Support Information

Cyclically Conjugated Porphyrin Trimers Linked through Benzo[4,5]imidazo[2,1-a]isoindole Bridges

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1. General Experimental Information

Chemicals

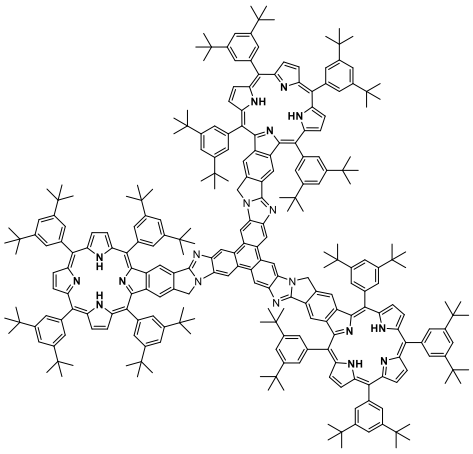
Chemicals used in synthesis were purchased either from Fischer or Sigma-Aldrich. Solvents used in reactions were ACS grade obtained from Fischer or ACRO Sand dried through a commercially available solvent purification system. C_{60} (>99%), was obtained from TCI Chemicals). Analytical thin-layer chromatography (TLC) was performed on Silicycle UltraPure SilicaGel 60 F254 TLC plates. Column chromatography was performed using 43 – 63 μm silica gels. Synthesis of dialdehydebenzoporphyrin was done using a previously published procedure[1].

Spectral measurements

NMR data of compounds were obtained on a Varian 500 MHz (^{1}HNMR)/126 MHz or 101 MHz (^{13}C NMR) spectrometer. All samples were prepared in $CDCl_3$ and chemical shifts were referenced to d-chloroform at d = 7.26 and 77.16 ppm, respectively. Coupling constants are given in Hz. Data for multiplicities were given as follows: s =singlet, d = doublet, t = triplet, q = quartet, m = multiple. Mass spectrometry experiments were done using a Thermoscientific MALDI-LTQ-XL-Orbitrap mass spectrometer. UV-Visible spectra were recorded on an Agilent CARY 5000 spectrometer and fluorescence data were recorded on a Horiba Fluoromax-4p fluorimeter. Ferrocene/ ferroceniumredox couple was used as an internal standard. All the solutions were purged prior to spectral measurements with nitrogen gas. Phosphorescence lifetimes were measured at liquid nitrogen temperature in Ar-purged toluene using a Xenon flash lamp on a Horiba Yvon Nanolog spectrometer. The emission was collected at the phosphorescence peak maxima of the given compound.

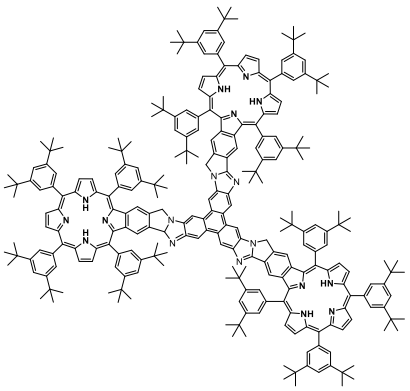
2. Synthesis

β,β'-Benzimidazole-Fused Free-Base Benzoporphyrin Trimer (FB-Trimer-1)



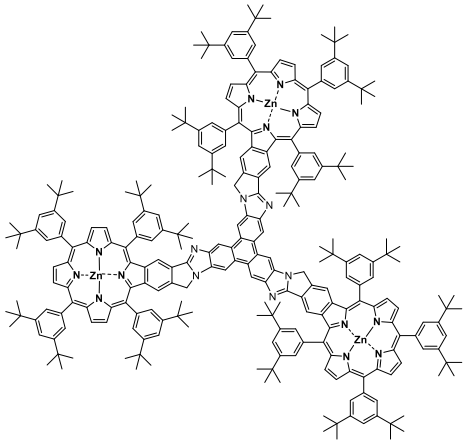
Monobenzodialdehyde porphyrin (40 mg, 0.03 mmol), 1,2,4,5-tetraaminobenzene tetrahydrochloride (6.08 mg, 0.011 mmol), Dichloromethane (2 mL), formic acid (0.5 mL), and triethylamine (TEA) (4 drops, 20 drops equal ~1 mL) were added together in an 8 mL vial. The reaction was then stirred at room temperature overnight. The reaction was then quenched with 0.5 mL TEA, diluted with methanol, and filtered. The products were redissolved in 1 % TEA in chloroform ($CHCl_3$), then a column chromatography was performed using 1 % TEA in $CHCl_3$ to collect the top spot, FB-Trimer-1. The fraction was then recrystallized in $CHCl_3$ and MeOH to yield 12 mg FB-Trimer-1 (28 % yield). UV-Vis λ_{max} (*o*-dichlorobenzene)/nm 437, 527, 600. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.18 (s, 3H), 9.04-9.01 (m, 9H), 8.94 (d, J = 4.7 Hz, 3H), 8.87 (s, 3H), 8.83-8.81 (m, 6H), 8.29-8.27 (m, 3H), 8.26-8.23 (m, 6H), 8.22-8.20 (m, 9H), 8.14-8.13 (m, 12H), 7.87 (s, 3H), 7.83-7.81 (m, 6H), 7.10 (s, 3H), 5.28 (s, 6H), 1.78 (d, J = 0.9 Hz, 36H), 1.98 – 1.59 (m, 216H), -2.50 (s, 6H).^{13}C NMR (126 MHz, $CDCl_3$) 160.92, 150.86, 150.69, 148.86, 148.83, 148.59, 143.13, 142.07, 142.07, 141.75, 141.19, 141.10, 134.04, 133.39, 129.67, 129.10, 128.71, 128.57, 128.08, 127.53, 127.02, 126.23, 121.92, 121.74, 122.41, 121.12, 120.43 118.87, 118.60, 114.24, 47.78, 37.45, 37.13, 35.46, 35.12, 32.79, 32.04 , 31.95, 30.08. MALDI-TOF-HRMS: calculated for $C_{264}H_{295}N_{18}$: 3720.39, found 3720.909.

