# Electronic Supplementary Information

## Benzoimidazole-2-one based macrocyclic arenes: Synthesis, and Solvent-induced structural changes

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## Contents

## 1. Materials and Methods.

All reactions were carried out with oven-dried glassware. Commercial reagents were used without further purification. Flash column chromatography was performed on 100-200 mesh silica gel. $^{1}H$ NMR, $^{13}C$ NMR spectra were recorded on a Bruker DMX400 NMR spectrometer. Melting points were determined using WRR melting point apparatus and were uncorrected. High Resolution atmospheric-pressure chemical ionization mass spectra (APCI-MS) were determined by Bruker Daltonics. Inc, APEX II. FT-ICRMS.

## 2. Synthesis of host 1 and 2.

To a mixture of 1,3-Dihydro-2H-benzimidazol-2-one (268.1 mg, 2.0 mmol) and 1,4-bis(bromomethyl)benzene (523.8 mg, 2.0 mmol) in *N,N*-dimethylformamide (100 mL) was added caesium carbonate (1.3 g, 4.0 mmol). The mixture was stirred at 110 °C for 24 h under $N_2$. Then the solvent was removed in vacuo and the residue was separated by column chromatography on silica gel (eluent: 80:1 DCM/Methanol) to give macrocyclic arenes **1** and **2**.

Host **1** (80.2 mg, 17%), $^{1}H$ NMR (400 MHz, Chloroform-*d*) δ 6.89 (dd, *J* = 5.8, 3.1 Hz, 1H), 6.76 (dd, *J* = 5.8, 3.2 Hz, 1H), 5.09 (s, 2H). $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 154.3, 135.6, 129.0, 127.4, 121.4, 108.2, 44.3. HRMS (APCI) m/z: $[M+H]^+$ calcd for $C_{30}H_{25}N_4O_2$, 473.1972; found, 473.1970.

Host **2** (108.6 mg, 23%), $^{1}H$ NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.26 (m, 12H), 6.96 (dt, *J* = 7.7, 3.3 Hz, 6H), 6.84 (ddd, *J* = 13.9, 6.0, 3.2 Hz, 6H), 5.14 – 4.99 (m, 12H). $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 154.5, 129.2, 127. 9, 127.8, 127.7, 127.4, 121.5, 108.4, 108.3, 65.0, 44.7, 44.6. HRMS (APCI) m/z: $[M+H]^+$ calcd for $C_{45}H_{37}N_6O_3$, 709.2922; found, 709.2921.

