

Supporting Information

The Synthesis and Topochemical Polymerisation of o-Carborane-based Diacetylene Macrocycles

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1. ^1H and ^{13}C NMR Spectra and HR-MS (ESI) of New Compounds

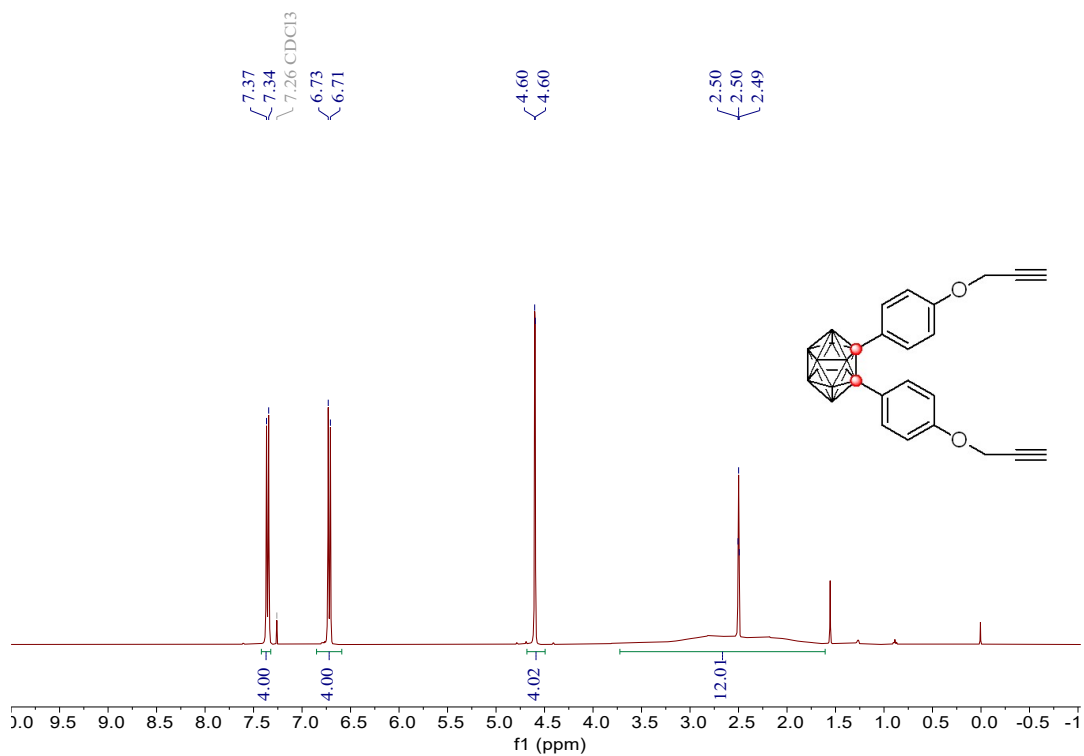


Figure S1 ^1H NMR spectrum of **1-4** (400 MHz, CDCl_3)