β,β'-Benzimidazole-Fused Free-Base Benzoporphyrin Trimer (FB-Trimer-2)



Monobenzodialdehyde porphyrin (40 mg, 0.03 mmol), 1,2,4,5-tetraaminobenzene tetrahydrochloride (6.08 mg, 0.011 mmol), Dichloromethane (2 mL), formic acid (0.5 mL), and triethylamine (TEA) (4 drops, 20 drops equal ~1 mL) were added together in an 8 mL vial. The reaction was then stirred at room temperature overnight. The reaction was then quenched with 0.5 mL TEA, diluted with methanol, and filtered. After elution of FB-Trimer-1, elute the bottom FB-Trimer-2. The fraction corresponding to FB-Trimer-2 was then recrystallized using 1 % TEA in CHCl3 and yielded 27 mg FB-Trimer-2 (44 % yield). UV-Vis λ_{max} (*o*-dichlorobenzene)/nm 437, 527, 600. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.38 – 9.17 (m, 3H), 9.05-9.01 (m, 9H), 8.96 – 8.57 (m, 12H), 8.37 – 8.24 (m, 9H), 8.23 – 8.19 (m, 9H), 8.16 – 8.14 (m, 13H), 7.87 – 7.76 (m, 9H), 7.15-7.03 (m, 3H), 5.32 – 5.21 (three singlets, 6H), 1.84 – 1.57 (m, 216H), -2.50 (s, 6H)

β,β'-Benzimidazole-Fused Zinc Benzoporphyrin Trimer (Zn-Trimer-1)



FB-Trimer-1 (11.7 mg, 0.0032 mmol) and 10 equivalents $Zn(OAc)_2$ (5.77 mg, 0.032 mmol) were mixed in $CHCl_3$/MeOH (1.5 mL/0.5 mL). The reaction was stirred overnight at room temperature, diluted with methanol, and filtered to yield 11 mg (87 % yield) Zn-Trimer-1. UV-Vis λ_{max} (*o*-dichlorobenzene)/nm 441, 463, 567, 605. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.22 (s, 3H), 9.09-9.06 (m, 9H), 9.05-9.03 (m, 3H), 8.97 (s, 6H), 8.91 (s, 3H), 8.31 (t, J = 1.9 Hz, 3H), 8.26-8.25 (m, 6H), 8.22-8.20 (m, 9H), 8.15-8.14 (m, 12H), 7.83 (t, J = 2.0 Hz, 9H), 7.31 (s, 3H), 5.36 (s, 6H), 1.84-1.66 (m, 216H). ^{13}C NMR (126 MHz, CDCl3) 161.00, 152.26, 151.79,150.85, 150.70, 150.24, 150.20, 149.23, 148.76, 145.72, 145.28, 142.78, 142.46, 141.85, 141.69, 141.52, 141.08, 133.58, 132.40, 131.86, 131.58, 129.61, 128.73, 128.35, 127.68, 126.35, 124.19, 121.81, 121.05, 119.53, 119.33, 47.86, 35.62, 35.57, 35.23, 32.15, 32.08, 32.02, 31.99 MALDI-TOF-HRMS: calculated for [M + 2MeOH]$C_{264}H_{297}N_{18}O_2$: 3972.16, found 3972.633.

3. Energy Level Diagram and Orbitals

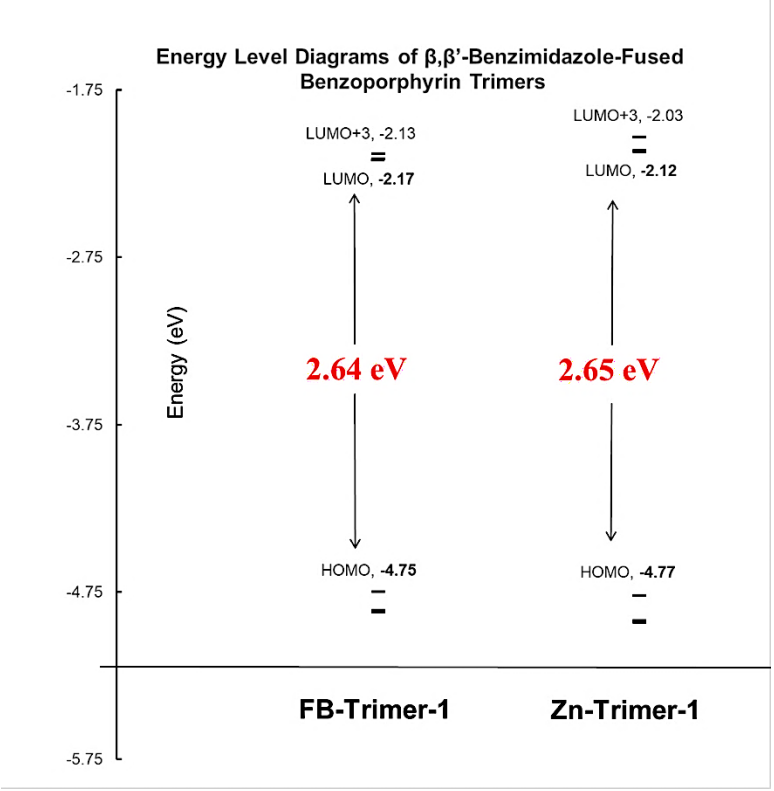


Figure S1. Energy Level Diagram of FB-Trimer-1 and Zn-Trimer-1 Based on Theoretical Calculation.

