Electronic Supplementary Information

Conformationally constrained aromatic oligoamide foldamers with supersecondary structure motifs

Hai-Yu Hu,[a,b] Jun-Feng Xiang,[a] and Chuan-Feng Chen[a,]*

[a]Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Molecular Recognition and Function, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China. [b]Graduate School, Chinese Academy of Sciences, Beijing 100049, China.

Email Address: cchen@iccas.ac.cn

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1. ^{1}H NMR and ^{13}C NMR spectra of new compounds.

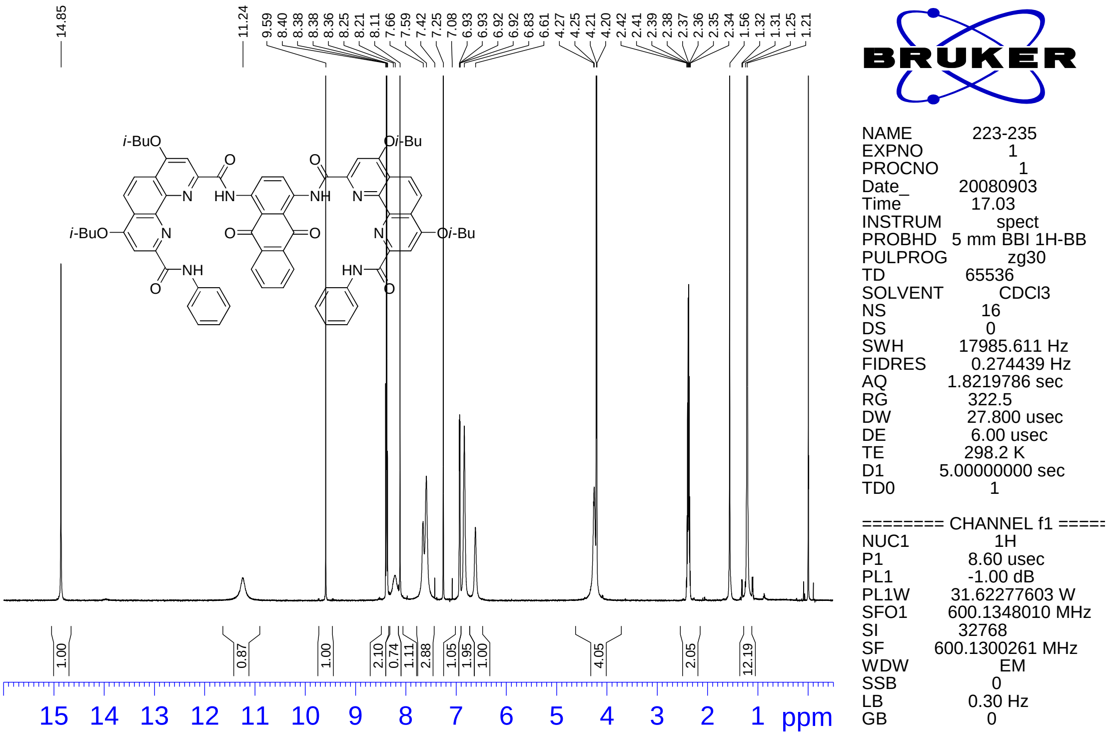


Figure S1. The ^{1}H NMR spectrum of compound 1.

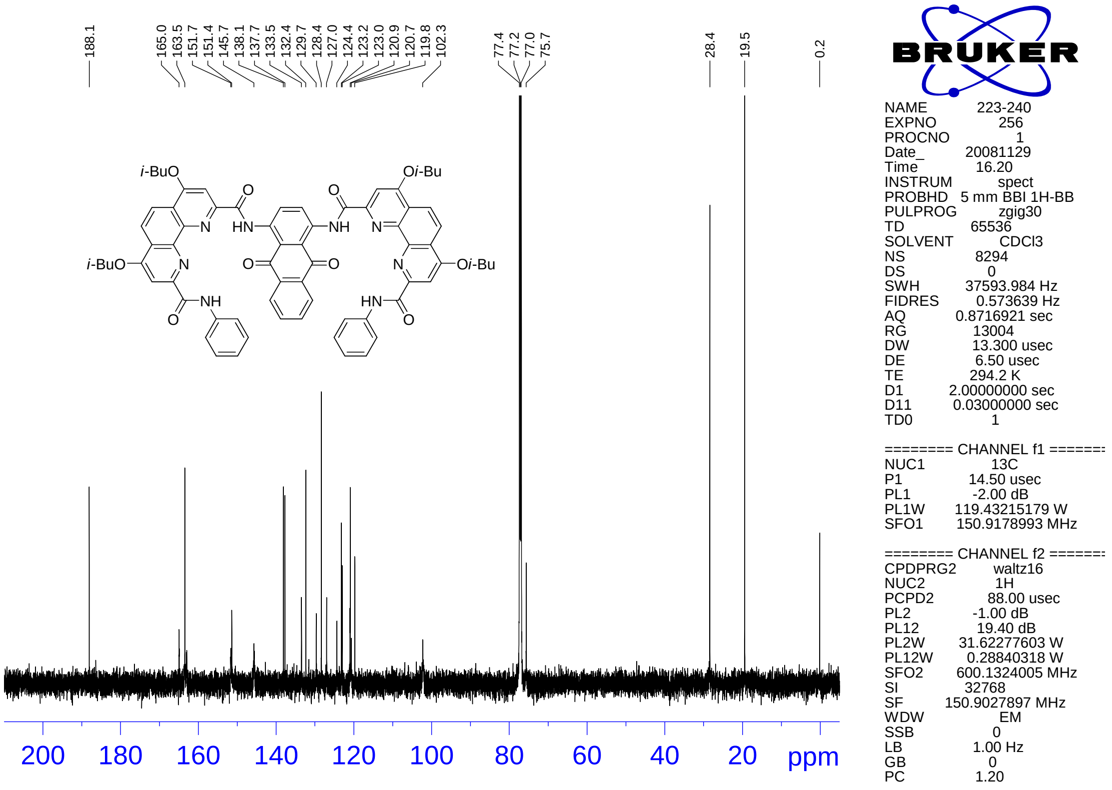
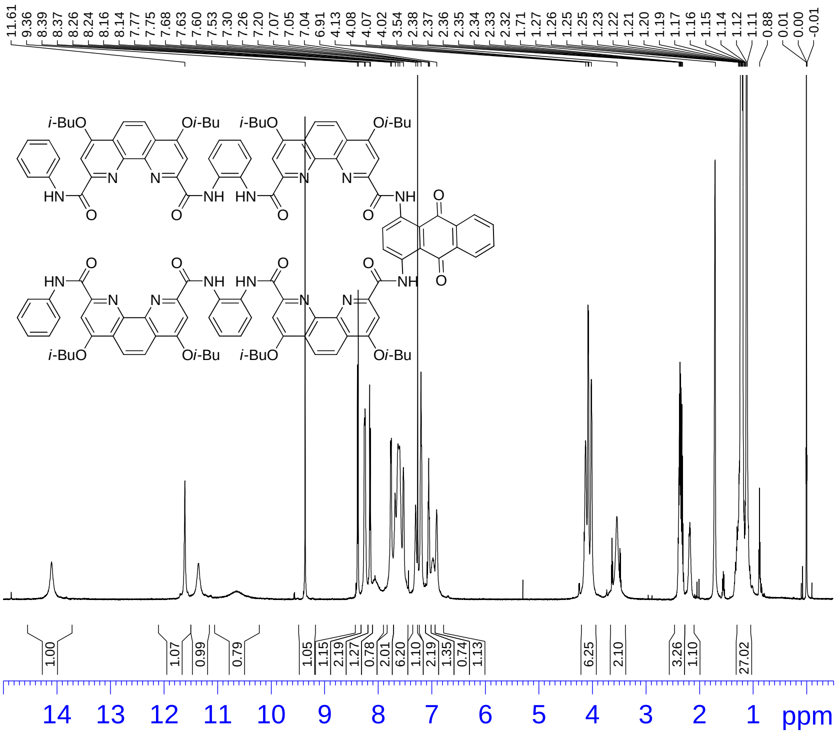


Figure S2. The ^{13}C NMR spectrum of compound 1.



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FIDRES       0.274439 Hz
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RG              161.3
DW             27.800 usec
DE               6.00 usec
TE              297.2 K
D1         5.00000000 sec
TD0                 1

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PL1             -1.00 dB
PL1W      31.62277603 W
SFO1      600.1348010 MHz
SI              32768
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WDW                EM
SSB                 0
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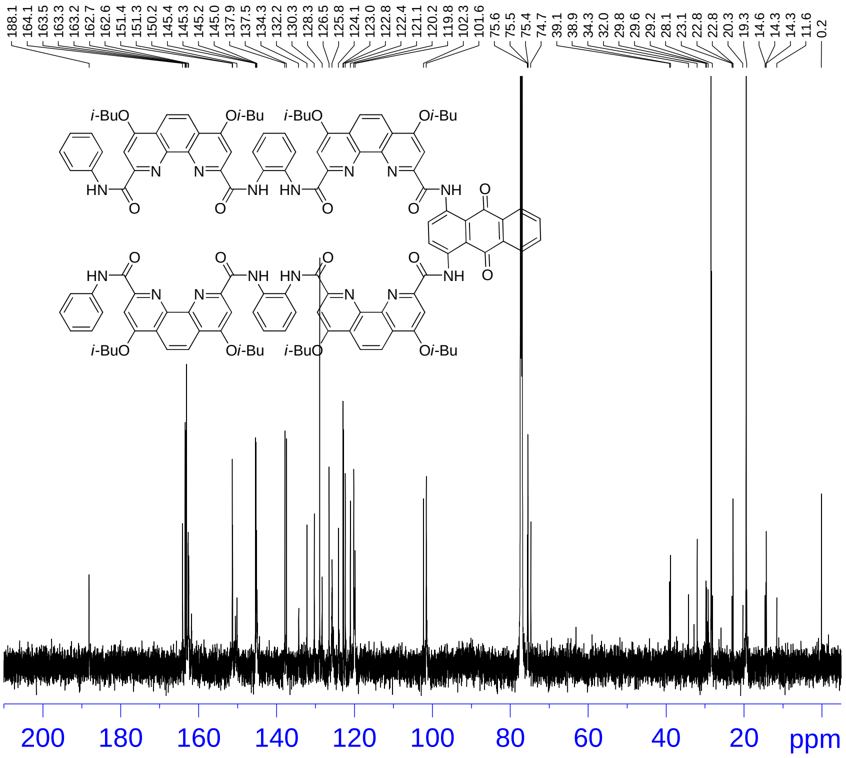
Figure S3. The ^{1}H NMR spectrum of compound 2.



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FIDRES       0.573639 Hz
AQ          0.8716921 sec
RG              13004
DW             13.300 usec
DE               6.50 usec
TE              289.4 K
D1         2.00000000 sec
D11        0.03000000 sec
TD0                 1

======== CHANNEL f1 ========
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P1              14.50 usec
PL1             -2.00 dB
PL1W     119.43215179 W
SFO1      150.9178993 MHz

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NUC2               1H
PCPD2           88.00 usec
PL2             -1.00 dB
PL12            19.40 dB
PL2W      31.62277603 W
PL12W      0.28840318 W
SFO2      600.1324005 MHz
SI              32768
SF        150.9027897 MHz
WDW                EM
SSB                 0
LB               1.00 Hz
GB                  0
PC               1.20
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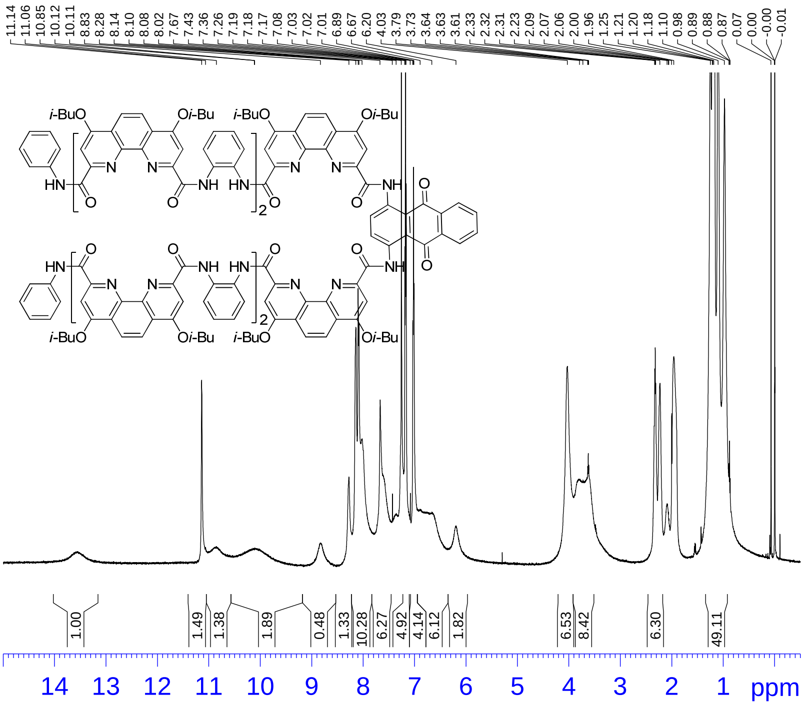
Figure S4. The ^{13}C NMR spectrum of compound 2.