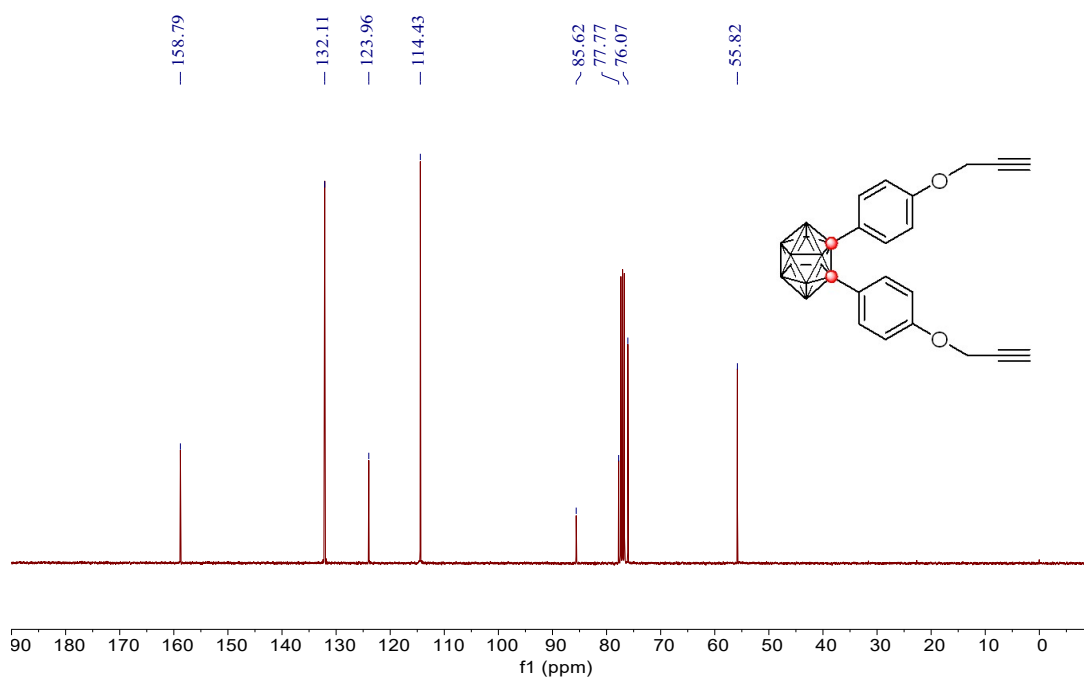
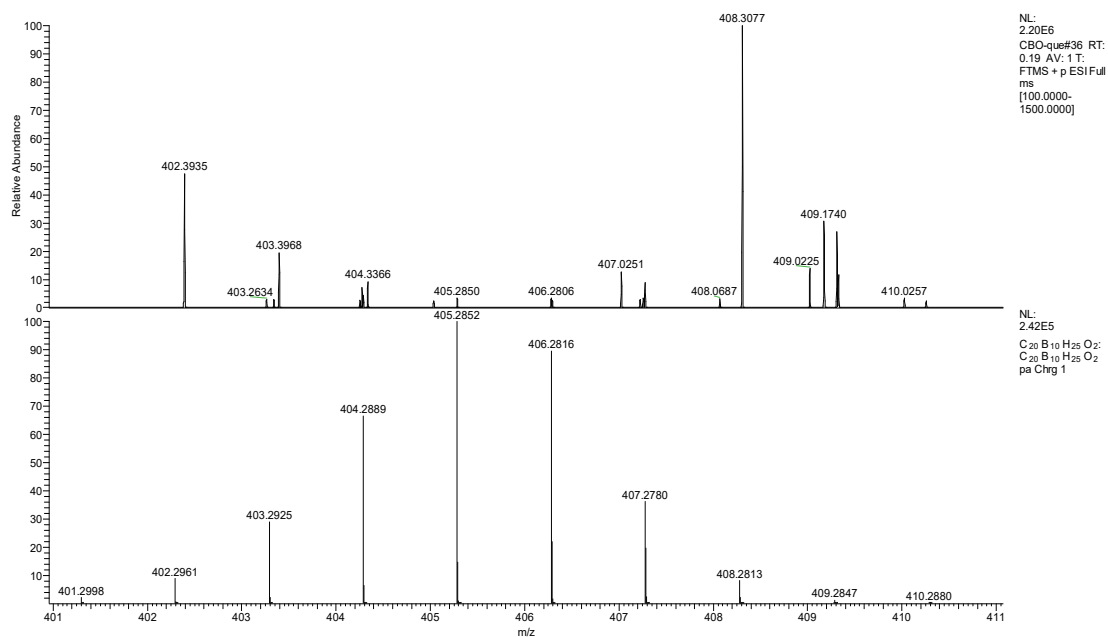
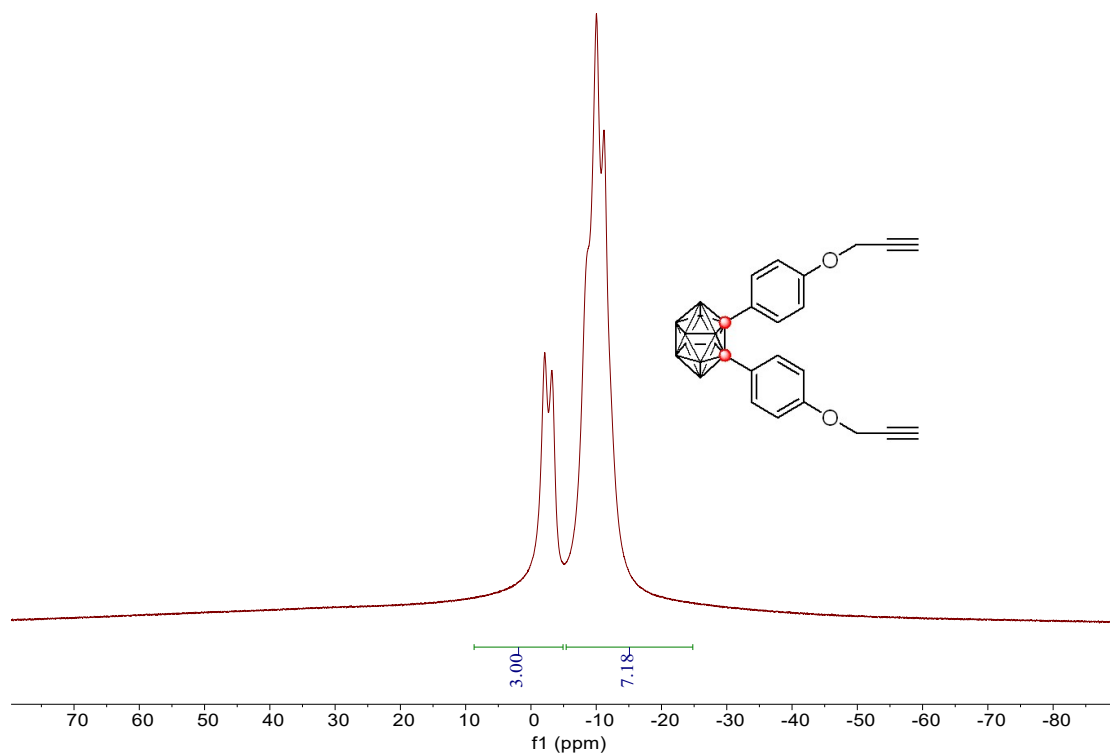


Figure S2 ^{13}C NMR spectrum of **1-4** (100 MHz, CDCl_3).



