Supporting Information

Synthesis and characterization of a luminescent and fully rigid tetrakisimidazolium macrocycle

*Hongjun Zhou, Zhi Wang, Chao Gao, Jingsong You and Ge Gao**

Key Laboratory of Green Chemistry and Technology of Ministry of Education, and College of Chemistry, Sichuan University, 29 Wangjiang Road, Chengdu 610064, PR China

Fax: 86-28-85412203; E-mail: gg2b@scu.ed.cn

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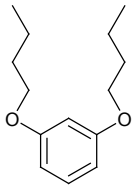
I. General remarks

Unless otherwise noted, all reagents were obtained from commercial suppliers and were used without further purification. Acetonitrile was firstly treated with phosphorus pentoxide and calcium hydride under reflux for several hours respectively and then distilled to store under nitrogen prior to use. *N*,*N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) were heated with calcium hydride at 60 ˚C for several hours and then distilled to store under nitrogen prior to use. Cuprous iodide was washed with THF using a soxhlet extractor before use to ensure satisfactory reactivity. Trichlolotriazine (TCT) was recrystallized twice from petroleum ether prior to use.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV-400 or a Varian INOVA-400. The ^{1}H NMR chemical shifts were measured relative to tetramethylsilane as the internal reference, while the ^{13}C NMR chemical shifts were recorded relative to $CDCl_3$ or DMSO-d_6 as the internal standard ($CDCl_3$: δ = 77.16 ppm; DMSO-d_6: δ = 39.52 ppm). High-resolution mass spectra (HRMS) were obtained on a Waters Q-TOF Premier (ESI), or a Shimadzu LCMS-IT-TOF. The MALDI-TOF mass spectrum was obtained on a Bruker autoflex III smartbeam, and the matrix was 2,5-dihydroxybenzoic acid (DHB). Melting points were determined with XRC-1 and uncorrected. Single crystal X-ray diffraction data were collected on an Oxford Xcalibur Eos Diffractometer. Absorption spectra were obtained on a HITACHI U-2910 spectrophotometer. Fluorescence spectra and absolute quantum yields were collected on a Horiba Jobin Yvon-Edison Fluoromax-4 fluorescence spectrometer with a calibrated integrating sphere system. Fluorescence microscopy image of the single crystal was taken on an OLYMPUS IX71 Fluorescence Microscope.

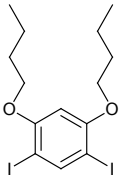
II. Synthesis of 1·2OTf

Synthesis of 1,3-di-*n*-butoxybenzene



It was synthesized according to the literature procedure[1] with a slight modification. Resorcinol (1.10 g, 10 mmol), 1-bromobutane (2.7 mL, 3.43 g, 25 mmol) and potassium carbonate (5.53 g, 40 mmol) was added into 10 mL DMF and stirred at 80 ˚C for 9 h. The resulting mixture was concentrated under vacuum, and then partitioned between water and dichloromethane. The organic layer was separated, and the aqueous layer was extracted with dichloromethane. The combined organic layers were dried over anhydrous sodium sulfate, filtered and evaporated to yield approximately quantitative 1,3-di-*n*-butoxybenzene as slightly colored oil, which was used for the next step without further purification. An analytical sample was obtained by column chromatography on silica gel eluted with petroleum ether/dichloromethane (20/1, v/v) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.97 (t, J = 7.4 Hz, 6H), 1.44-1.53 (m, 4H), 1.72-1.79 (m, 4H), 3.94 (t, J = 6.6 Hz, 4H), 6.47 (s, 2H), 6.49 (s, 1H), 7.15 (t, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 19.4, 31.5, 67.8, 101.6, 106.8, 129.9, 160.6. MS (ESI, m/z): 223 $[M+H]^+$.

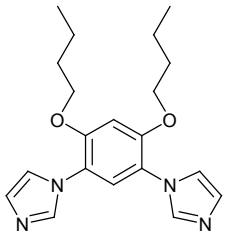
Synthesis of 1,3-di-*n*-butoxy-4,6-diiodobenzene 2



It was synthesized according to the literature.[2] To a solution of 1,3-di-*n*-octyloxybenzene (2.22 g, 10 mmol) in 45 mL acetic acid was added dropwise iodine monochloride (1.1 mL, 3.44 g, 21 mmol) in 10 mL acetic acid and the solution was stirred at room temperature for 3 h. The reaction mixture was poured into water and the organic layer was separated. The aqueous layer was extracted with dichloromethane, and the combined

