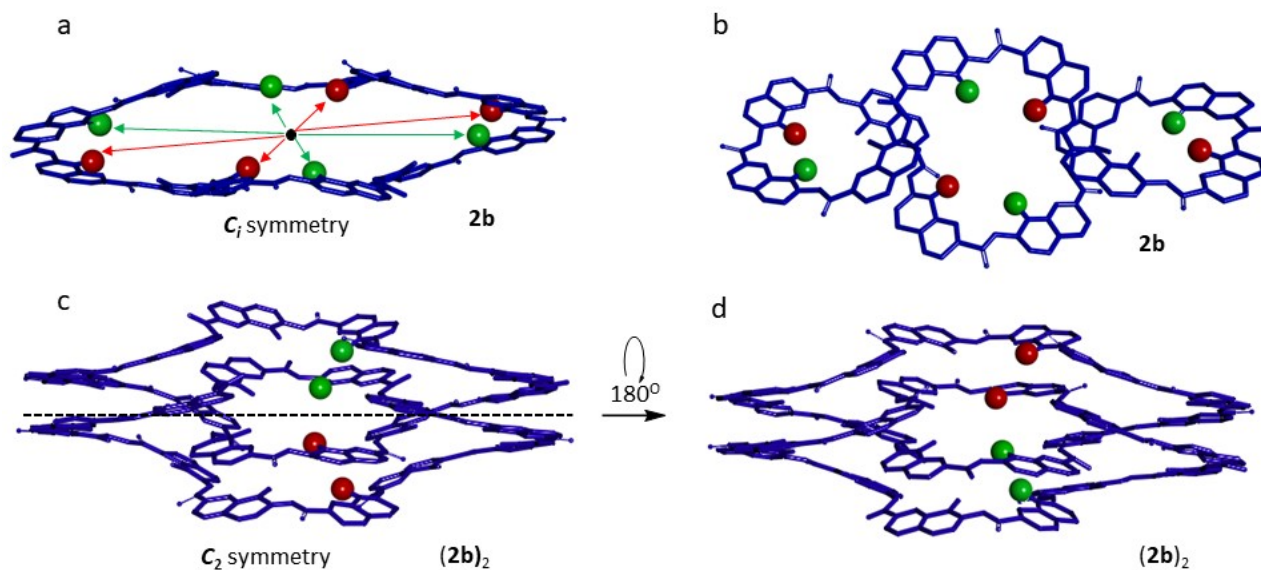
<i>CCDC code</i>	<b>2161479</b>
<i>Empirical formula</i>	C <sub>348</sub> H <sub>321</sub> Cl <sub>2</sub> F <sub>24</sub> N <sub>48</sub> O <sub>48</sub>
<i>Formula weight</i>	6470.41
<i>Temperature/K</i>	135
<i>Crystal system</i>	triclinic
<i>Space group</i>	P-1
<i>a/Å</i>	24.6529(8)
<i>b/Å</i>	28.2336(8)
<i>c/Å</i>	32.8540(10)
<i>α/°</i>	76.852(2)
<i>β/°</i>	72.247(3)
<i>γ/°</i>	74.951(3)
<i>Volume/Å<sup>3</sup></i>	20757(1)
<i>Z</i>	2
<i>ρ<sub>calc</sub>/cm<sup>3</sup></i>	1.035
<i>μ/mm<sup>-1</sup></i>	0.760
<i>F(000)</i>	6758.0
<i>Crystal size/mm<sup>3</sup></i>	0.05 × 0.05 × 0.05
<i>Radiation</i>	Cu Kα (λ = 1.54178)
<i>2θ range for data collection/°</i>	3.844 to 87.974
<i>Index ranges</i>	-22 ≤ h ≤ 22, -25 ≤ k ≤ 21, -29
<i>Reflections collected</i>	101599
<i>Independent reflections</i>	31689 [R <sub>int</sub> = 0.0908, R <sub>sigma</sub> =
<i>Data/restraints/parameters</i>	31689/72118/3679
<i>Goodness-of-fit on F<sup>2</sup></i>	2.082
<i>Final R indexes [I ≥ 2σ (I)]</i>	R <sub>1</sub> = 0.2225, wR <sub>2</sub> = 0.4996
<i>Final R indexes [all data]</i>	R <sub>1</sub> = 0.2792, wR <sub>2</sub> = 0.5454

### 4.3 Symmetry of **1b**



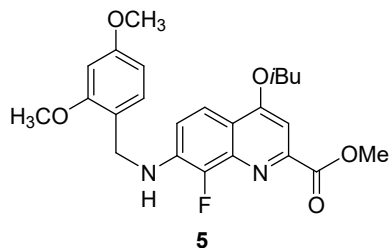
**Figure S15.** X-ray structure of **1b**, a) top view of monomeric **1b** which is one strand in the crystal packing, two side F atoms were marked as green and red balls; b) **1b**, rotated 180° horizontal from a); c) top view of  $(\mathbf{1b})_2$ , picked F atoms were marked as green and red; d)  $(\mathbf{1b})_2$ , rotated 180° horizontal from c). Side chains (*O**i*Bu groups) and included solvent molecules have been removed for clarity.

#### 4.4 Symmetry of 2b

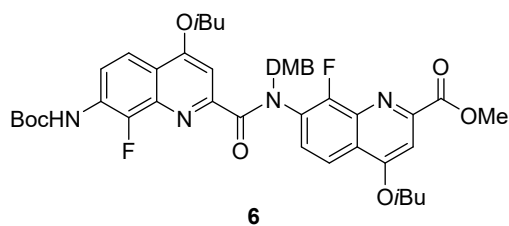


**Figure S16.** X-ray structure of macrocycle **2b**, a) front view of macrocycle monomeric **2b** only one strand is shown, fluorine atoms are marked as green and red balls, equal distance between a pair of antipodal fluorine atoms and inversion center were marked as different color arrow (green and red); b) top view of **2b**; c) side view of macrocycle dimeric  $(2b)_2$ ; d) side view of  $(2b)_2$ , rotated 180° vertical from c). Side chains (O*t*Bu groups) and included solvent molecules have been removed for clarity.

## 5. Synthetic procedures



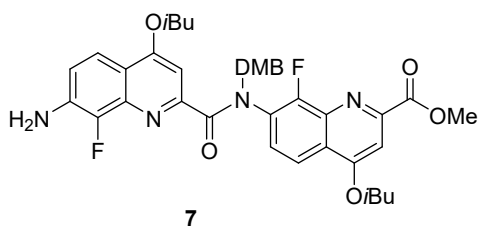
Compound **5**: amine **3**<sup>[5]</sup> (610 mg, 1.98 mmol), 2,4-dimethoxybenzaldehyde (659 mg, 3.97 mmol) were dissolved in 1,2-dichloroethane (5 ml), under inert atmosphere of N<sub>2</sub>. The slurry was stirred at room temperature for 2 hours. Then sodium triacetoxyborohydride (841 mg, 3.97 mmol) was added to the slurry. The mixture was stirred at room temperature under a N<sub>2</sub> atmosphere for 18 h. The reaction mixture was quenched by adding aqueous saturated NaHCO<sub>3</sub>, and the product was extracted with dichloromethane. The organic layer was washed with brine, and dried over anhydrous MgSO<sub>4</sub>. After the solvent was removed in vacuo, the residue was purified by flash column chromatography (silica gel, ethyl acetate / cyclohexane = 1 / 6) to give **5** as yellow solid (731 mg, 83 %). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298 K) δ 7.90 (dd, *J*(H, H) = 1.5, *J*(H, H) = 9.1, 1H), 7.37 (s, 1H), 7.26-7.18 (m, 2H), 6.50 (d, *J*(H, H) = 2.3, 1H), 6.45-6.41 (m, 1H), 4.91 (br, 1H), 4.49 (d, *J*(H, H) = 6.2, 2H), 4.07 (s, 3H), 4.03 (d, *J*(H, H) = 6.4, 2H), 3.87 (s, 3H), 3.81 (s, 3H), 2.34-2.20 (m, 1H), 1.15 (s, 3H), 1.12 (s, 3H) <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 166.4, 162.7, 160.4, 158.4, 149.6, 145.3, 142.8, 138.9, 136.9, 129.3, 118.9, 117.5, 116.0, 114.7, 103.8, 98.7, 98.3, 74.9, 55.3, 53.0, 42.9, 28.1, 19.2. HRMS (ESI): *m/z* calcd for C<sub>24</sub>H<sub>28</sub>FN<sub>2</sub>O<sub>5</sub> [M+H]<sup>+</sup> 443.1977, found 443.1989.



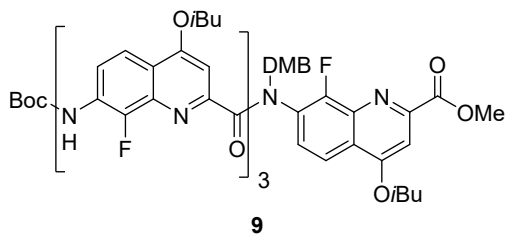
Compound **6**: A solution of **4**<sup>[1]</sup> (645 mg, 1.7 mmol) in dry CHCl<sub>3</sub> (3 mL) was cooled to 0°C. 1-Chloro-N,N,2-trimethyl-1-propenylamine (0.75 mL, 3.0 eq.) was added. The solution was stirred at room temperature for 3 h under inert atmosphere of N<sub>2</sub>. The solvent was removed under high-vacuum for at least 2 hours to yield the corresponding acid chloride. The resulting acid chloride was dissolved in dry CHCl<sub>3</sub> (3 mL) and added to a solution of **5** (630 mg, 0.9 eq.) and dry DIPEA (0.73 mL, 4.0 eq.) in dry CHCl<sub>3</sub> (1 mL). The mixture was stirred



for 12 h. The solvent was removed under reduced pressure and the residue was dissolved in dichloromethane, washed with saturated aqueous  $\text{NH}_4\text{Cl}$ , saturated aqueous  $\text{NaHCO}_3$  and brine, dried over  $\text{MgSO}_4$ , filtered and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, ethyl acetate / cyclohexane = 1 / 4) to give **6** as yellow solid (1.1 g, 89 %).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  8.19 (t,  $J(\text{H}, \text{H}) = 7.9$ , 1H), 7.82 (t,  $J(\text{H}, \text{H}) = 10.9$ , 2H), 7.58-7.49 (m, 3H), 7.25 (s, 1H), 6.75 (s, 1H), 6.46 (d,  $J(\text{H}, \text{H}) = 8.1$ , 1H), 6.30 (s, 1H), 5.21 (dd,  $J(\text{H}, \text{H}) = 14.5$ , 2H), 4.01 (br, 7H), 3.78 (s, 3H), 3.47 (s, 3H), 2.35-2.18 (m, 2H), 1.52 (s, 9H), 1.15-1.10 (m, 12H)  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  168.6, 165.9, 162.4, 162.0, 160.4 158.5, 154.6, 154.1, 152.1, 151.6, 149.3, 146.6, 144.1, 138.9, 136.9, 131.6, 131.3, 129.6, 126.6, 122.2, 118.9, 117.9, 117.1, 116.9, 116.0, 104.1, 101.6, 100.2, 98.1, 81.4, 75.2, 75.0, 55.2, 54.9, 53.2, 47.7, 38.6, 37.0, 35.5, 28.2, 28.1, 28.0, 19.1. HRMS (ESI):  $m/z$  calcd for  $\text{C}_{43}\text{H}_{49}\text{F}_2\text{N}_4\text{O}_9$   $[\text{M}+\text{H}]^+$  803.3462, found 803.3486.

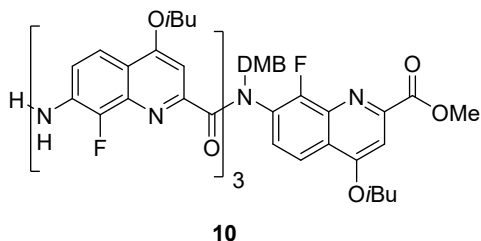


Synthesis of compound **7**: **6** (200 mg, 0.24 mmol) was dissolved in dioxane (0.2 mL). HCl in dioxane (4M, 2mL) was added to the solution, and stirred at room temperature for 4 h. The mixture was diluted with DCM, the organic layer was washed with saturated aqueous  $\text{NaHCO}_3$  and brine, dried over  $\text{MgSO}_4$ , filtered and concentrated in vacuo to give **7** as yellow solid (169 mg, 98%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  7.82 (d,  $J(\text{H}, \text{H}) = 8.9$ , 1H), 7.64 (d,  $J(\text{H}, \text{H}) = 8.8$ , 1H), 7.55 (t,  $J(\text{H}, \text{H}) = 7.8$ , 1H), 7.49-7.47 (m, 2H), 7.12 (s, 1H), 6.84 (t,  $J(\text{H}, \text{H}) = 8.1$ , 1H), 6.42 (d,  $J(\text{H}, \text{H}) = 8.1$ , 1H), 6.27 (s, 1H), 5.19 (dd,  $J(\text{H}, \text{H}) = 14$ , 2H), 3.98-3.94 (m, 7H), 3.75 (s, 3H), 3.44 (s, 3H), 2.30-2.16 (m, 2H), 1.12-1.06 (m, 12H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  168.9, 165.9, 162.4, 162.1, 160.3, 158.5, 154.3, 151.6, 149.2, 144.9, 142.5, 139.0, 138.9, 138.1, 138.0, 133.8, 131.6, 131.4, 129.8, 122.2, 118.2, 117.0, 116.0, 115.2, 104.1, 101.5, 98.8, 98.1, 75.2, 74.8, 67.0, 55.2, 54.9, 53.2, 47.7, 28.2, 19.1. HRMS (ESI):  $m/z$  calcd for  $\text{C}_{38}\text{H}_{40}\text{F}_2\text{N}_4\text{O}_7$   $[\text{M}+\text{H}]^+$  702.7558, found 703.7089.