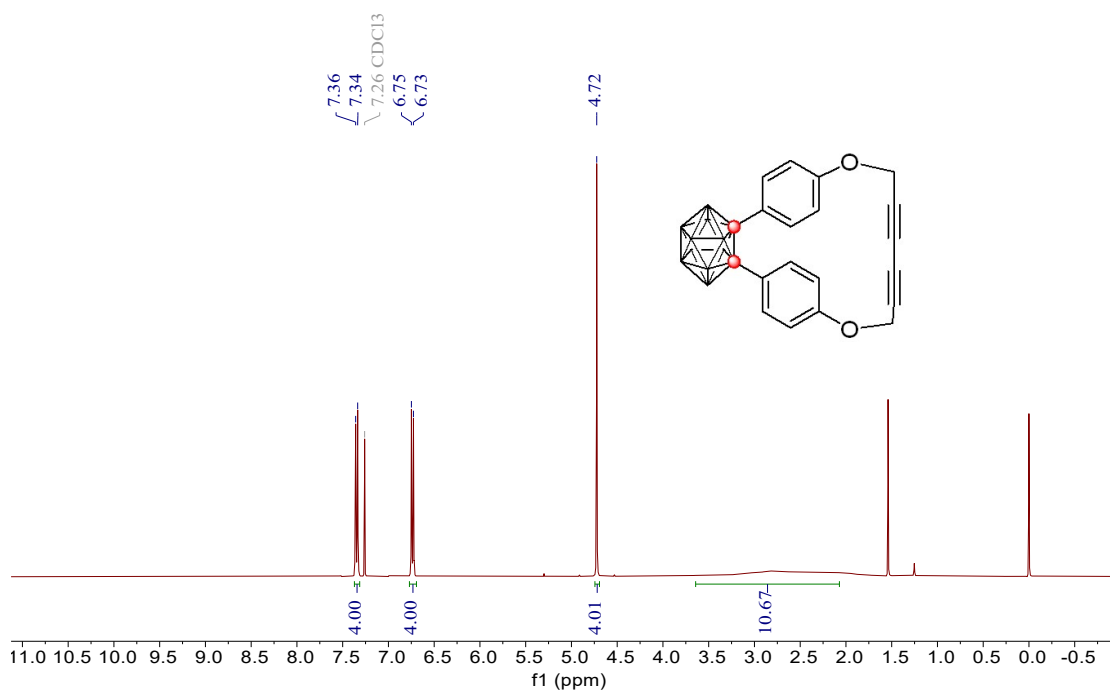


Figure S5 ¹H NMR spectrum of **CBMC-1** (400 MHz, CDCl₃)

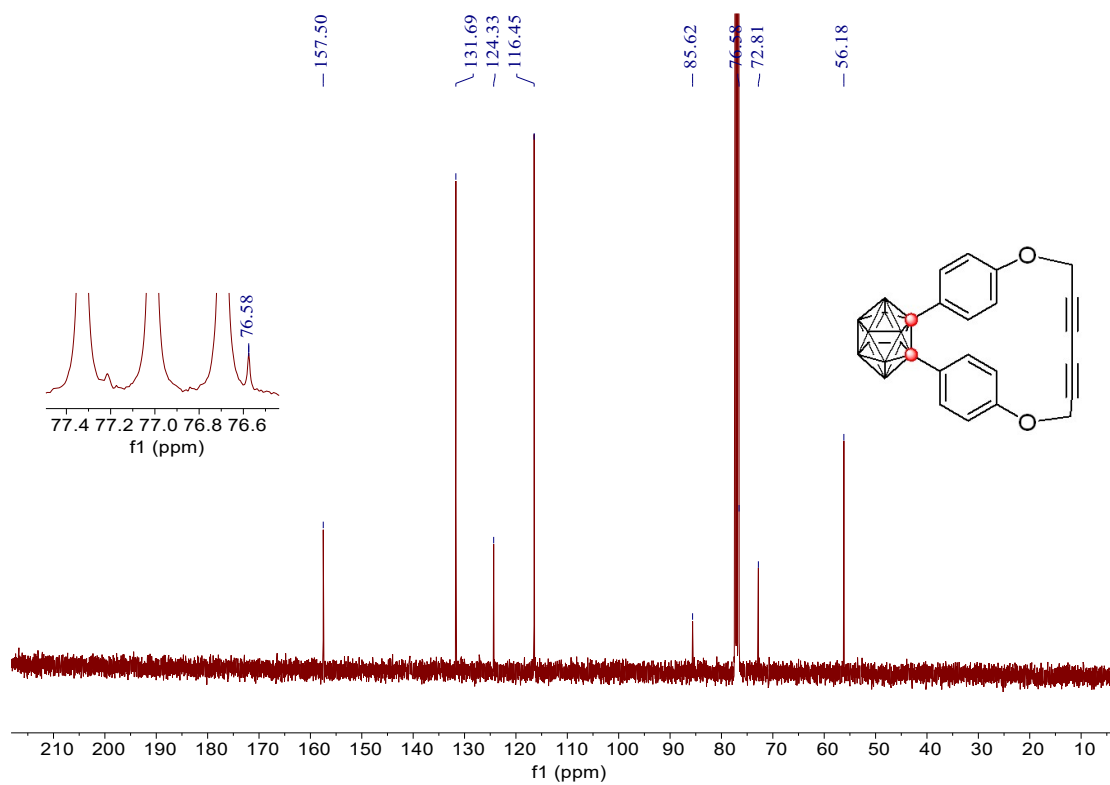


Figure S6 ¹³C NMR spectrum of **CBMC-1** (100 MHz, CDCl₃).