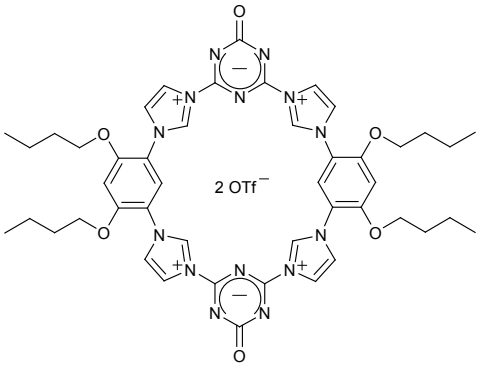
organic layers were washed with aqueous sodium thiosulfate, saturated aqueous sodium bicarbonate and water. The organic layers was dried over anhydrous sodium sulfate, filtered and evaporated under vacuum to afford 1,3-di-*n*-octyloxy-4,6-diiodobenzene **2** as an offwhite solid (4.43 g, 94%), which was used for the next step without further purification. An analytical sample was obtained by recrystallization from petroleum ether/dichloromethane. mp 91-92 ˚C (lit.,[2] 90-91 ˚C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.99 (t, J = 7.2 Hz, 6H), 1.53-1.60 (m, 4H), 1.79-1.85 (m, 4H), 3.99 (t, J = 6.2 Hz, 4H), 6.33 (s, 1H), 8.02 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 19.4, 31.2, 69.3, 76.1, 98.0, 146.7, 159.2. MS (ESI, m/z): 475 $[M+H]^+$.

Synthesis of 1,3-di-*n*-butoxy-4,6-di(1*H*-imidazol-1-yl) benzene 3[3]



A flask was charged with cuprous iodide (1.52 g, 8 mmol), *N*,*N*-dimethylglycine (2.23 g, 16 mmol), **2** (18.96 g, 40 mmol), potassium carbonate (33.17 g, 240 mmol) and imidazole (10.89 g, 160 mmol). The system was then evacuated twice and back filled with N_2, followed by addition of 160 mL DMSO. The mixture was heated at 110 °C for 90 h. After the reaction, the resulting mixture was diluted with dichloromethane, filtered, and concentrated under vacuum. The residue was then loaded on a silica gel column and eluted with petroleum ether/acetone (3/2, v/v) and dichloromethane/methanol (20/1, v/v) to afford an offwhite solid, which was further purified by recrystallization from petroleum ether/dichloromethane to afford pure **3** (10.55 g, 74%). mp 137-138 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.94 (t, J = 7.4 Hz, 6H), 1.38-1.47 (m, 4H), 1.71-1.78 (m, 4H), 4.04 (t, J = 6.4 Hz, 4H), 6.70 (s, 1H), 7.14 (s, 2H), 7.16 (s, 2H), 7.23 (s, 1H), 7.73 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.6, 19.1, 30.9, 69.2, 99.3, 119.4, 120.3, 122.7, 128.9, 137.7, 152.7. HRMS (ESI^+): calcd for $C_{20}H_{27}N_4O_2$ $[M+H]^+$ 355.2129, found 355.2131.

Synthesis of 1·2OTf



Under nitrogen, a solution of trichlorotriazine (55.3 mg, 0.3 mmol) in 15 mL acetonitrile and a solution of **3** (106.3 mg, 0.3 mmol) in 15 mL acetonitrile were simultaneously added dropwise to 16 mL acetonitrile via a syringe pump under reflux over a period of 2.5 h. After addition, the solution was stirred for additional 2.5 h and cooled down to room temperature. The reaction mixture was then filtered and the filtrate was concentrated to afford a light yellow solid. The crude product was dissolved in 12 mL methanol and lithium triflate (187.2 mg, 1.2 mmol) in 1 mL methanol/water (1/1, v/v) was added for anion exchange. The mixture was stirred at room temperature for 1 h. The white precipitates were collected by filtration, washed with methanol and dried in a vacuum desiccator to yield **1**·2OTf as a white solid (122.5 mg, 68%). mp 278 ˚C (decomposed). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 0.91 (t, J = 7.4 Hz, 12H), 1.34-1.43 (m, 8H), 1.69-1.76 (m, 8H), 4.30 (t, J = 6.2 Hz, 8H), 7.31 (s, 2H), 8.09 (s, 2H), 8.33 (s, 4H), 8.68 (s, 4H), 10.05 (s, 4H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 13.5, 18.4, 30.1, 69.7, 100.2, 115.4, 118.3, 118.7, 124.6, 126.1, 135.6, 155.2, 159.2, 164.9. MS (MALDI-TOF; DHB): calcd for $C_{47}H_{52}F_3N_{14}O_9S$ $[M\text{-}OTf]^+$ 1045.4, found 1046.0. HRMS (ESI^+): calcd for $C_{47}H_{52}F_3N_{14}O_9S$ $[M\text{-}OTf]^+$ 1045.3709, found 1045.3701.