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NS                 16
DS                  0
SWH       17985.611 Hz
FIDRES     0.274439 Hz
AQ       1.8219786 sec
RG                181
DW          27.800 usec
DE           6.00 usec
TE            297.6 K
D1     5.00000000 sec
TD0                 1

======== CHANNEL f1 ========
NUC1               1H
P1            8.60 usec
PL1           -1.00 dB
PL1W      31.62277603 W
SFO1     600.1348010 MHz
SI              32768
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WDW                EM
SSB                 0
LB            0.30 Hz
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PC               1.20
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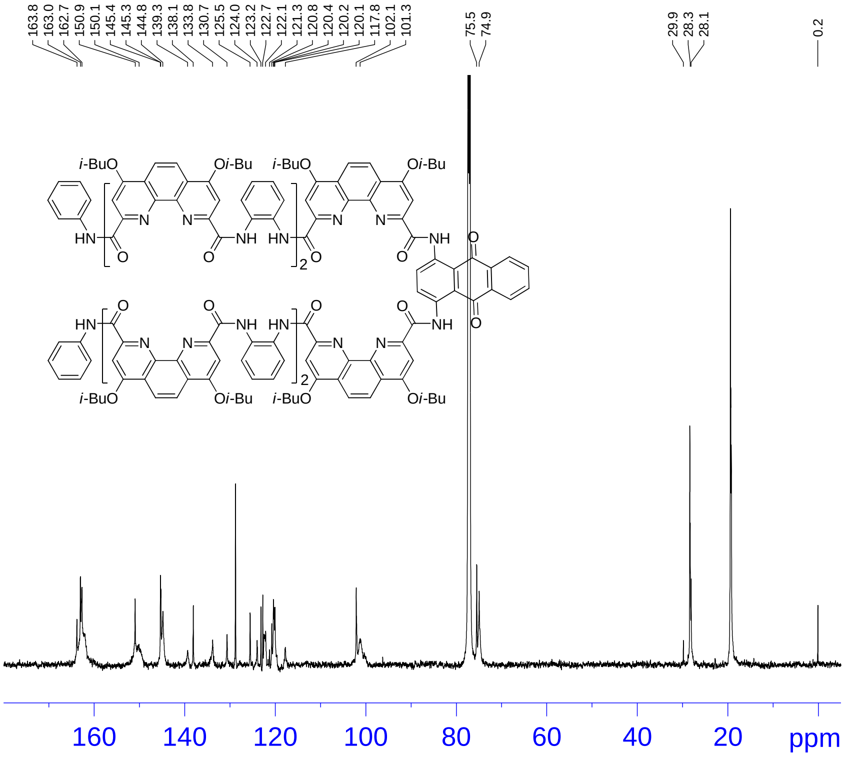
Figure S5. The ^{1}H NMR spectrum of compound 3.



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FIDRES     0.573639 Hz
AQ       0.8716921 sec
RG              13004
DW          13.300 usec
DE           6.50 usec
TE            293.2 K
D1     2.00000000 sec
D11    0.03000000 sec
TD0                 1

======== CHANNEL f1 ========
NUC1              13C
P1           14.50 usec
PL1           -2.00 dB
PL1W     119.43215179 W
SFO1     150.9178993 MHz

======== CHANNEL f2 ========
CPDPRG2        waltz16
NUC2               1H
PCPD2        88.00 usec
PL2           -1.00 dB
PL12          19.40 dB
PL2W      31.62277603 W
PL12W      0.28840318 W
SFO2     600.1324005 MHz
SI              32768
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WDW                EM
SSB                 0
LB            5.00 Hz
GB                  0
PC               1.20
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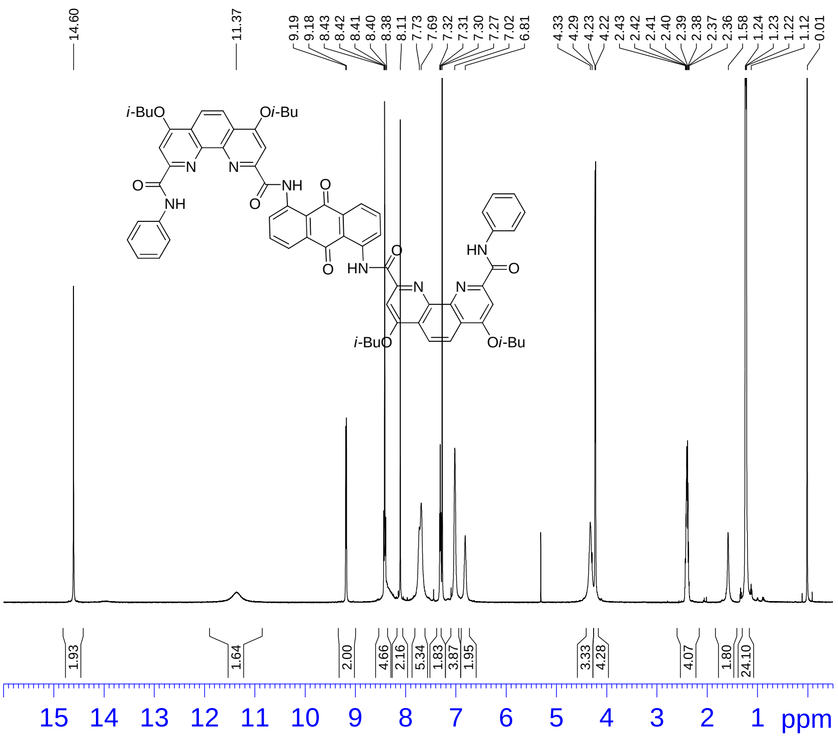
Figure S6. The ^{13}C NMR spectrum of compound 3.



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PROCNO 1
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PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219786 sec
RG 322.5
DW 27.800 usec
DE 6.00 usec
TE 298.1 K
D1 5.00000000 sec
TD0 1

======== CHANNEL f1 =====
NUC1 1H
P1 8.60 usec
PL1 -1.00 dB
PL1W 31.62277603 W
SFO1 600.1348010 MHz
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SF 600.1300146 MHz
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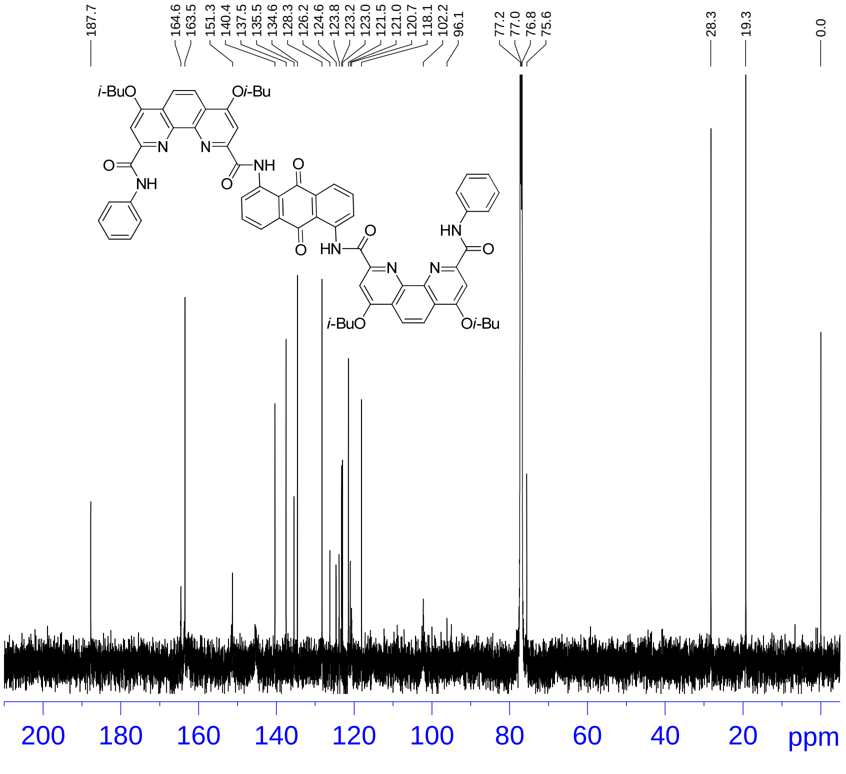
Figure S7. The ^{1}H NMR spectrum of compound 4.



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SOLVENT CDCl3
NS 24758
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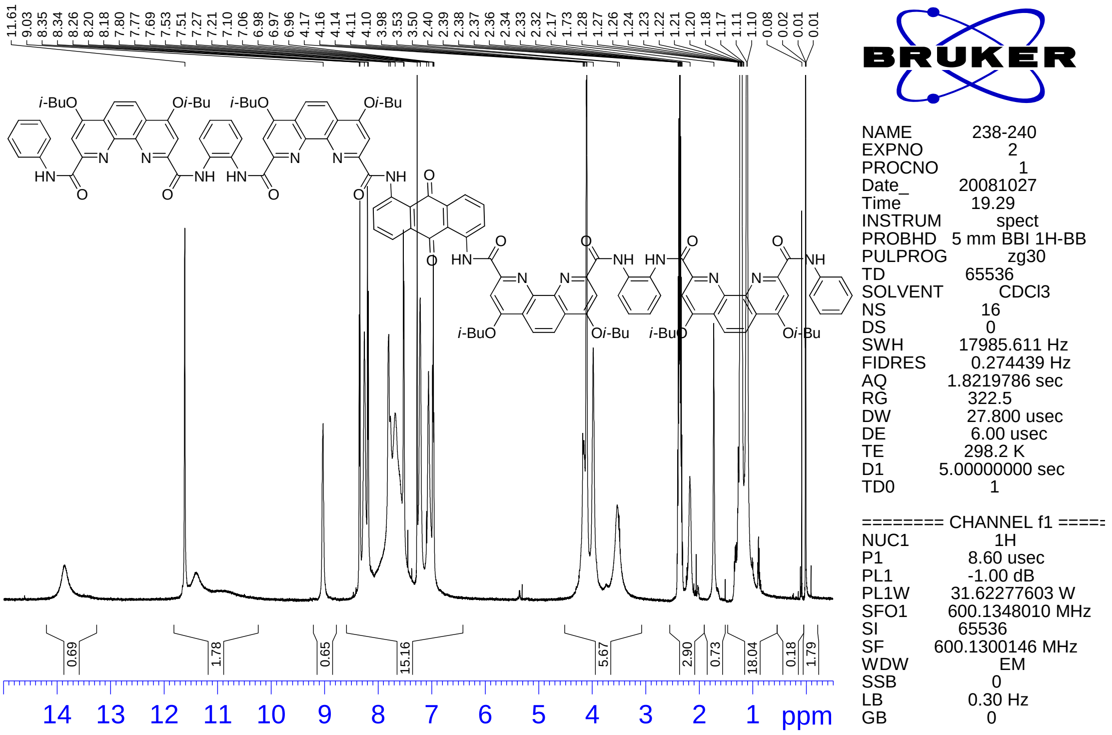
FIDRES 0.573639 Hz
AQ 0.8716921 sec
RG 13004
DW 13.300 usec
DE 6.50 usec
TE 293.8 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 =======
NUC1 13C
P1 14.50 usec
PL1 -2.00 dB
PL1W 119.43215179 W
SFO1 150.9178993 MHz

======== CHANNEL f2 =======
CPDPRG2 waltz16
NUC2 1H
PCPD2 88.00 usec
PL2 -1.00 dB
PL12 19.40 dB
PL2W 31.62277603 W
PL12W 0.28840318 W
SFO2 600.1324005 MHz
SI 32768
SF 150.9028121 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.20

Figure S8. The ^{13}C NMR spectrum of compound 4.



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SOLVENT CDCl3
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FIDRES 0.274439 Hz
AQ 1.8219786 sec
RG 322.5
DW 27.800 usec
DE 6.00 usec
TE 298.2 K
D1 5.00000000 sec
TD0 1

======== CHANNEL f1 =====
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PL1W 31.62277603 W
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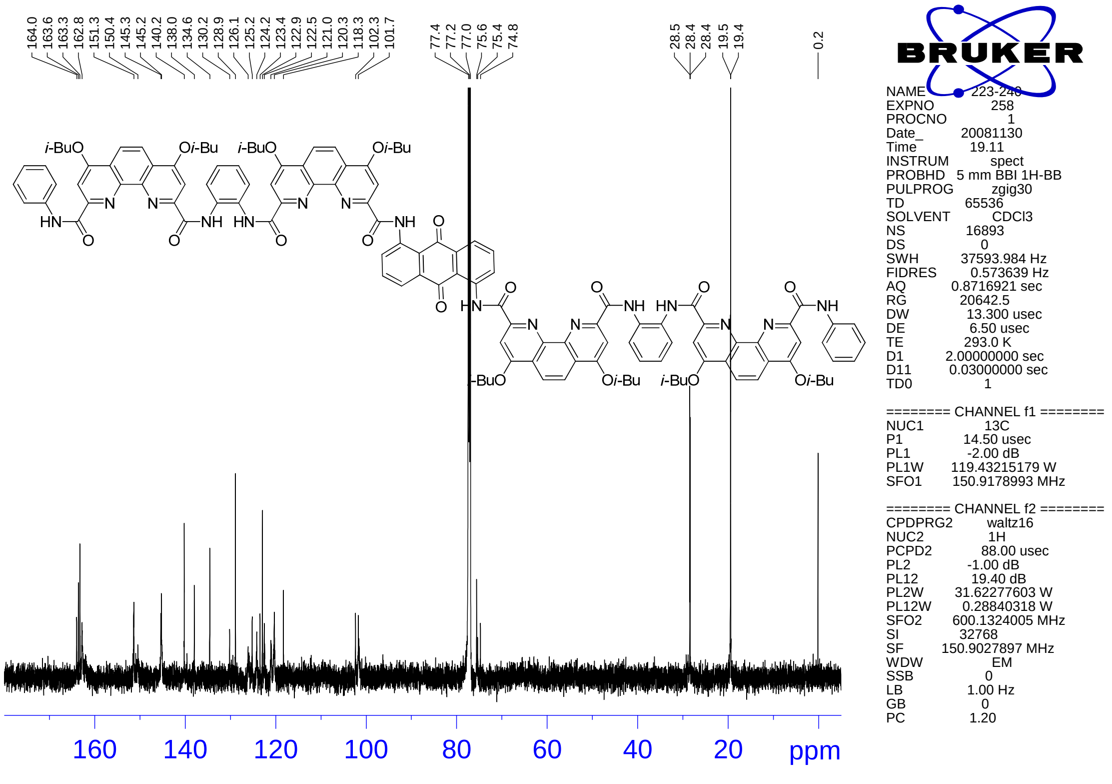
LB 0.30 Hz
GB 0

Figure S9. The ^{1}H NMR spectrum of compound 5.



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D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
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======== CHANNEL f2 ========
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PCPD2 88.00 usec
PL2 -1.00 dB
PL12 19.40 dB
PL2W 31.62277603 W
PL12W 0.28840318 W
SFO2 600.1324005 MHz
SI 32768
SF 150.9027897 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.20

Figure S10. The ^{13}C NMR spectrum of compound 5.