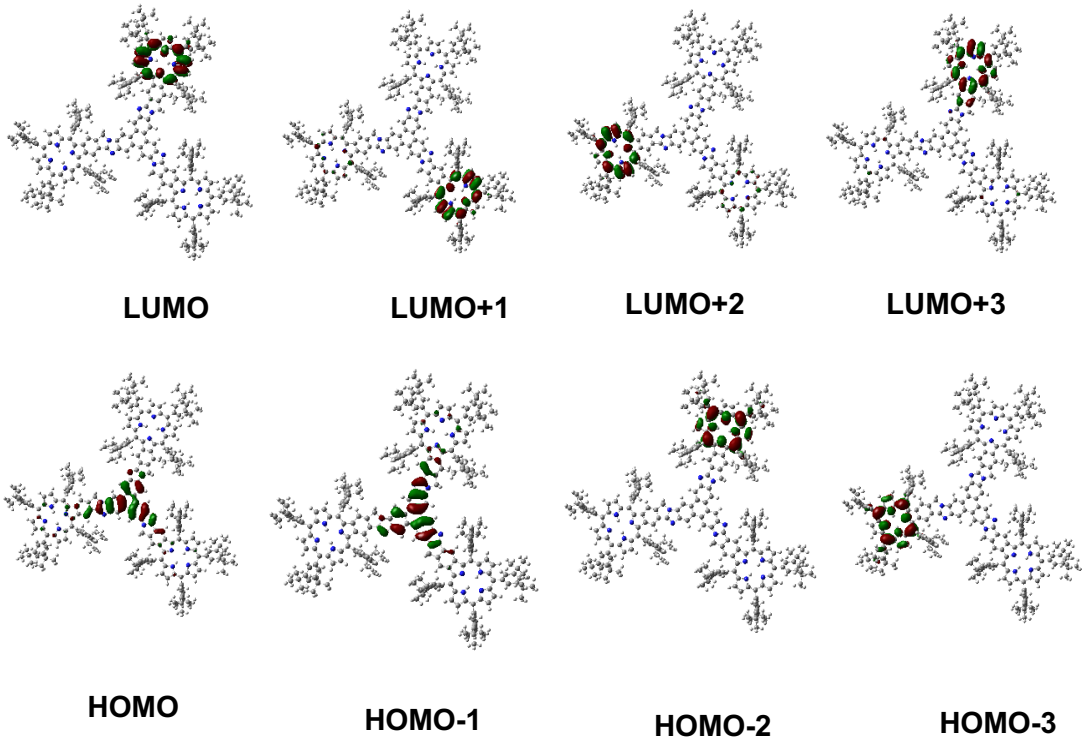


Figure S2. HOMO-LUMO Orbitals of FB-Trimer-1

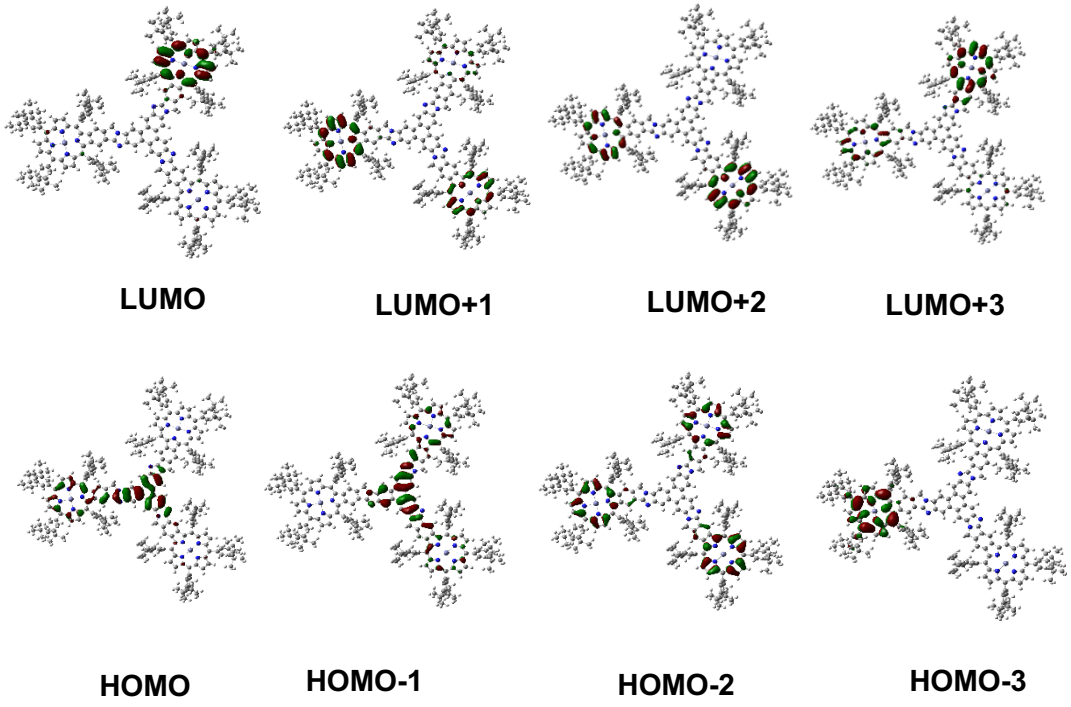


Figure S3. HOMO-LUMO Orbitals of Zn-Trimer-1

4. NMR Spectra

β,β'-Benzimidazole-Fused Free-Base Benzoporphyrin Trimer (FB-Trimer-1)