III. MALDI-TOF mass spectrum of 1·2OTf

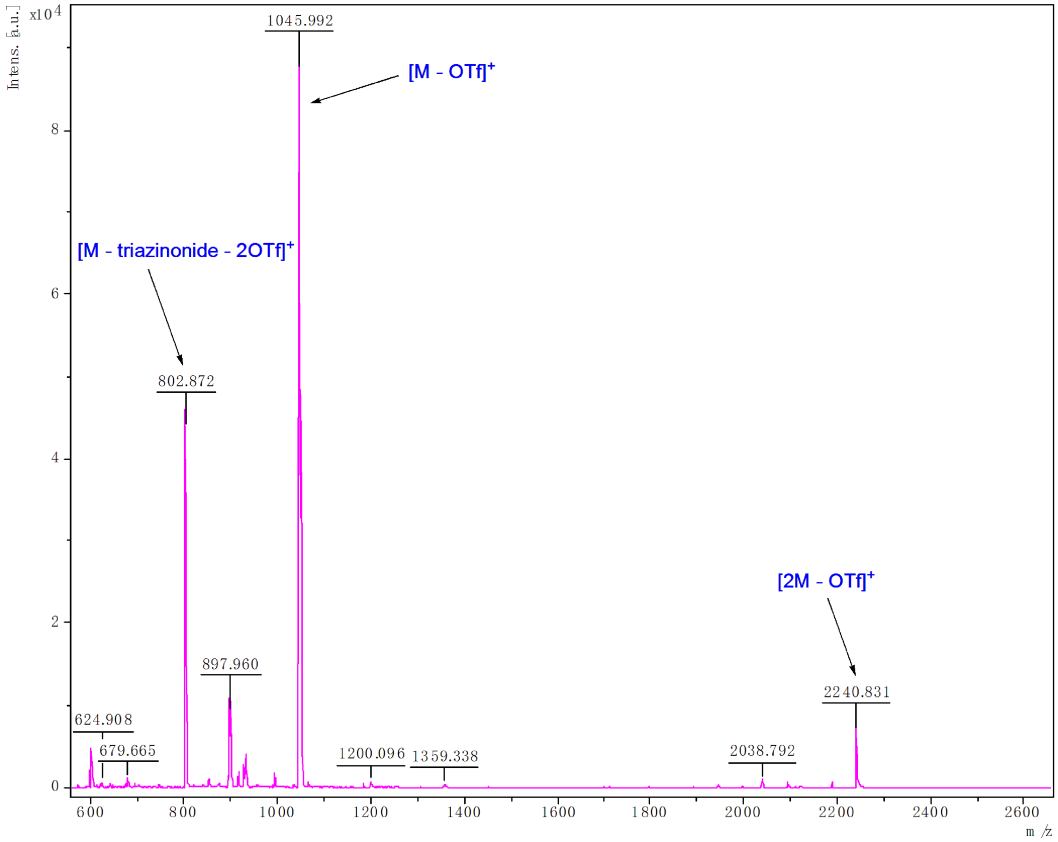


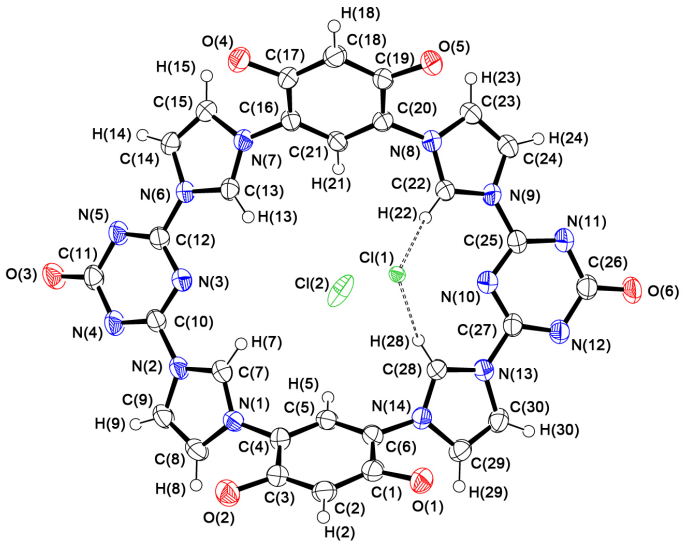
Figure S1 MALDI-TOF mass spectrum of **1**·2OTf.

