Supporting information

A new *meso-meso* directly-linked corrole-porphyrin-corrole hybrid: synthesis and photophysical properties

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General Methods

All solvents were purified according to standard methods. Chemicals received from commercial sources were used without purification except $POCl_3$ which was distilled over P_2O_5 prior to use. Dipyrromethane, [1] 3, 5-di-tert-butylbenzaldehyde, [2] 5, 15-Bis-formyl-10, 20-bis-(3, 5-di-*t*-butylphenyl)-porphinato copper (II) [3] were prepared by literature methods. Characterization through standard techniques including NMR (^{1}H NMR, ^{19}F NMR, and 2D NMR) and MASS (MALDI-ToF/HR-LCMS) recorded on Bruker Advance 500 MHz spectrometer and Bruker Daltonics flex Analysis mass spectrometer respectively. Chemical shifts expressed in ppm relative to chloroform. UV-vis spectral measurements were done on a Shimadzu spectrophotometer UV-1800 using Hellma quartz cells of 10mm path length. Steady state emission measurements were carried out on a Horiba Jobin Yvon fluorolog 3-111. Spectroscopic grade solvents were used for measuring optical properties. The measurements of fluorescence decay were done on time correlated single-photon-counting system from HORIBA. All the molecules were excited at 407 nm using N-405L picosecond diodes (IBH-NanoLed) and emission was collected at magic angle polarization using a Hamamatsu MCP photomultiplier (Model R-3809U-50). The TCSPC set up consists of an Ortec 9327 pico-timing amplifier. The data was collected with a PCI-6602 interface card as a multi-channel analyzer. FWHM at 407nm excitation was around 140 ps.

Synthetic procedures

Synthesis of **1**[3]

Compound **1** was obtained by demetalation of 5, 15-Bis-formyl-10, 20-bis-(3, 5-di-t-butylphenyl)-porphinato copper[1] with 1:1 trifluoroacetic acid and sulfuric acid mixture.[2] The analytical data are identical with reports.

Data for **1:** ^{1}H NMR- (500MHz; CDCl$_3$): δ 12.56 (s, 2H), 10.02 (d, *J*=4.4 Hz, 4H), 9.02 (d, *J*=4.8 Hz, 4H), 8.06 (d, *J*=1.6Hz, 4H), 7.88 (t, *J*=1.7Hz, 2H), 1.56(s, 36H), -2.25 (s, 2H), MS (LR-LCMS, positive mode): found 742.415 for $C_{50}H_{52}N_4O_2$ Calcd 742.425.
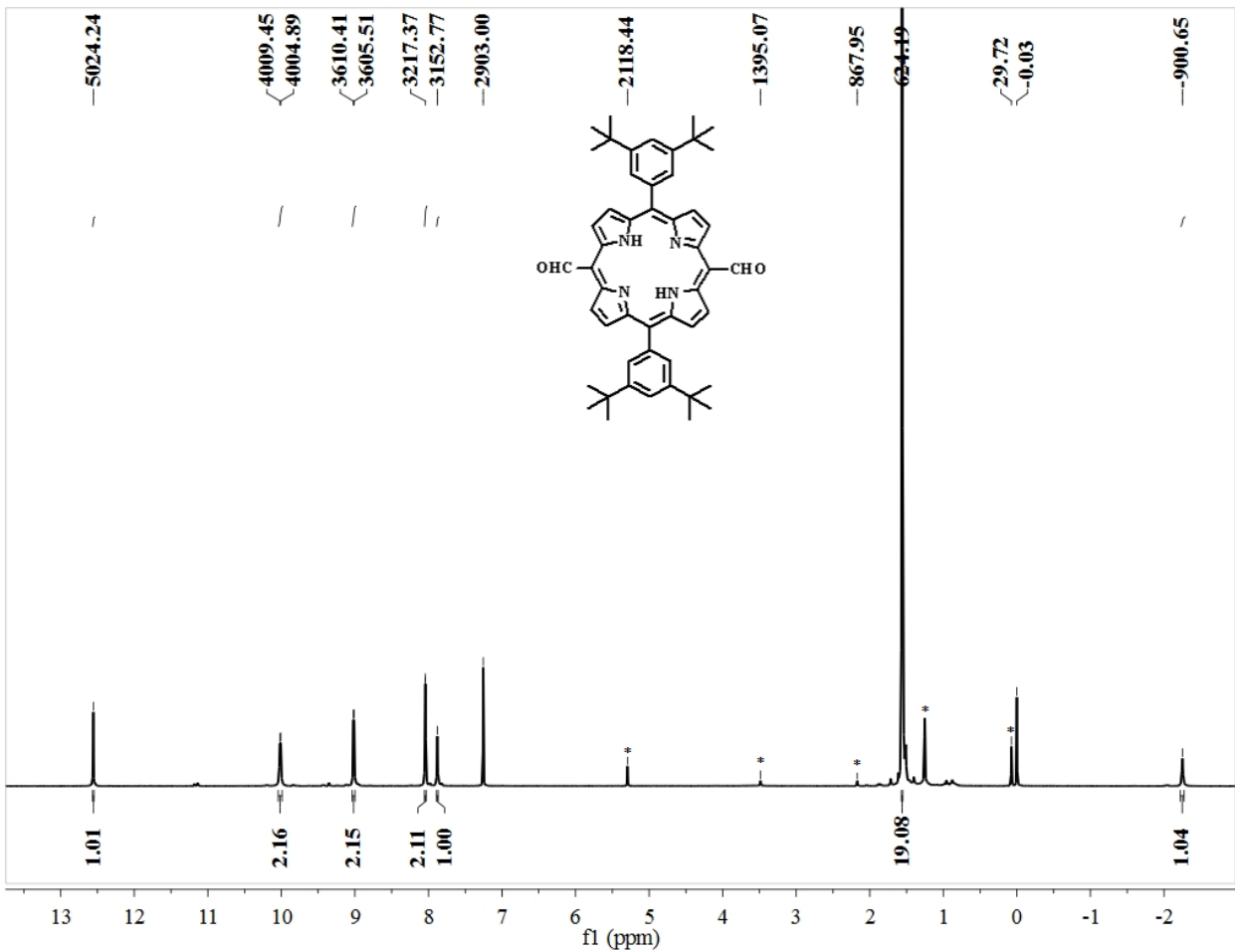
500 MHz ^{1}H NMR of Compound **1** in CDCl$_3$
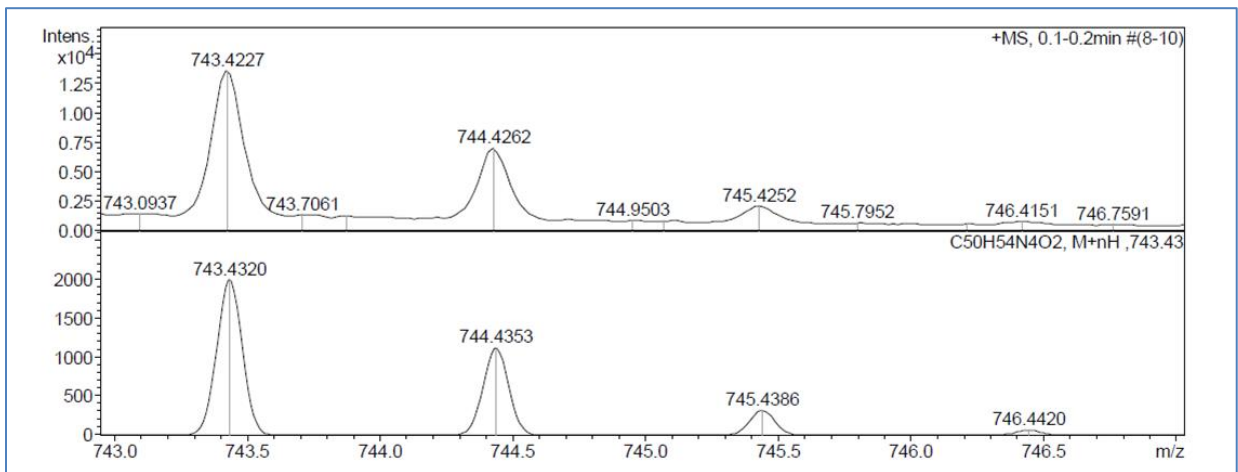
LR-LCMS of **1** in positive mode