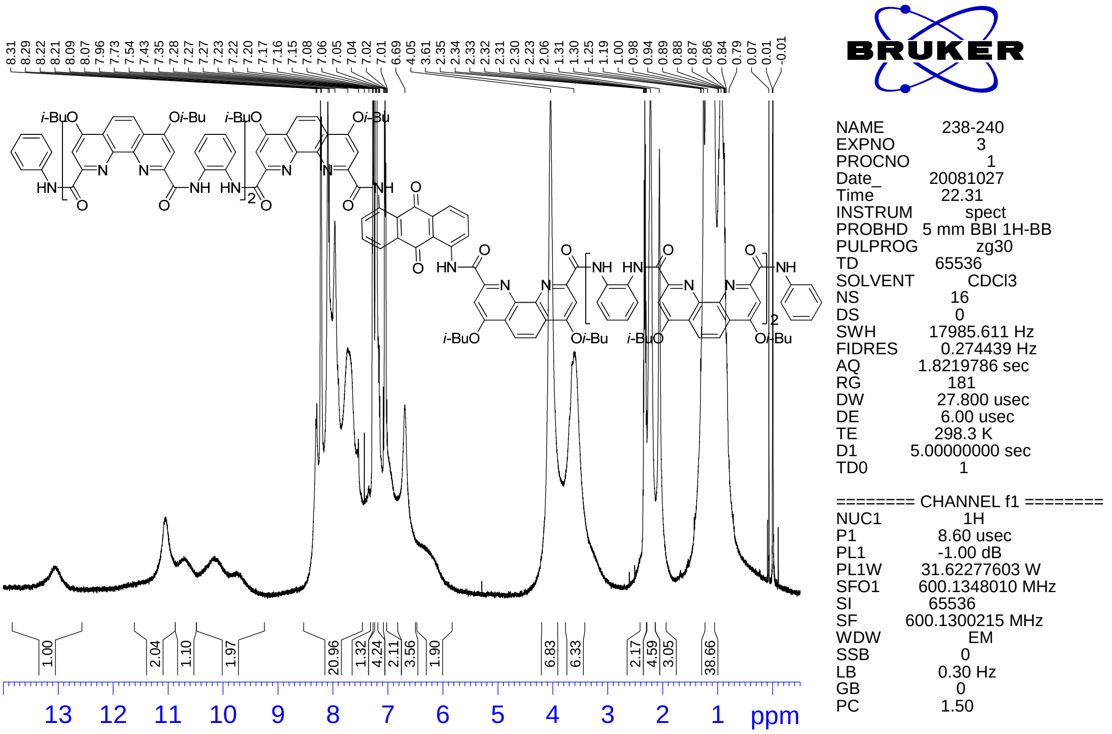


Figure S11. The ^{1}H NMR spectrum of compound 6.

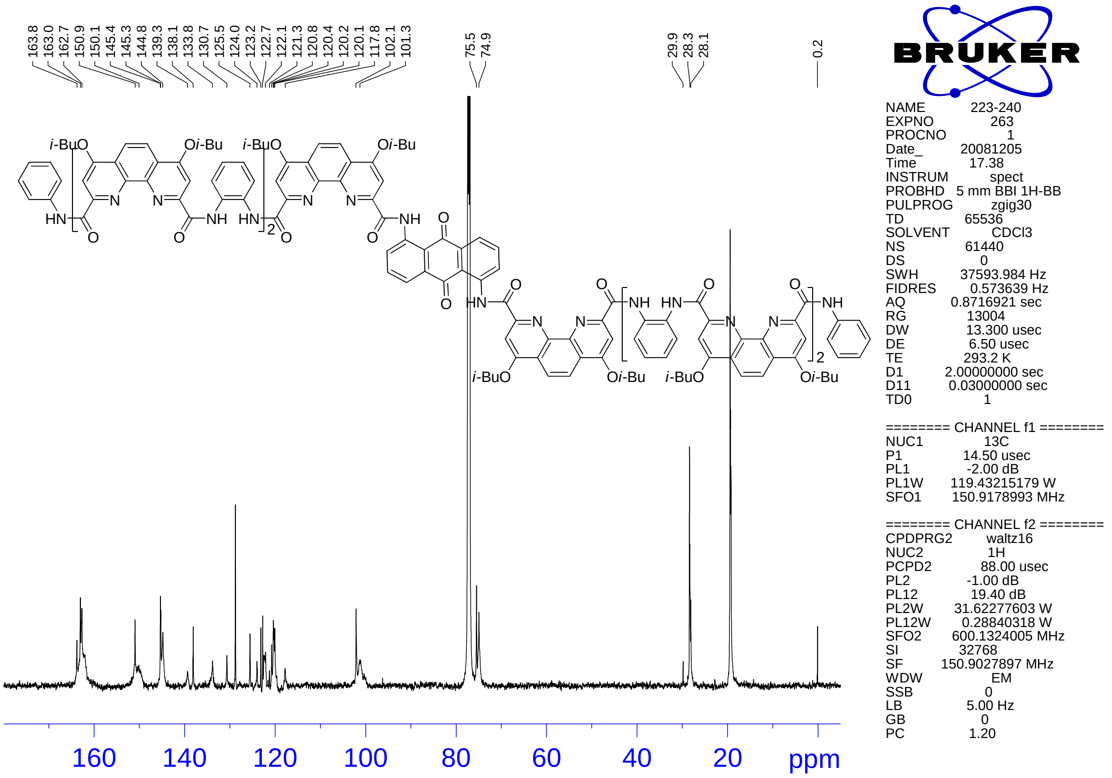
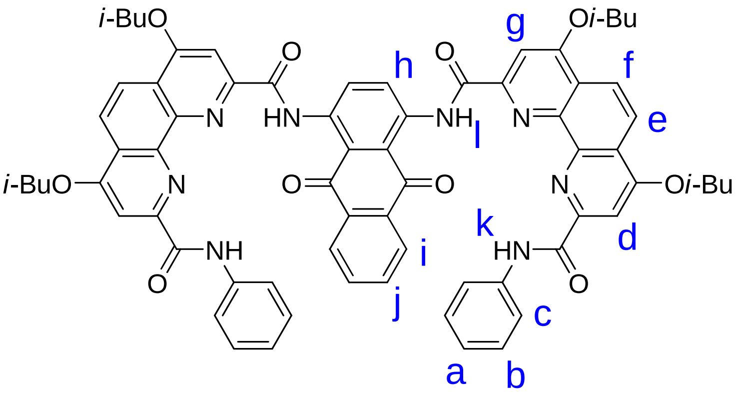


Figure S12. The ^{13}C NMR spectrum of compound 6.

2. TOCSY and NOESY spectra of compounds 1~6.



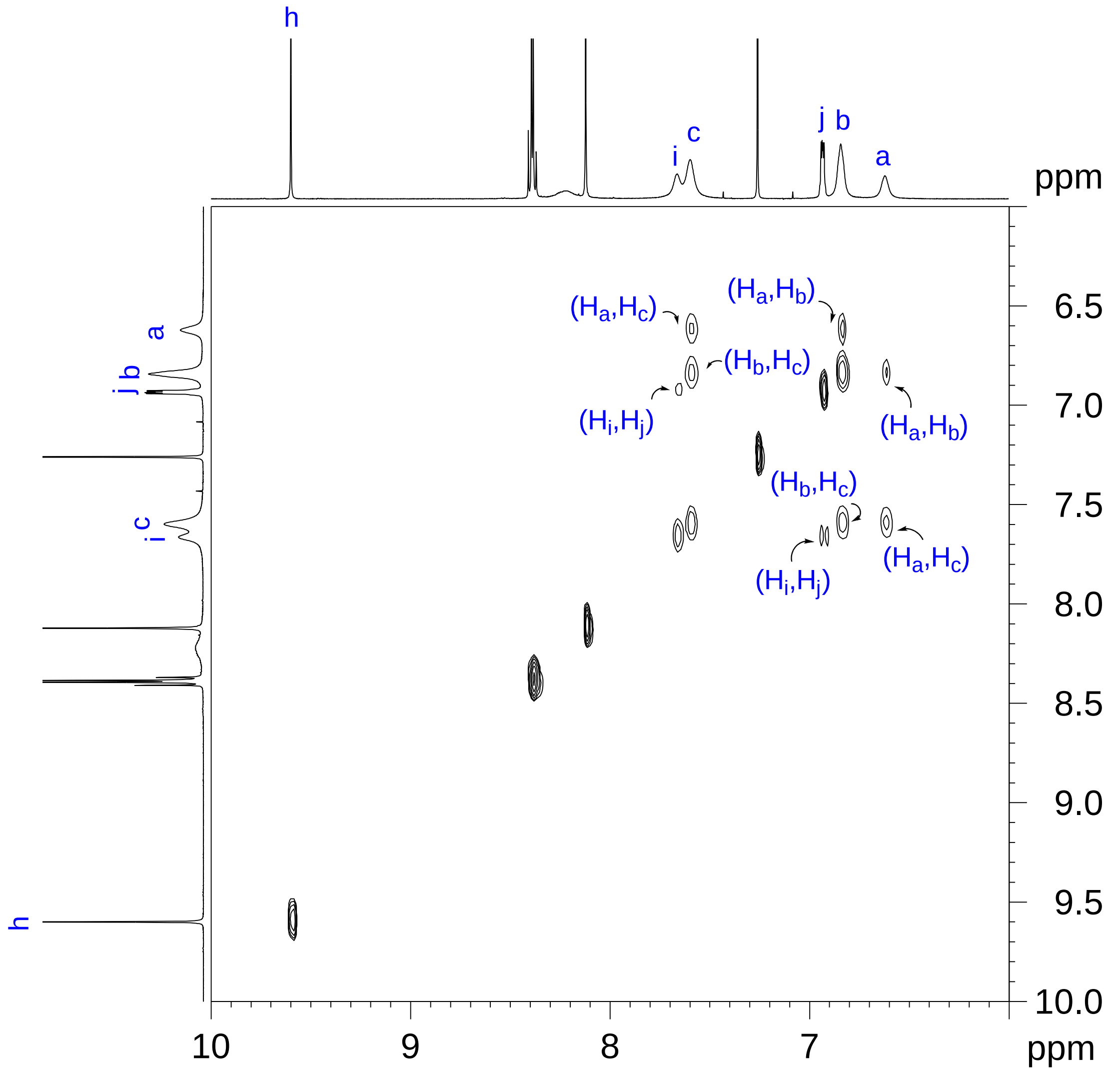
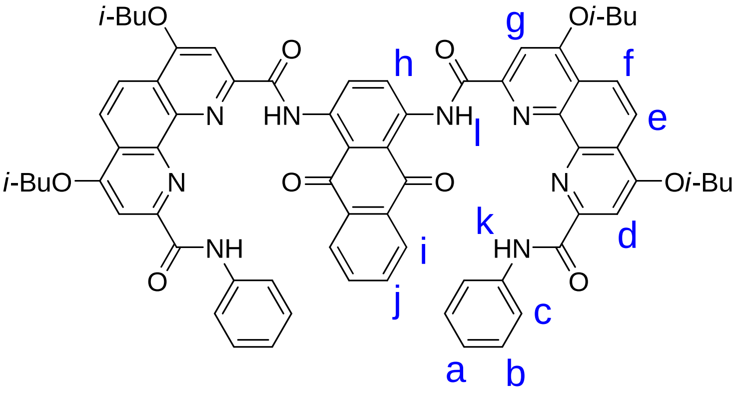


Figure S13. The TOCSY spectrum (600MHz, $CDCl_3$) of compound 1.



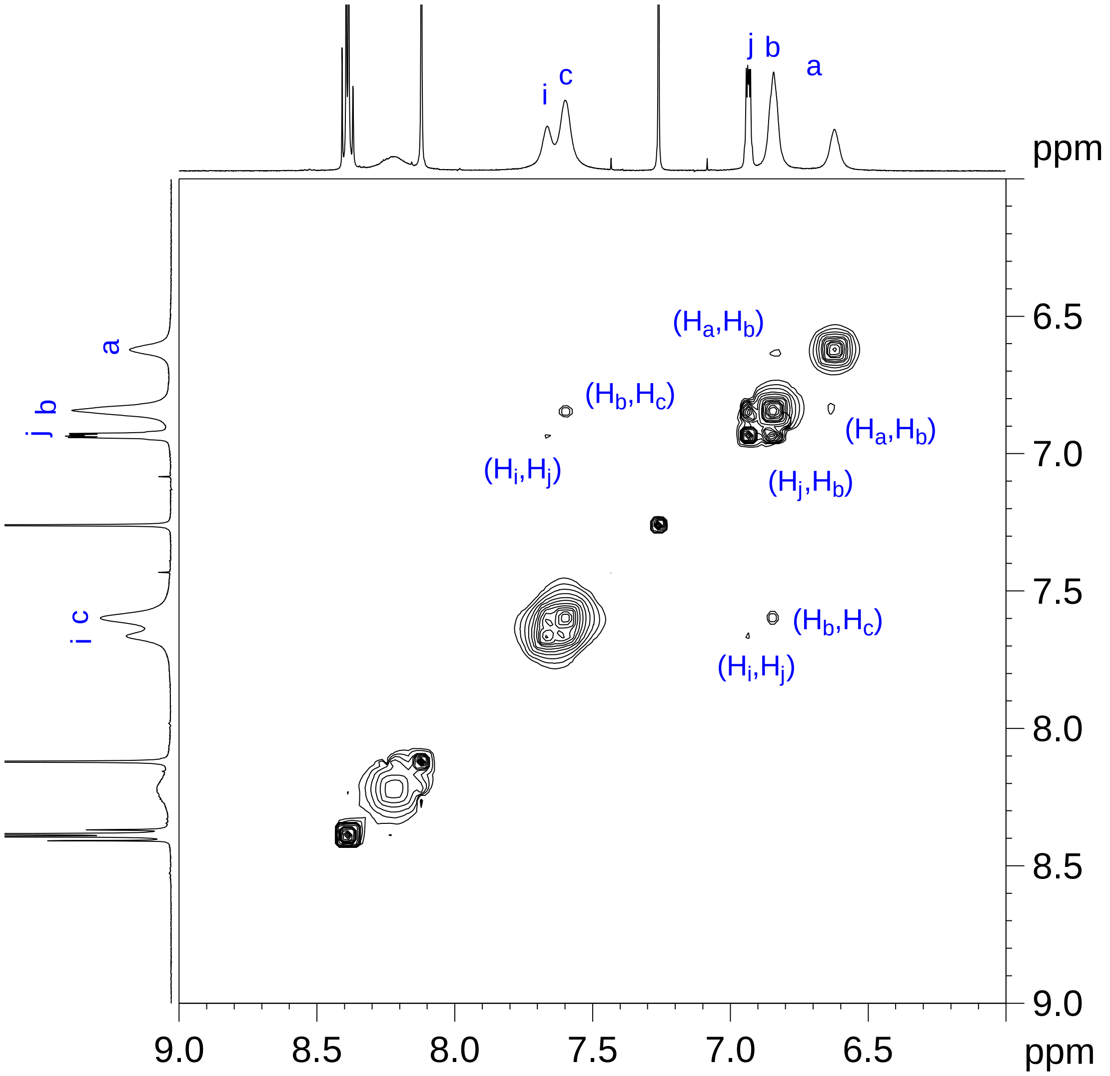


Figure S14. The NOESY spectrum (600MHz, $CDCl_3$) of compound 1.