IV. Single crystal structure of 1·2Cl

Table S1 Crystallographic data of **1**·2Cl.

Empirical formula	$C_{48}H_{66}Cl_2N_{14}O_{11}$	F(000)	2296.0
Formula weight	1086.05	Crystal size/mm^3	0.32 × 0.28 × 0.25
Temperature/K	130.0	2Θ range for data collection	5.96 to 50.06°
Crystal system	monoclinic	Index ranges	-16 ≤ h ≤ 17, -26 ≤ k ≤ 27, -20 ≤ l ≤ 18
Space group	$P2_1/n$		
a/Å	14.9174(6)	Reflections collected	21229
b/Å	22.8283(7)	Independent reflections	9188[R(int)=0.0256]
c/Å	16.9320(6)	Data/restraints/parameters	9188/828/767
α/°	90.00	Goodness-of-fit on F^2	1.062
β/°	113.615(4)	Final R indexes [I>=2σ (I)]	R_1 = 0.0743, wR_2 = 0.1843
γ/°	90.00		
Volume/Å^3	5283.2(3)	Final R indexes [all data]	R_1 = 0.1008, wR_2 = 0.2037
Z	4		
ρ_{calc} mg/mm^3	1.365	Largest diff. peak/hole / e Å^{-3}	1.10/-0.51
m/mm^{-1}	0.195		

Table S2 The main bond lengths (Å), bond angles (°) and dihedral angles (°) in **1**·2Cl.



O(3)-C(11)	1.232(6)	O(6)-C(26)	1.233(6)
N(3)-C(10)	1.330(6)	N(3)-C(12)	1.325(6)
N(4)-C(10)	1.304(6)	N(4)-C(11)	1.384(6)
N(5)-C(11)	1.392(6)	N(5)-C(12)	1.304(6)
N(10)-C(25)	1.340(6)	N(10)-C(27)	1.319(6)
N(11)-C(25)	1.298(6)	N(11)-C(26)	1.388(6)
N(12)-C(26)	1.392(6)	N(12)-C(27)	1.311(6)
C(10)-N(3)-C(12)	110.3(4)	C(10)-N(4)-C(11)	115.5(4)
C(11)-N(5)-C(12)	114.9(4)	C(25)-N(10)-C(27)	110.6(4)
C(25)-N(11)-C(26)	115.3(4)	O(26)-N(12)-C(27)	114.6(4)
N(3)-C(10)-N(4)	129.5(4)	N(3)-C(12)-N(5)	130.0(4)
N(4)-C(11)-N(5)	119.7(4)	N(10)-C(25)-N(11)	129.3(2)
N(10)-C(27)-N(12)	129.9(5)	N(11)-C(26)-N(12)	120.1(4)
C(7)-N(1)-C(4)-C(5)	-55.0(6)	C(7)-N(2)-C(10)-N(3)	2.2(6)
C(13)-N(6)-C(12)-N(3)	1.1(6)	C(13)-N(7)-C(16)-C(21)	51.9(6)
C(22)-N(8)-C(20)-C(21)	-55.3(6)	C(22)-N(9)-C(25)-N(10)	7.7(7)
C(28)-N(13)-C(27)-N(10)	-7.3(6)	C(28)-N(14)-C(6)-C(5)	61.0(6)

Table S3 The main hydrogen bonding interactions in the crystal structure of **1**·2Cl.[a]

D-H···A	D-H/Å	H···A/Å	D···A/Å	D-H···A/°
C(9)–H(9)···O(6)$^{\#1}$	0.93	2.60	3.212(7)	124
C(9)–H(9)···N(11)$^{\#1}$	0.93	2.62	3.509(8)	159
C(14)–H(14)···Cl(2)$^{\#2}$	0.93	2.61	3.488(5)	157
C(22)–H(22)···Cl(1)	0.93	2.68	3.492(5)	146
C(24)–H(24)···O(3)$^{\#3}$	0.93	2.49	3.094(6)	123
C(28)–H(28)···Cl(1)	0.93	2.76	3.539(5)	142
C(30)–H(30)···Cl(2)$^{\#4}$	0.93	2.62	3.482(5)	154

[a] Symmetry codes: #1: -1+x, y, z; #2: -1/2+x, 1/2-y, -1/2+z; #3: 1+x, y, z; #4: 1/2+x, 1/2-y, 1/2+z.