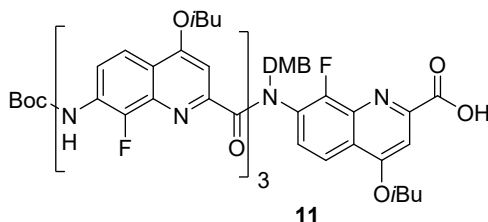


Compound **9**: A solution of **8**<sup>III</sup> (845 mg, 1.3 mmol) in dry  $\text{CHCl}_3$  (3 mL) was cooled to  $0^\circ\text{C}$ . 1-Chloro-N,N,2-trimethyl-1-propenylamine (0.27 mL, 1.5 eq.) was added. The solution was stirred at room temperature for 3 h under inert atmosphere of  $\text{N}_2$ . The solvent was removed under high-vacuum for at least 2 hours to yield the

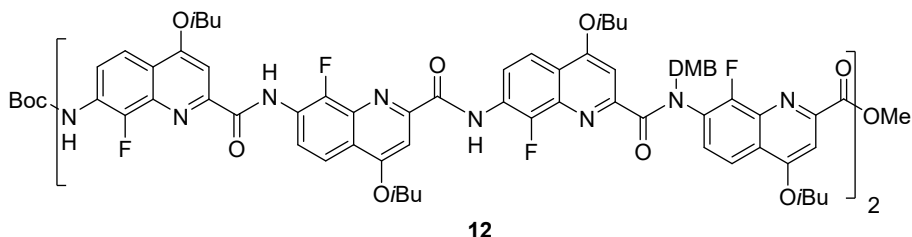
corresponding acid chloride. The resulting acid chloride was dissolved in dry  $\text{CHCl}_3$  (3 mL) and added to a solution of **7** (929 mg, 1.0 eq.) and dry DIPEA (0.70 mL, 3.0 eq.) in dry  $\text{CHCl}_3$  (2 mL). The mixture was stirred for 12 h. The solvent was removed under reduced pressure and the residue was dissolved in dichloromethane and washed with saturated aqueous  $\text{NH}_4\text{Cl}$ , saturated aqueous  $\text{NaHCO}_3$  and brine, dried over  $\text{MgSO}_4$ , filtered and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, ethyl acetate / cyclohexane = 1 / 4) to give **9** as yellow solid (1.3 g, 74 %).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  10.96 (s, 1H), 10.59 (s, 1H), 8.87 (q,  $J(\text{H}, \text{H}) = 6.8$ , 1H), 8.60 (t,  $J(\text{H}, \text{H}) = 7.9$ , 1H), 8.53 (q,  $J(\text{H}, \text{H}) = 5.3$ , 1H), 8.12 (q,  $J(\text{H}, \text{H}) = 3.5$ , 1H), 8.04 (d,  $J(\text{H}, \text{H}) = 5.2$ , 1H), 7.91 (d,  $J(\text{H}, \text{H}) = 8.9$ , 2H), 7.74 (s, 1H), 7.69 (s, 1H), 7.60 (t,  $J(\text{H}, \text{H}) = 7.9$ , 1H), 7.55 (s, 1H), 7.50 (s, 1H), 7.47 (s, 1H), 7.31 (s, 1H), 6.45 (q,  $J(\text{H}, \text{H}) = 3.4$ , 1H), 6.31 (s, 1H), 5.47 (d,  $J(\text{H}, \text{H}) = 7.3$ , 1H), 4.97 (d,  $J(\text{H}, \text{H}) = 7.3$ , 1H), 4.14-4.09 (m, 4H), 4.02-3.98 (m, 7H), 3.76 (s, 3H), 3.50 (s, 3H), 2.40-2.12 (m, 4H), 1.59 (s, 9H), 1.17-1.10 (m, 24H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  168.6, 166.0, 163.5, 163.4, 162.7, 162.6, 162.4, 162.1, 160.5, 158.7, 154.7, 152.4, 151.4, 151.2, 149.4, 148.6, 147.1, 145.2, 143.8, 137.8, 137.6, 137.3, 131.6, 130.0, 127.8, 126.8, 126.0, 122.5, 120.9, 120.0, 119.1, 118.8, 117.8, 116.3, 104.2, 101.8, 100.7, 98.3, 97.9, 81.8, 75.6, 75.3, 55.4, 55.1, 53.3, 48.0, 30.4, 29.8, 28.1, 19.1. HRMS (ESI):  $m/z$  calcd for  $\text{C}_{71}\text{H}_{74}\text{F}_4\text{N}_8\text{O}_{13}$   $[\text{M}+\text{H}]^+$  1323.4096, found 1324.5714.



Compound **10**: **9** (0.20 g, 0.15 mmol) was dissolved in dioxane (0.2 mL). HCl in dioxane (4M, 2mL) was added to the solution, and stirred at room temperature for 4 h. The mixture was diluted with DCM, the organic layer was washed with saturated aqueous  $\text{NaHCO}_3$  and brine, dried over  $\text{MgSO}_4$ , filtered and concentrated in vacuo to give **10** as yellow solid (180 mg, 98%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  11.07 (s, 1H), 10.64 (s, 1H), 8.90 (q,  $J(\text{H}, \text{H}) = 5.3$ , 1H), 8.61 (t,  $J(\text{H}, \text{H}) = 7.8$ , 1H), 8.12 (d,  $J(\text{H}, \text{H}) = 9.1$ , 1H), 7.98-7.89 (m, 3H), 7.70-7.64 (m, 3H), 7.55 (s, 1H), 7.50 (d,  $J(\text{H}, \text{H}) = 8.3$ , 1H), 7.32 (s, 1H), 7.14 (t,  $J(\text{H}, \text{H}) = 8.3$ , 1H), 6.47 (d,  $J(\text{H}, \text{H}) = 8.2$ , 1H), 6.34 (s, 1H), 5.50 (d,  $J(\text{H}, \text{H}) = 14.6$ , 1H), 4.98 (d,  $J(\text{H}, \text{H}) = 14.6$ , 1H), 4.13-3.99 (m, 8H), 3.79 (s, 3H), 3.72 (s, 3H), 3.53 (s, 3H), 2.34-2.16 (m, 4H), 1.26 (s, 3H), 1.18-1.12 (m, 18H), 0.97 (d,  $J(\text{H}, \text{H}) = 6.6$ , 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  168.8, 166.0, 163.3, 162.9, 162.7, 162.3, 162.0, 160.6, 158.7, 154.6, 151.2, 150.7, 149.4, 148.2, 145.2, 144.9, 142.0, 139.1, 138.4, 137.4, 135.3, 131.5, 130.1, 127.0, 126.8, 125.9, 122.6, 120.3, 119.5, 119.2, 118.8, 117.5, 117.1, 116.5, 115.9, 104.3, 101.8, 100.5, 98.4, 98.1, 96.4, 75.5, 75.2, 67.2, 55.4, 55.2, 53.3, 48.1, 31.7, 29.8, 28.2, 22.7, 19.3, 19.1, 14.2. HRMS (ESI):  $m/z$  calcd for  $\text{C}_{66}\text{H}_{66}\text{F}_4\text{N}_8\text{O}_{11}$   $[\text{M}+\text{H}]^+$  1223.2926, found 1224.5142.

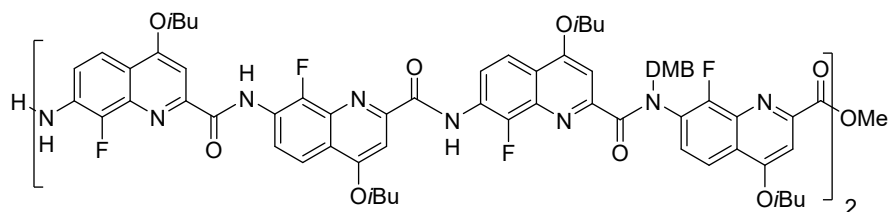


Compound **11**: **9** (750 mg, 0.56 mmol) was dissolved in a mixture of THF (10 mL) and H<sub>2</sub>O (2 mL). To this solution was added LiOH (71 mg, 3.0 equiv.). The solution was stirred at room temperature for 3 h. Then solution was neutralized with 1N HCl to pH = 4~5, and concentrated under reduced pressure to remove THF. H<sub>2</sub>O (30 mL) was added to the residue. The aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3×20 mL). The combined organic phases were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, then evaporated to give dimer acid **11** as a yellow solid (702 mg, 97%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298 K) δ 10.99 (s, 1H), 10.56 (s, 1H), 8.89 (q, *J*(H, H) = 5.3, 1H), 8.61 (t, *J*(H, H) = 7.6, 1H), 8.52 (t, *J*(H, H) = 8.1, 1H), 8.12 (d, *J*(H, H) = 9.5, 1H), 8.04 (d, *J*(H, H) = 9.3, 1H), 7.91 (t, *J*(H, H) = 7.8, 2H), 7.73 (s, 1H), 7.68 (s, 1H), 7.61 (s, 1H), 7.53 (t, *J*(H, H) = 7.9, 1H), 7.45 (s, 1H), 7.36 (s, 1H), 6.47 (d, *J*(H, H) = 7.7, 1H), 6.29 (s, 1H), 5.42 (d, *J*(H, H) = 13.5, 1H), 5.08 (d, *J*(H, H) = 14.8, 1H), 4.14-4.09 (m, 4H), 4.05-4.03 (m, 4H), 3.76 (s, 3H), 3.46 (s, 3H), 2.40-2.15 (m, 4H), 1.59 (s, 9H), 1.25 (s, 3H), 1.17-1.11 (m, 18H), 0.95 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 168.3, 164.4, 163.9, 162.8, 162.5, 160.6, 158.7, 154.5, 152.5, 147.7, 145.1, 143.8, 137.7, 131.7, 129.9, 127.9, 126.9, 122.7, 120.9, 120.2, 119.9, 119.1, 118.8, 117.7, 117.0, 104.2, 100.63, 99.7, 98.3, 97.9, 81.7, 75.7, 75.6, 75.3, 55.4, 55.0, 31.7, 30.4, 29.8, 28.4, 28.2, 28.0, 22.7, 19.3, 19.1, 14.2. HRMS (ESI): *m/z* calcd for C<sub>70</sub>H<sub>72</sub>F<sub>4</sub>N<sub>8</sub>O<sub>13</sub> [M+H]<sup>+</sup> 1309.3823, found 1310.5554.