## 3. $^{1}$H NMR and $^{13}$C NMR Spectral of New compounds

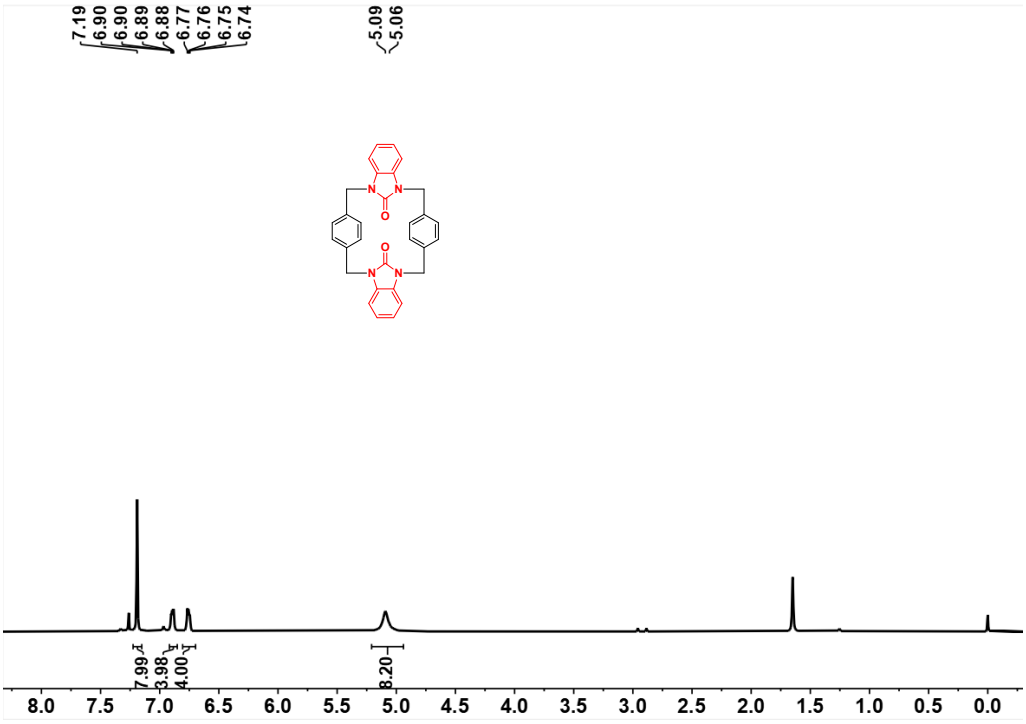


**Figure S1.**$^{1}$H NMR spectrum (400 MHz, $CDCl_3$, 298K) of **1**

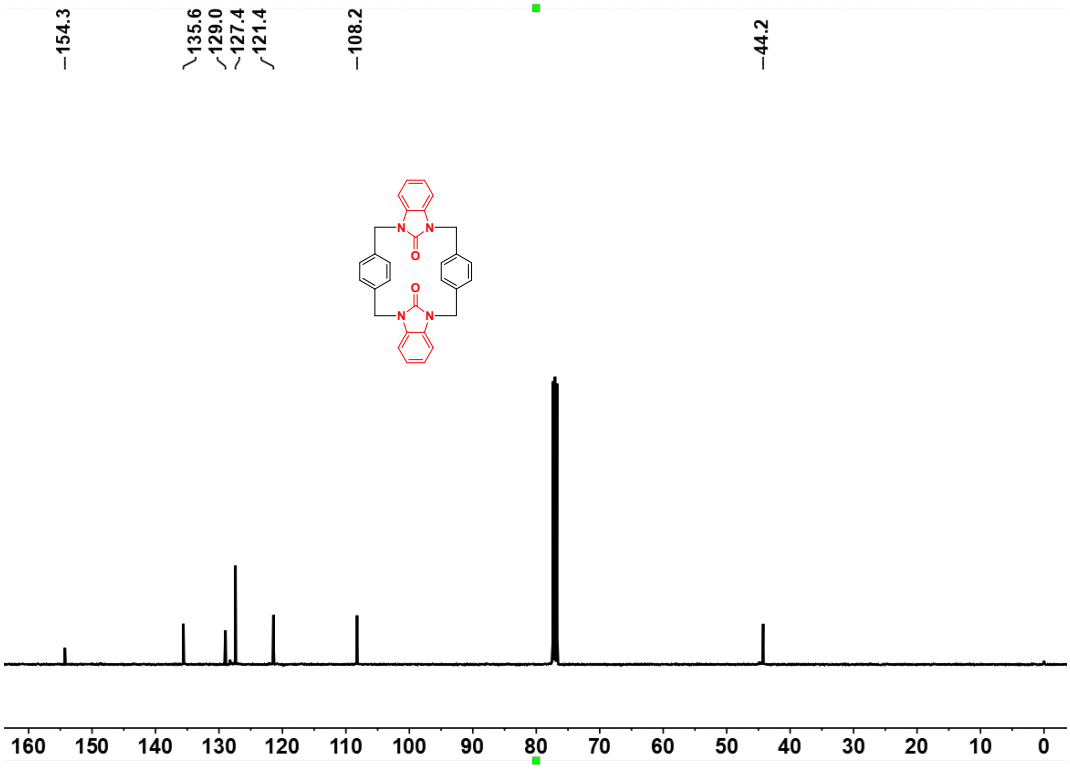


**Figure S2.**$^{13}$C NMR spectrum (101 MHz, $CDCl_3$, 298K) of **1**

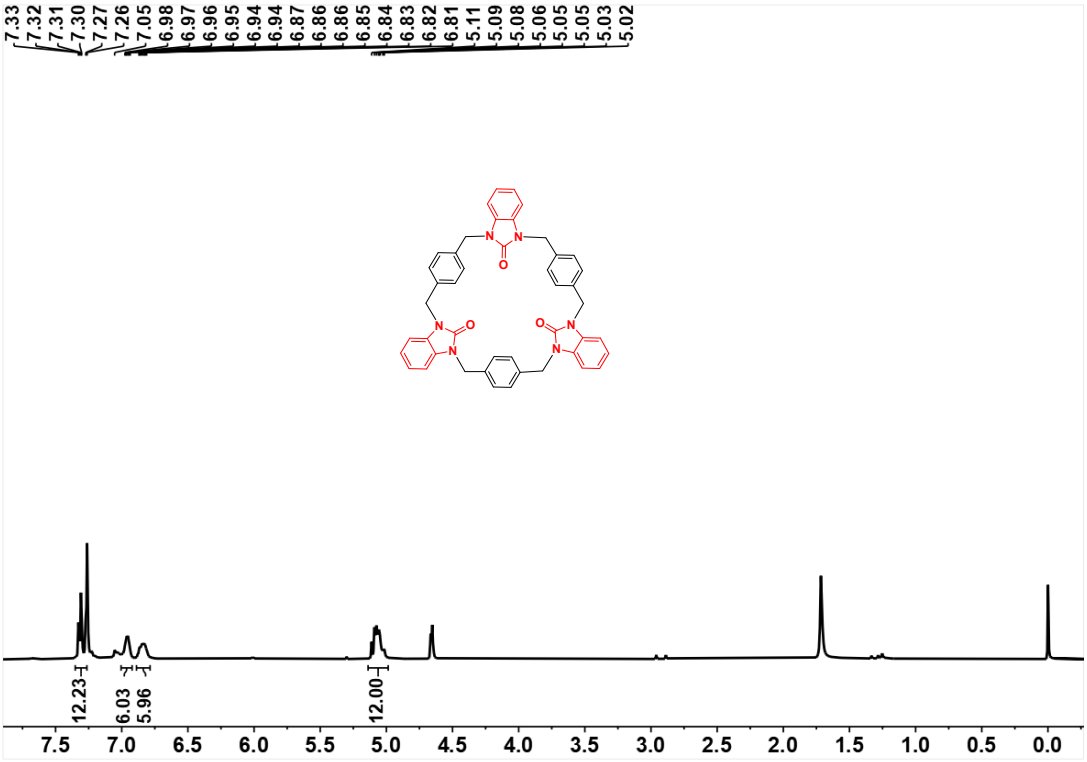


**Figure S3.** $^{1}$H NMR spectrum (400 MHz, $CDCl_3$, 298K) of **2**

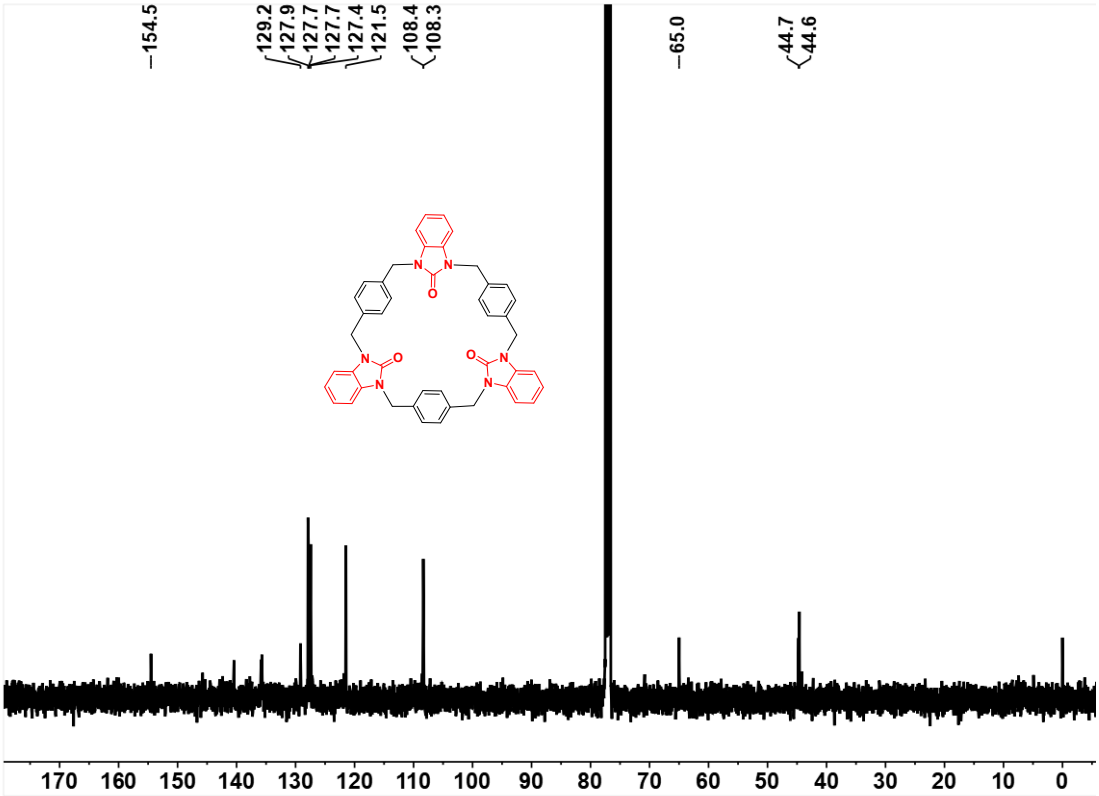


**Figure S4.** $^{13}$C NMR spectrum (101 MHz, $CDCl_3$, 298K) of **2**

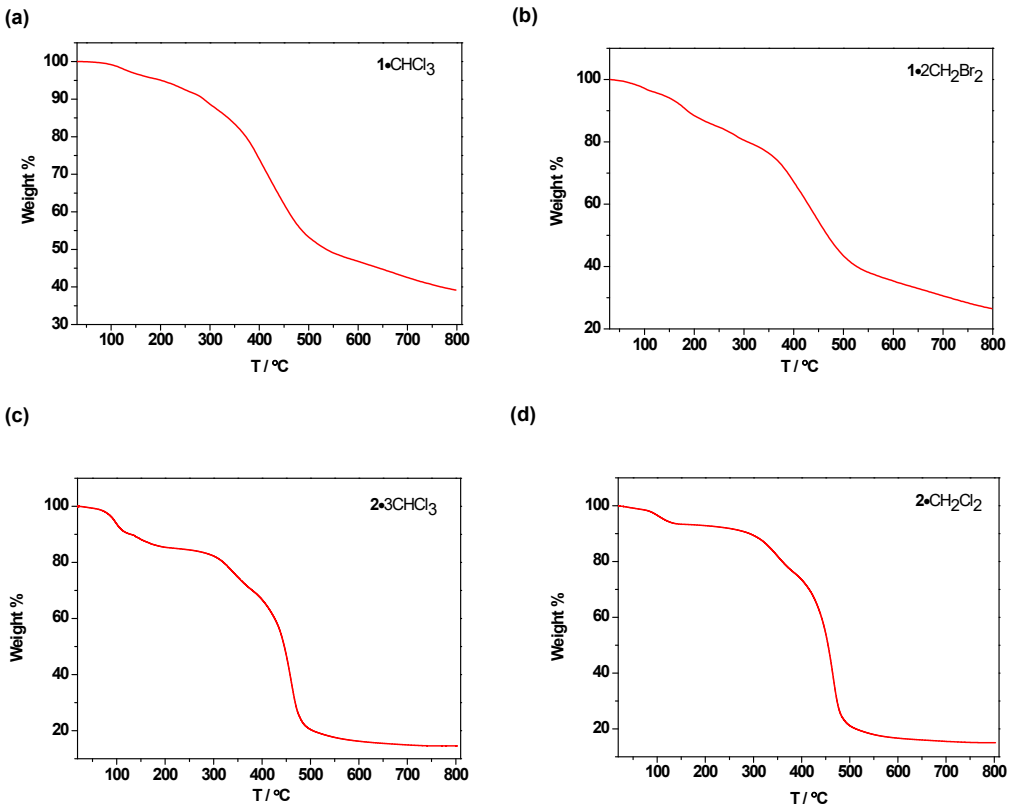


**Figure S5.** Thermogravimetric analysis of **1**•$CHCl_3$, **1**•$2CH_2Br_2$, **2**•$3CHCl_3$ and **2**•$CH_2Cl_2$

## 4. Crystal structures data of **1**•$CHCl_3$, **1**•**2**$CH_2Br_2$, **2**•$3CHCl_3$ and **2**•$CH_2Cl_2$

**Crystal data and structure refinement for 1•$CHCl_3$.**

| | |