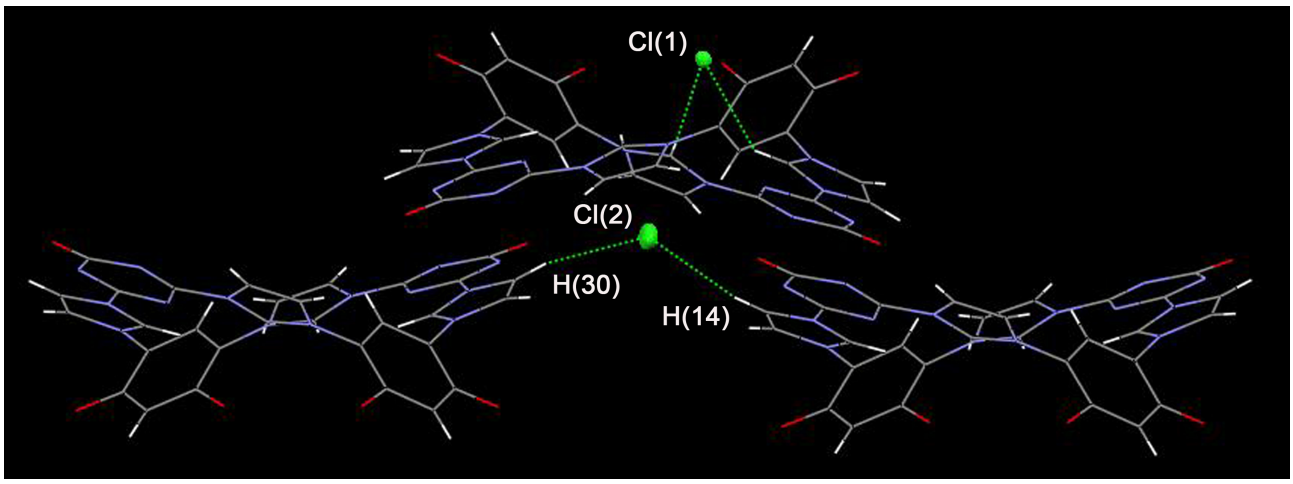


Figure S2 The hydrogen bonds (2.61 Å of Cl2-H14 and 2.62 Å of Cl2-H30) between the chloride sat in the middle of the lower cleft and C4/5 hydrogens of the imidazoliums in the adjacent two macrocycles.

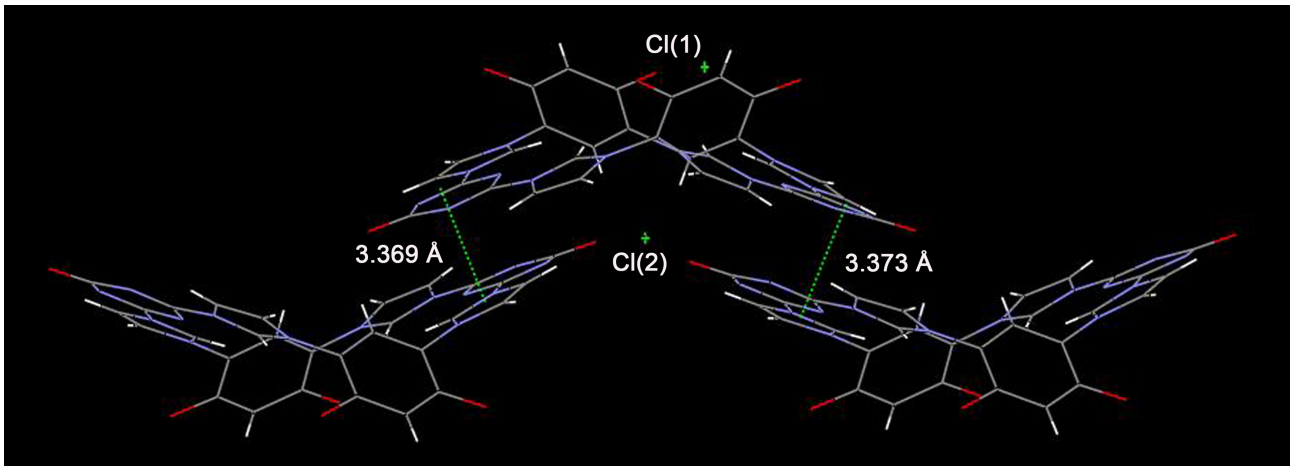


Figure S3 The intermolecular π-π stacking between the macrocycles.