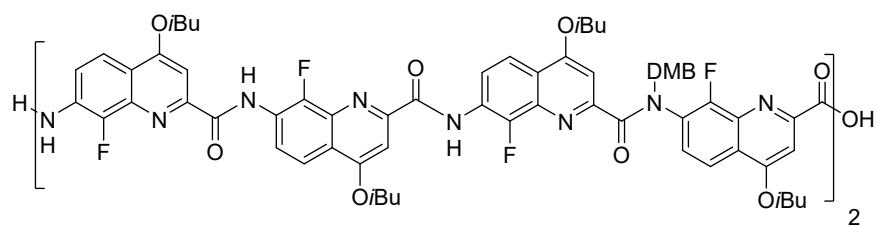
Compound **12**: A solution of **11** (400 mg, 0.30 mmol) in dry CHCl<sub>3</sub> (3 mL) was cooled to 0°C. 1-Chloro-N,N,2-trimethyl-1-propenylamine (0.10 mL, 2.2 eq.) was added. The solution was stirred at room temperature for 3 h under N<sub>2</sub>. The solvent was removed under high-vacuum for at least 2 hours to yield the corresponding acid chloride. The resulting acid chloride was dissolved in dry CHCl<sub>3</sub> (3 mL) and added to a solution of **10** (377 mg, 1.0 eq.) and dry DIPEA (0.16 mL, 3.0 eq.) in dry CHCl<sub>3</sub> (2 mL). The mixture was stirred for 12 h. The organic layer was washed with saturated aqueous NH<sub>4</sub>Cl, saturated aqueous NaHCO<sub>3</sub> and brine, dried over MgSO<sub>4</sub>, filtered and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, ethyl acetate / cyclohexane = 1 / 3) to give **12** as yellow solid (594 mg, 77 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) δ 11.44-10.28 (m, 5H), 9.09-8.33 (m, 5H), 8.16-7.31 (m, 20H), 7.19-6.97 (m, 2H), 6.51-5.99 (m, 3H), 5.47-4.85 (m,

4H), 4.12-3.36 (m, 31H), 2.39-2.09 (m, 8H), 1.66-1.51 (m, 12H), 1.22-1.07 (m, 45H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 167.6, 164.8, 162.1, 161.4, 160.9, 159.4, 159.2, 157.4, 153.5, 151.3, 150.2, 150.1, 149.9, 148.0, 146.8, 137.6, 136.4, 130.7, 130.2, 128.4, 128.1, 126.6, 125.8, 125.5, 124.8, 121.5, 120.8, 119.4, 118.9, 118.7, 118.1, 117.6, 116.4, 116.0, 115.3, 103.1, 99.7, 99.5, 98.2, 97.0, 76.2, 74.3, 74.0, 54.2, 54.1, 53.9, 52.0, 46.6. HRMS (ESI): m/z calcd for C<sub>136</sub>H<sub>136</sub>F<sub>8</sub>N<sub>16</sub>O<sub>23</sub> [M+H]<sup>+</sup> 2514.6602, found 2515.0552.



**13**

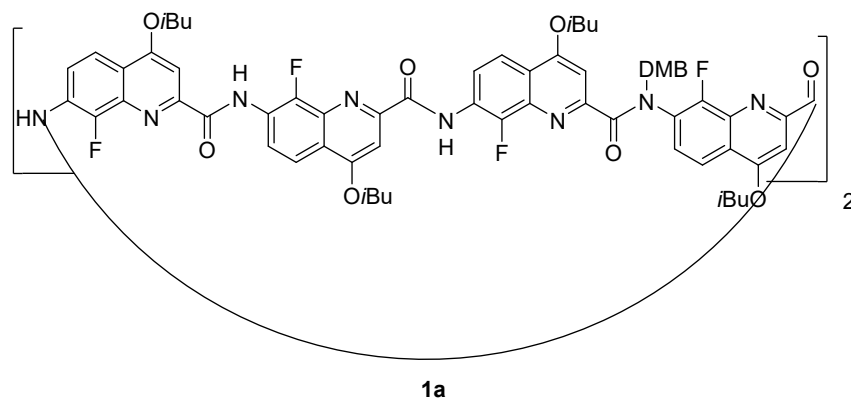
Compound **13**: **12** (100 mg, 0.039 mmol) was dissolved in dioxane (0.1 mL). HCl in dioxane (4M, 1.0 mL) was added to the solution, and stirred at room temperature for 4 h. The mixture was diluted with DCM and the organic layer was washed with saturated aqueous NaHCO<sub>3</sub> and brine, dried over MgSO<sub>4</sub>, filtered and concentrated in vacuo to give **13** as yellow solid (93 mg, 97%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) δ 11.30-10.37 (m, 5H), 9.13-8.32 (m, 4H), 8.22-7.37 (m, 20H), 7.22-6.92 (m, 3H), 6.51-6.18 (m, 3H), 5.47-4.94 (m, 4H), 4.35-3.91 (m, 25H), 3.77-3.36 (m, 6H), 2.42-2.11 (m, 8H), 1.72-1.62 (m, 6H), 1.24-0.95 (m, 42H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 168.6, 165.8, 163.1, 162.7, 162.4, 161.9, 160.5, 160.3, 160.0, 158.6, 158.4, 154.6, 151.1, 150.5, 138.8, 137.7, 137.1, 135.1, 131.7, 11.4, 129.5, 126.9, 125.9, 122.5, 121.9, 120.0, 119.1, 118.9, 117.4, 117.0, 116.3, 104.1, 101.6, 101.2, 100.7, 100.4, 99.2, 98.1, 96.1, 95.3, 72.2, 71.1, 61.5, 59.4, 53.1, 47.6, 42.8, 37.6, 35.6, 30.2, 29.6. HRMS (ESI): m/z calcd for C<sub>131</sub>H<sub>128</sub>F<sub>8</sub>N<sub>16</sub>O<sub>21</sub> [M+H]<sup>+</sup> 2414.5432, found 2414.9951.



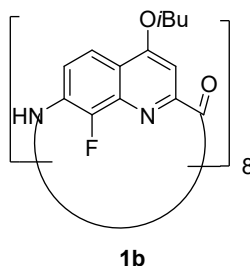
**14**

Compound **14**: **13** (90 mg, 0.037 mmol) was dissolved in THF (1.0 mL). LiOH (7.45 mg, 0.186 mmol) was added to the solution, followed with H<sub>2</sub>O (0.1 mL) and stirred at room temperature for 4 h. The organic layer was washed with citric acid (5%, 25 mL) and brine, dried over MgSO<sub>4</sub>, filtered and concentrated in vacuo to give **14** as yellow solid (82 mg, 98%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) δ 11.27-10.34 (m, 5H), 9.10-8.32 (m, 4H), 8.07-7.30 (m, 20H), 7.19-6.90 (m, 3H), 6.64-6.04 (m, 3H), 5.44-4.87 (m, 4H), 4.42-3.79 (m, 18H), 3.76-3.30 (m, 10H), 2.40-2.07 (m, 8H), 1.23-0.94 (m, 48H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 167.2, 163.2, 162.6, 162.1, 161.3,

160.9, 160.4, 159.5, 159.0, 157.5, 153.3, 150.0, 149.4, 146.6, 144.1, 136.1, 134.0, 130.7, 130.4, 128.7, 125.9, 124.8, 124.4, 121.4, 118.9, 118.1, 117.8, 116.4, 115.2, 114.6, 103.1, 102.9, 102.7, 102.5, 99.4, 98.0, 97.0, 95.0, 94.2, 66.9, 66.0, 58.4, 50.0, 47.0, 36.0, 34.5, 28.6, 28.4, 24.5. HRMS (ESI):  $m/z$  calcd for  $C_{130}H_{126}F_8N_{16}O_{21}$   $[M+H]^+$  2400.5162, found 2400.9805.

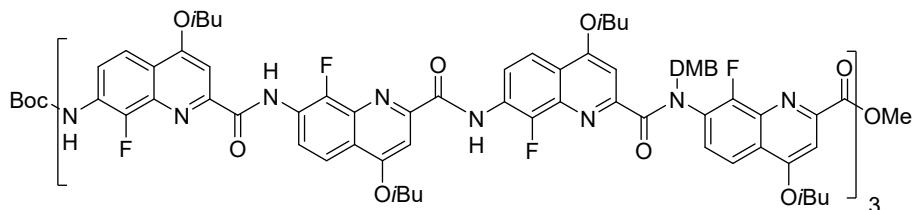


Compound **1a**: **14** (350 mg, 0.15 mmol) and triphenylphosphine (582 mg, 15 eq.) were mixed in dry chloroform (5 mL) and then trichloroacetonitrile (250  $\mu$ L, 17 eq.) and dry DIPEA (384  $\mu$ L, 15 eq.) were added. The mixture was stirred at room temperature for 48 h. The solvent was removed under reduced pressure and the residue was dissolved in dichloromethane and washed with saturated aqueous  $NH_4Cl$ ,  $NaHCO_3$  and extracted with chloroform. The organic layer was washed with brine, and dried over anhydrous  $MgSO_4$ . After the solvent was removed in vacuo, the residue was purified by column chromatography (silica gel, ethyl acetate / *n*-hexane = 1 / 2) and GPC to give **1a** as yellow solid (127 mg, 36%).  $^1H$  NMR (300 MHz,  $CDCl_3$ , 298 K)  $\delta$  11.15-10.80 (m, 2H), 10.68 (s, 2H), 10.44-10.23 (m, 2H), 8.97-8.46 (m, 4H), 8.37-8.26 (m, 2H), 8.17-8.02 (m, 3H), 7.95-7.40 (m, 11H), 7.30 (s, 4H), 6.59 (br, 1H), 6.40 (d,  $J(H, H) = 7.9$ , 2H), 6.22-6.18 (m, 3H), 5.64 (d,  $J(H, H) = 14.2$ , 2H), 5.03 (d,  $J(H, H) = 14.2$ , 2H), 4.17-3.96 (m, 12H), 3.85 (s, 4H), 3.68 (s, 6H), 3.47-3.33 (m, 6H), 2.30-2.07 (m, 8H), 1.24-1.05 (m, 24H), 1.02-0.94 (m, 24H). HRMS (ESI):  $m/z$  calcd for  $C_{130}H_{125}F_8N_{16}O_{20}$   $[M+2H]^{2+}$  1191.9615, found 1191.8117.



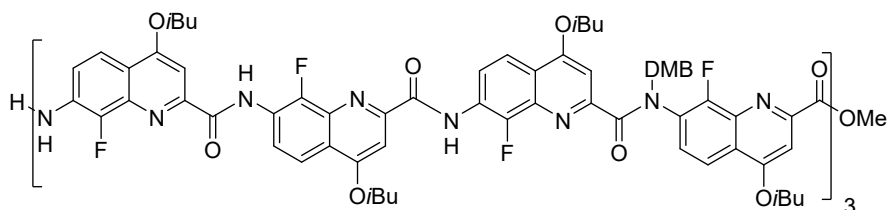
Compound **1b**: Trifluoroacetic acid (5 mL) was added to **1a** (100.0 mg, 0.04 mmol) and the mixture was stirred at  $60^\circ C$  for 2 h. The reaction mixture was quenched by adding sat.  $NaHCO_3$  aq. and extracted with chloroform. The organic layer was washed with brine, and dried over  $MgSO_4$ . After the solvent was removed in vacuo, the residue

was purified by GPC to give **1b** as yellow solid (87.4 mg, quant.). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298 K) δ 11.37-9.92 (m, 8H), 9.17-8.73 (m, 4H), 8.51-8.06 (m, 6H), 7.97-7.32 (m, 10H), 7.06-6.64 (m, 4H), 4.38-3.69 (m, 16H), 1.37-1.04 (m, 48H). HRMS (ESI): m/z calcd for C<sub>112</sub>H<sub>104</sub>F<sub>8</sub>N<sub>16</sub>O<sub>16</sub> [3M+3H]<sup>3+</sup> 2082.4450, found 2082.4993.



**15**

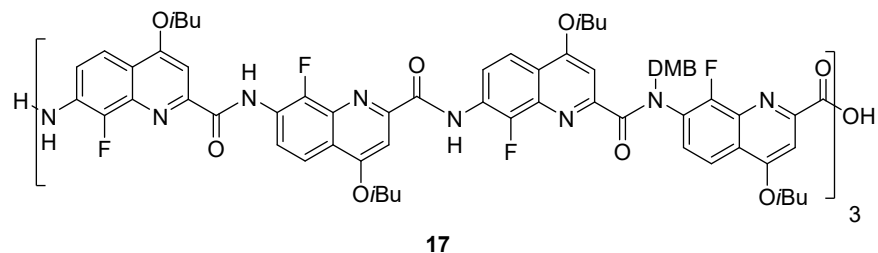
Compound **15**: A solution of **11** (107 mg, 0.08 mmol) in dry CHCl<sub>3</sub> (1 mL) was cooled to 0°C. 1-Chloro-N,N,2-trimethyl-1-propenylamine (0.04 mL, 3.0 eq.) was added. The solution was stirred at room temperature for 3 h. The solvent was removed under high-vacuum. The resulting acid chloride was dissolved in dry CHCl<sub>3</sub> (3 mL) and added to a solution of **13** (200 mg, 1.0 eq.) and dry DIPEA (0.05 mL, 3.0 eq.) in dry CHCl<sub>3</sub> (2 mL). The mixture was stirred for 12 h. The solvent was removed under reduced pressure and the residue was dissolved in dichloromethane and washed with saturated aqueous NH<sub>4</sub>Cl, saturated aqueous NaHCO<sub>3</sub> and brine, dried over MgSO<sub>4</sub>, filtered and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, ethyl acetate / cyclohexane = 1 / 3) to give **15** as yellow solid (162 mg, 54%). <sup>1</sup>H NMR δ (400 MHz, CDCl<sub>3</sub>, 298 K) δ 10.96-10.40 (m, 8H), 9.01-8.51 (m, 8H), 8.10-7.48 (m, 28H), 6.48-6.24 (m, 9H), 5.50-4.96 (m, 6H), 4.24-3.83 (m, 27H), 3.73-3.67 (m, 9H), 3.52-3.41 (m, 9H), 2.43-2.11 (m, 12H), 1.32-1.00 (m, 81H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 167.6, 167.1, 164.8, 162.0, 161.4, 160.8, 159.2, 157.4, 153.5, 151.3, 150.0, 148.1, 147.3, 146.7, 145.5, 145.0, 144.2, 137.7, 136.5, 130.5, 128.8, 125.7, 125.4, 124.5, 121.3, 120.1, 119.2, 118.7, 118.7, 118.2, 117.4, 116.4, 116.0, 115.2, 103.0, 100.5, 99.6, 97.0, 96.6, 80.3, 79.9, 74.3, 74.0, 54.1, 53.8, 46.8, 27.1, 18.2. HRMS (ESI): m/z calcd for C<sub>201</sub>H<sub>199</sub>F<sub>12</sub>N<sub>24</sub>O<sub>33</sub> [M+H]<sup>+</sup> 3706.4501, found 3706.4991.