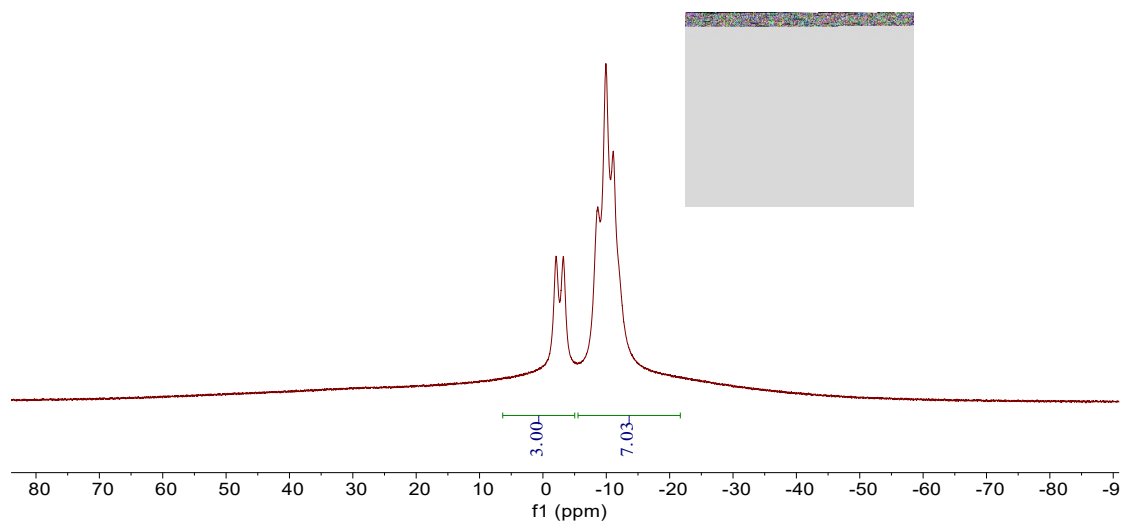


Figure S7 ^{11}B NMR spectrum of **CBMC-1** (128 MHz, CDCl_3).

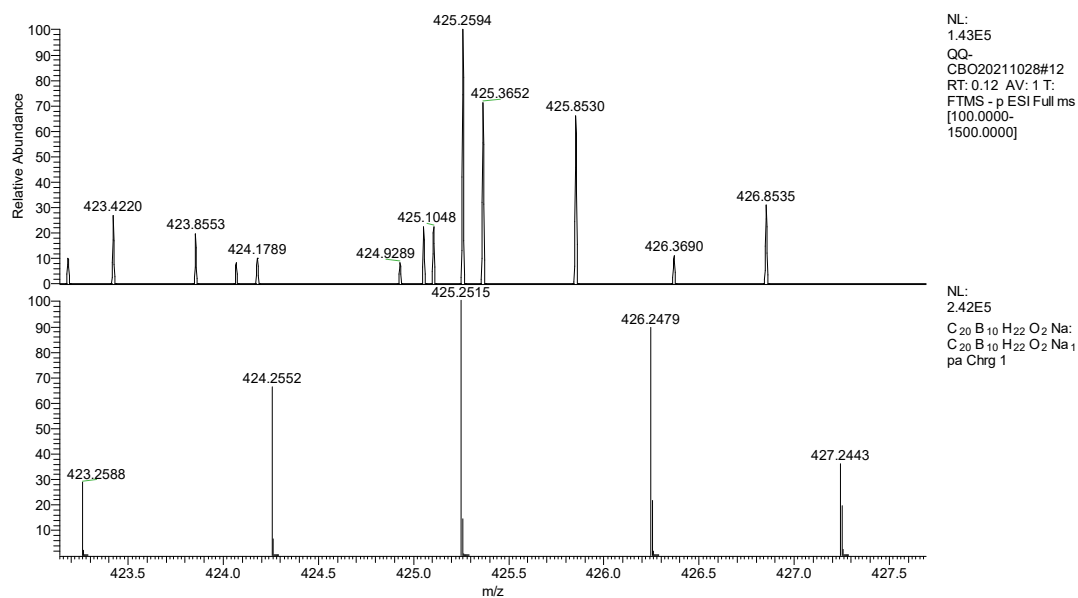


Figure S8 HR-MS (ESI) spectra of **CBMC-1**.

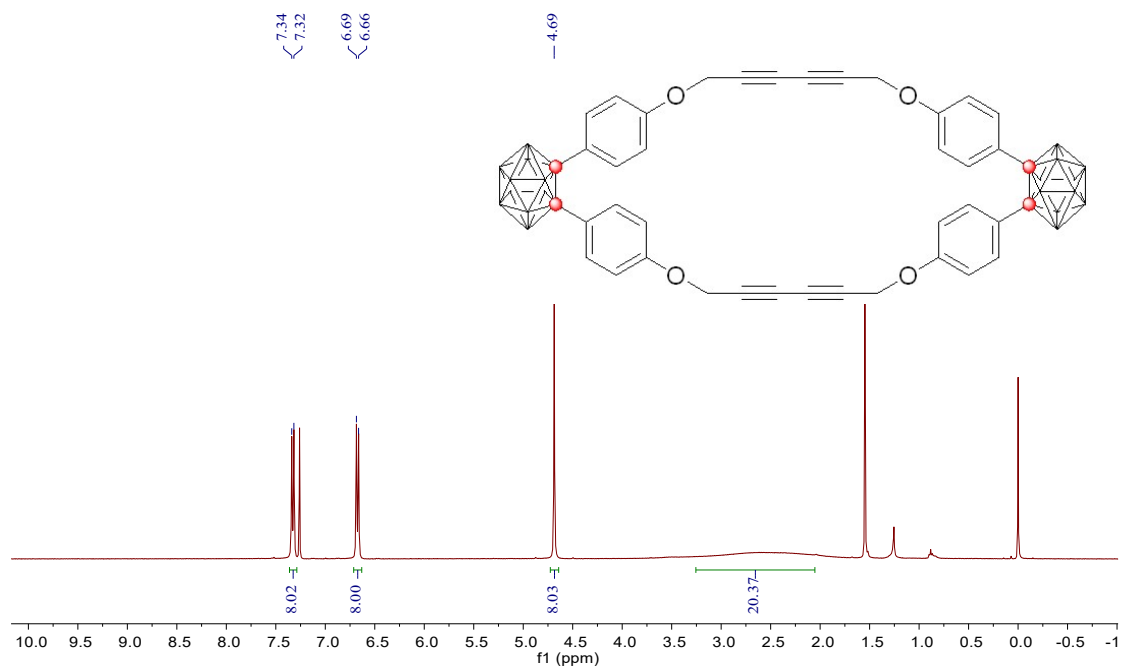


Figure S9 ^1H NMR spectrum of **CBMC-2** (400 MHz, CDCl_3).