|---|---|
| Identification code | **1**•$CHCl_3$ |
| Empirical formula | $C_{31}H_{25}Cl_3N_4O_2$ |
| Formula weight | 591.90 |
| Temperature/K | 296.15 |
| Crystal system | monoclinic |
| Space group | C2/c |
| a/Å | 33.696(7) |
| b/Å | 10.737(2) |
| c/Å | 17.724(4) |
| α/° | 90 |
| β/° | 115.638(3) |
| γ/° | 90 |

| | |
|---|---|
| Volume/Å$^3$ | 5781(2) |
| Z | 8 |
| $\rho_{calc}$g/cm$^3$ | 1.360 |
| μ/mm$^{-1}$ | 0.353 |
| F(000) | 2448.0 |
| Crystal size/mm$^3$ | 0.1 × 0.1 × 0.1 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 2.682 to 55.064 |
| Index ranges | -43 ≤ h ≤ 43, -13 ≤ k ≤ 13, -22 ≤ l ≤ 22 |
| Reflections collected | 31811 |
| Independent reflections | 6561 [$R_{int}$ = 0.0783, $R_{sigma}$ = 0.0757] |
| Data/restraints/parameters | 6561/0/361 |
| Goodness-of-fit on $F^2$ | 0.998 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0592, w$R_2$ = 0.1321 |
| Final R indexes [all data] | $R_1$ = 0.1518, w$R_2$ = 0.1697 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.31/-0.28 |

**Crystal data and structure refinement for 1•2$CH_2Br_2$.**

| | |
|---|---|
| Identification code | **1**•2$CH_2Br_2$ |
| Empirical formula | $C_{16}H_{14}Br_2N_2O$ |
| Formula weight | 410.11 |
| Temperature/K | 296.15 |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 9.02(2) |
| b/Å | 9.39(2) |
| c/Å | 10.71(3) |
| α/° | 84.17(3) |
| β/° | 67.13(3) |
| γ/° | 66.09(3) |
| Volume/Å$^3$ | 763(3) |

| | |
|---|---|
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.786 |
| $\mu$/mm$^{-1}$ | 5.314 |
| F(000) | 404.0 |
| Crystal size/mm$^3$ | 0.1 × 0.1 × 0.1 |
| Radiation | MoK$\alpha$ ($\lambda$ = 0.71073) |
| 2$\Theta$ range for data collection/° | 4.136 to 52.998 |
| Index ranges | $-11 \leq h \leq 11$, $-11 \leq k \leq 11$, $-13 \leq l \leq 13$ |
| Reflections collected | 7846 |
| Independent reflections | 3137 [$R_{int}$ = 0.0875, $R_{sigma}$ = 0.1122] |
| Data/restraints/parameters | 3137/0/242 |
| Goodness-of-fit on F$^2$ | 0.879 |
| Final R indexes [I>=2$\sigma$ (I)] | $R_1$ = 0.0444, $wR_2$ = 0.0802 |
| Final R indexes [all data] | $R_1$ = 0.1132, $wR_2$ = 0.0999 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.40/-0.40 |