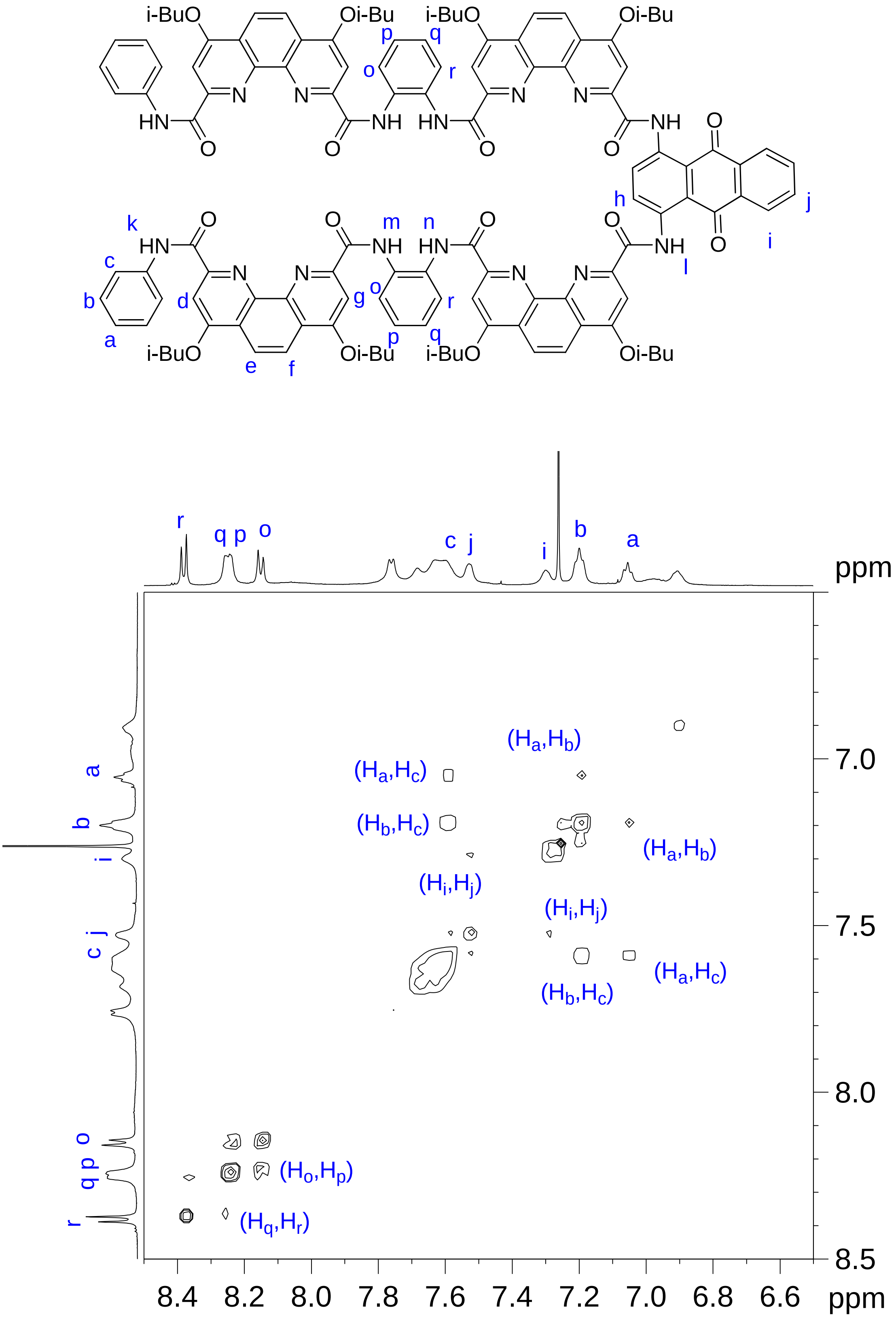


Figure S15. The TOCSY spectrum (600MHz, CDCl$_3$) of compound 2.

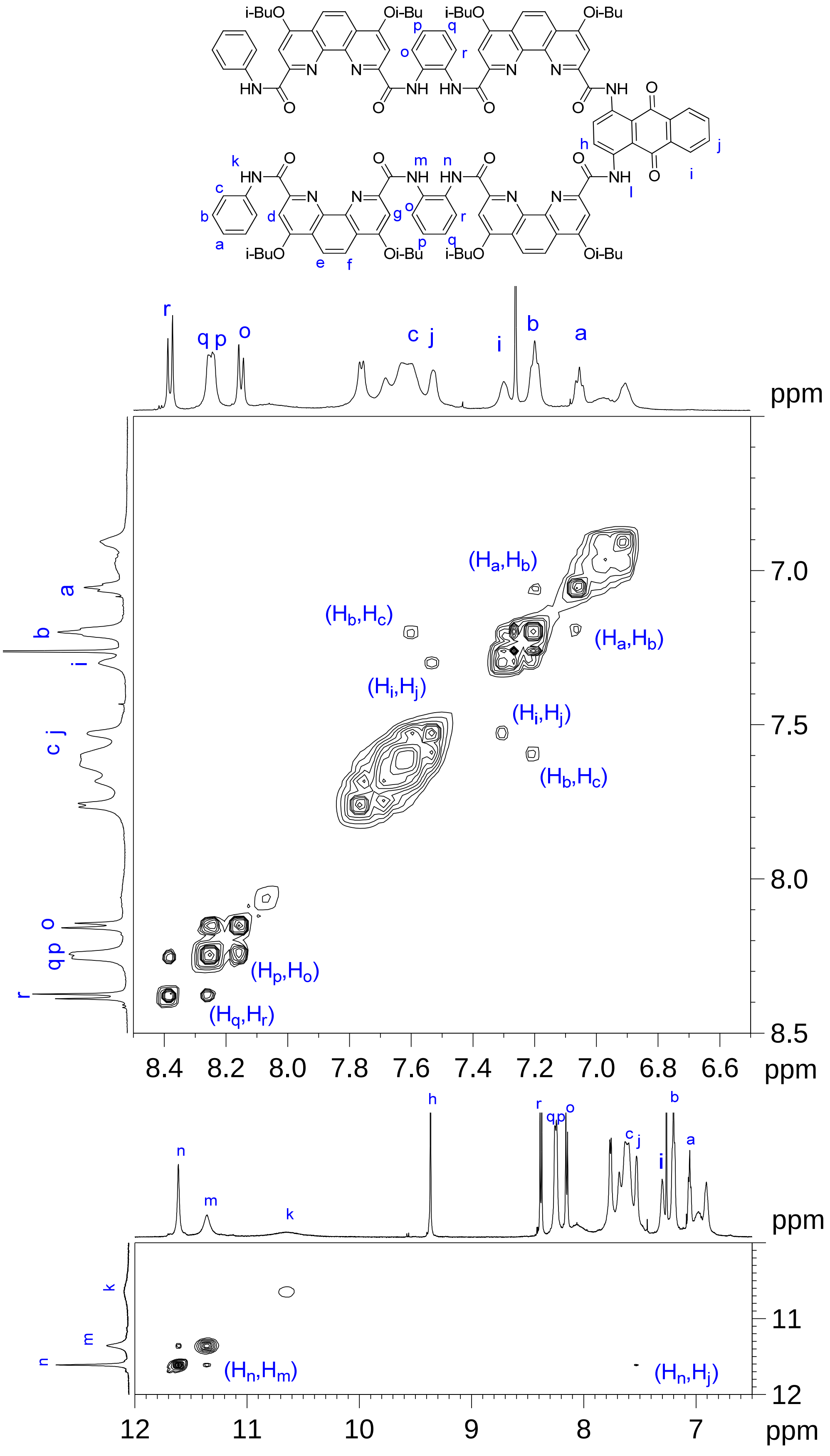
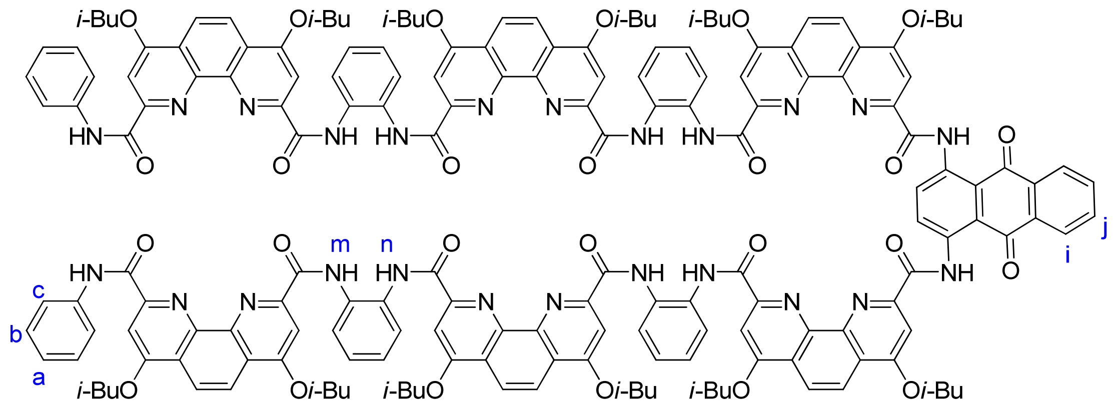


Figure S16. The NOESY spectrum (600MHz, $CDCl_3$) of compound 2.



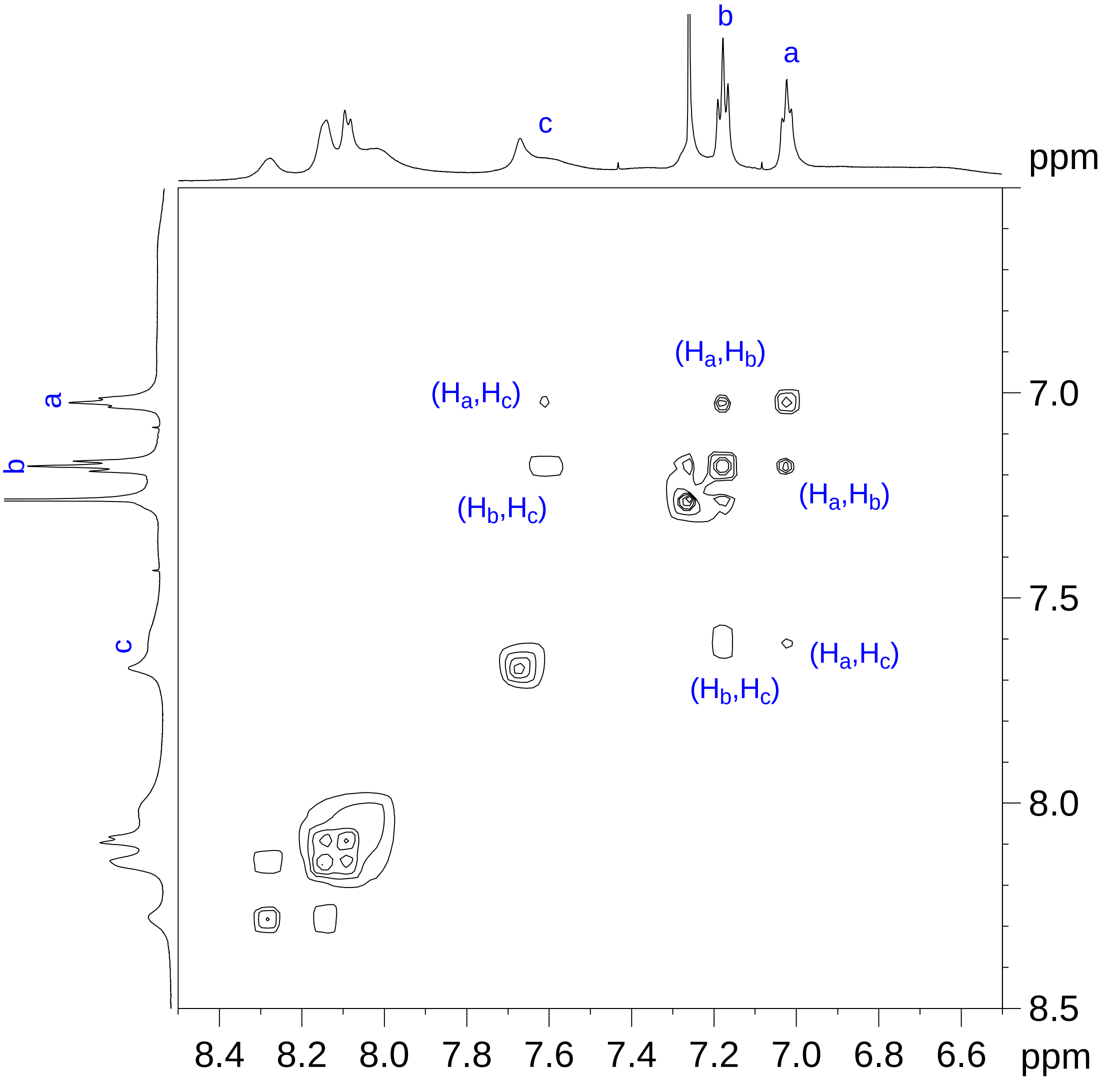


Figure S17. The TOCSY spectrum (600MHz, $CDCl_3$) of compound 3.