V. Temperature effect on the fluorescence spectra of 1·2OTf

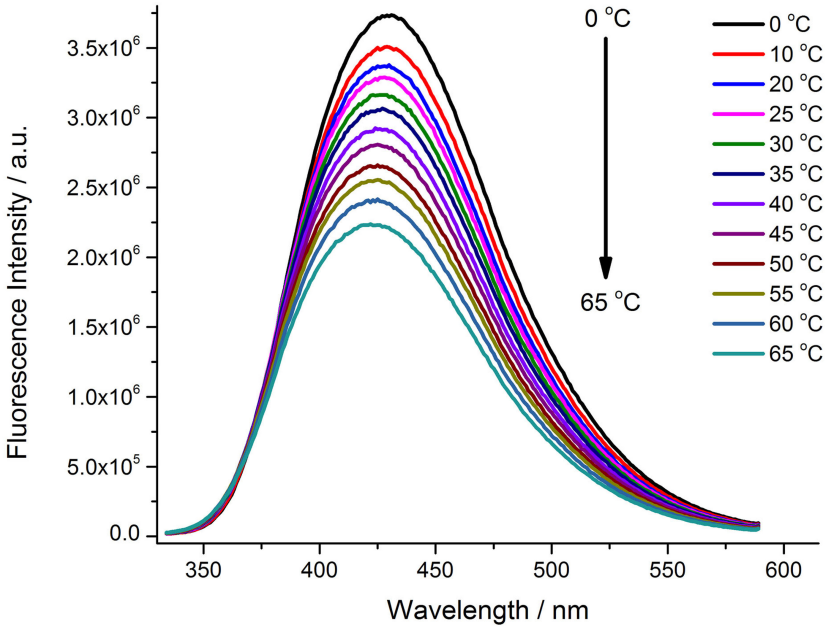


Figure S4 Fluorescent emission of **1**·2OTf (5 μM) in acetonitrile at different temperature excited at 297 nm.