Figure S4

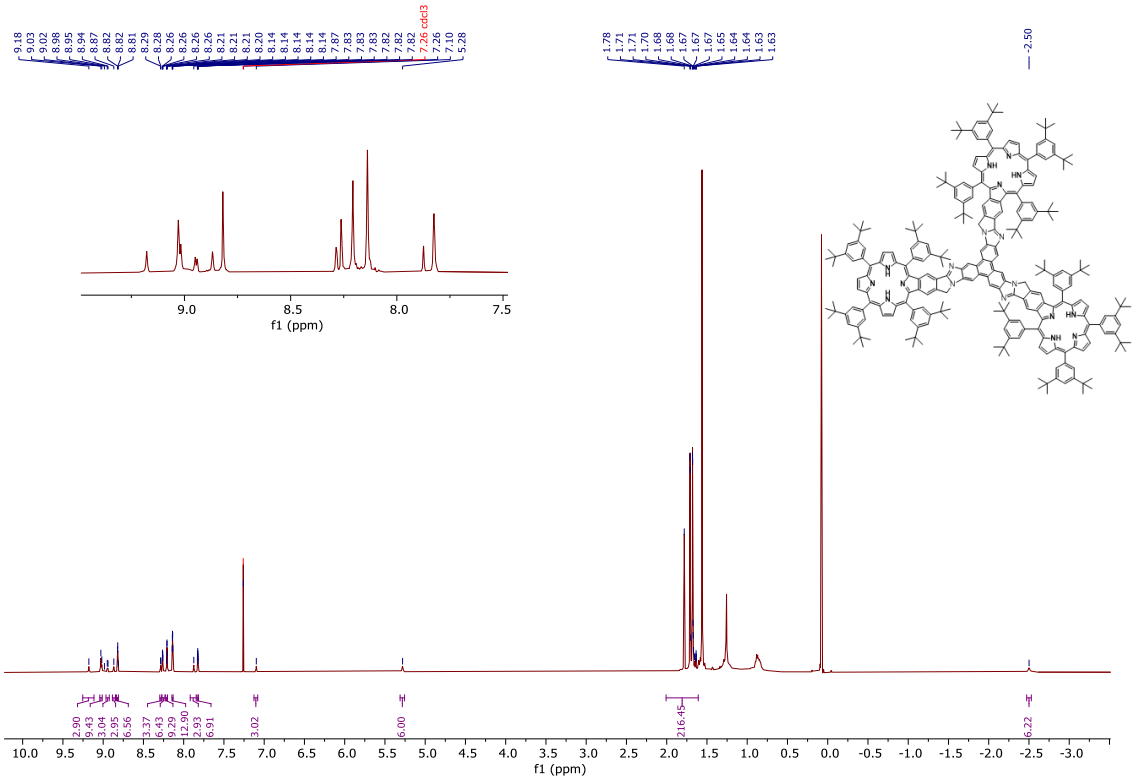
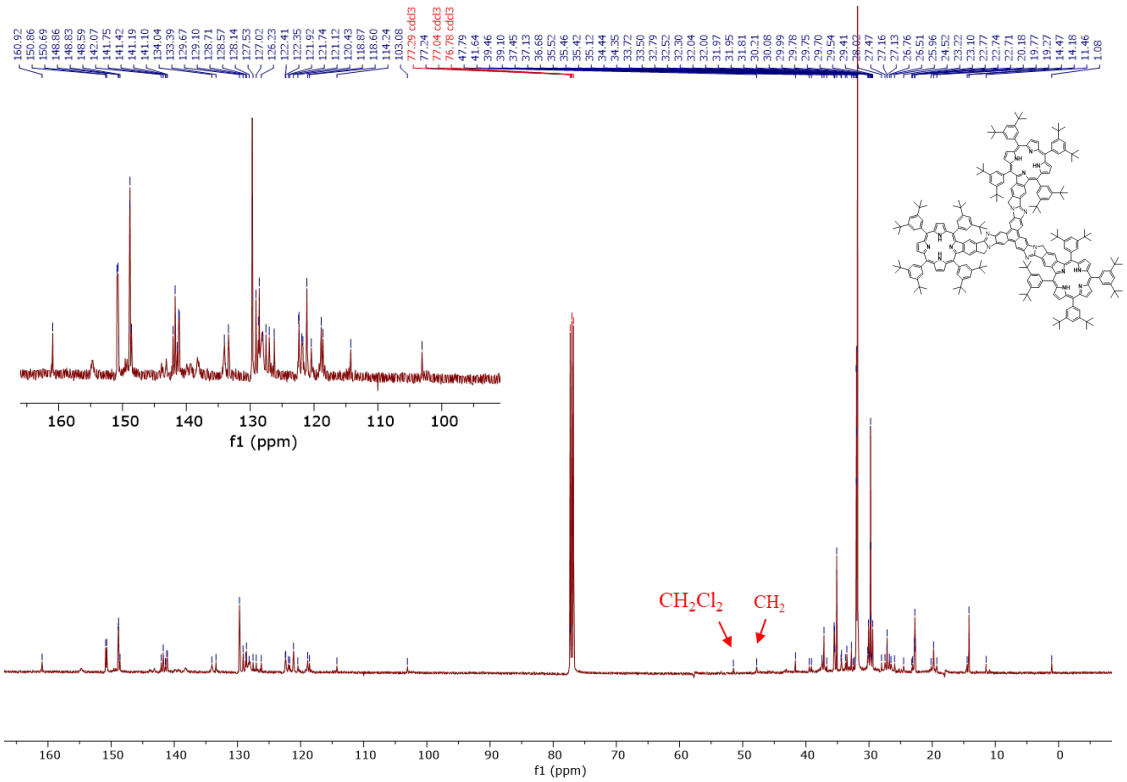
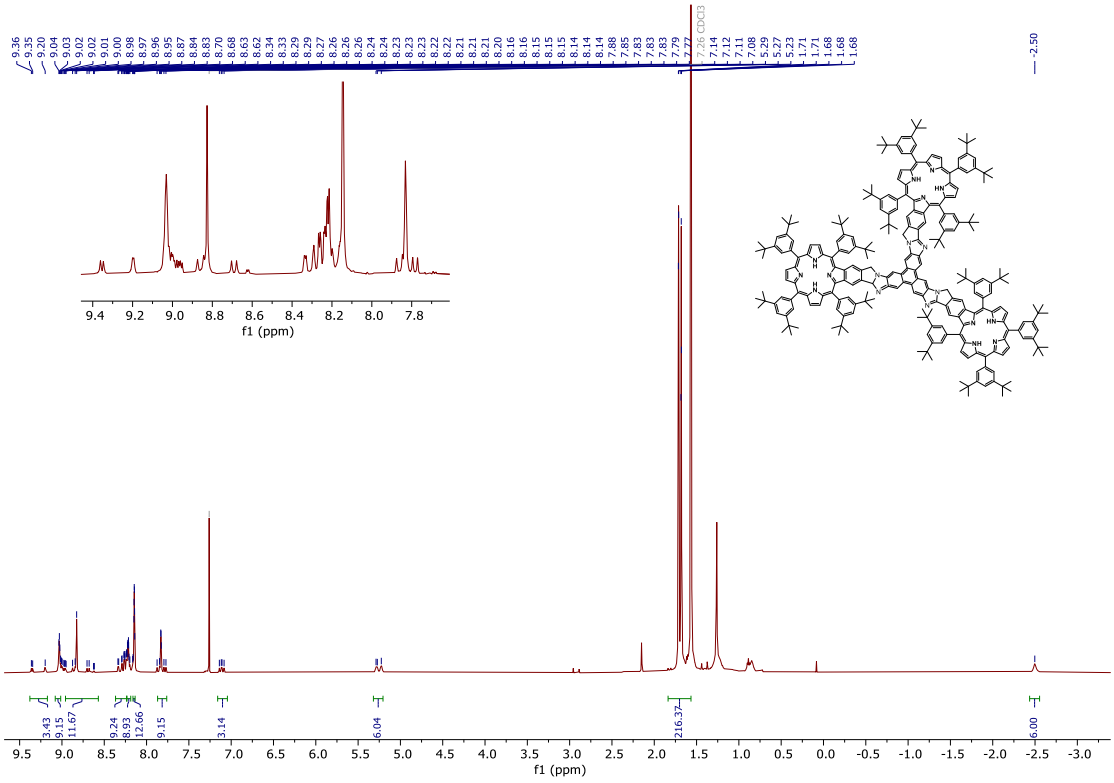