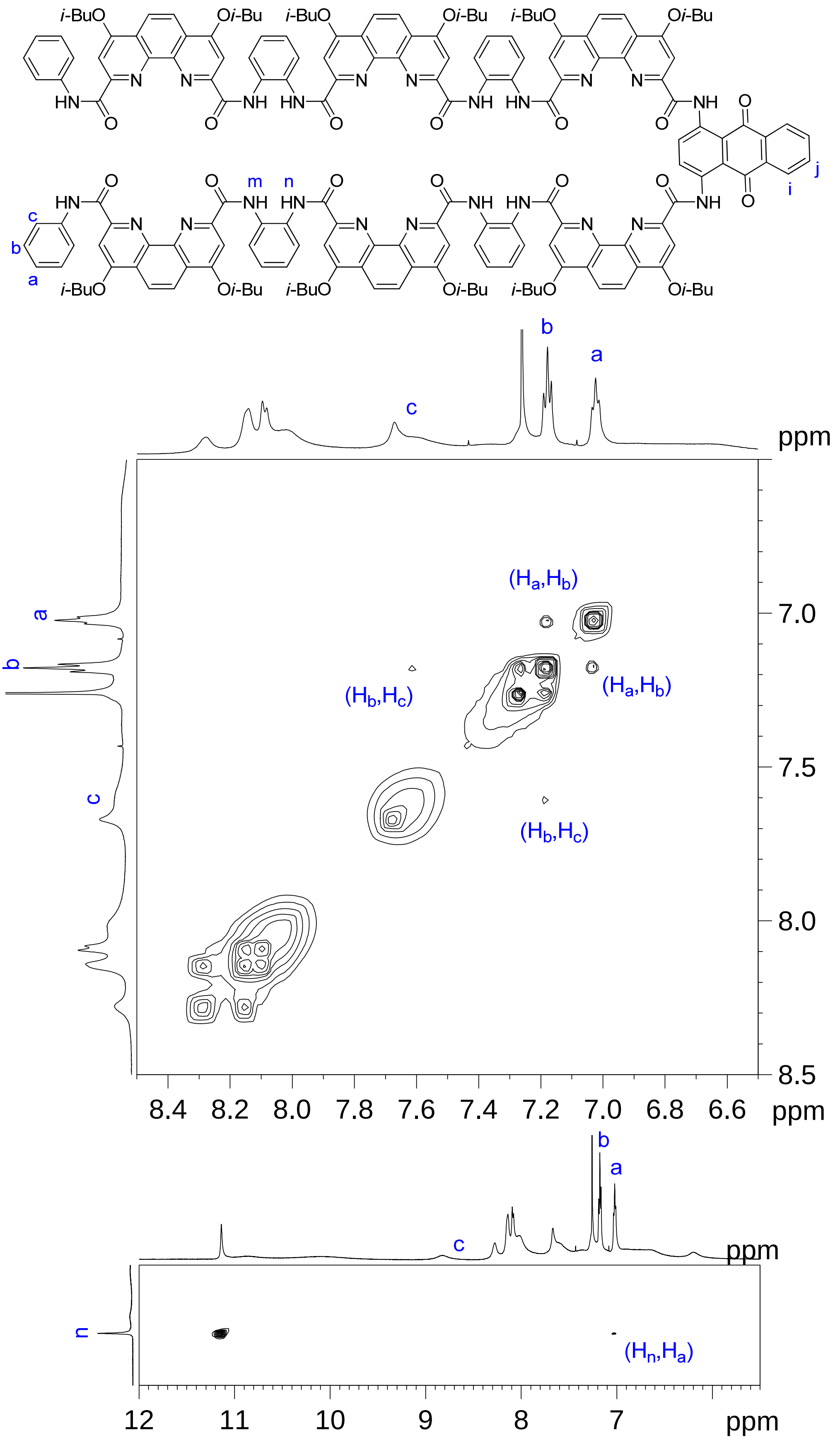
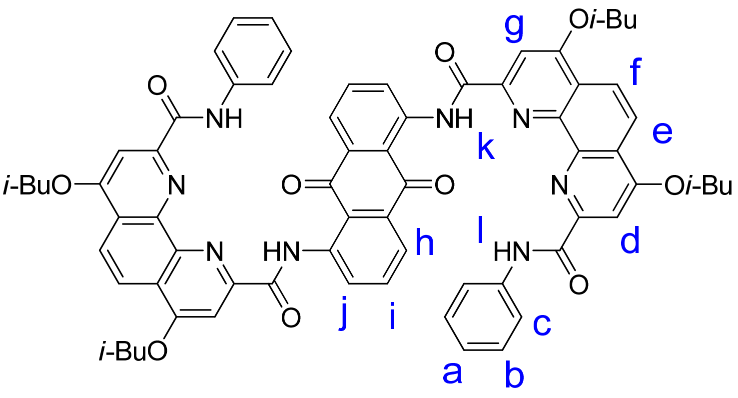


Figure S18. The NOESY spectrum (600MHz, $CDCl_3$) of compound 3.



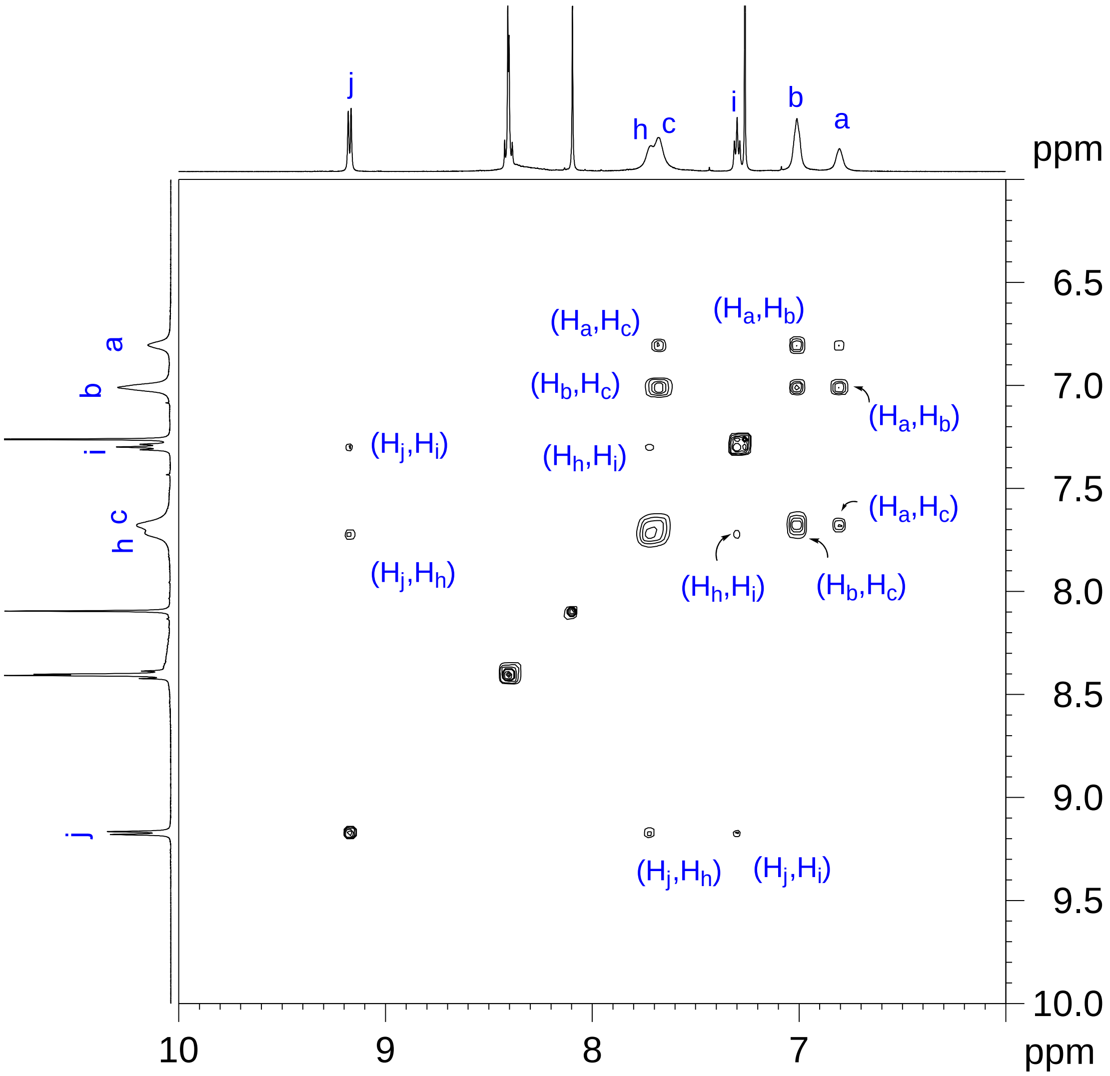
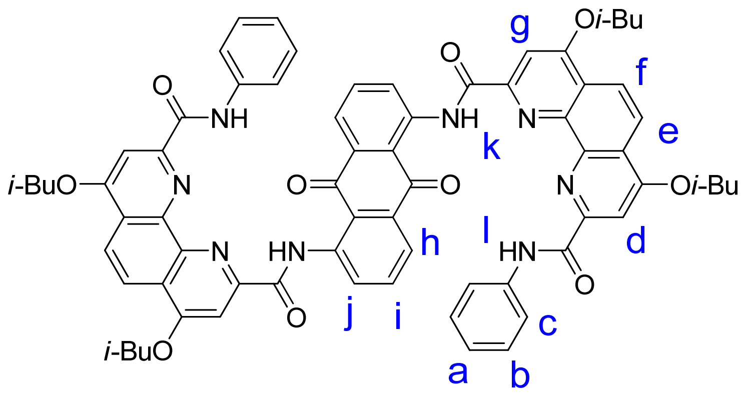


Figure S19. The TOCSY spectrum (600MHz, $CDCl_3$) of compound 4.



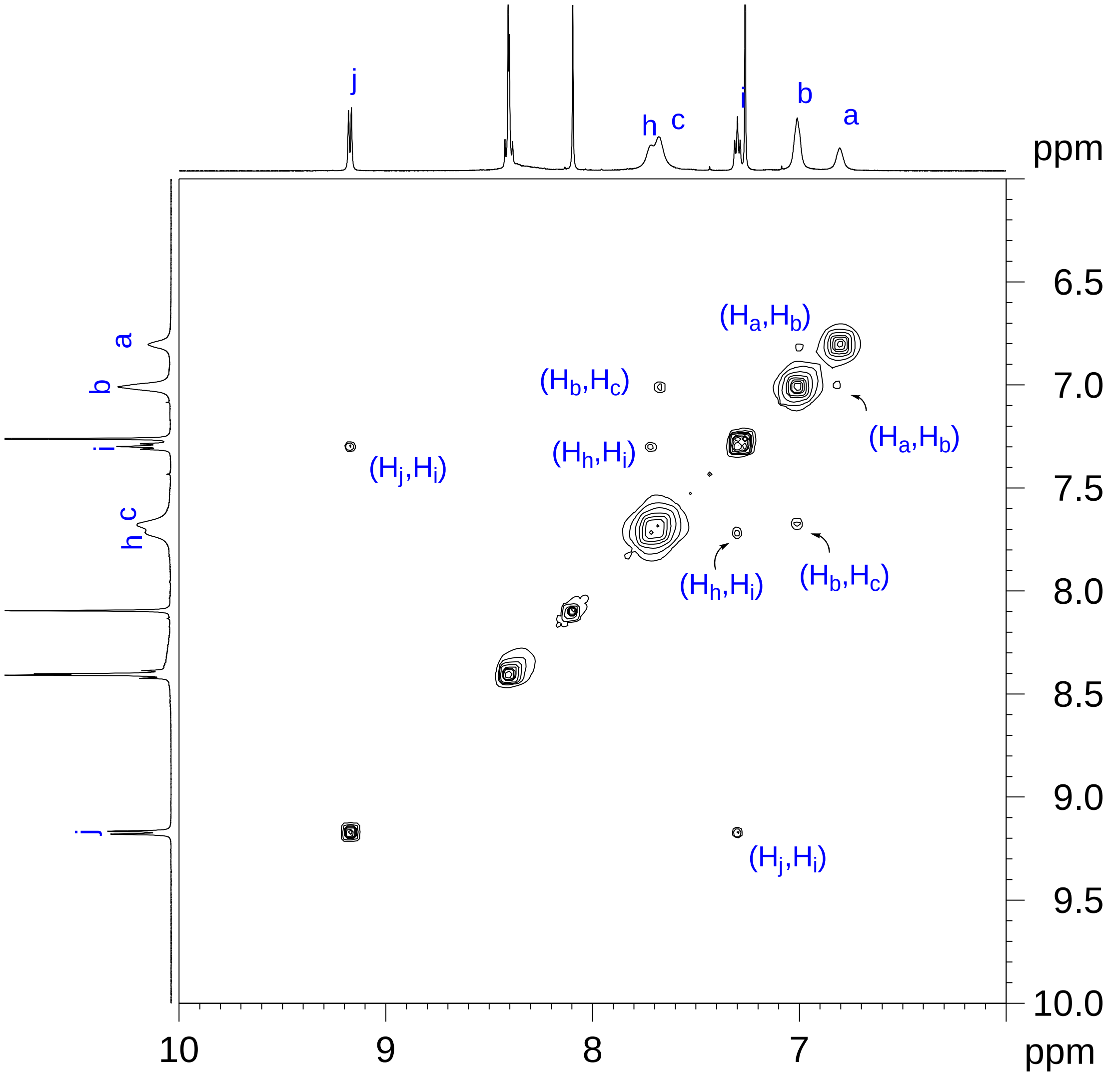


Figure S20. The NOESY spectrum (600MHz, $CDCl_3$) of compound 4.