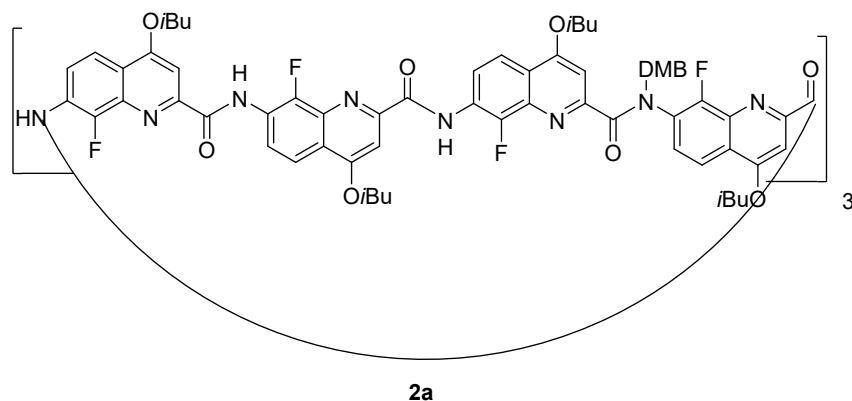
**16**

Compound **16**: **15** (80 mg, 0.021 mmol) was dissolved in dioxane (0.1 mL). HCl in dioxane (4M, 1mL) was added to the solution, and stirred at room temperature for 4 h. The mixture was diluted with DCM and washed with saturated aqueous NaHCO<sub>3</sub> and brine, the organic layer was dried over MgSO<sub>4</sub>, filtered and concentrated in vacuo to give **16** as yellow solid (75 mg, 98%). <sup>1</sup>H NMR δ (400 MHz, CDCl<sub>3</sub>, 298 K) 11.07-10.55 (m, 8H), 8.93-

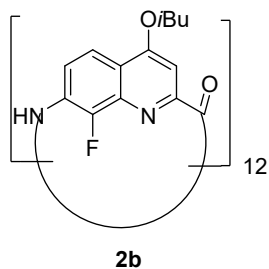
8.51 (m, 8H), 8.17-7.40 (m, 26H), 7.22-7.09 (m, 2H), 6.50-6.22 (m, 9H), 5.50-5.03 (m, 6H), 4.18-3.45 (m, 45H), 2.45-2.17 (m, 12H), 1.29-0.83 (m, 72H).



Compound **17**: **16** (80 mg, 0.021 mmol) was dissolved in THF (1.0 mL). LiOH (5.09 mg, 0.121 mL) was added to the solution, followed with H<sub>2</sub>O (0.1 mL) and stirred at room temperature for 4 h. The organic layer was washed with citric acid (5%, 25 mL) and brine, dried over MgSO<sub>4</sub>, filtered and concentrated in vacuo to give **17** as yellow solid (78 mg, 98%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) δ 10.73-10.48 (m, 8H), 8.70-8.39 (m, 8H), 8.00-7.39 (m, 26H), 6.32-6.13 (m, 9H), 5.37-5.03 (m, 6H), 4.21-3.23 (m, 42H), 2.42-2.19 (m, 12H), 1.03-0.78 (m, 72H).



Compound **2a**: **17** (85 mg, 0.023 mmol) and triphenylphosphine (93.4 mg, 15 eq.) were mixed in dry chloroform (3 mL) and then trichloroacetonitrile (47 μL, 17 eq.) and dry DIPEA (61 μL, 15 eq.) were added. The mixture was stirred at room temperature for 48 h under argon. The solvent was removed under reduced pressure and the residue was dissolved in dichloromethane and washed with saturated aqueous NH<sub>4</sub>Cl, NaHCO<sub>3</sub> and extracted with chloroform. The organic layer was washed with brine, and dried over anhydrous MgSO<sub>4</sub>. After the solvent was removed in vacuo, the residue was purified by column chromatography (silica gel, ethyl acetate / n-hexane = 1 / 2) and GPC to give **2a** as yellow solid (52 mg, 61%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) δ 11.01-10.46 (m, 9H), 9.03-8.37 (m, 9H), 8.20-7.34 (m, 24H), 7.20-7.01 (m, 4H), 6.44-6.12 (m, 8H), 5.09 (br, 6H), 4.21-3.94 (m, 20H), 3.81-3.53 (m, 12H), 3.46-3.22 (m, 10H), 2.42-2.04 (m, 12H), 1.16-0.84 (m, 72H).

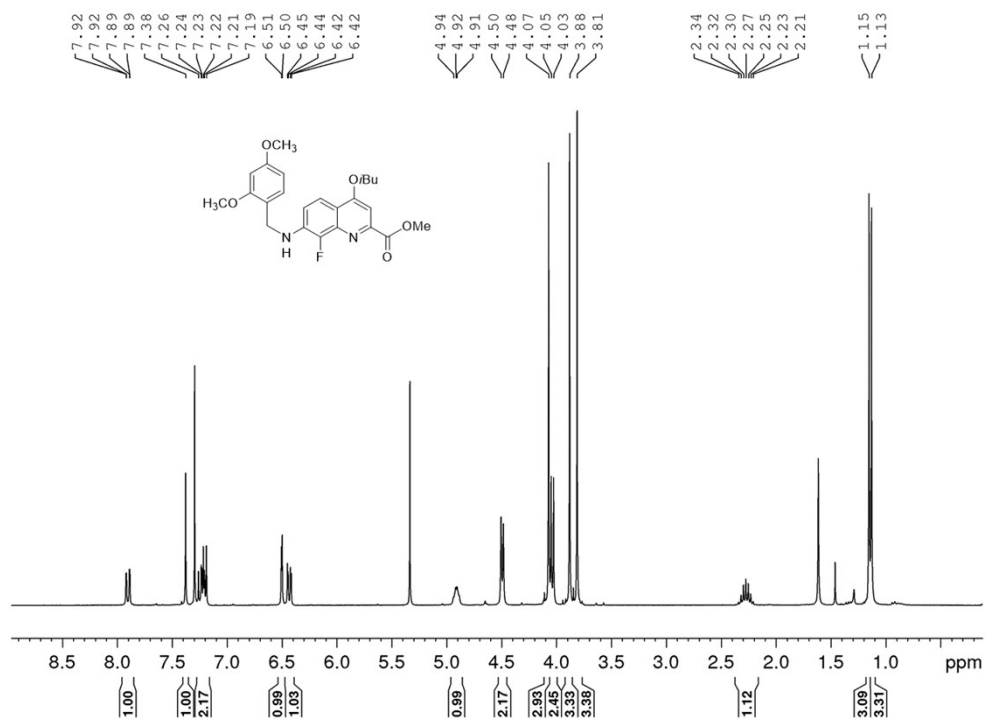


Compound **2b**: Trifluoroacetic acid (5 mL) was added to **2a** (56.0 mg, 0.015 mmol) and the mixture was stirred at 60°C for 2 h. The reaction mixture was quenched by adding sat. NaHCO<sub>3</sub> aq. and extracted with chloroform. The organic layer was combined and washed with brine, dried over MgSO<sub>4</sub>. After the solvent was removed in vacuo, the residue was purified by GPC to give **2b** as yellow solid (48.2 mg, quant.). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) δ 12.01 (s, 1H), 11.87 (s, 1H), 11.74 (s, 1H), 11.57 (s, 1H), 11.50 (s, 1H), 11.48 (s, 1H), 11.44 (s, 1H), 11.36 (s, 2H), 10.50 (s, 1H), 10.37 (s, 1H), 9.24 (t, *J*(H, H) = 7.2, 1H), 9.11 (s, 1H), 9.07 (t, *J*(H, H) = 7.8, 1H), 9.00-8.89 (m, 3H), 8.81 (t, *J*(H, H) = 7.6, 1H), 8.63 (t, *J*(H, H) = 7.3, 1H), 8.46 (t, *J*(H, H) = 7.2, 1H), 8.20 (q, *J*(H, H) = 7.8, 2H), 8.14 (t, *J*(H, H) = 7.2, 1H), 8.09 (s, 1H), 8.07-8.01 (m, 1H), 7.87 (d, *J*(H, H) = 9.0, 1H), 7.80-7.71 (m, 4H), 7.65 (s, 1H), 7.51 (s, 1H), 7.47 (d, *J*(H, H) = 11.0, 1H), 7.42 (d, *J*(H, H) = 9.0, 1H), 7.35-7.29 (m, 2H), 7.18-7.07 (m, 5H), 6.99 (s, 1H), 6.64 (s, 1H), 6.60 (d, *J*(H, H) = 4.6, 2H), 6.41 (s, 1H), 6.18 (s, 1H), 4.35 (br, 2H), 4.20-4.14 (m, 5H), 4.12-4.03 (m, 2H), 3.92-3.86 (m, 3H), 3.81-3.72 (m, 5H), 3.70-3.57 (m, 5H), 3.40 (t, *J*(H, H) = 8.1, 1H), 3.03 (t, *J*(H, H) = 8.1, 1H), 2.42-2.03 (m, 12H), 1.31-1.00 (m, 72H). HRMS (ESI): *m/z* calcd for C<sub>168</sub>H<sub>156</sub>F<sub>12</sub>N<sub>24</sub>O<sub>24</sub> [M+2H]<sup>2+</sup> 1562.0856, found 1562.0332, [2M+3H]<sup>3+</sup>: 2082.7795, found 2082.7056 .

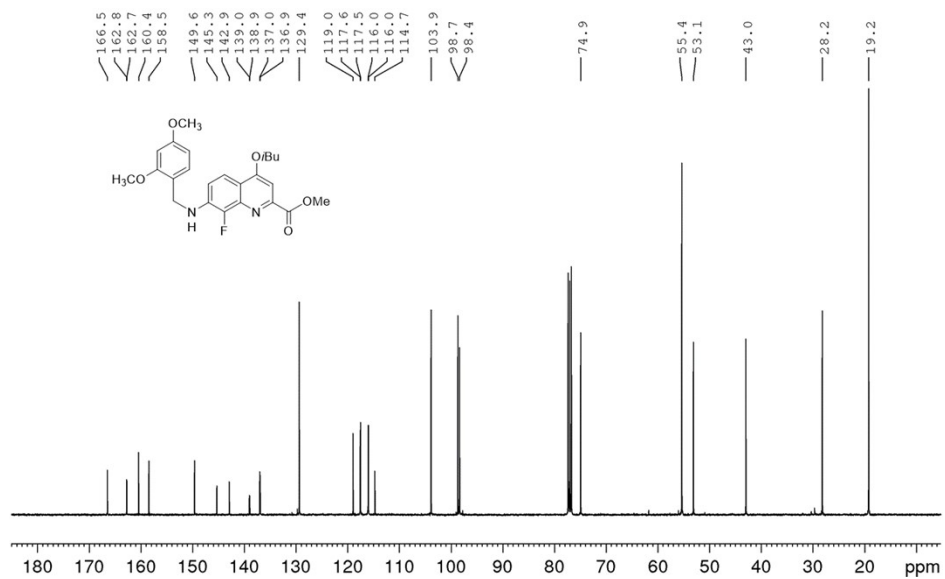


## 6. $^1\text{H}$ and $^{13}\text{C}$ NMR spectra

### Compound 5

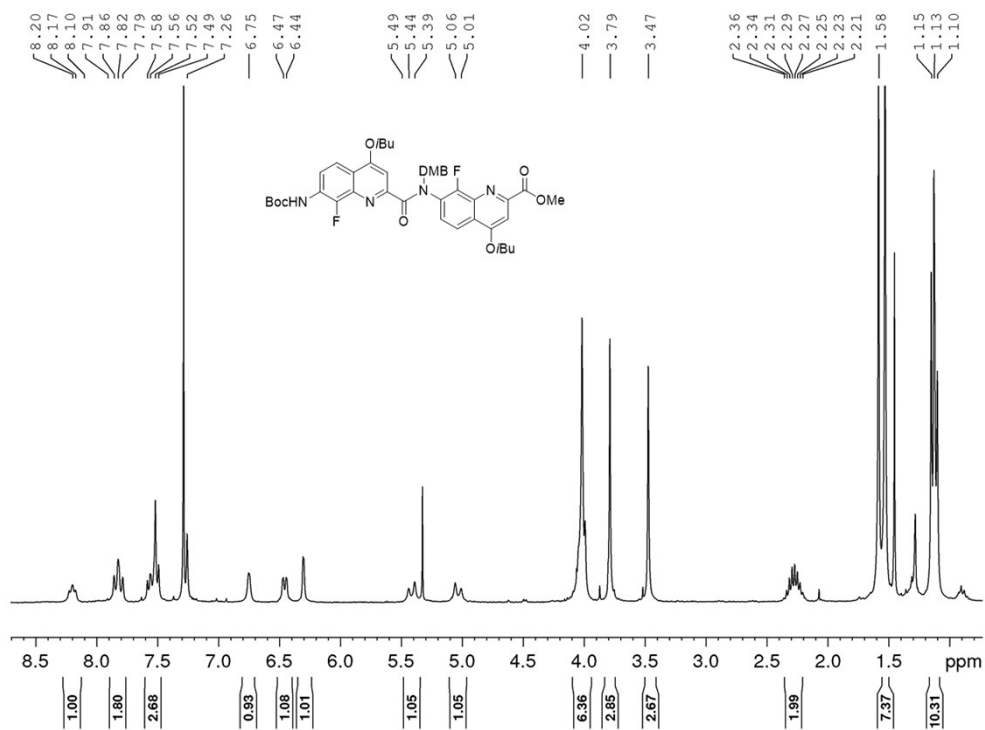


$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25°C)