Figure S5



β,β'-Benzimidazole-Fused Free-Base Benzoporphyrin Trimer (FB-Trimer-2)

Figure S6



β,β'-Benzimidazole-Fused Zinc Benzoporphyrin Trimer (Zn-Trimer-1)

Figure S7

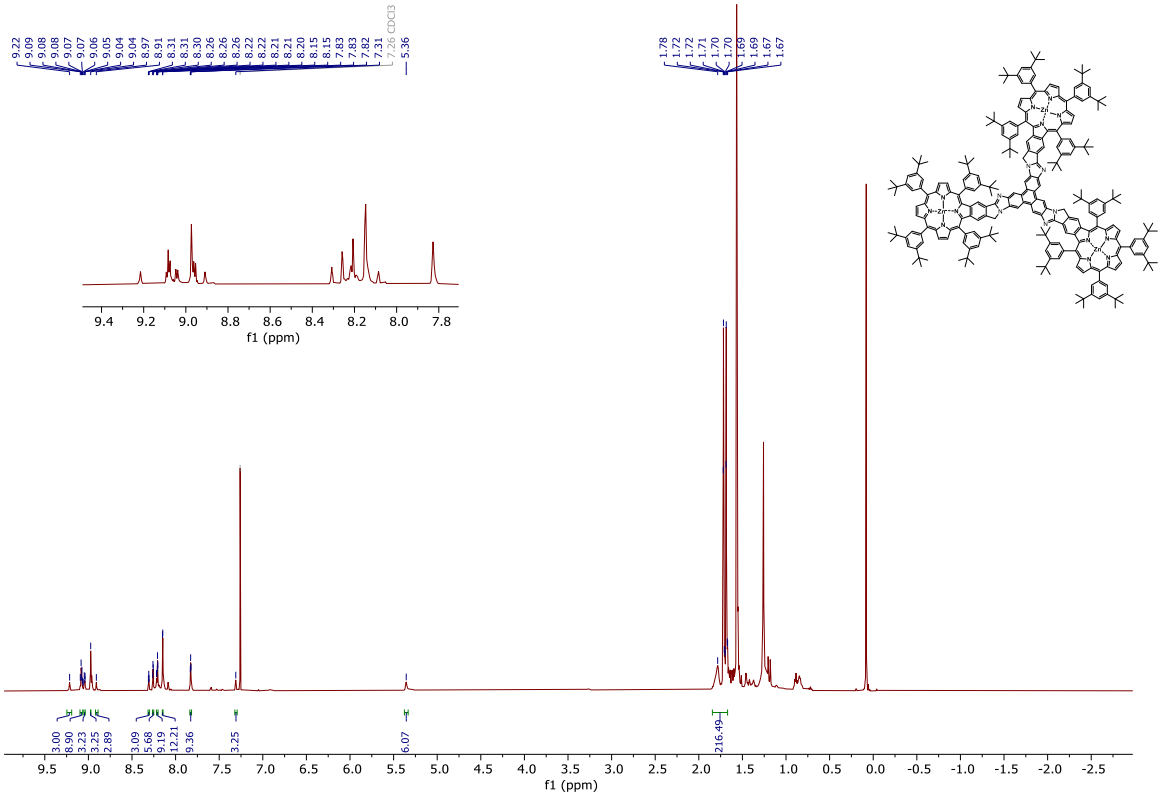
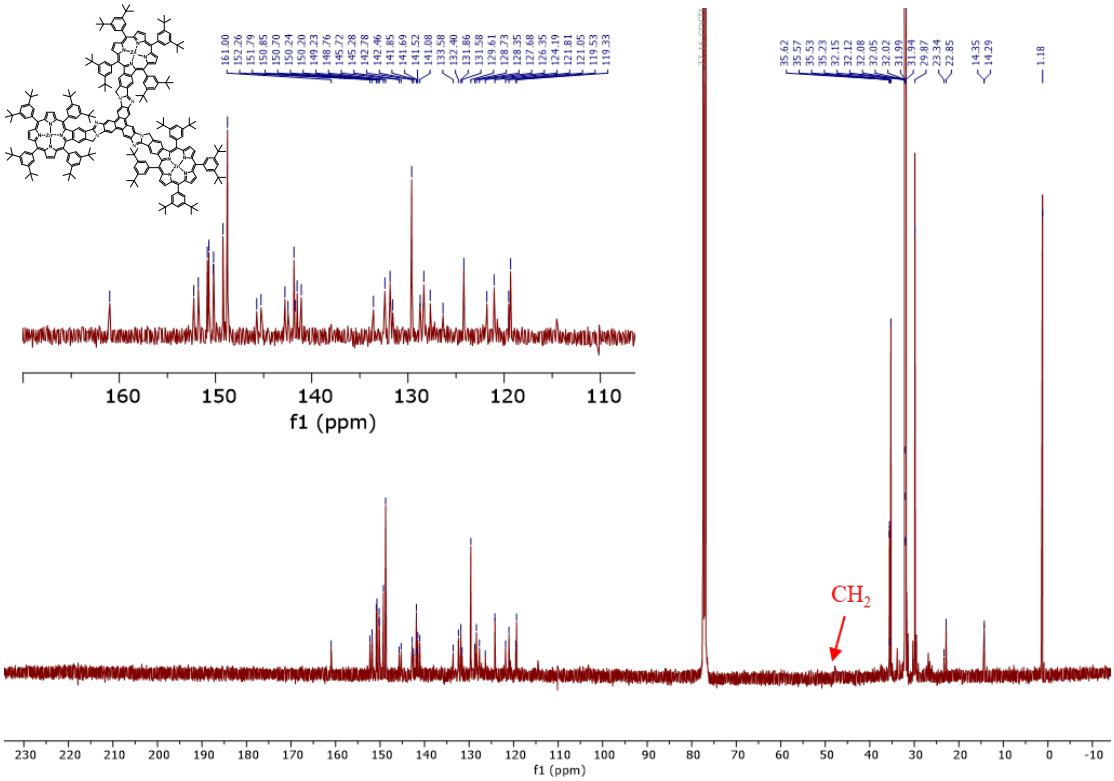