**Crystal data and structure refinement for 2●3$CHCl_3$.**

| | |
|---|---|
| Identification code | **2**●3$CHCl_3$ |
| Empirical formula | $C_{48}H_{39}Cl_9N_6O_3$ |
| Formula weight | 1066.90 |
| Temperature/K | 296.15 |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 13.234(7) |
| b/Å | 13.892(7) |
| c/Å | 16.543(9) |
| $\alpha$/° | 109.362(7) |
| $\beta$/° | 96.339(7) |
| $\gamma$/° | 102.534(7) |
| Volume/Å$^3$ | 2746(3) |

| | |
|---|---|
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.291 |
| $\mu$/mm$^{-1}$ | 0.502 |
| F(000) | 1092.0 |
| Crystal size/mm$^3$ | 0.15 × 0.12 × 0.11 |
| Radiation | MoK$\alpha$ ($\lambda$ = 0.71073) |
| 2$\Theta$ range for data collection/° | 2.662 to 50.054 |
| Index ranges | -15 ≤ h ≤ 15, -16 ≤ k ≤ 16, -19 ≤ l ≤ 19 |
| Reflections collected | 26432 |
| Independent reflections | 9686 [$R_{int}$ = 0.0934, $R_{sigma}$ = 0.1304] |
| Data/restraints/parameters | 9686/513/595 |
| Goodness-of-fit on F$^2$ | 0.984 |
| Final R indexes [I>=2$\sigma$ (I)] | $R_1$ = 0.0918, w$R_2$ = 0.2449 |
| Final R indexes [all data] | $R_1$ = 0.2085, w$R_2$ = 0.3105 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.59/-0.48 |

**Crystal data and structure refinement for 2●$CH_2Cl_2$.**

| | |
|---|---|
| Identification code | **2●**$CH_2Cl_2$ |
| Empirical formula | $C_{46}H_{38}Cl_2N_6O_3$ |
| Formula weight | 793.72 |
| Temperature/K | 296.15 |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 12.106(6) |
| b/Å | 13.118(6) |
| c/Å | 13.961(7) |
| $\alpha$/° | 76.807(6) |
| $\beta$/° | 75.289(6) |
| $\gamma$/° | 84.733(7) |
| Volume/Å$^3$ | 2086.7(17) |

| | |
|---|---|
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.263 |
| $\mu$/mm$^{-1}$ | 0.204 |
| F(000) | 828.0 |
| Crystal size/mm$^3$ | 0.14 × 0.11 × 0.09 |
| Radiation | MoK$\alpha$ ($\lambda$ = 0.71073) |
| 2$\Theta$ range for data collection/° | 3.086 to 50.054 |
| Index ranges | $-14 \leq h \leq 14$, $-15 \leq k \leq 15$, $-16 \leq l \leq 16$ |
| Reflections collected | 20197 |
| Independent reflections | 7357 [$R_{int}$ = 0.0684, $R_{sigma}$ = 0.1096] |
| Data/restraints/parameters | 7357/468/541 |
| Goodness-of-fit on F$^2$ | 1.176 |
| Final R indexes [I>=2$\sigma$ (I)] | $R_1$ = 0.1270, $wR_2$ = 0.3448 |
| Final R indexes [all data] | $R_1$ = 0.2213, $wR_2$ = 0.4085 |
| Largest diff. peak/hole / e Å$^{-3}$ | 1.13/-0.32 |