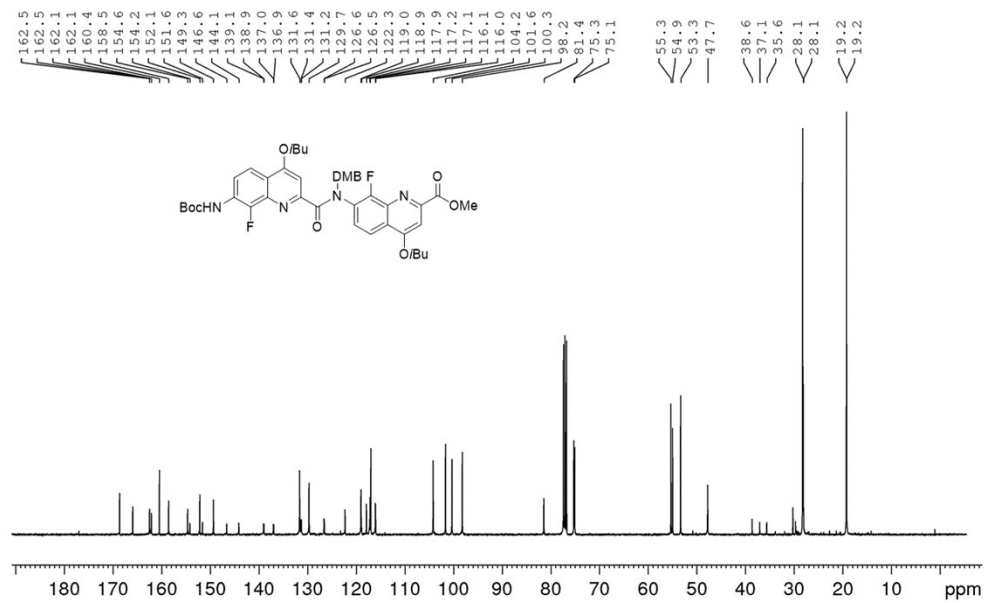


$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 25°C)

# Compound 6

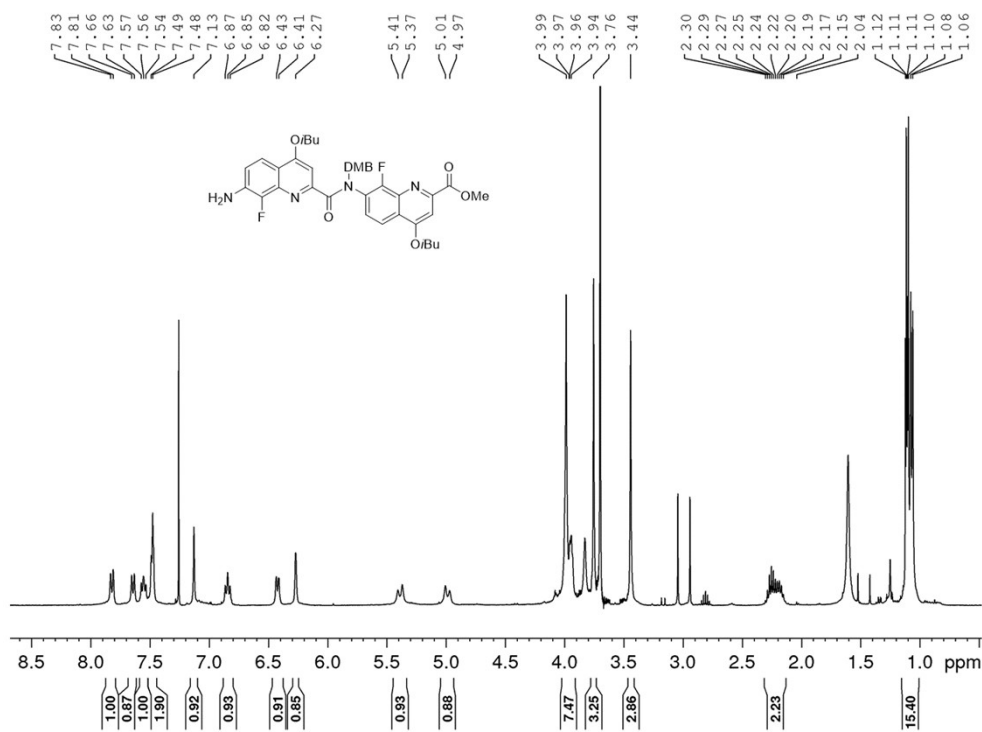


<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C)

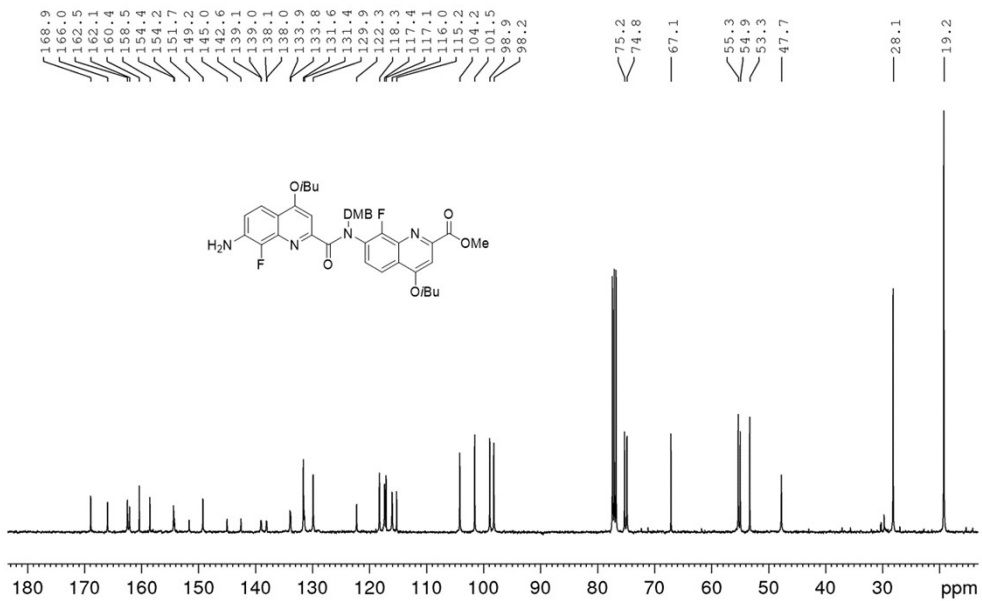


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C)

# Compound 7

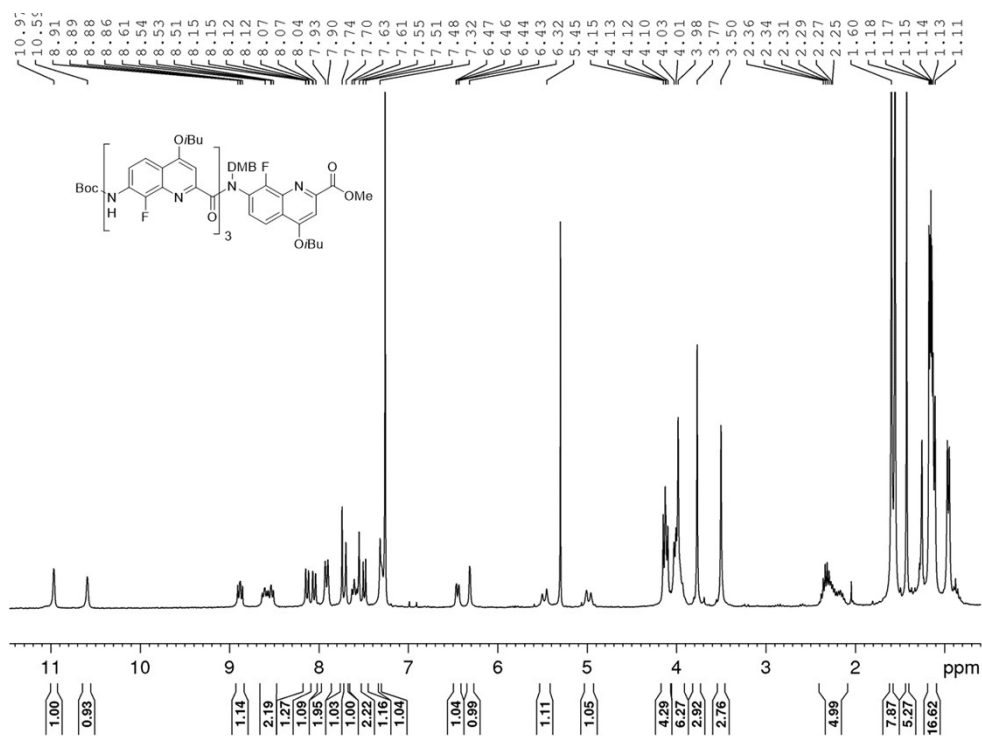


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K)

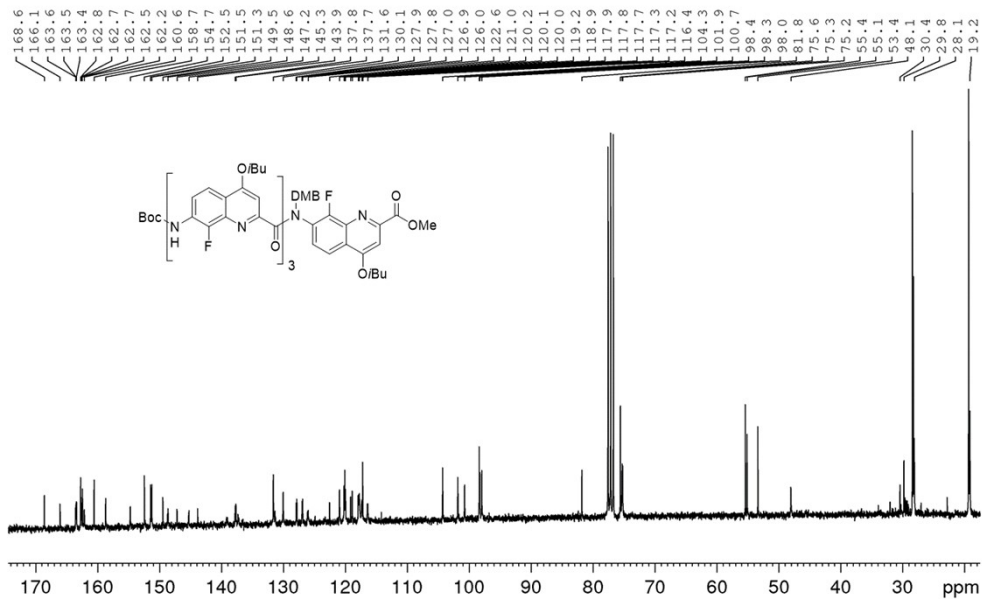


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C)