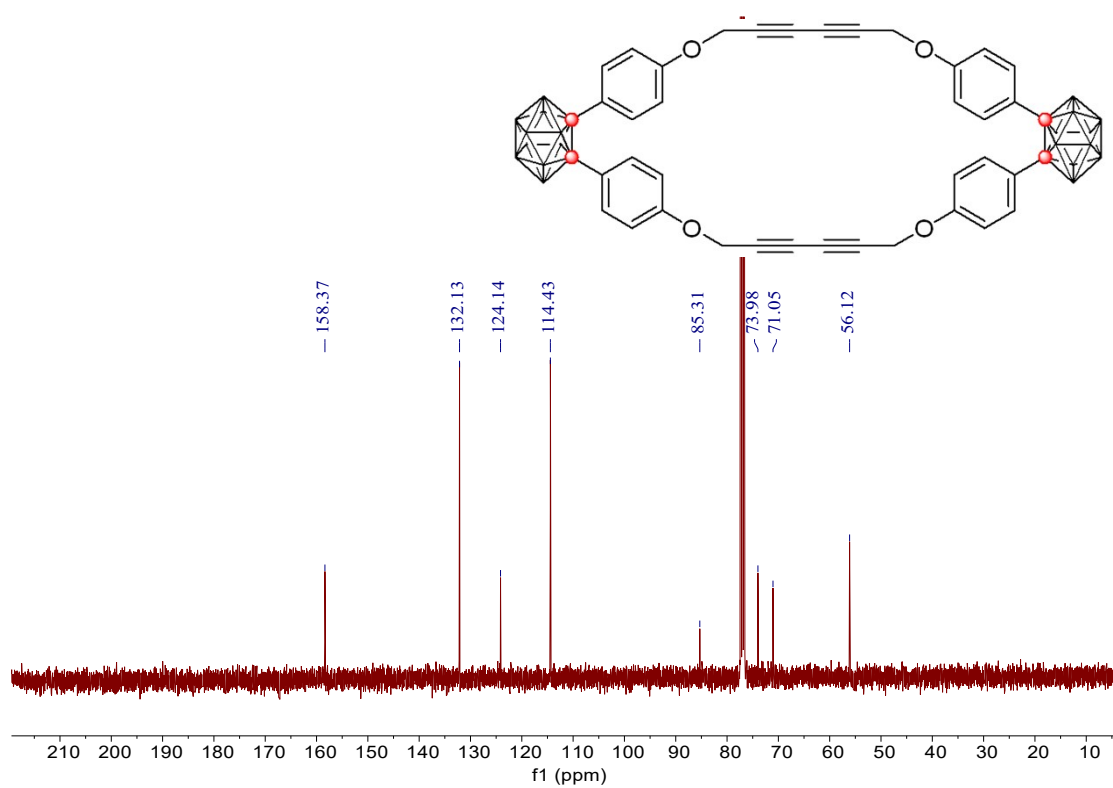


Figure S10 ^{13}C NMR spectrum of **CBMC-2** (100 MHz, CDCl_3).

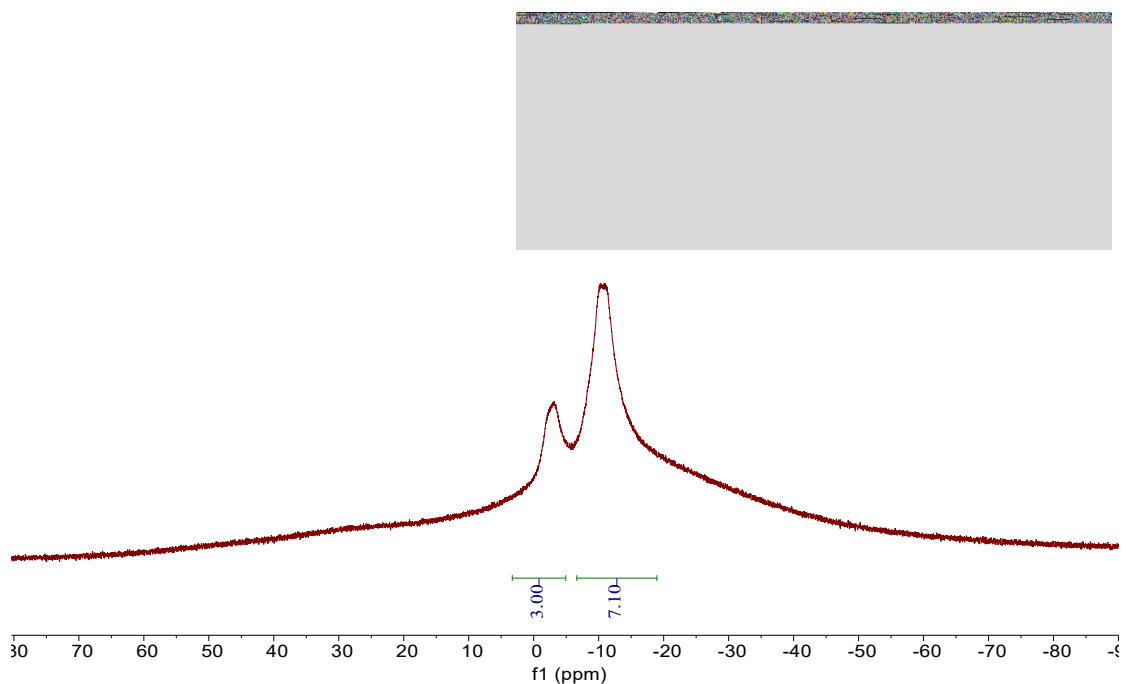


Figure S11 ^{11}B NMR spectrum of **CBMC-2** (128 MHz, CDCl_3).