Figure S8



5. 2D NMR

Figure S11 gCOSY spectrum of β,β'-Benzimidazole-Fused Free-Base Benzoporphyrin Trimer (FB-Trimer-2)

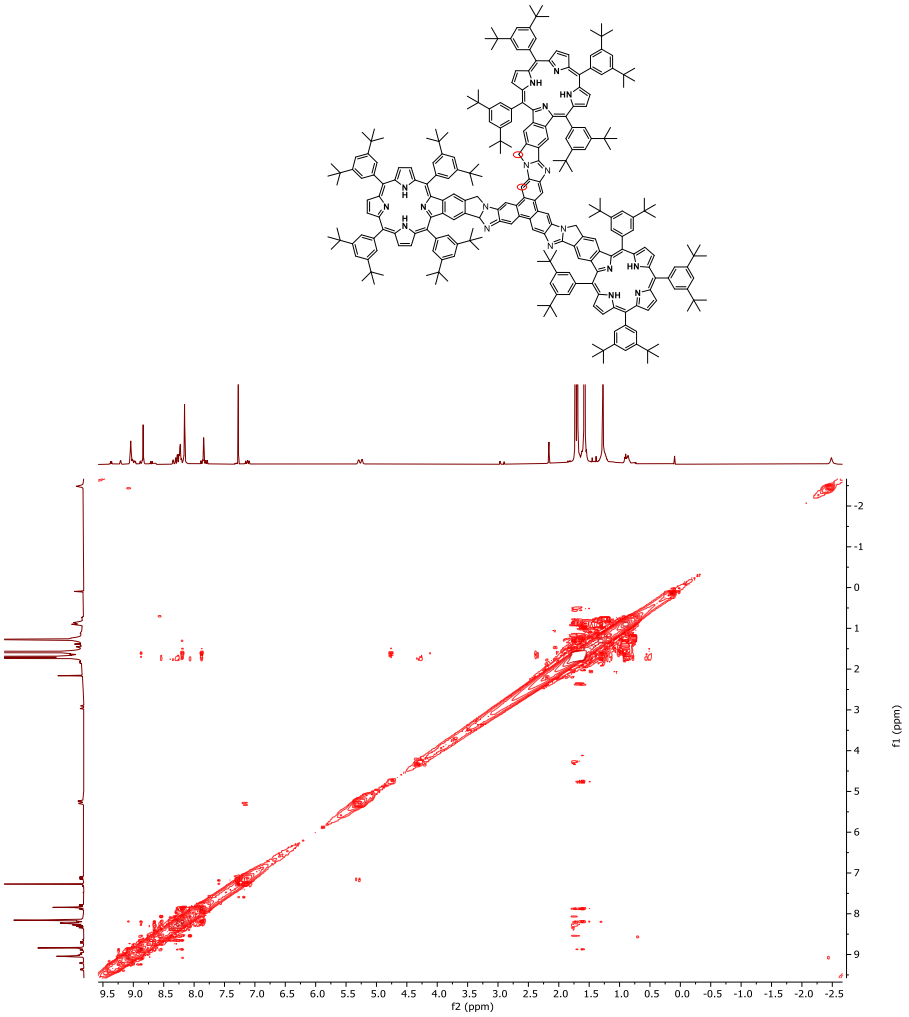


Figure S11. gCOSY Spectrum of FB-Trimer-2 in $CDCl_3$, 500 MHZ

From this COSY spectrum, a weak correlation between the peaks at 5.2-5.3 ppm for -CH_2 proton and the-CH of triphenylene at 7.07-7.14 ppm is visible.

Figure S12 NOESY spectrum of β,β'-Benzimidazole-Fused Free-Base Benzoporphyrin Trimer (FB-Trimer-2)