## Compound 9

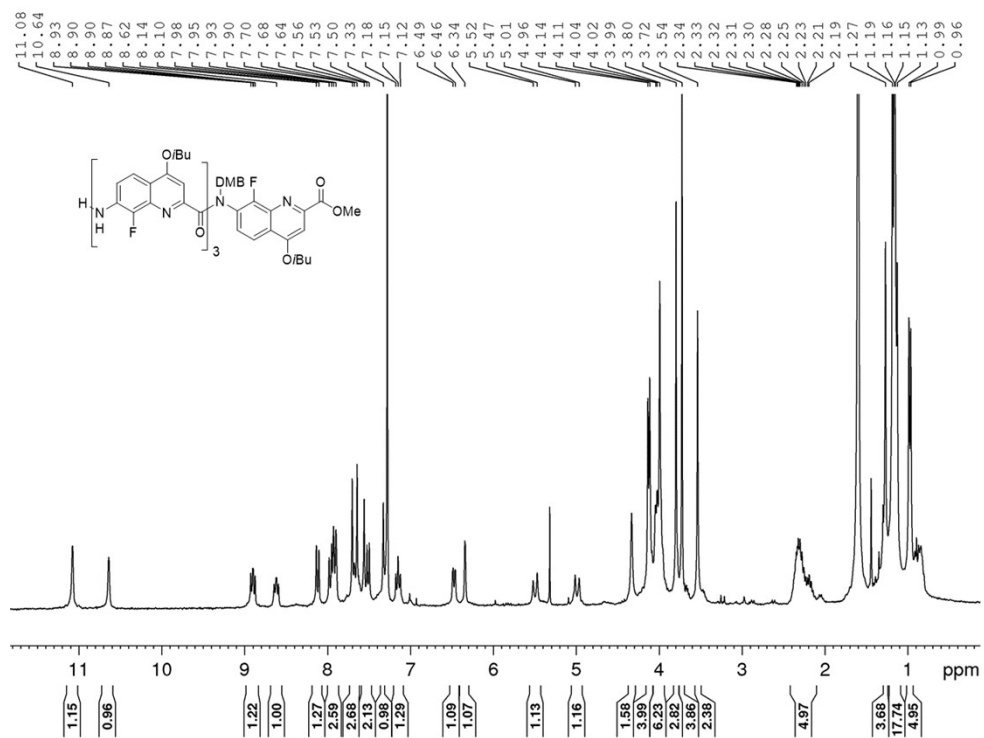


$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 298 K)

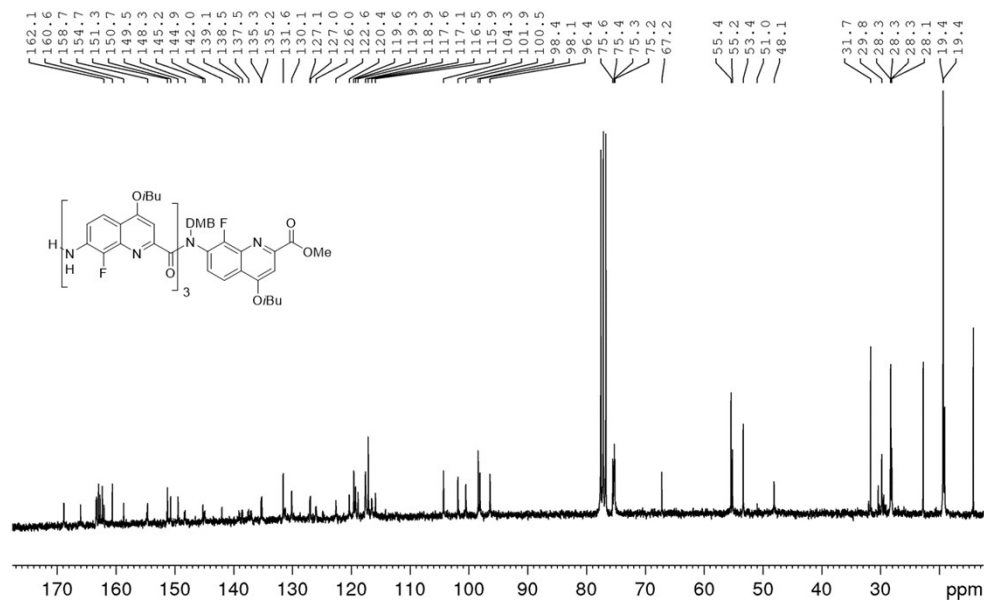


$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 25°C)

# Compound 10

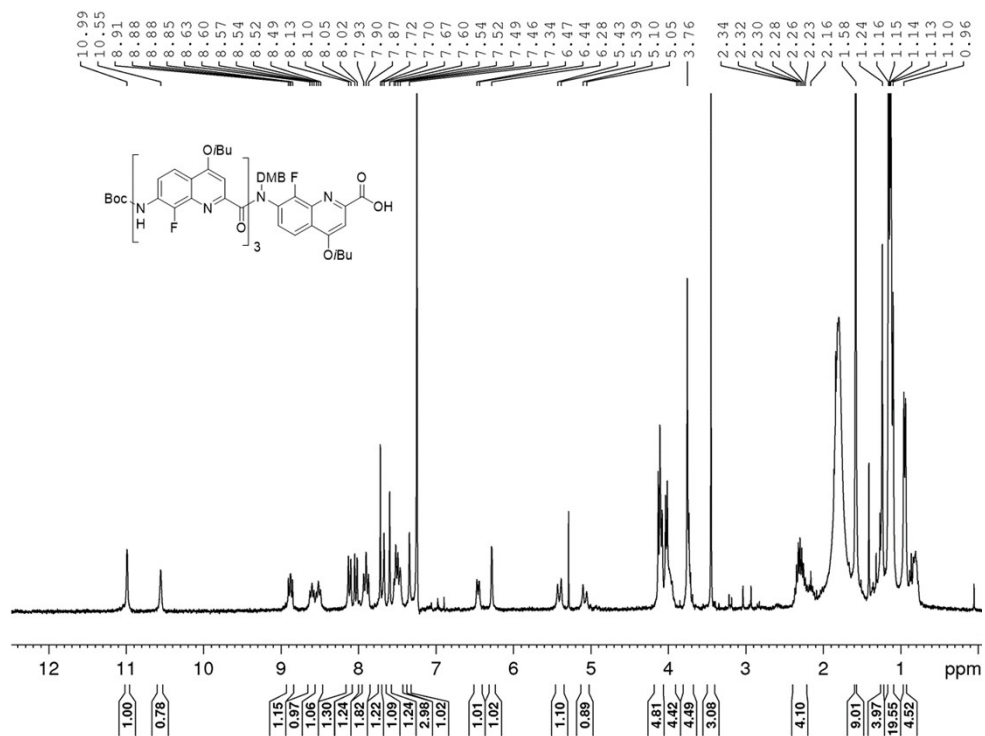


<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298 K)

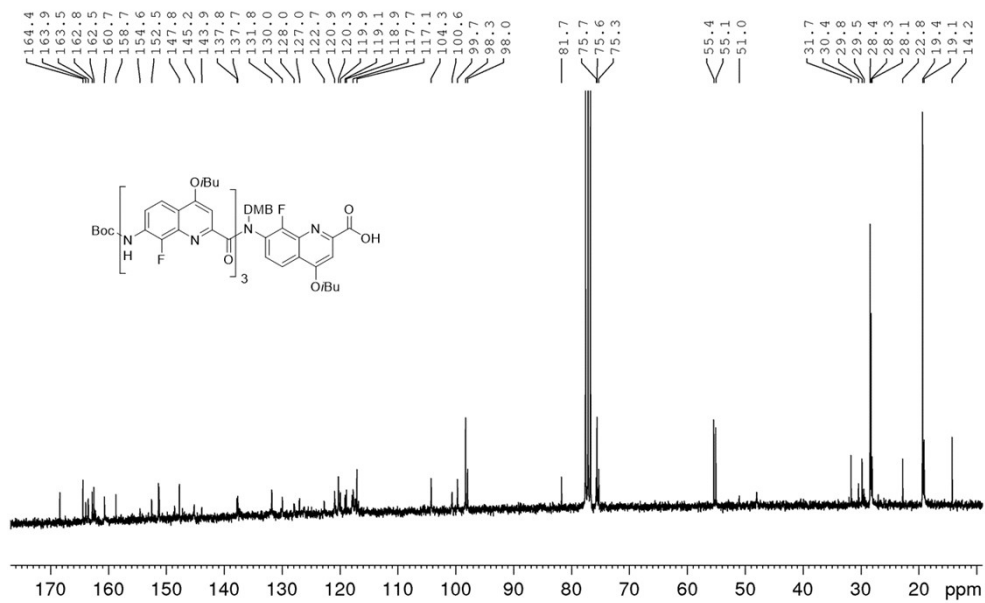


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C)

# Compound 11

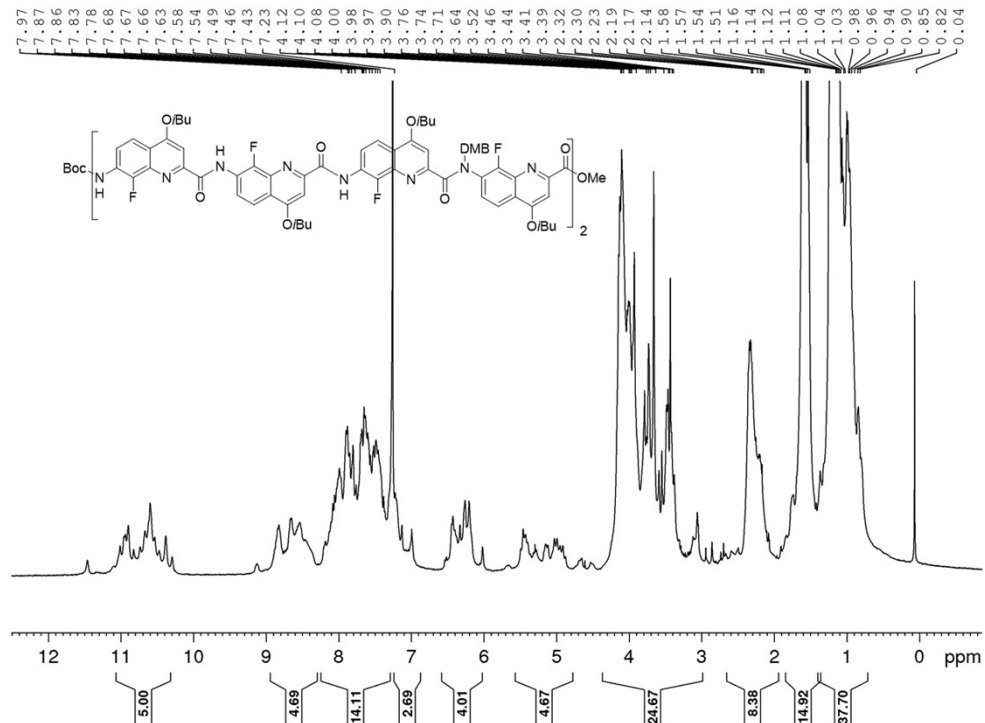


<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298 K)

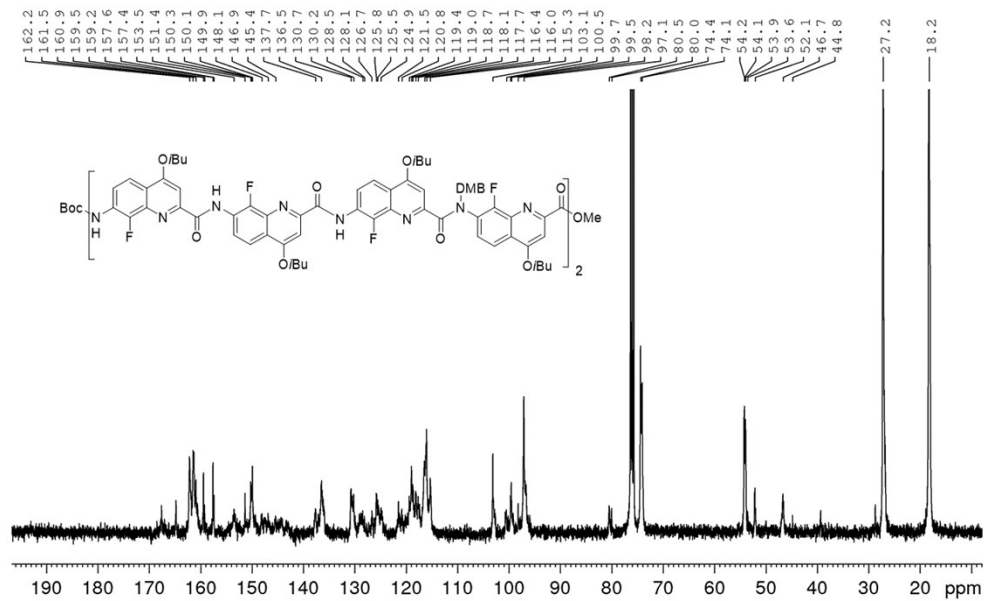


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C)