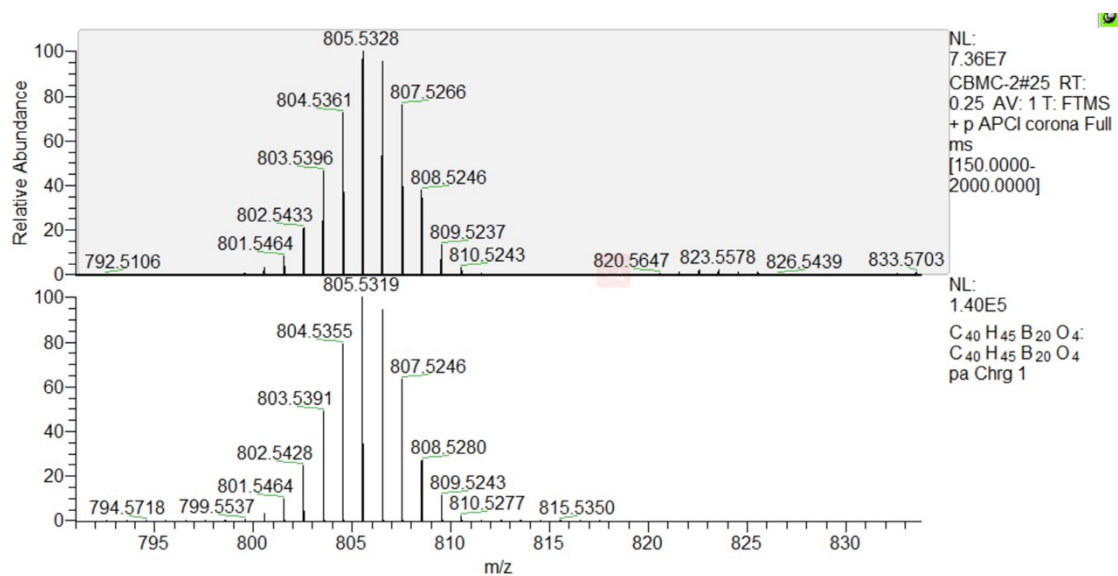


Figure S12 HR-MS (ESI)spectrum of **CBMC-2**.

2. DSC plots of crystals of macrocycle **CBMC-2**

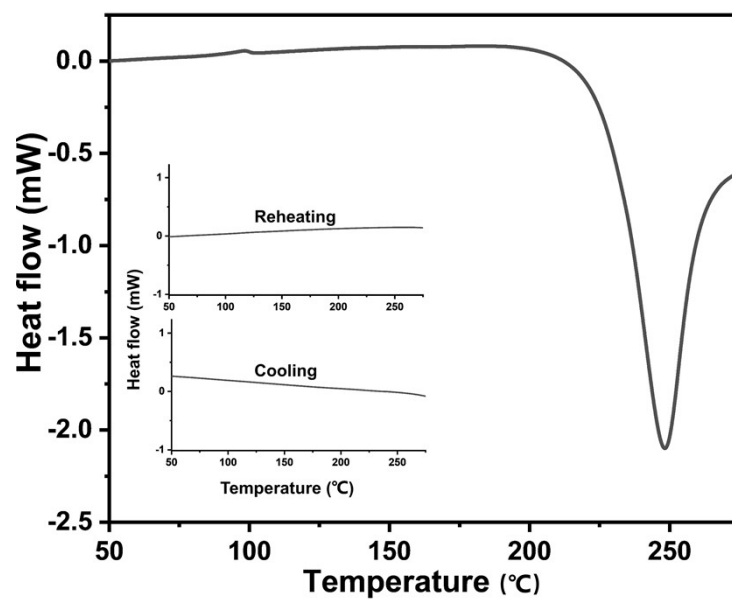


Figure S13 DSC plots of crystals of macrocycle **CBMC-2** (heating rate 10 °C/min). Cooling (10 °C/min) and reheating experiments (Inset).

3. TGA plot of crystals of macrocycle CBMC-2

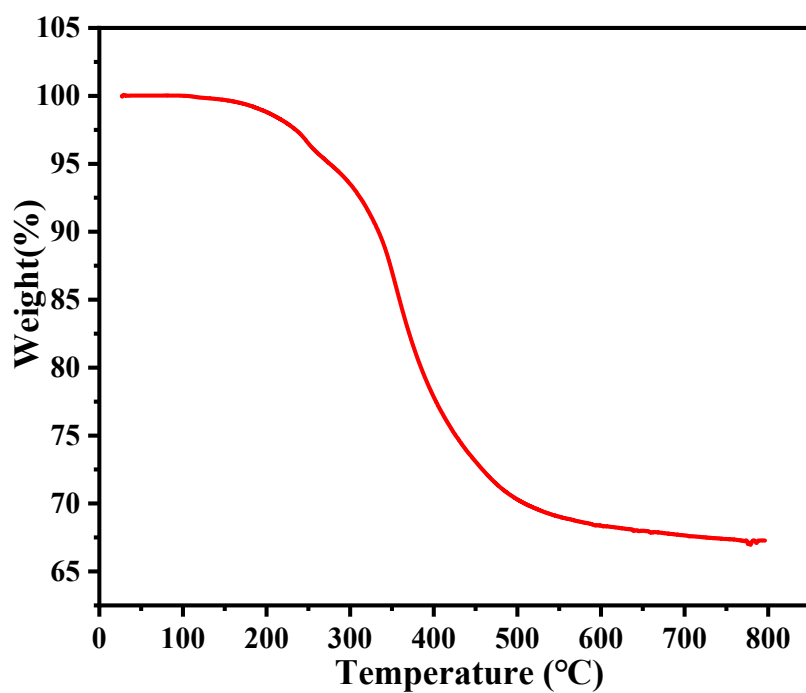


Figure S14 TGA analysis of crystals of macrocycle **CBMC-2** from 25 to 800 °C.