Synthesis of **3a**

meso-bis-formylporphyrin **1** (20mg, 0.03mmol), 5-pentafluorophenyldipyrromethane **2** (67mg, 0.22 mmol) and EtOH (2μL, 0.03 mmol) were dissolved in 4ml DCM at 0°C. $BF_3.Et_2O$ (7.7μL, 0.06 mmol) was added to the solution, the mixture was then stirred for 30 min and one drop of Et_3N was added. The reaction mixture was diluted to 25ml with DCM. The resulting diluted reaction mixture was dropped into a solution of 49mg DDQ in 0.5 ml THF/25ml DCM over a period of 30 min. The reaction mixture was passed over a silica column and eluted with DCM. All fractions were combined and evaporated to dryness. Subsequent chromatography (silica, DCM/hexane, 2:8) afforded pure **3a**.
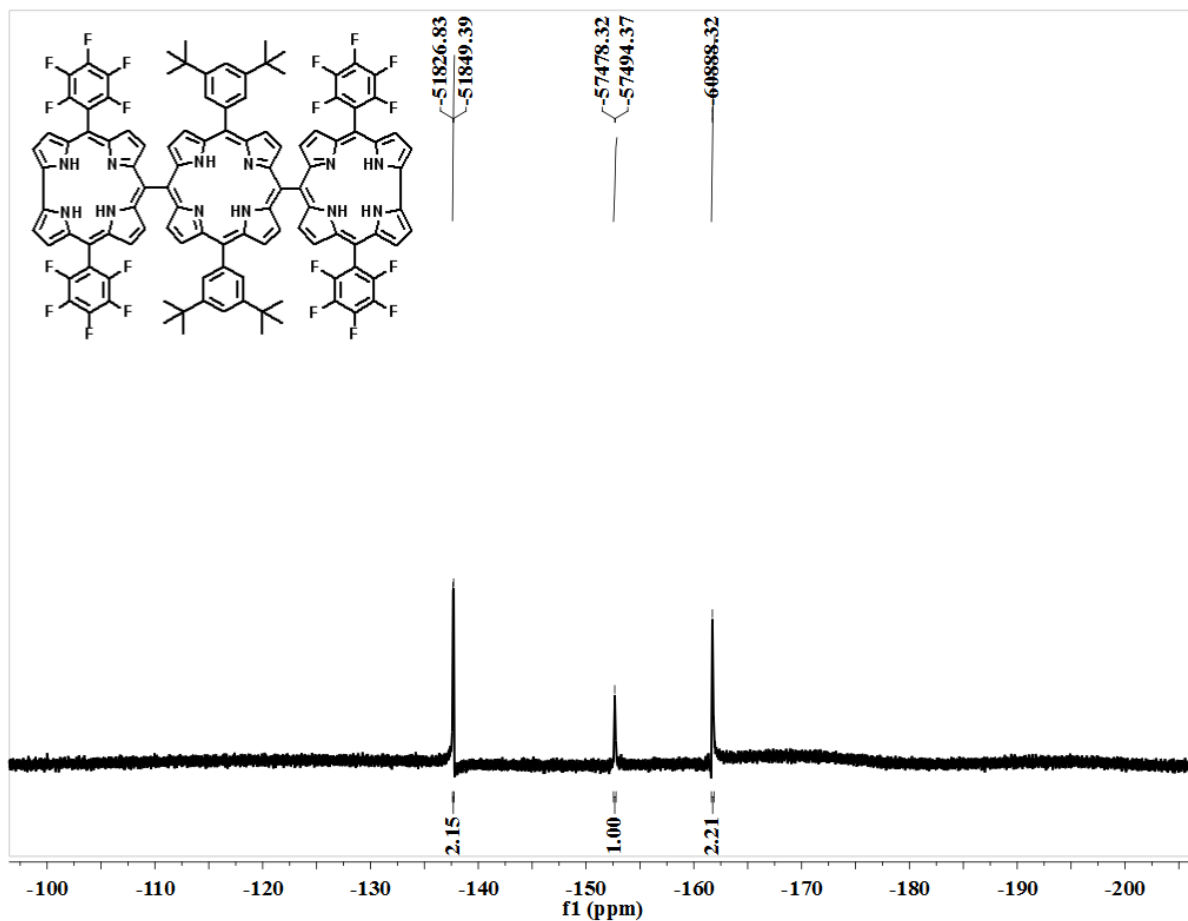