## Compound 12

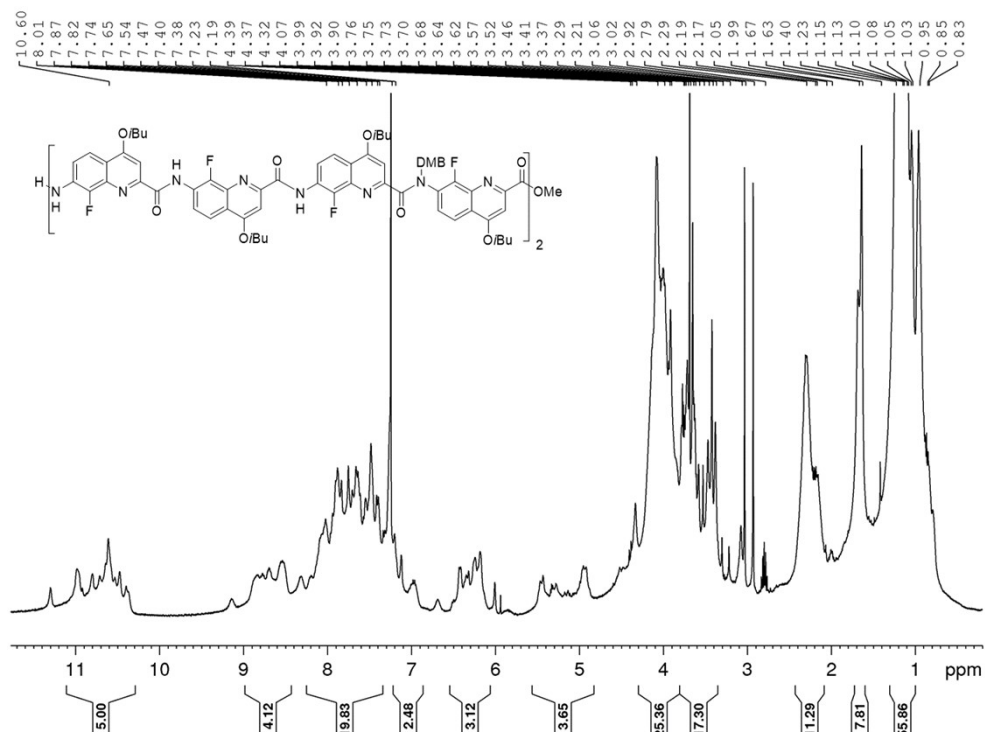


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K)

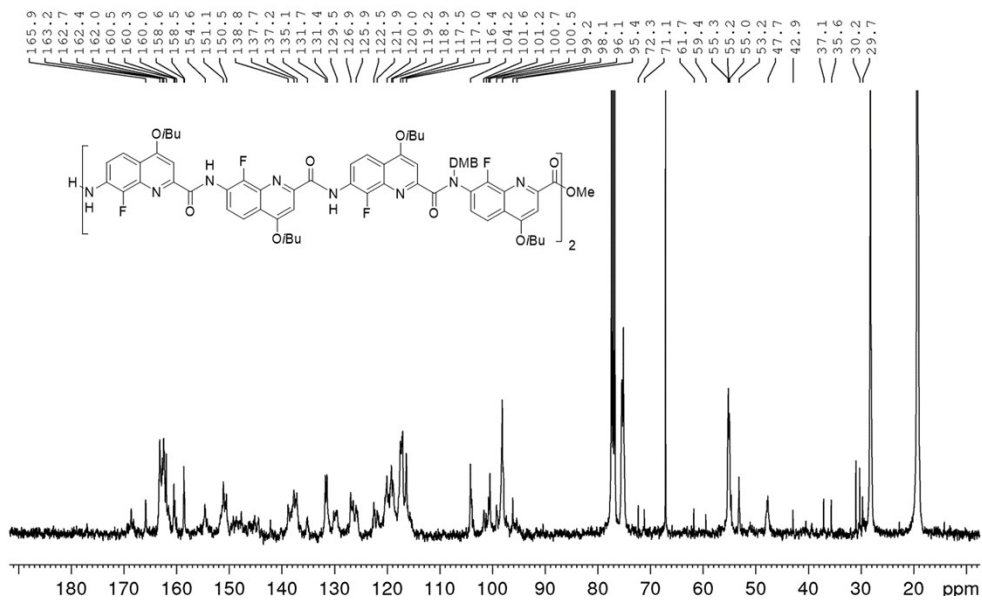


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C)

# Compound 13



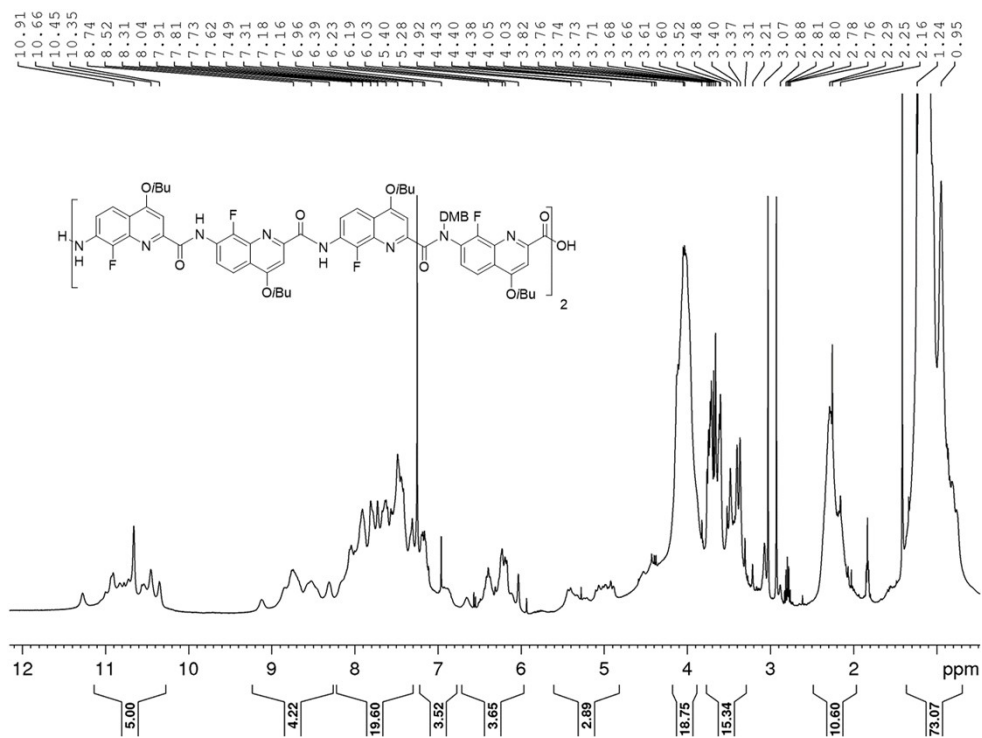
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K)



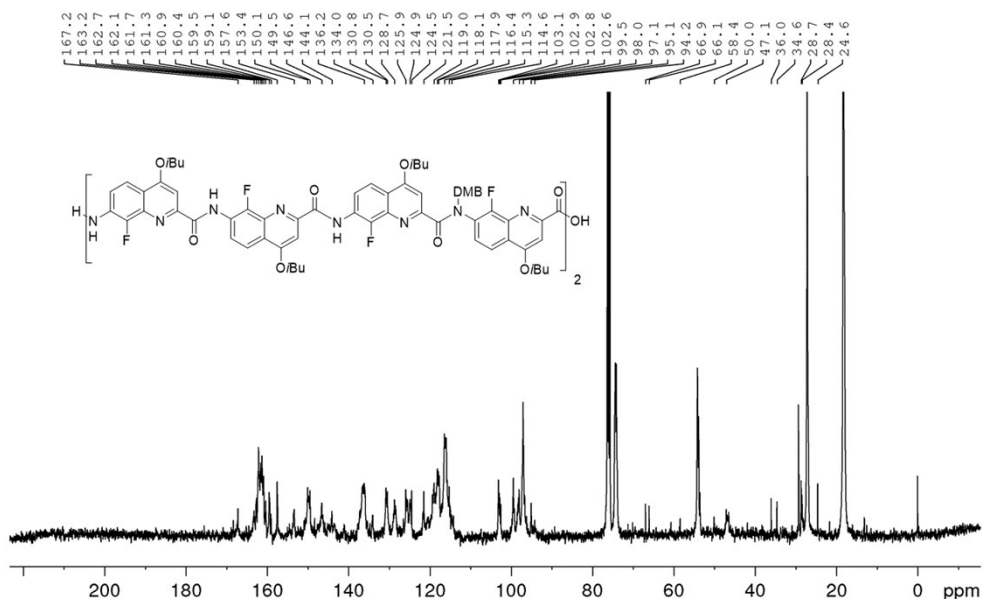
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C)



# Compound 14

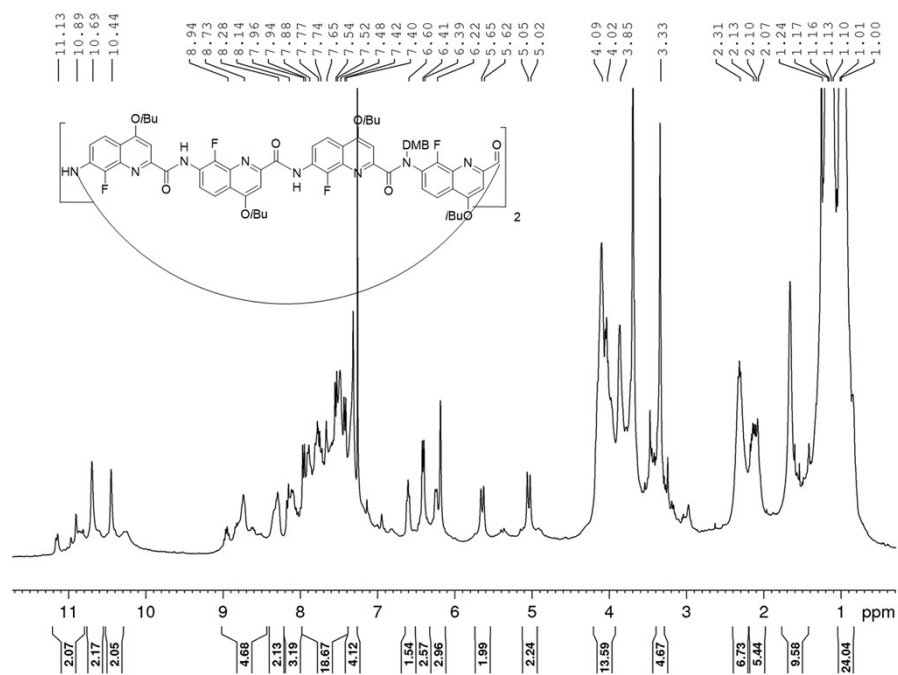


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K)



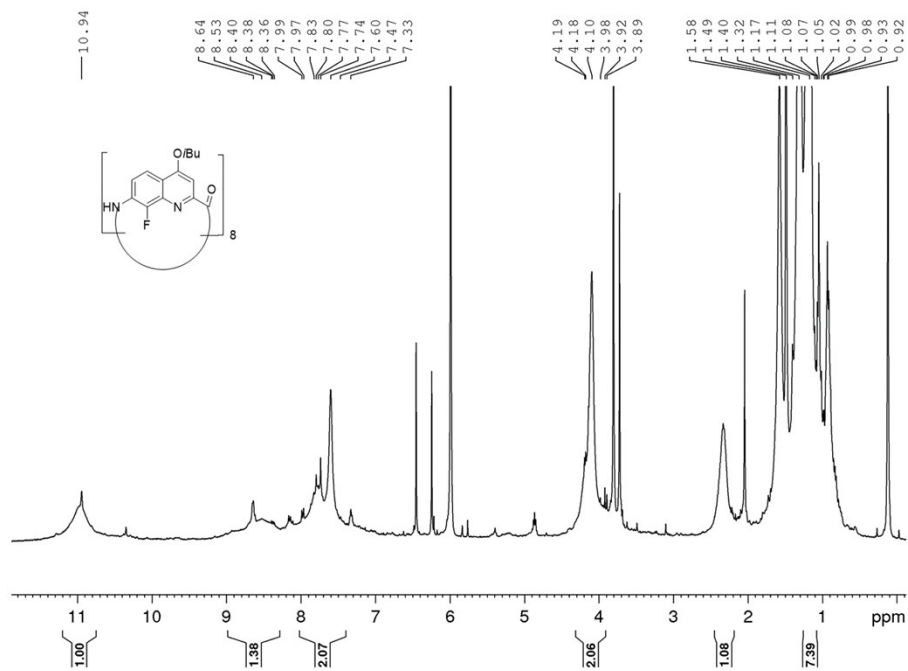
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C)