4. X-ray crystallography data of macrocycle **CBMC-1** and **CBMC-2**

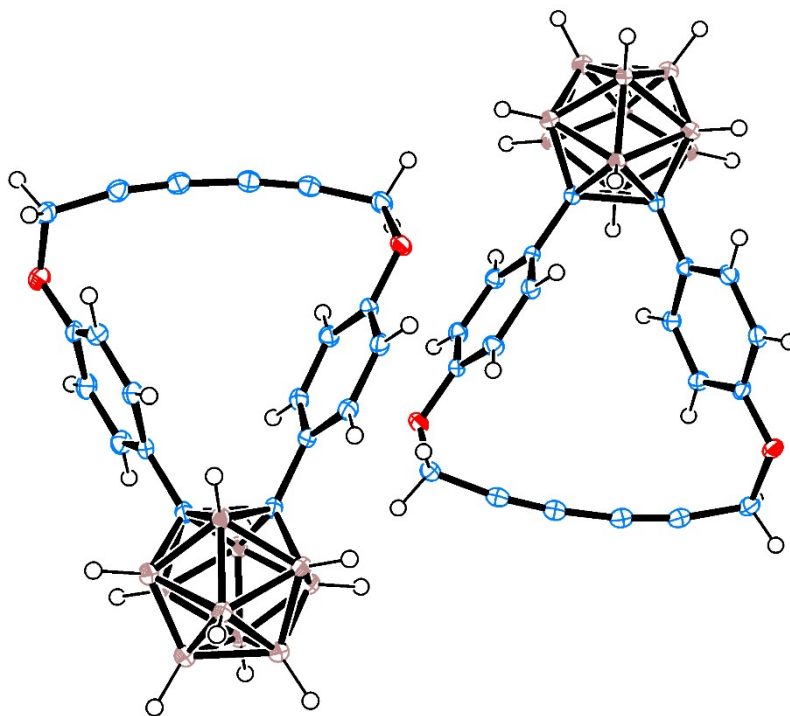


Figure S15 Ortep drawing of 2 in crystal **CBMC-1**(30% probability).

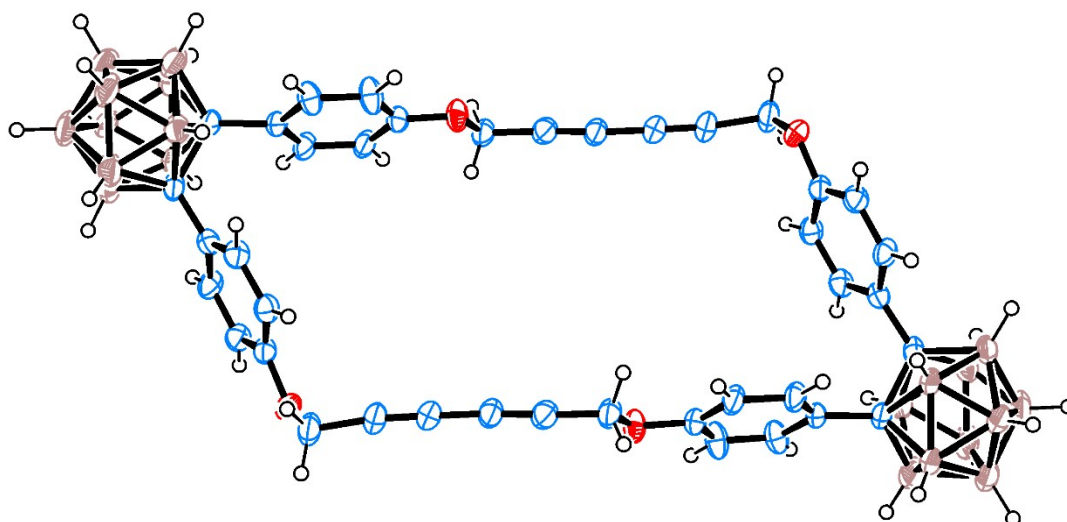


Figure S16 Ortep drawing of 2 in crystal **CBMC-2**(30% probability).

Table S1. Crystal data and structure refinement for **CBMC-1** and **CBMC-2**.

Identification code	CBMC-1	CBMC-2
Empirical formula	C ₄₀ H ₄₄ B ₂₀ O ₄	C _{41.5} H ₄₇ B ₂₀ Cl ₃ O ₄
Formula weight	805.278	932.676
Temperature/K	100.15	100.15
Crystal system	monoclinic	monoclinic
Space group	P2 ₁ /n	P2 ₁ /c
a/Å	16.25641(16)	10.8158(3)
b/Å	13.27791(13)	27.3194(6)
c/Å	20.2000(2)	9.4186(3)
α/°	90	90
β/°	107.8418(11)	113.082(3)
γ/°	90	90
Volume/Å³	4150.50(8)	2560.22(13)
Z	4	2
ρ_{calc}/cm³	1.289	1.210
μ/mm⁻¹	0.547	1.916
F(000)	1668.7	962.7
Crystal size/mm³	0.12×0.11×0.1	0.1×0.02×0.01
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2θ range for data collection/°	6.14 to 153.44	8.88 to 153.58
Index ranges	-9 ≤ h ≤ 20, -16 ≤ k ≤ 16, -25 ≤ l ≤ 25	-11 ≤ h ≤ 13, -30 ≤ k ≤ 34, -11 ≤ l ≤ 11
Reflections collected	30042	18953
Independent reflections	8441 [R _{int} = 0.0242, R _{sigma} = 0.0226]	5137 [R _{int} = 0.0374, R _{sigma} = 0.0350]
Data/restraints/parameters	8441/0/974	5137/0/289
Goodness-of-fit on F²	1.087	1.037
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0201, wR ₂ = 0.0522	R ₁ = 0.0686, wR ₂ = 0.1669
Final R indexes [all data]	R ₁ = 0.0238, wR ₂ = 0.0533	R ₁ = 0.0781, wR ₂ = 0.1735
CCDC number	2130685	2130906