Data for **3a:** ^{1}H NMR - (400MHz, $CDCl_3$) δ 9.22 (d, *J*=4.2Hz, 4H), 8.66 (m, 8H), 8.52 (d, *J*=4.5Hz, 4H), 8.17 (d, *J*=4.7, 4H), 8.05 (m, 8H), 7.62 (t, *J*=1.7Hz, 2H), 1.36 (s, 36H), -1.68 (s, 2H), ^{19}F NMR (376MHz, $CDCl_3$) δ: -137.6 (4F), -152.6 (2F), -161.7 (4F). MS (HR-LCMS, positive mode): found M+nH=1943.5956 Calcd for $C_{110}H_{74}F_{20}N_{12}$ 1942.5840.
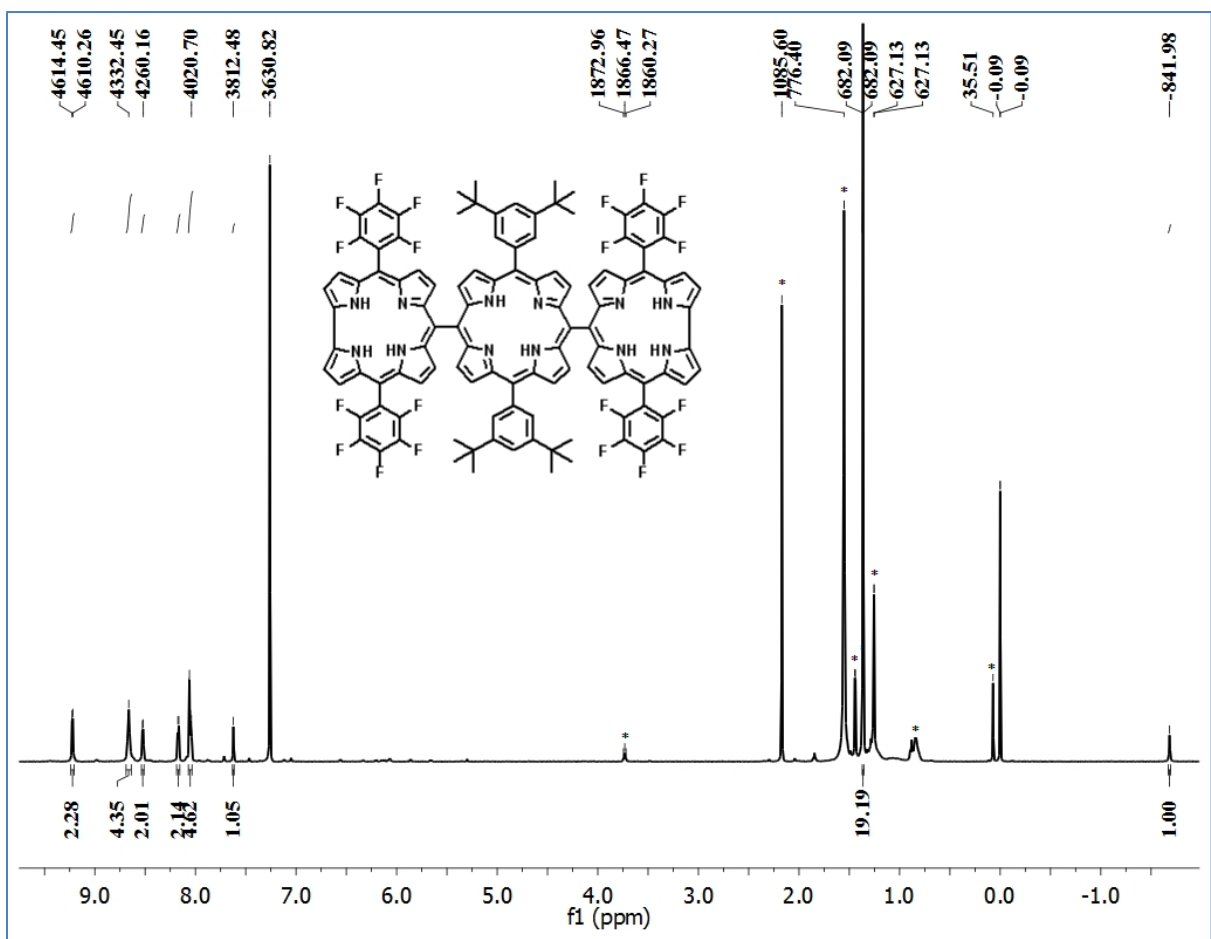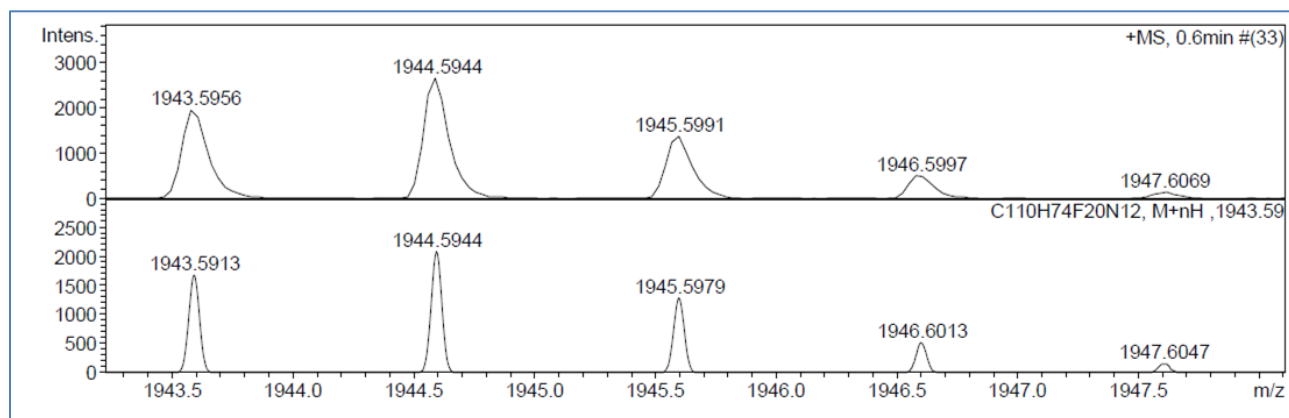
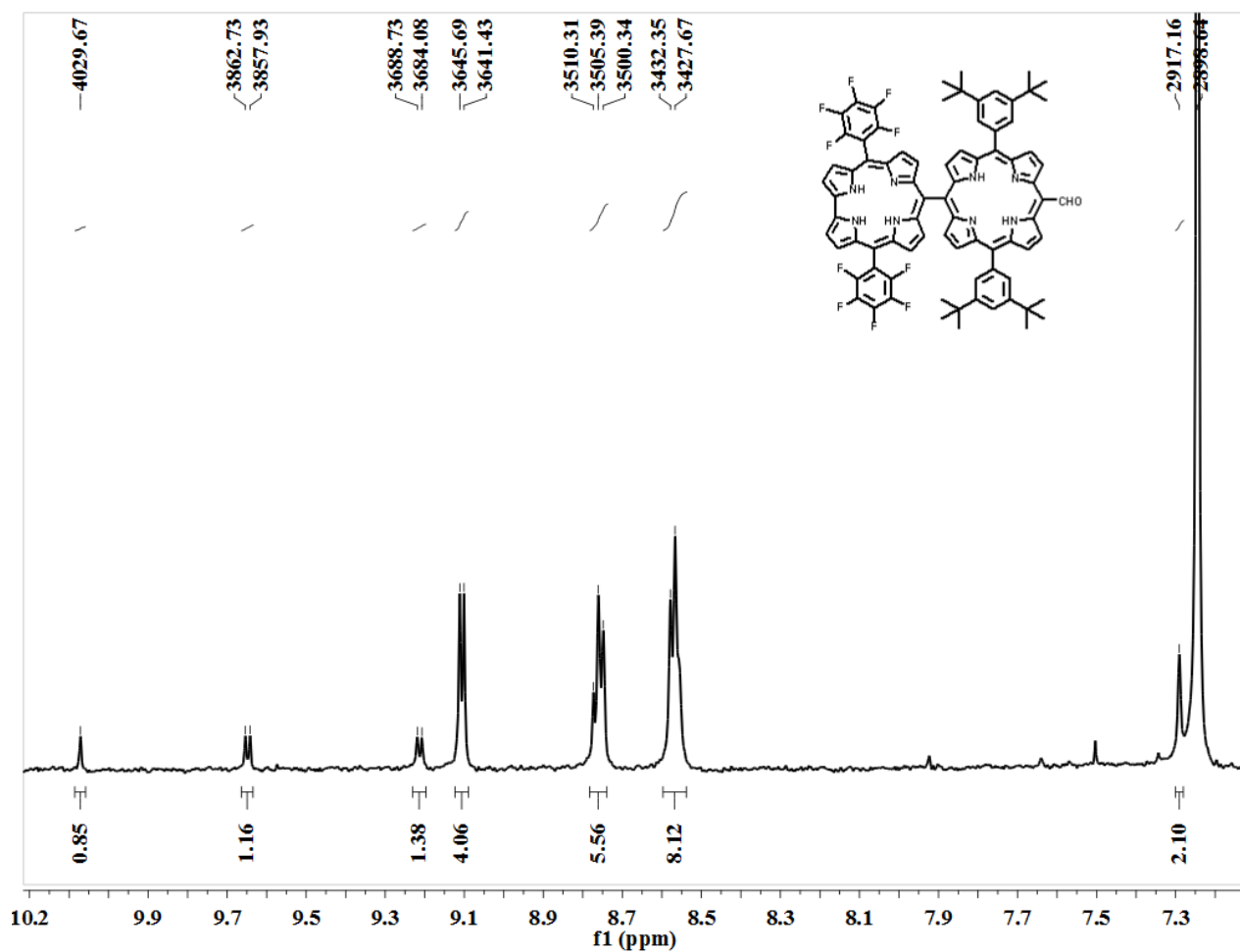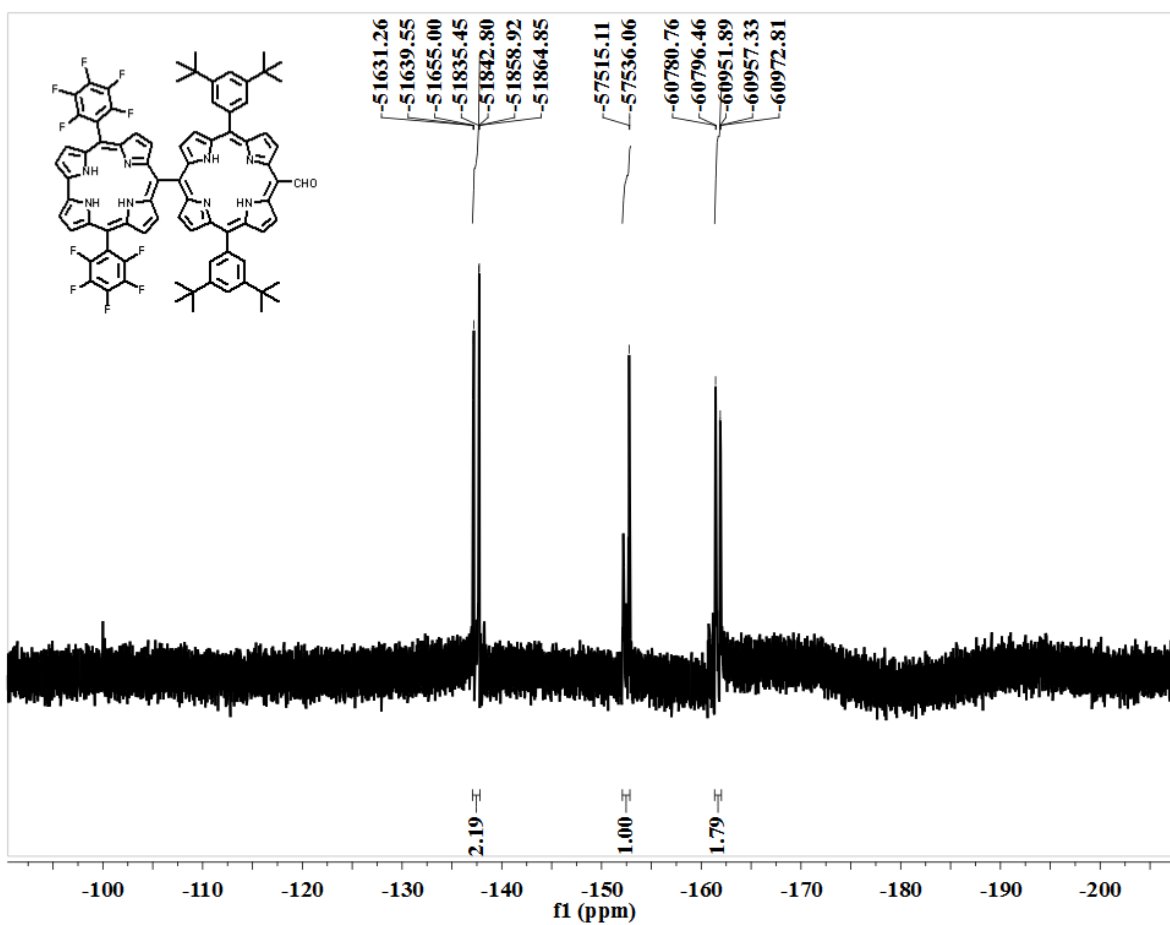500MHz ^{1}H NMR spectrum of **3a** in CDCl$_3$
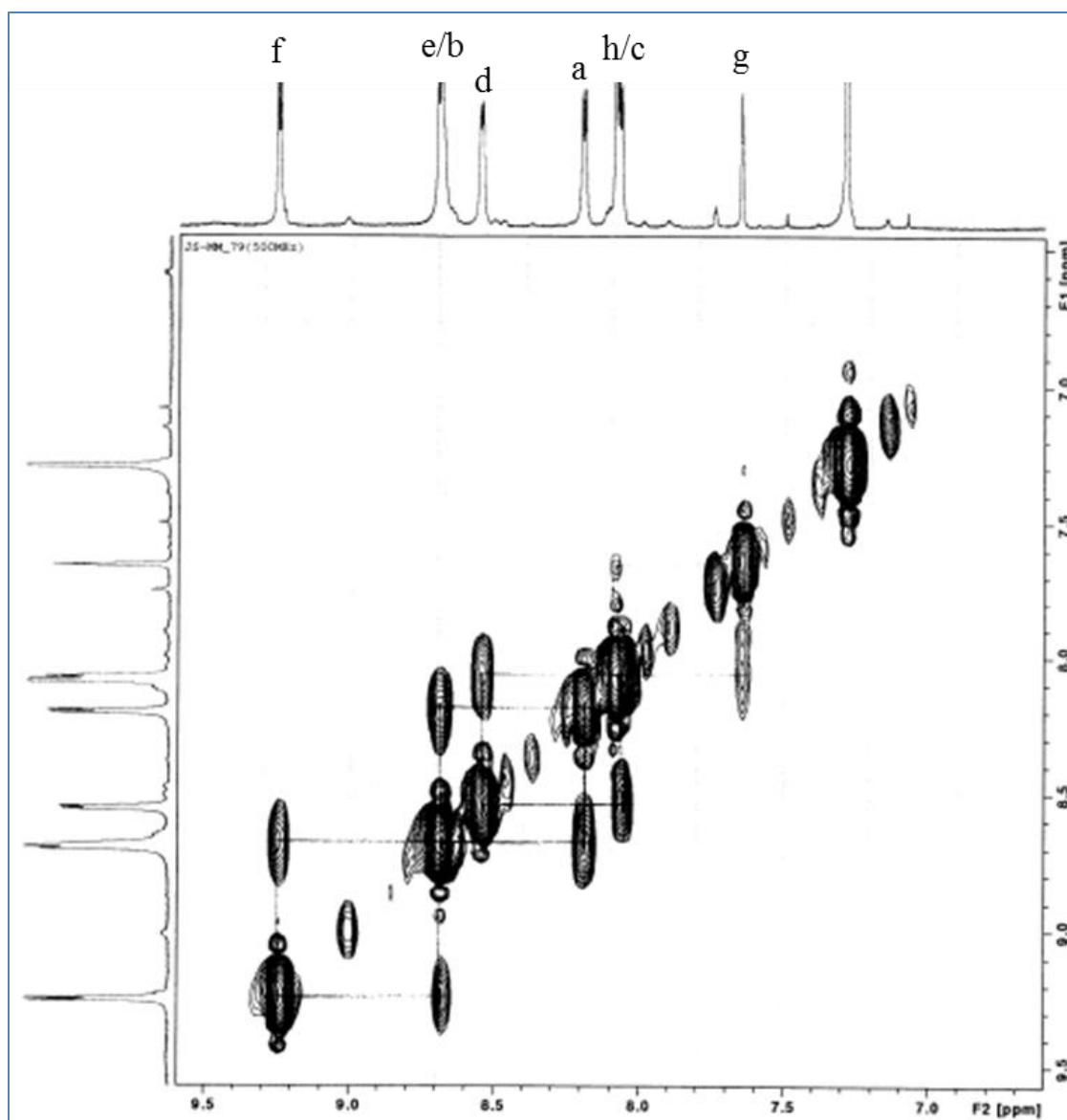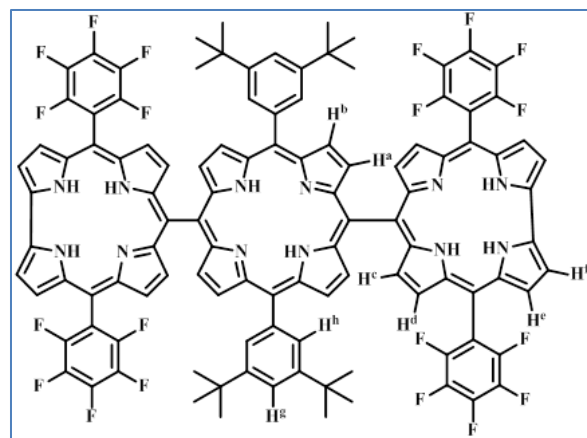
$^1H - {}^1H$ COSY spectrum of **3a** in CDCl$_3$