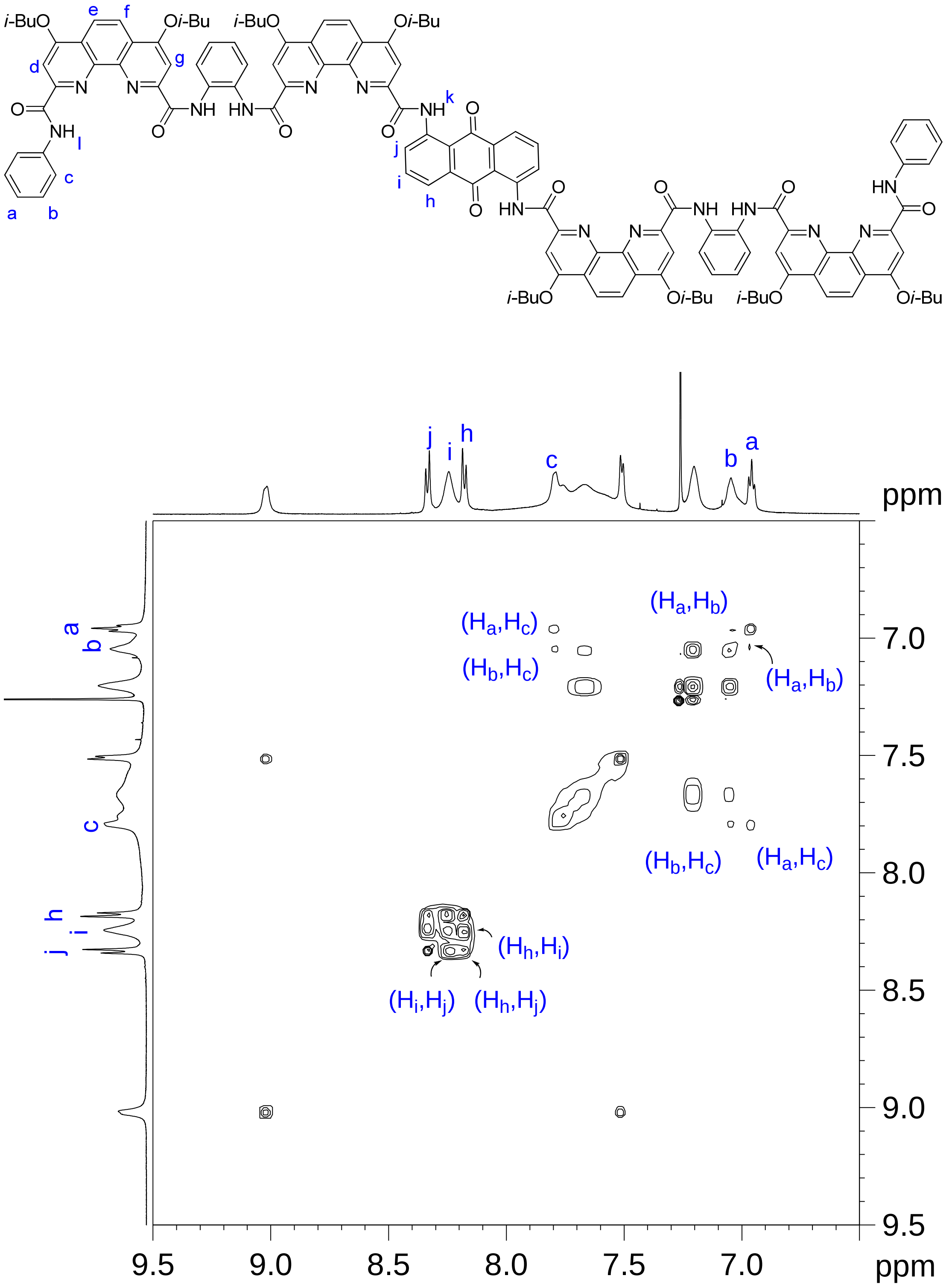


Figure S21. The TOCSY spectrum (600MHz, $CDCl_3$) of compound 5.

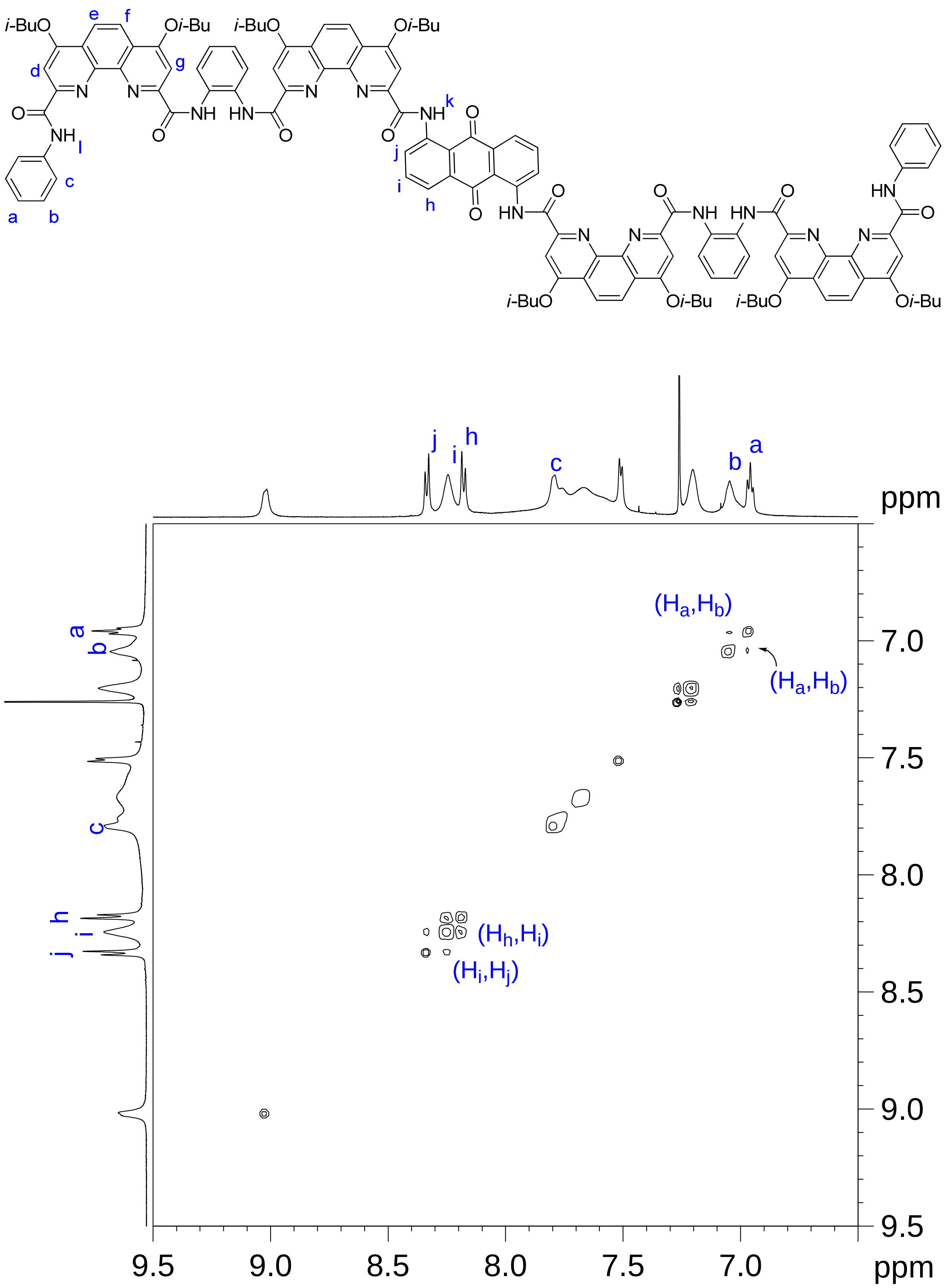


Figure S22. The NOESY spectrum (600MHz, $CDCl_3$) of compound 5.

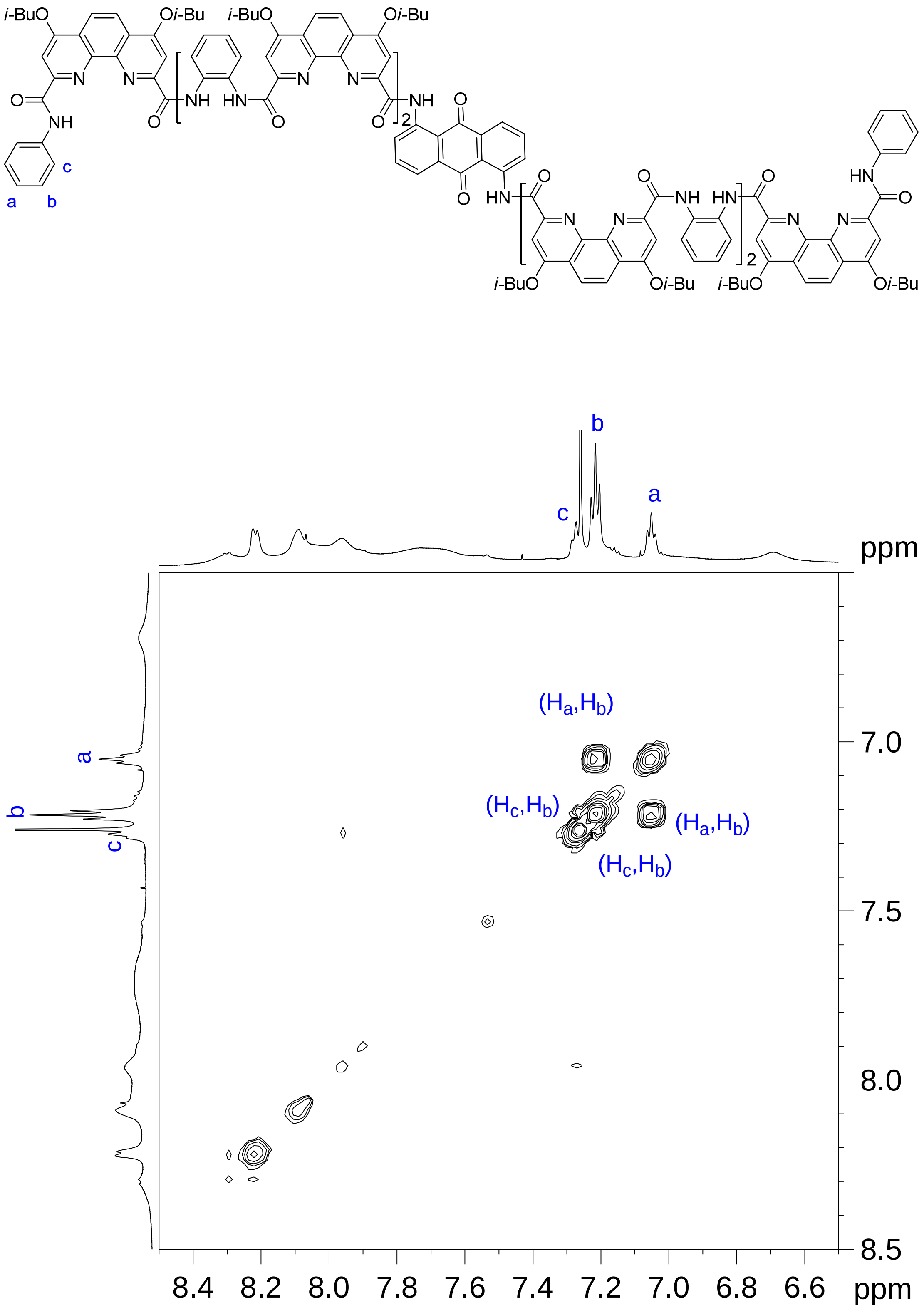


Figure S23. The TOCSY spectrum (600MHz, $CDCl_3$) of compound 6.

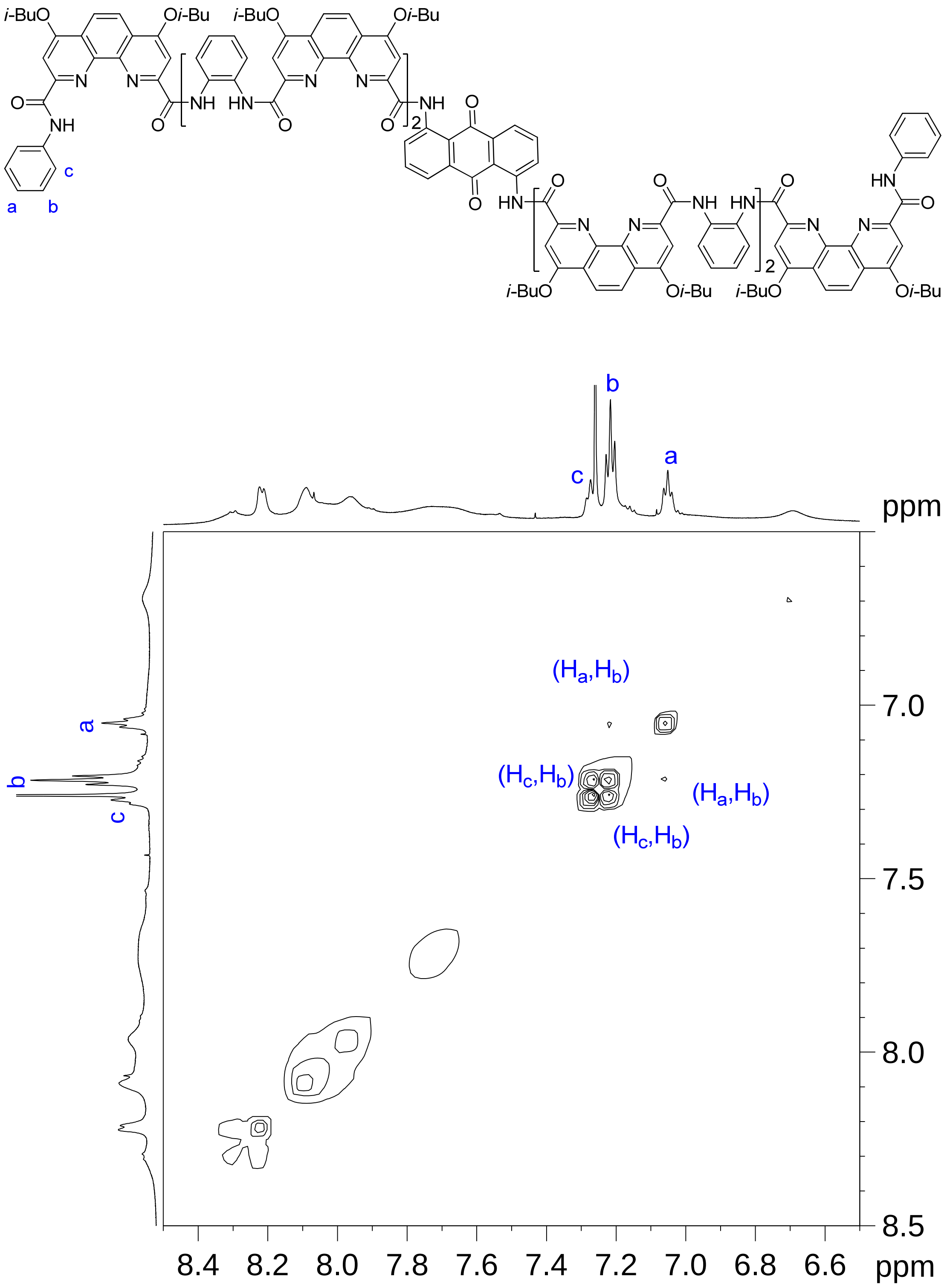


Figure S24. The NOESY spectrum (600MHz, $CDCl_3$) of compound 6.