## Compound 1a



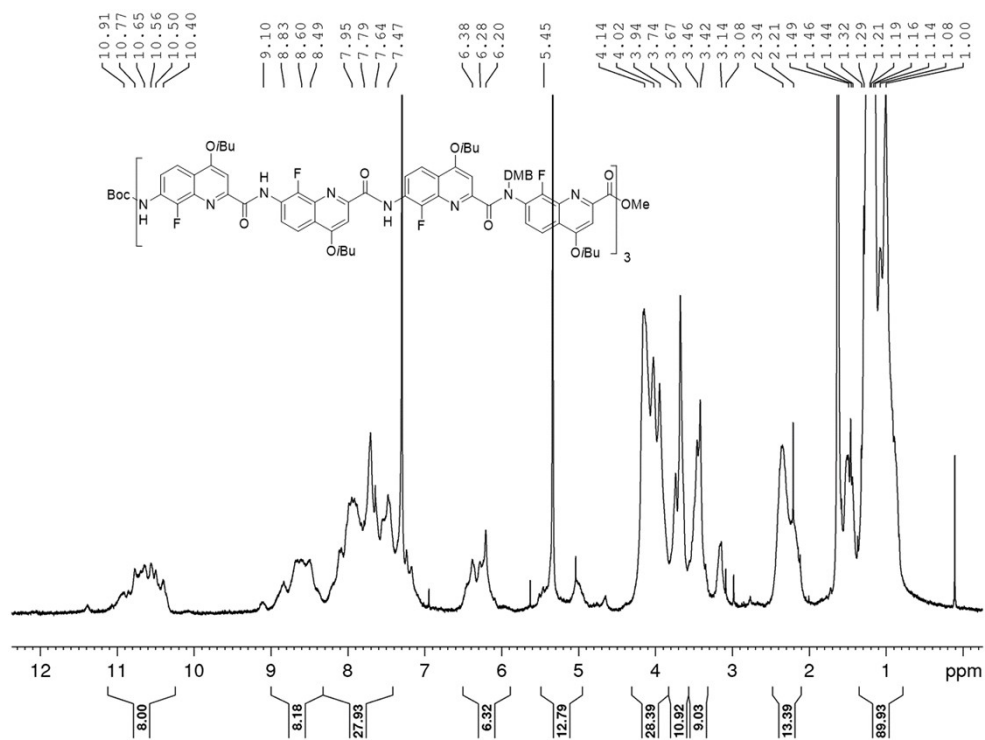
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298 K)

## Compound 1b

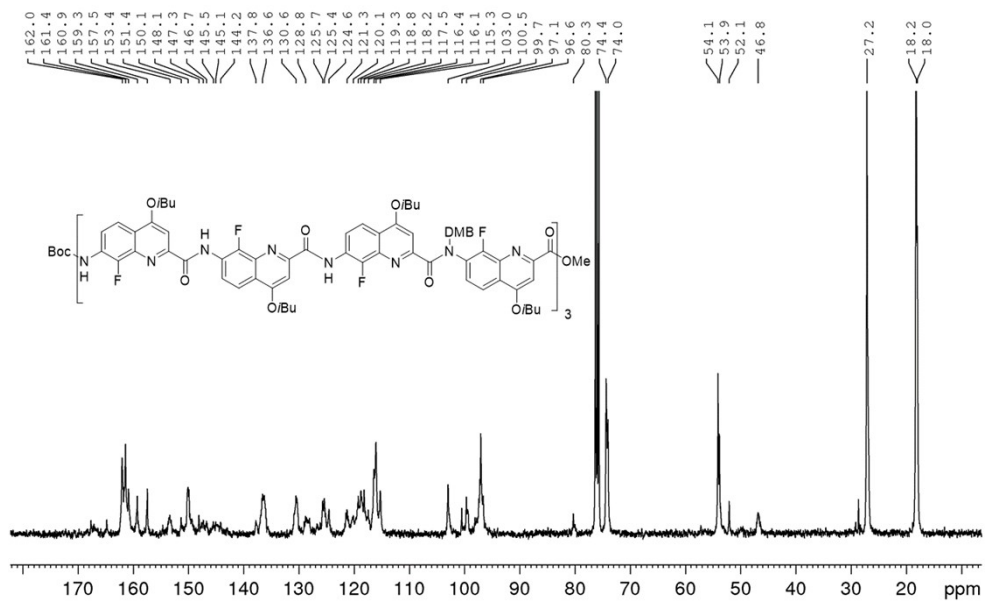


<sup>1</sup>H NMR (300 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 353 K)

# Compound 15

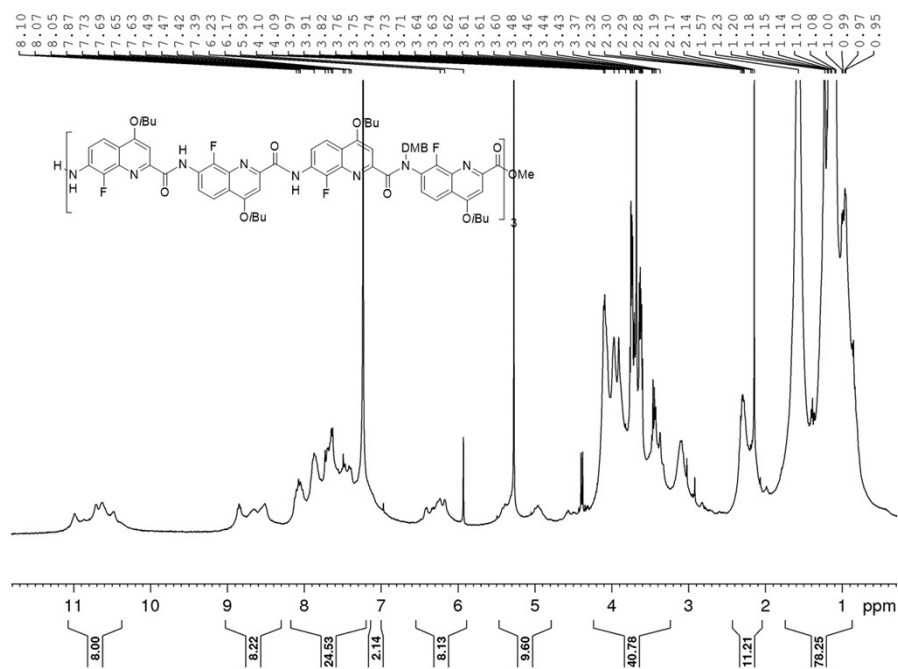


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K)



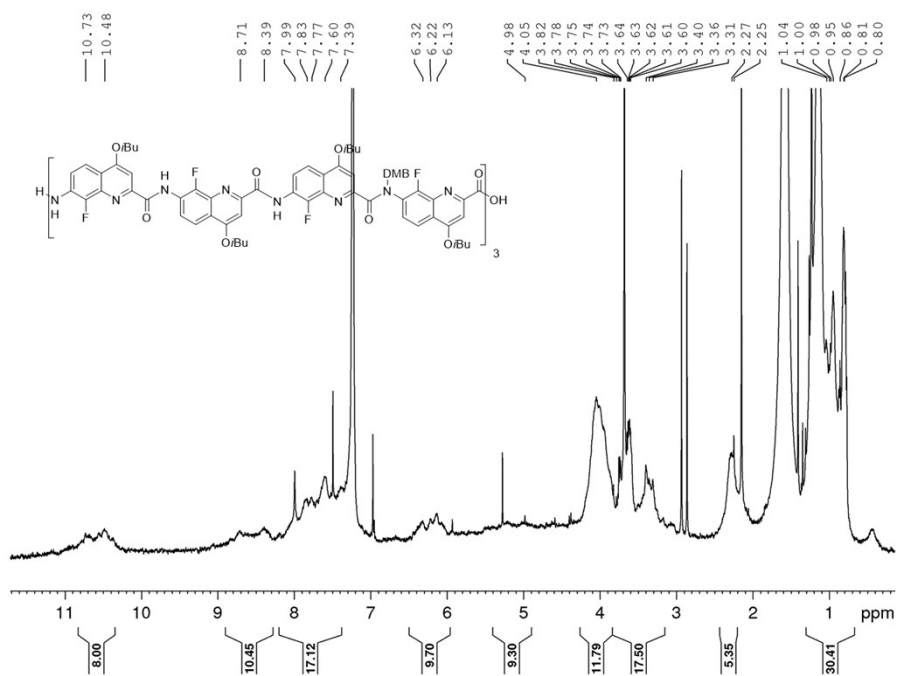
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 25°C)

## Compound 16



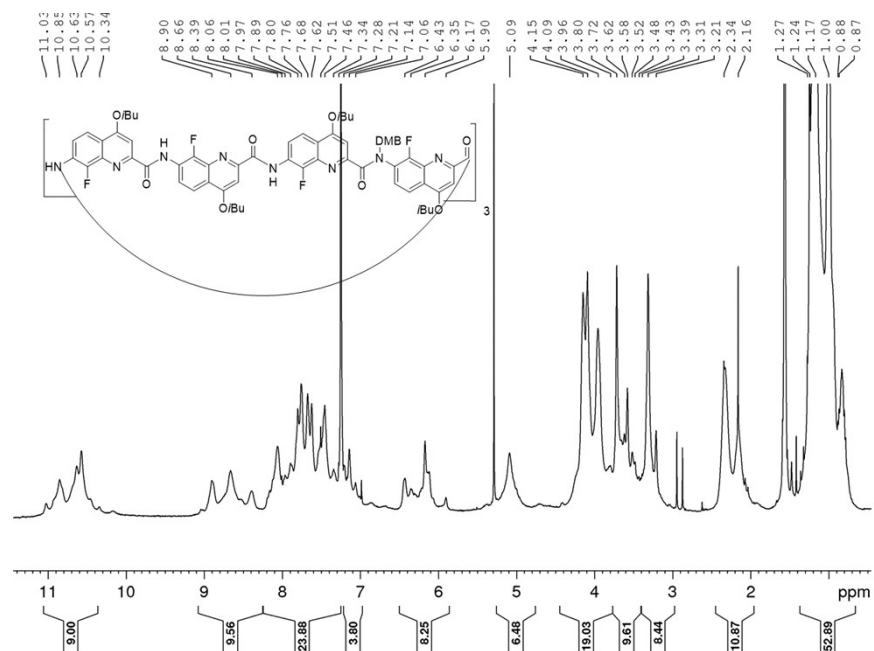
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K)

## Compound 17



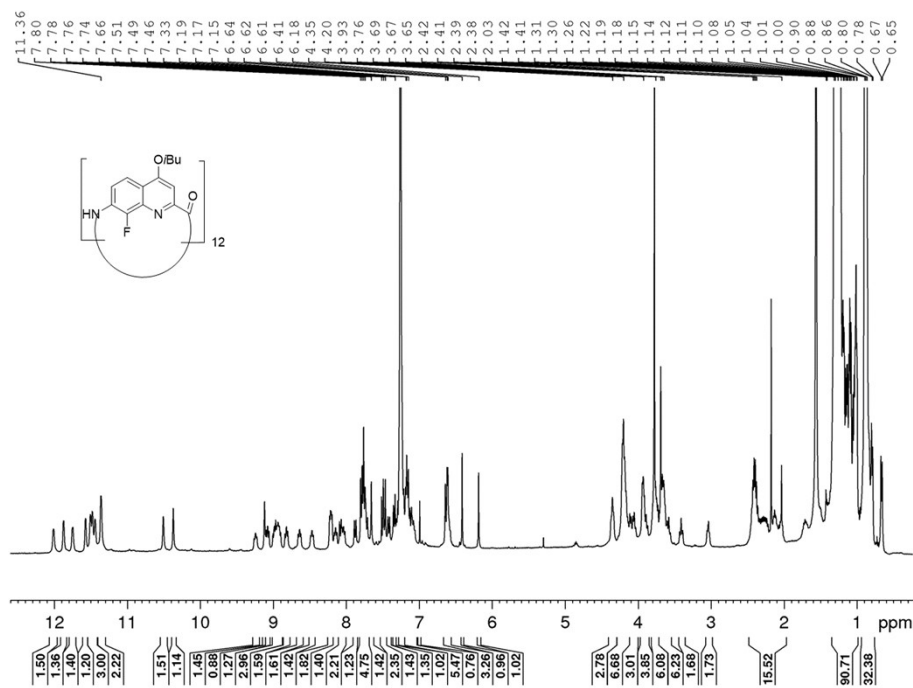
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K)

## Compound 2a



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K)

## Compound 2b



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K)

## 7. Reference

- [1] CrysAlisPRO: CrysAlisPRO, Oxford Diffraction /Agilent Technologies UK Ltd, Yarnton, England.
- [2] Sheldrick, G. M. *Acta Cryst.* **2015**, A71, 3–8.
- [3] OLEX2: O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann. *J. Appl. Cryst.* **2009**, 42, 339–341.
- [4] Spek, A. *Acta Cryst.* **2015**, C71, 9–18.
- [5] Gan, Q.; Bao, C.; Kauffmann, B.; Grélard, A.; Xiang, J.; Liu, S.; Huc, I.; Jiang, H. *Angew. Chem., Int. Ed.* **2008**, 47, 1715–1718.