376 MHz ^{19}F NMR spectrum of **3a** in CDCl$_3$

HR-LCMS of 3a in positive mode

Data for **3b:** ^{1}H NMR - (400MHz, CDCl$_3$) δ 10.07 (s, 1H), 9.64 (d, *J*=4.8Hz, 1H), 9.21 (d, *J*=4.6Hz, 1H), 9.1 (d, *J*=4.3Hz, 4H) 8.7 (m, 6H), 8.5 (m, 8H), 7.2 (s, 2H), 1.24 (s, 36H), ^{19}F NMR (376MHz, CDCl$_3$) δ: -137.6 (4F), -152.8 (2F), -161.8 (4F). MS (HR-LCMS, positive mode): found M+nH = 1343.5116, Calcd for C$_{80}$H$_{64}$F$_{10}$N$_8$O 1342.504.

500MHz ^{1}H NMR spectrum of **3b** in CDCl$_3$

376 MHz ^{19}F NMR spectrum of **3b** in CDCl$_3$

Peak labels: -51631.26, -51639.55, -51655.00, -51835.45, -51842.80, -51858.92, -51864.85, -57515.11, -57536.06, -60780.76, -60796.46, -60951.89, -60957.33, -60972.81

Integrations: 2.19, 1.00, 1.79

+MS, 0.0-0.4min #(2-23)

1343.5116, 1344.5127, 1345.5164, 1346.5181

C80H64F10N8O, M+nH ,1343.51

1343.5116, 1344.5149, 1345.5183, 1346.5217
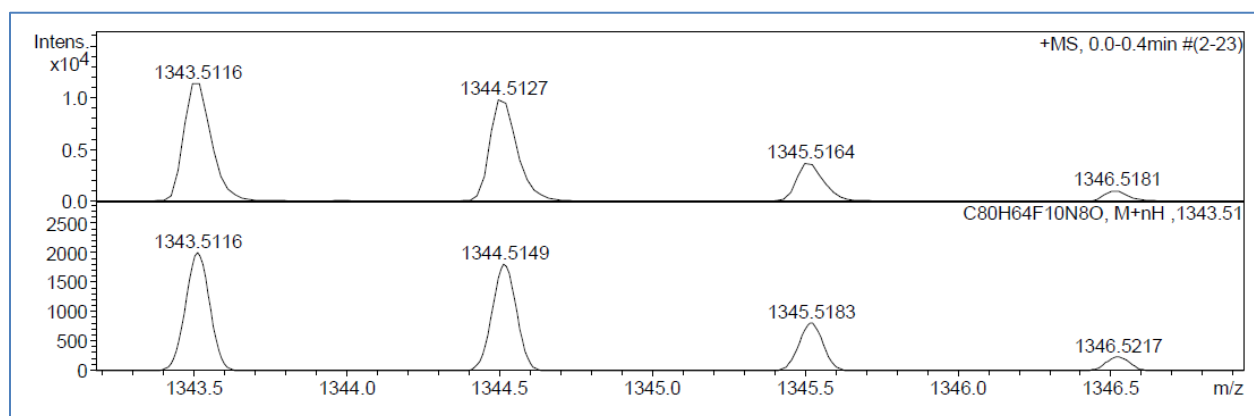
HR-LCMS of compound **3b**