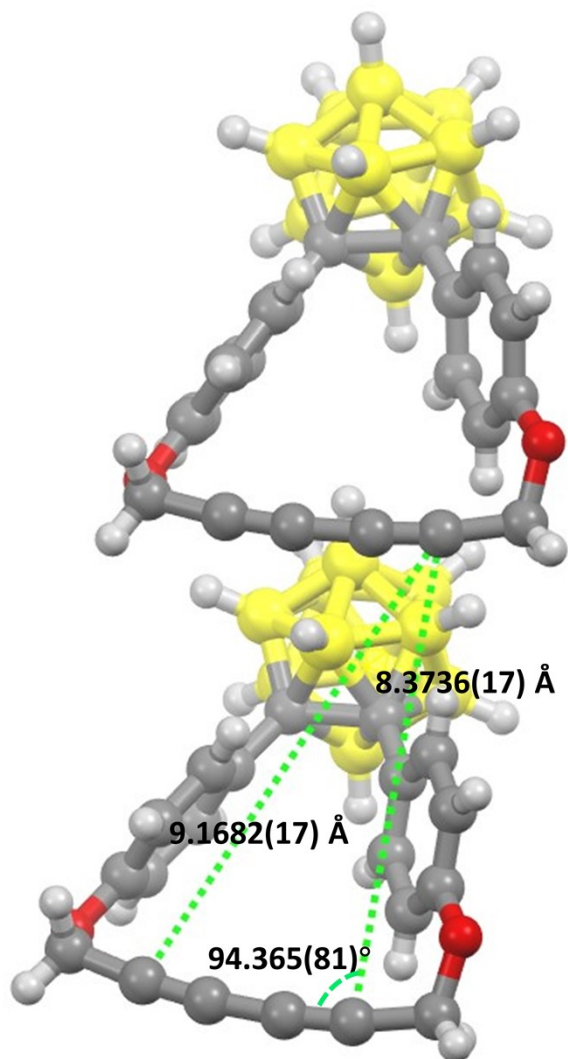


Figure S17 Spatial parameters for topochemical polymerization of **CBMC-1**.

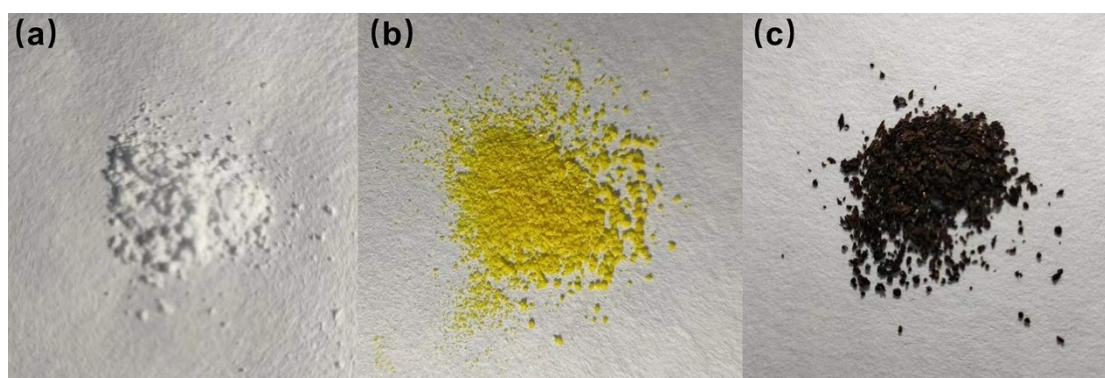


Figure S18 (a) fresh crystals of macrocycle **CBMC-2** after grinding, (b) crystals of macrocycle **CBMC-2** that turned yellow after oven-dry at 60 °C, (c) crystals of macrocycle **CBMC-2** that turned dark black after heating at 250 °C under vacuum atmosphere for 30 min.



5. FT-IR spectra of CBMC-2 and PDAs

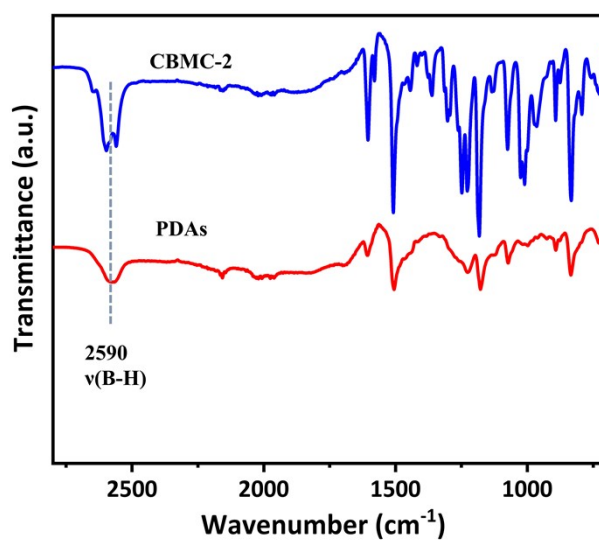


Figure S19 FT-IR spectra of **CBMC-2** (blue line) and **PDAs** (red line)