3. UV-vis spectra of oligomers 1~6 at various concentrations.

To rule out intermolecular association, the ε for each oligomer was determined by using a range of concentrations. For each compound, Beer’s law behavior was observed, which indicated that the oligomers were in an ordered conformation consistent with the helix formation.

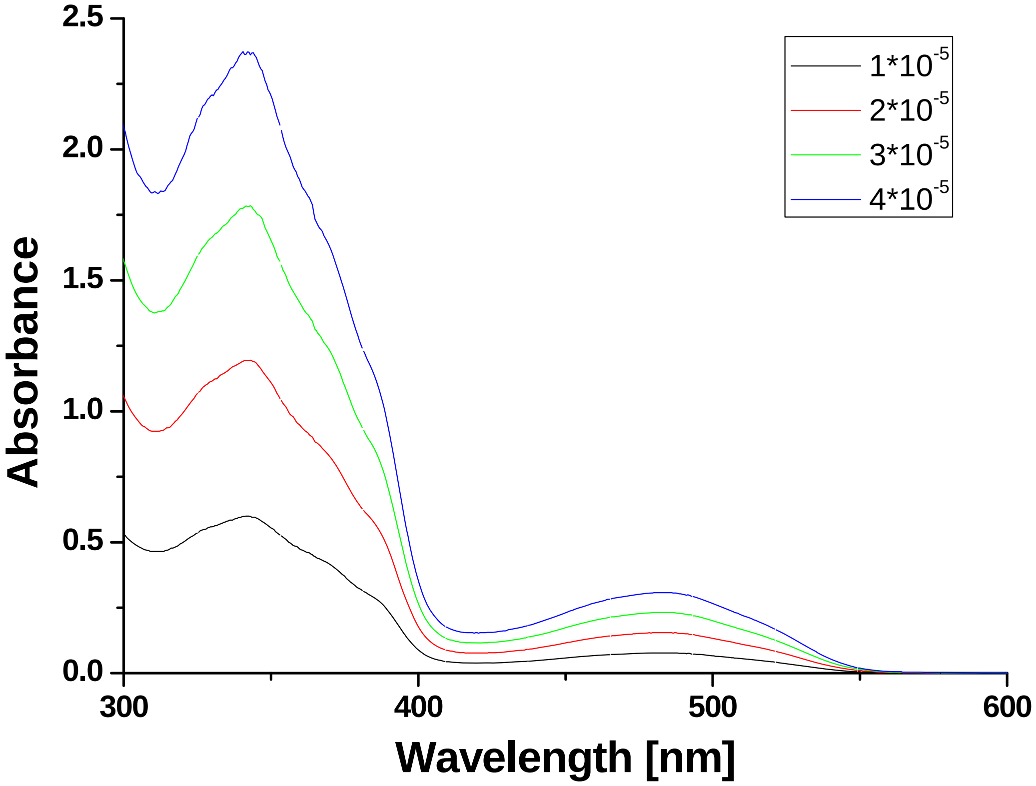


Figure S25. Representative UV-vis spectra of 1 in CHCl$_3$ at various concentrations.

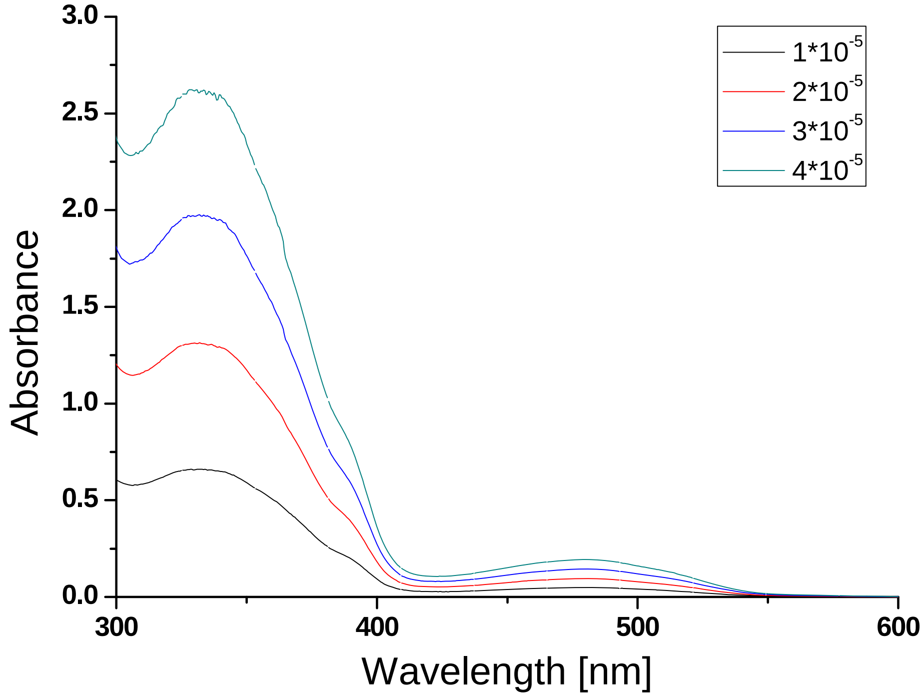


Figure S26. Representative UV-vis spectra of 2 in $CHCl_3$ at various concentrations.

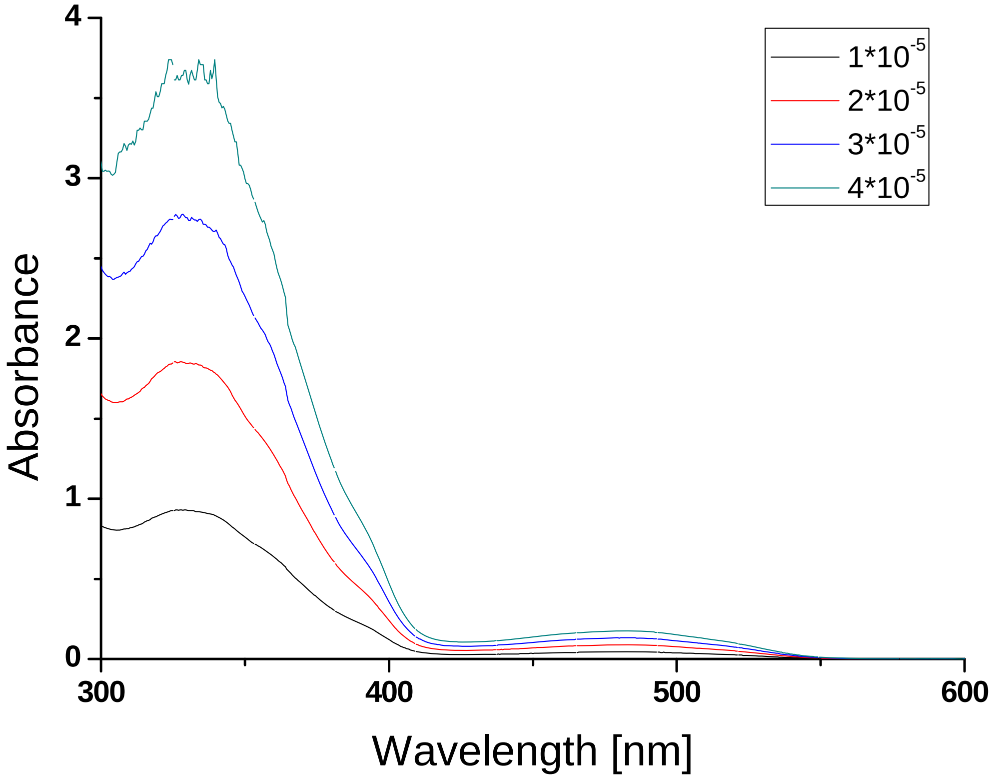


Figure S27. Representative UV-vis spectra of 3 in $CHCl_3$ at various concentrations.

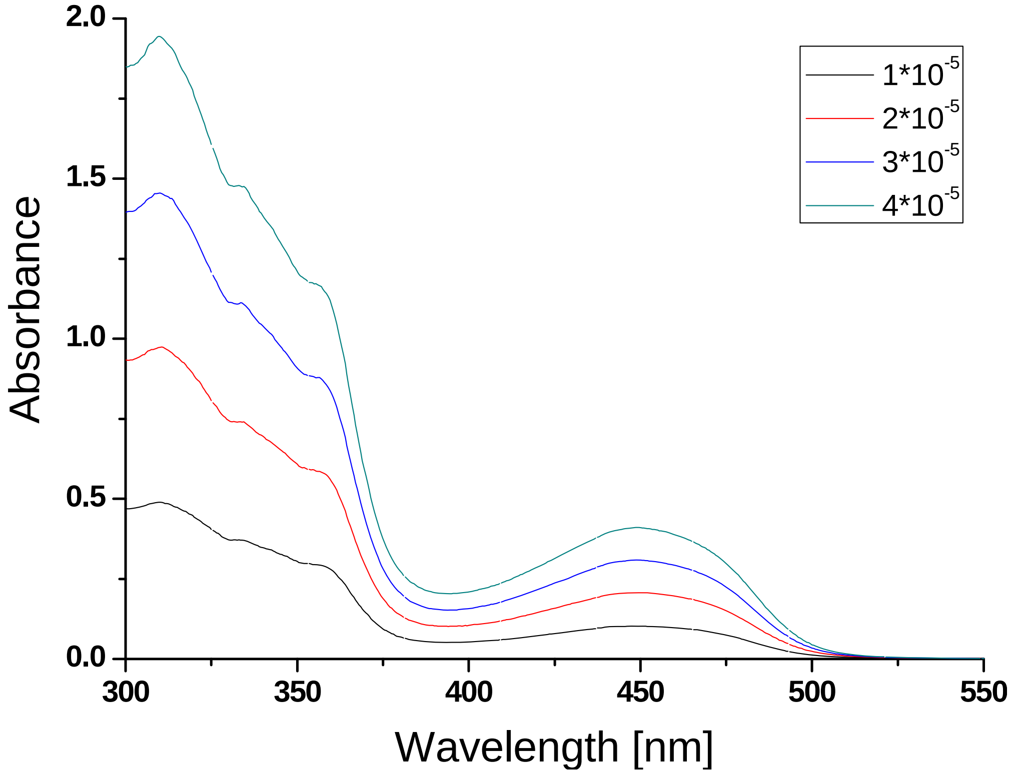


Figure S28. Representative UV-vis spectra of 4 in CHCl$_3$ at various concentrations.

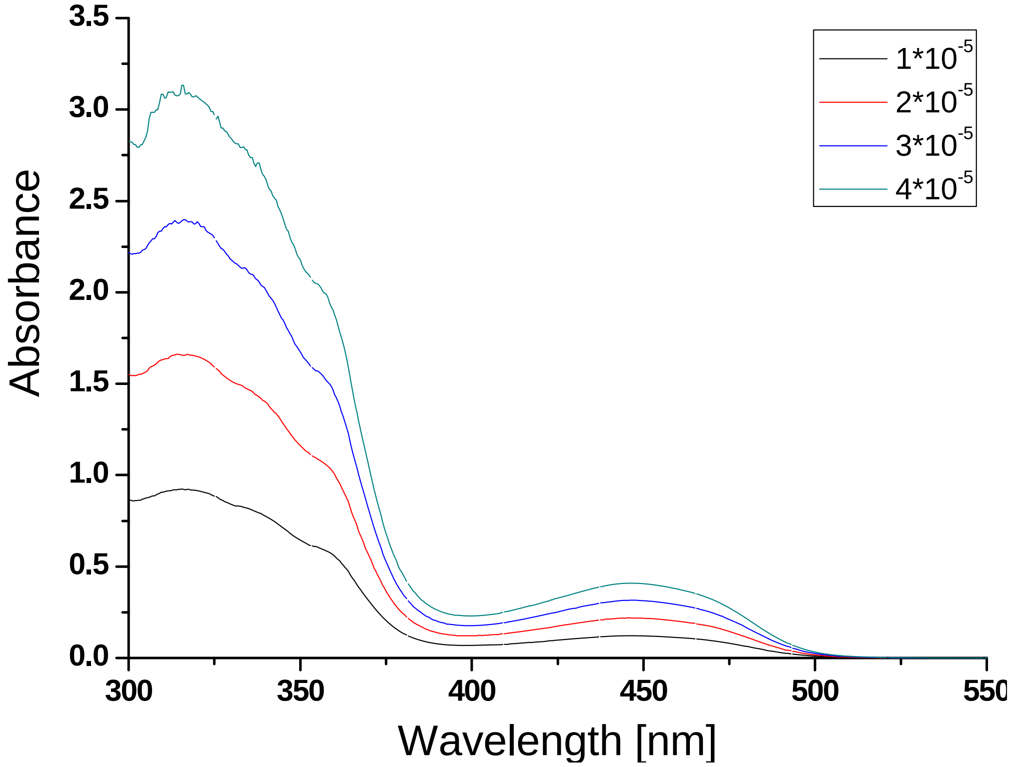


Figure S29. Representative UV-vis spectra of 5 in CHCl$_3$ at various concentrations.