Synthesis of **4**[4]

5-pentafluorophenyl dipyrromethane (312.237, 1 mmol) and 3, 5-di-tert-butylbenzaldehyde (109.165mg, 0.5mmol) were dissolved in a solution of 50mL MeOH and 50mL of H_2O. Conc. HCl (36%, 2.5mL) was added, and the reaction was stirred at room temperature for 1 h. The mixture was extracted with $CHCl_3$, and the organic layer was washed twice with H_2O, dried with Na_2SO_4, filtered, and diluted to 250mL with $CHCl_3$. *p*-Chloranil (470mg, 1.5mmol) was added, and the mixture was stirred for 3h at room temperature. The reaction mixture was concentrated to half the volume and passed over a silica column. All fractions containing corrole were combined and evaporated to dryness. Subsequent chromatography afforded pure corrole **4**.

Data for **4:** ^{1}H NMR- (500MHz; $CDCl_3$): δ 9.09 (d, *J*=4.2Hz, 2H), 8.7 (d, *J*=4.7Hz, 2H), 8.6 (d, *J*=4.6Hz, 2H), 8.5 (d, *J*= 3.5Hz, 2H), 8.0 (d, *J*=1.6Hz, 2H), 7.7(t, *J*=1.6Hz, 1H), 1.5 (s, 18H)
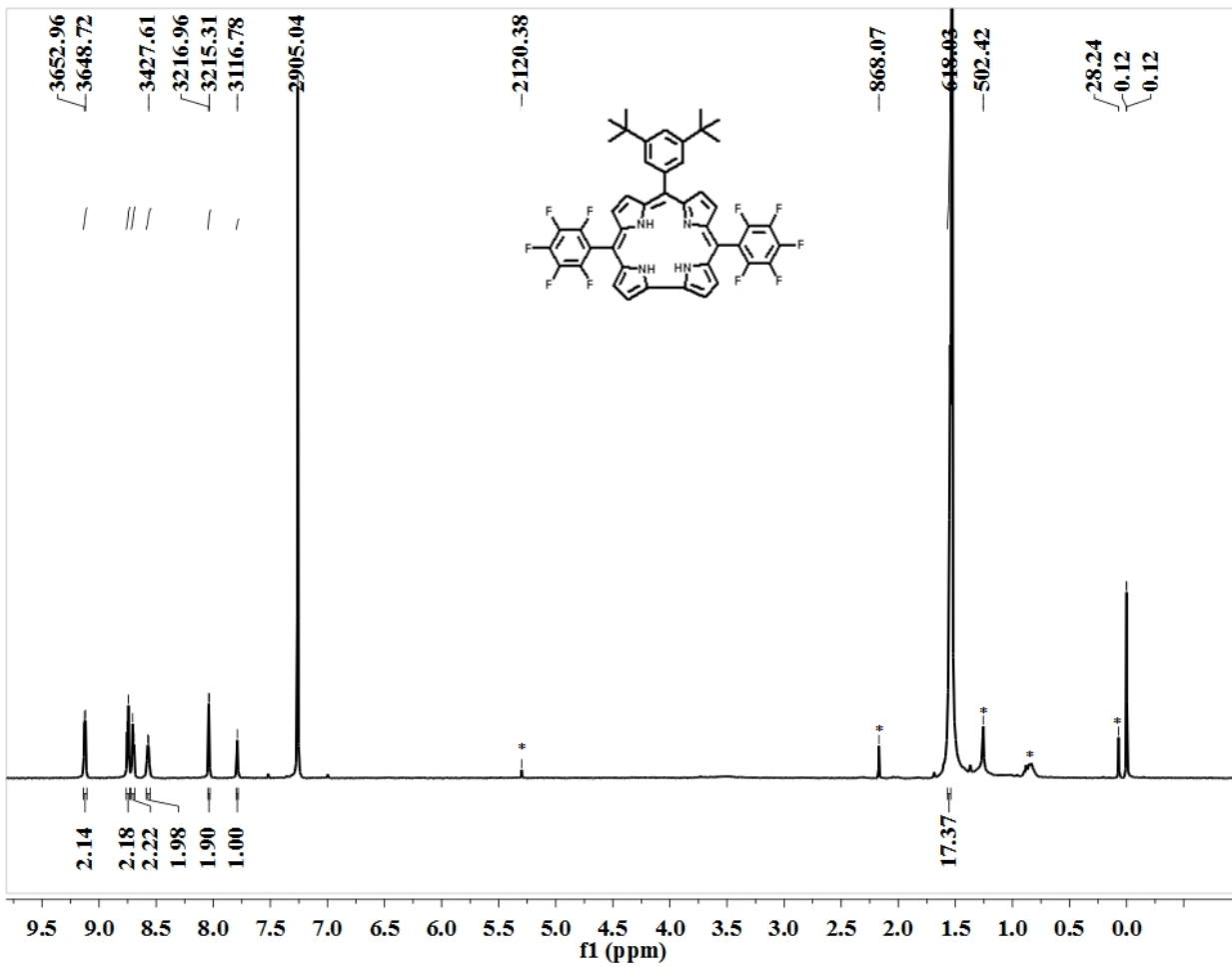
500MHz ^{1}H NMR spectrum of **4** in CDCl$_3$