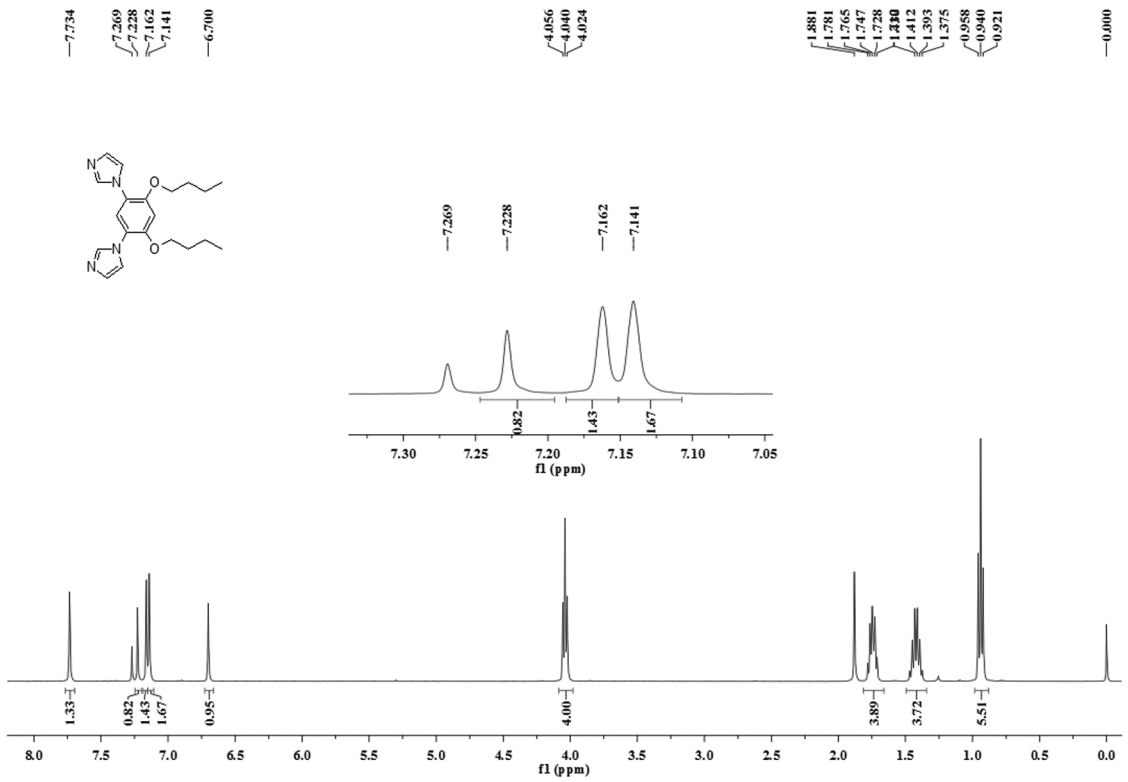
VI. References

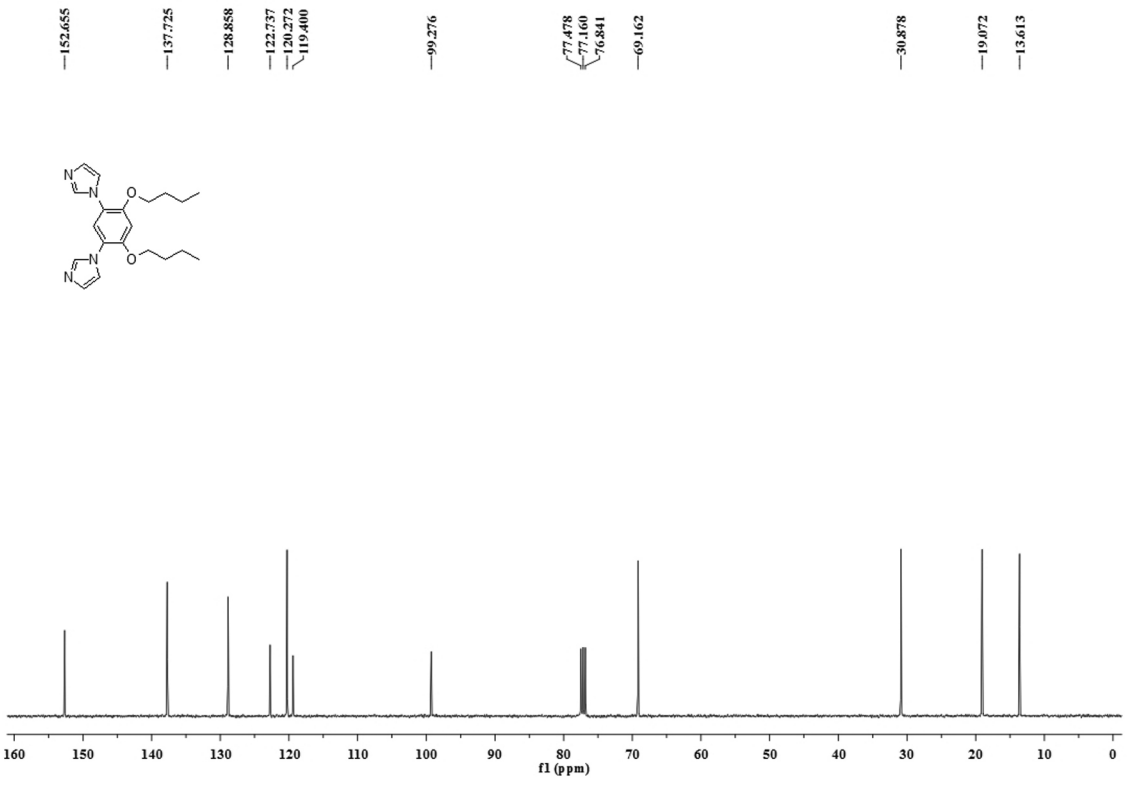
1 B. Mohr, V. Enkelmann and G. Wegner, *J. Org. Chem.*, 1994, **59**, 635.

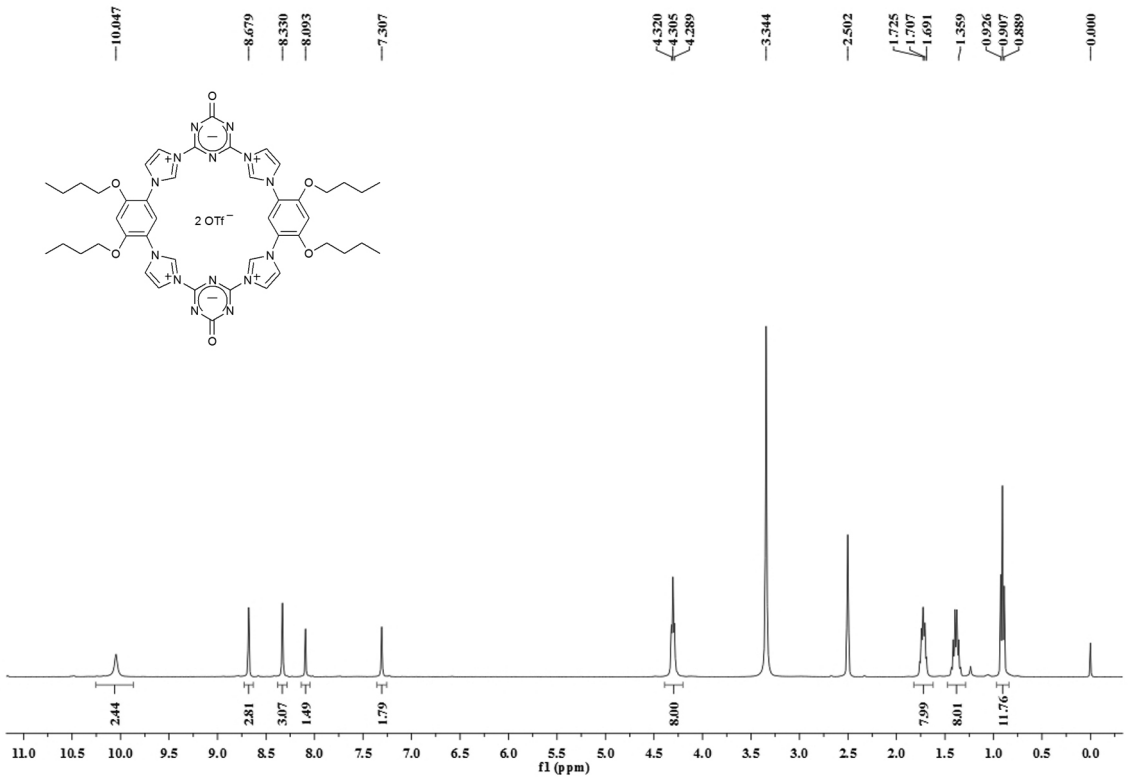
2 S. Sasaki, M. Mizuno, K. Naemura and Y. Tobe, *J. Org. Chem.*, 2000, **65**, 275.