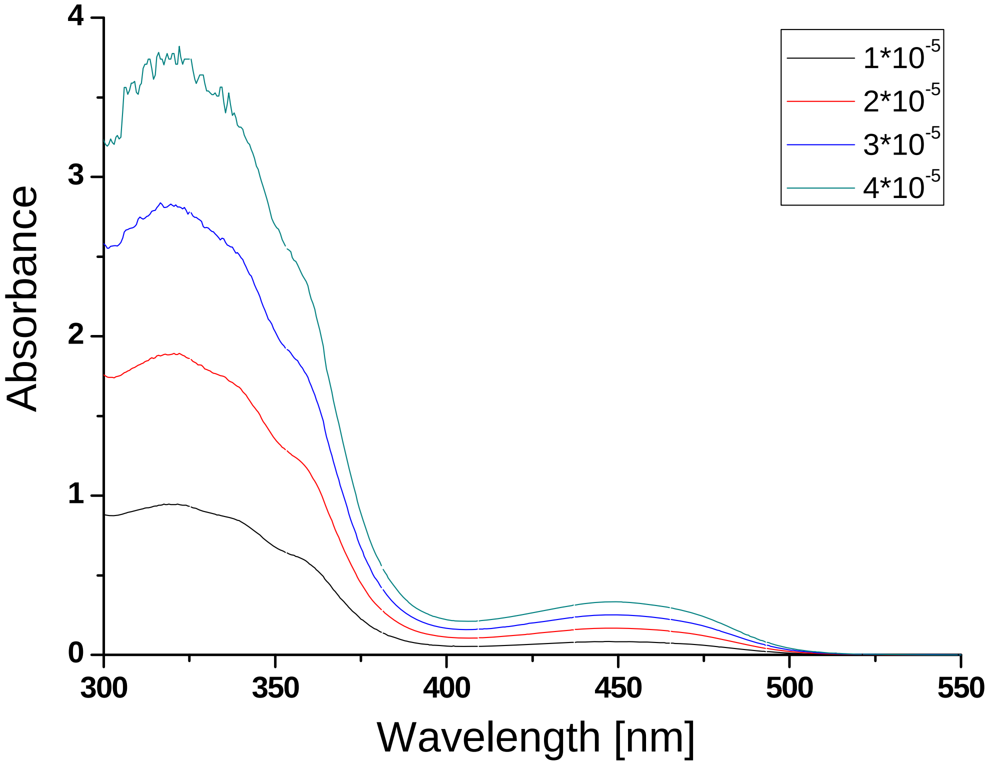


Figure S30. Representative UV-vis spectra of 6 in $CHCl_3$ at various concentrations.

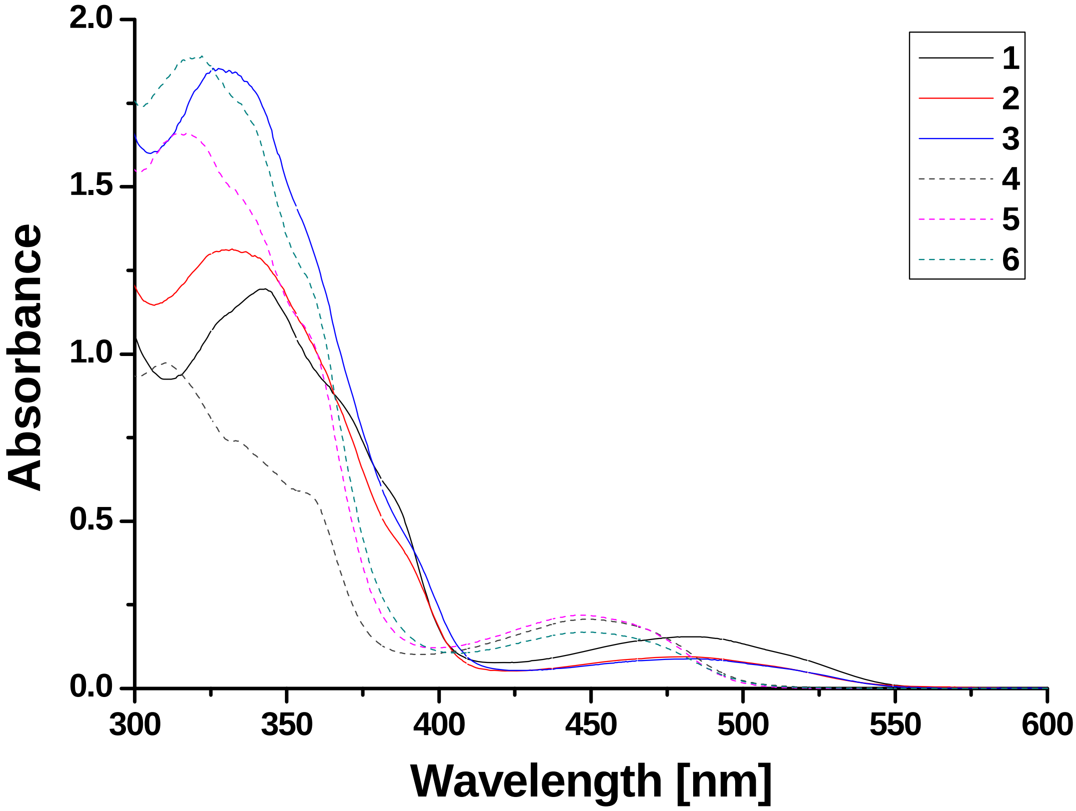
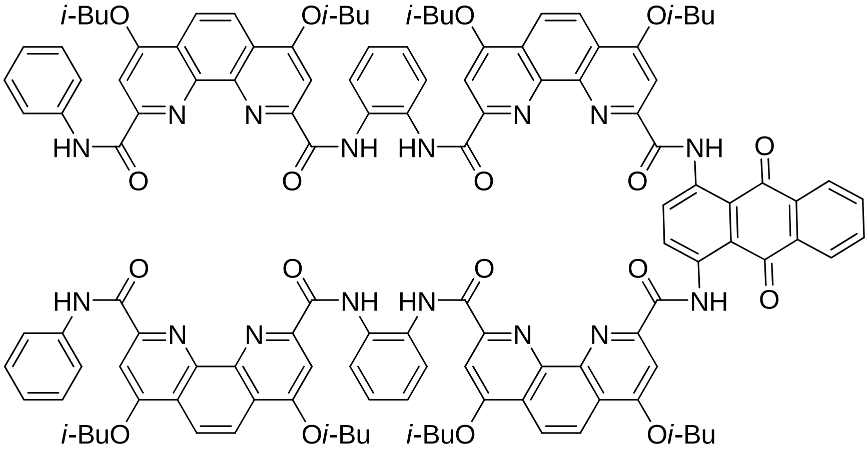


Figure S31. UV-Vis spectra of the molecular strands 1~6 in $CHCl_3$ ($c = 2\times10^{-5}$ M).

4. X-ray crystallographic analysis of oligomers 2 and 4.

Single crystals of **2** ($C_{126}H_{120}N_{16}O_{18}\cdot3.5CH_2Cl_2\cdot2.5CH_3OH\cdot CH_3CH_2OH\cdot0.5H_2O$ M_w = 2578.8) suitable for X-ray analysis were grown from the mixture solution of CH_2Cl_2/CH_3OH, CH_3CH_2OH through a slow evaporation at room temperature of **2**, and an orange single crystal was selected for intensity measurements.



2

Table S1. Crystal Data and Structure Refinement for Compound **2**.

Empirical formula	C134 H144 Cl7 N16 O22	
Formula weight	2578.80	
Temperature	113(2) K	
Wavelength	0.71073 Å	
Crystal system	*Triclinic*	
Space group	*P-1*	
Unit cell dimensions	*a* = 15.396(3) Å	*α* = 99.21(3)°
	b = 16.278(3) Å	*β* = 104.19(3)°
	c = 29.093(6) Å	*γ* = 100.30(3)°
Volume	6794(2) Å^3	
Z	2	
Density (calculated)	1.261 g/cm^3	
Absorption coefficient	0.218 mm^{-1}	
F(000)	2710	
Theta range for data collection	1.48 to 25°	

Index ranges	-18 <= h <= 17, -19 <= k <= 19, -34 <= l <=20
Reflections collected	38568
Independent reflections	23468 [R(int) = 0.1804]
Completeness to theta = 26°	98.0%
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	23468 / 11 / 1470
Goodness-of-fit on F^2	1.176
Final R indices [I>2sigma(I)]	R_1 = 0.1587, wR_2 = 0.3256
R indices (all data)	R_1 = 0.3304, wR_2 = 0.4091
Largest diff. peak and hole	0.744 and -1.244 e·Å^3

The poor quality of the crystal structure may be attributed to the weak diffraction intensity, strong disorganization of isobutyl side chains and included solvent molecules. Both CH_2Cl_2 (C135, Cl9, Cl10) and H_2O (O20) are half-occupied, i.e. the sum of the SOF of these two groups are 1.00, in other words, they do not appear at the same time. The O23 atom is also half-occupied, i.e. O23 is disordered in two positions. The C136/O23 are belong to one CH_3OH molecule (H for O23 was not added).

Since the X-ray diffraction data were weak and the quality was not good enough, DFIX restrains are used to keep the bonds and angles in a reasonable range, and isor simu restrains are used to restrict the anisotropic atomic displacement parameters.

Restrains List

DFIX 1.50 0.01 C95 O4

DFIX 1.55 0.01 C95 C96

DFIX 1.55 0.01 C96 C97

DFIX 1.55 0.01 C96 C98

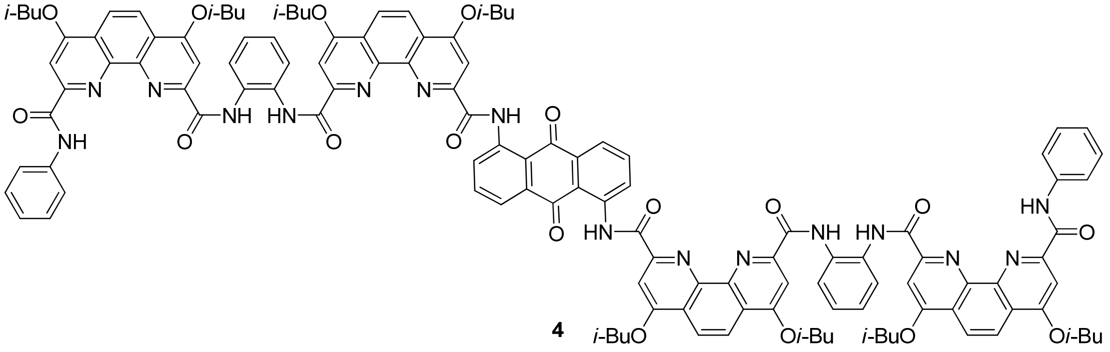
DFIX 1.55 0.01 C111 C112

DFIX 1.55 0.01 C112 C113

DFIX 1.55 0.01 C112 C114

```
DFIX 1.55 0.01 C111 C12B
DFIX 1.55 0.01 C12B C13B
DFIX 1.55 0.01 C12B C14B
EADP C112 C12B
EADP C113 C13B
EADP C114 C14B
DFIX 1.55 0.01 C136 O23
ISOR 0.01 C95 C96 C97 C98
```

Single crystals of **4** ($C_{126}H_{120}N_{16}O_{18}\cdot 4.5CHCl_3\cdot 2CH_3OH$ M_w = 2753.63) suitable for X-ray analysis were grown from the mixture solution of $CHCl_3$/ CH_3OH, CH_3CH_2OH through a slow evaporation at room temperature of **4**, and an orange single crystal was selected for intensity measurements.



4

Table S2. Crystal Data and Structure Refinement for Compound **4**.

Empirical formula	C 132.5 H 132.5 Cl 13.50 N 16 O20	
Formula weight	2753.63	
Temperature	113(2) K	
Wavelength	0.71073 Å	
Crystal system	*Triclinic*	
Space group	*P-1*	
Unit cell dimensions	a = 14.041(3) Å	α = 110.78(3)°
	b = 15.327(3)) Å	β = 102.06(3)°
	c = 18.740(4) Å	γ = 104.06(3)°
Volume	3458.6(12) Å^3	
Z	1	
Density (calculated)	1.322 g/cm^3	
Absorption coefficient	0.339 mm^{-1}	
F(000)	1432	
Crystal size	0.14 × 0.12 × 0.06 mm^3	
Theta range for data collection	1.77 to 25.00°	
Index ranges	-16 <= h <= 16, -18 <= k <=13, -22 <= l <= 22	
Reflections collected	23723	
Independent reflections	12103 [R(int) = 0.1890]	

Completeness to theta = 26°	99.2%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9799 and 0.9541
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12103 / 197 / 948
Goodness-of-fit on F^2	1.103
Final R indices [I>2sigma(I)]	$R_1 = 0.1473$, $wR_2 = 0.3631$
R indices (all data)	$R_1 = 0.2973$, $wR_2 = 0.4435$
Largest diff. peak and hole	0.908 and -0.621 e·Å^3

DFIX restrains are used to keep the bonds and angles of C-Cl Cl-C-Cl in $CHCl_3$ in a reasonable range. Isor simu restrains are used to restrict the anisotropic atomic displacement parameters.

Restrains List

ISOR 0.01 O10 > last

DFIX 1.45 0.01 O10 C67 O11 C68 O12 C69 O13 C70

DFIX 1.54 0.01 C25 C27

DFIX 1.72 0.01 C64 CL1 C64 CL2 C64 CL3 C64 CL1' C64 CL2' C64 CL3'

ISOR 0.01 CL1 CL2 CL3 CL1' CL2' CL3' CL4 CL5 CL6 CL7 CL8

ISOR 0.01 CL7 CL8 CL9 C27

ISOR 0.01 CL4 CL5 CL6 CL4' CL5' CL6'

DFIX 1.72 0.01 C66 CL7 C66 CL8 C66 CL9

DFIX 1.72 0.01 C65 CL4 C65 CL5 C65 CL6 C65 CL4' C65 CL5' C65 CL6'

DFIX 2.8 0.01 CL4' CL5' CL4' CL6' CL5' CL6'

EADP Cl6 Cl6'

EADP Cl5 Cl5'

EADP Cl4 Cl4'