Spectral studies
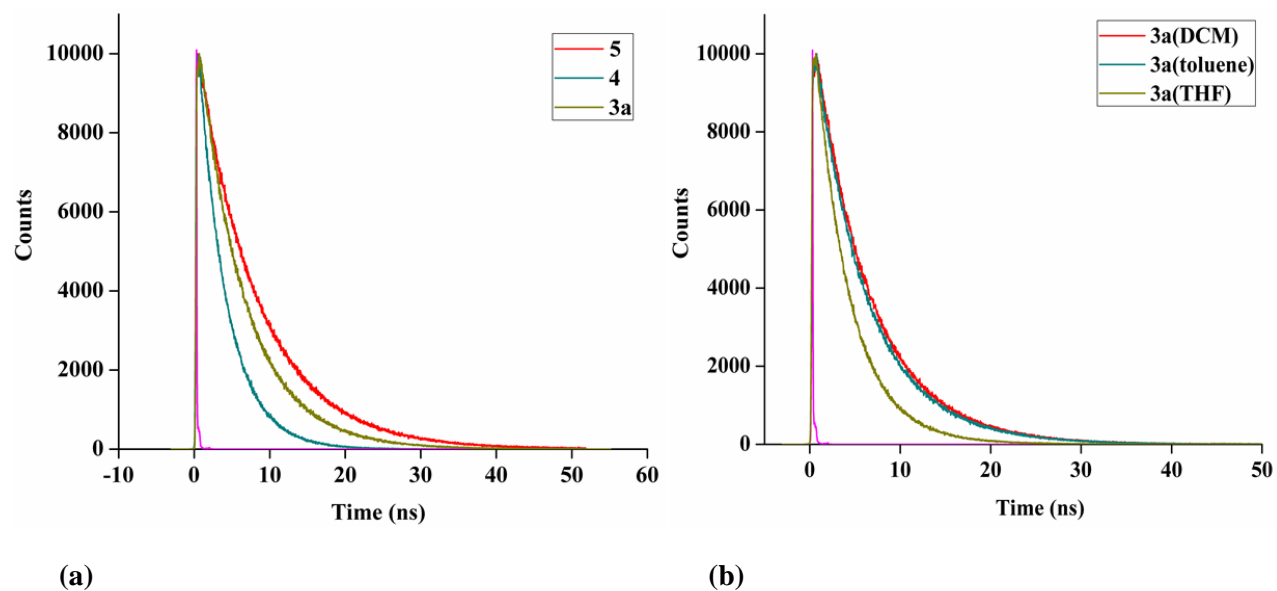
Time-resolved fluorescence decay of (a) **3a, 4, 5** in CH_2Cl_2 and (b) **3a** in CH_2Cl_2, THF, and toluene

Density Functional Theory (DFT) Calculations

All Theoretical calculations were carried out using the density functional theory (DFT) method with Beckee's three-parameter hybrid exchange functional and the Lee-Yang-Parr correlation functional (B3LYP) employing the 6-31G(d) basis set for all atoms by Gaussian09 program suite.[5] Frequency analysis was performed to confirm the stability of the optimized geometry which was visualized by Jmol viewer.[6]

a)   (b)
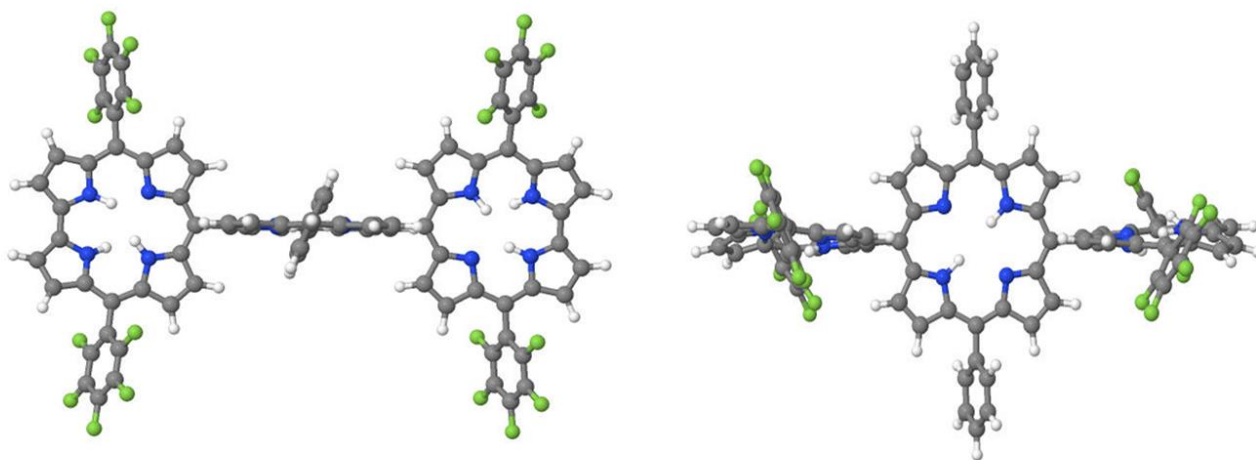
Optimized geometry of **3a** (a) front and (b) top view)

References:

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3. T. S. Balaban, A. D. Bhise, M. Fischer, M. Linke-Schaetzel, C. Roussel, N. Vanthuyne *Angew. Chem. Int. Ed.,* 2003, **42**, 2140.
4. B. Koszarna, D. T. Gryko, *J.Org.Chem*., 2006, **71,** 3707.
5. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian 09, Revision A.02, Gaussian, Inc., Wallingford CT, 2009.
6. Jmol: an open-source Java viewer for chemical structures in 3D. http://www.jmol.org/