3 H. Zhang, Q. Cai and D. Ma, *J. Org. Chem.*, 2005, **70**, 5164.

VII. Copies of ^{1}H and ^{13}C NMR spectra



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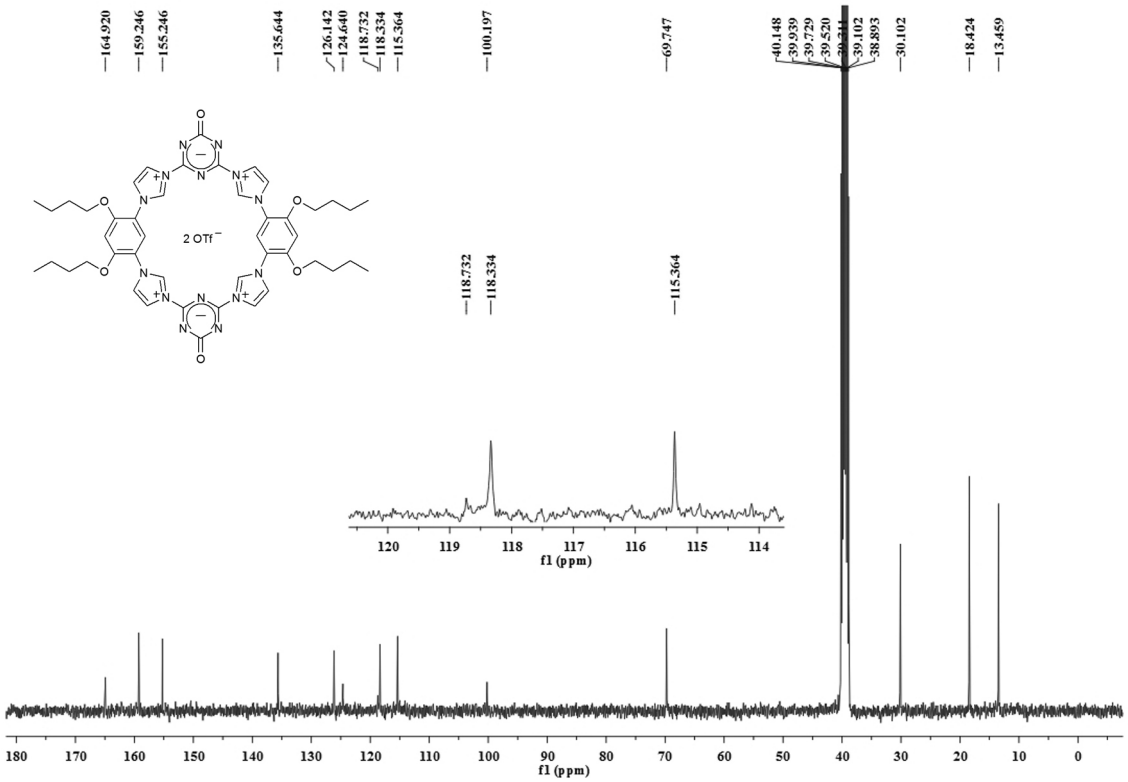
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f1 (ppm)
f1 (ppm)