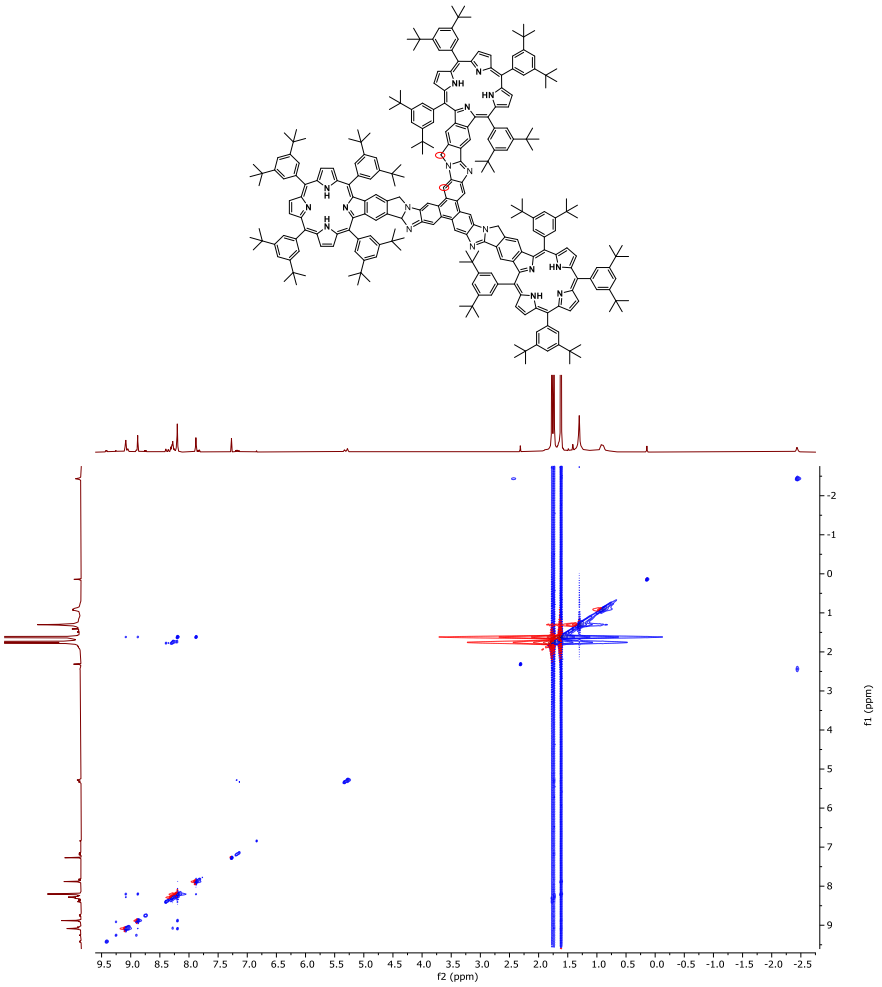


Figure S12. NOESY Spectrum of FB-Trimer-2 in in $CDCl_3$, 500 MHZ

Like the COSY spectrum, a very weak correlation between the peaks at 5.2-5.3 ppm for -CH_2 proton and the-CH of triphenylene at 7.07-7.14 ppm is visible on this NOESY spectrum.

Figure S13 HMBC spectrum of β,β'-Benzimidazole-Fused Free-Base Benzoporphyrin Trimer (FB-Trimer-2)

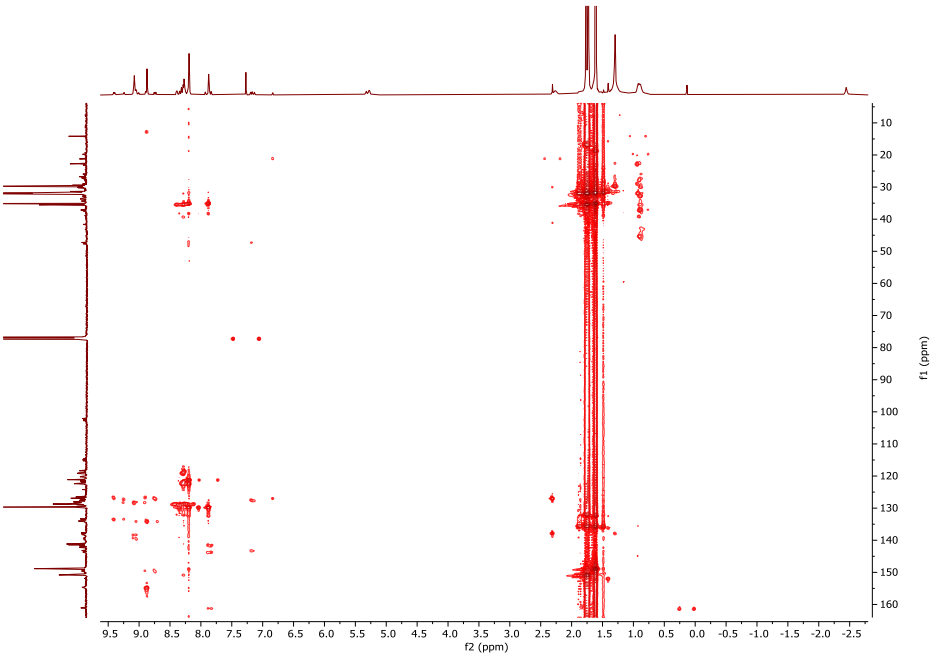


Figure S13. HMBC Spectrum of FB-Trimer-2 in $CDCl_3$, 500 MHZ

Not much information was able to be gathered from HMBC

6. DEPT (Distortionless Enhancement by Polarization Transfer)

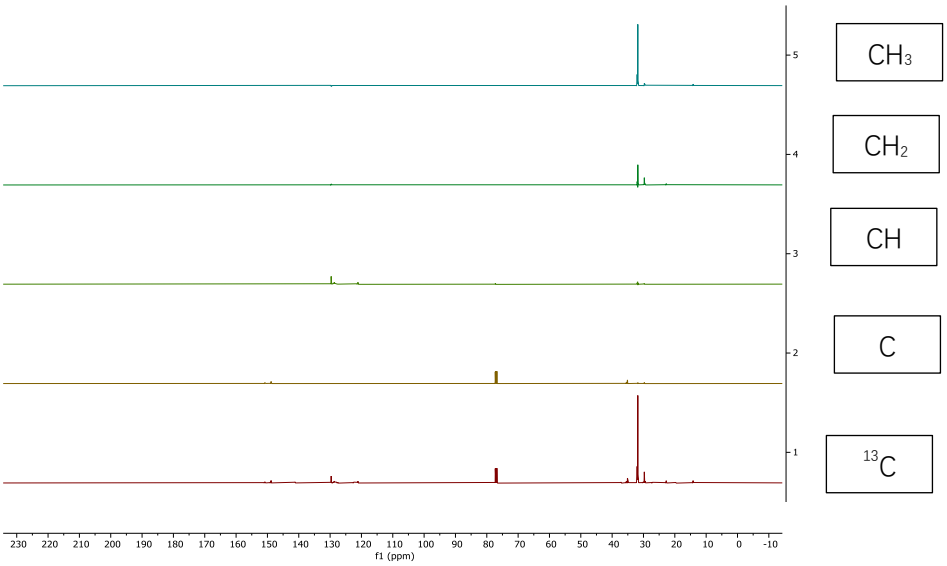


Figure S14. DEPT Spectra in $CDCl_3$, 500 MHZ

All the signals were too weak since the molecule is too big. The nature of FB-Trimer-2 being assymetric, and the solubility of the compound being low make it hard to get chemical shifts with good (visible) intensity. We also performed APT to see if we can

observe -any CH_2 peaks as negative.

7. APT (Attached Proton Test)

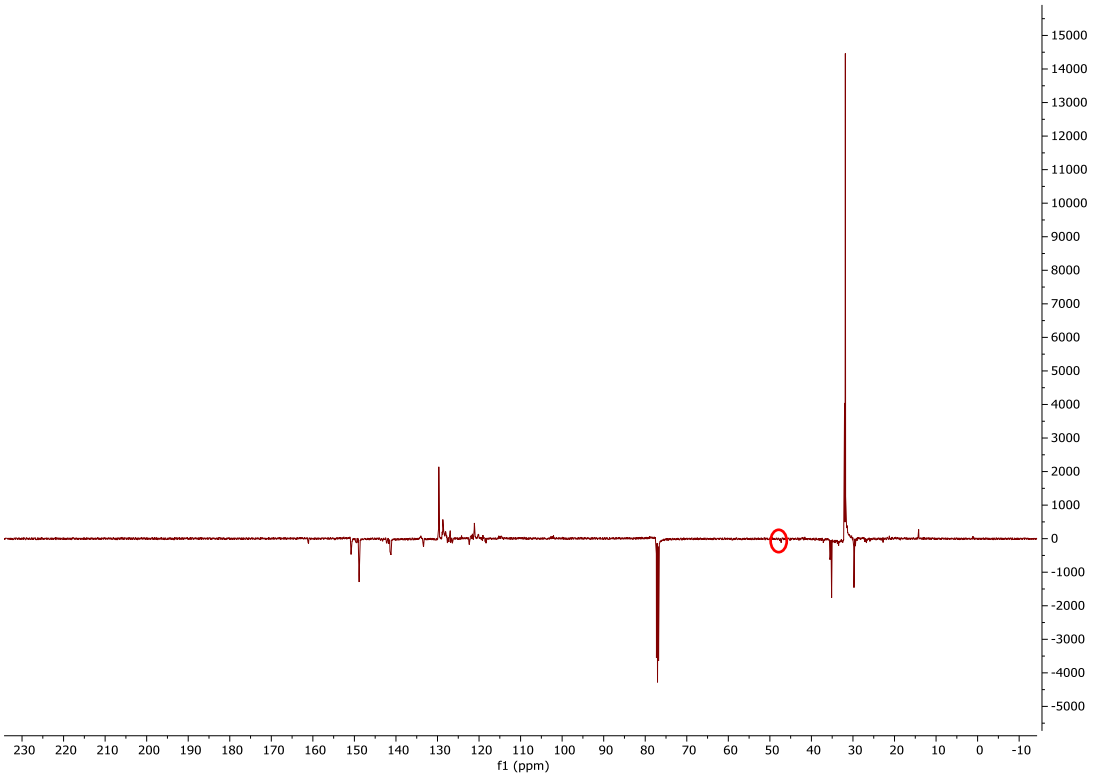


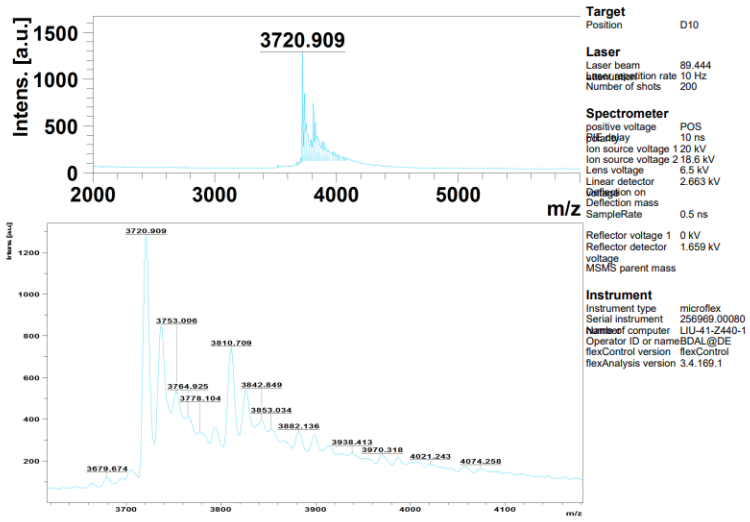
Figure S15. APT Spectra in $CDCl_3$, 500 MHZ

We can observe a couple of very weak negative peaks at ~47 ppm, where the -CH_2 is expected to show up.

8. MALDI-TOF

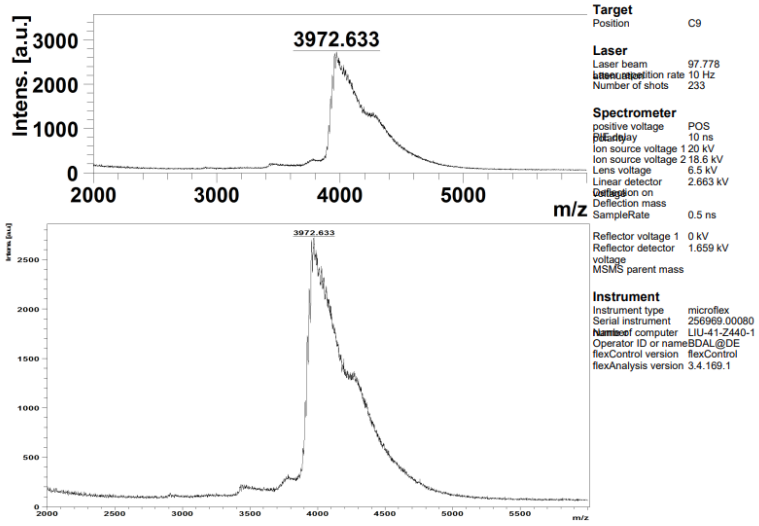
β,β'-Benzimidazole-Fused Free-Base Benzoporphyrin Trimer (FB-Trimer-1)

Figure S9



β,β'-Benzimidazole-Fused Zinc Benzoporphyrin Trimer (Zn-Trimer-1)

Figure S10



9. Reference

1. Hu, Y.; Thomas, M. B.; Webre, W. A.; Moss, A.; Jinadasa, R. G. W.; Nesterov, V. N.; D'Souza, F.; Wang, H. Nickel(II) Bisporphyrin-Fused Pentacenes Exhibiting Abnormal High Stability. *Angew. Chem. Int. Ed.* 2020, 59, 20075-20082.