Electronic supplementary information

2,2’-Biphen[n]arenes (n = 4–8): one-step, high-yield synthesis and host–guest properties

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Experimental

Materials and methods

Organic cationic guests $1^+\sim 4^{2+}$ with tetrakis[3,5-bis(trifluoromethyl)phenyl]borate counter anions were prepared from their chloride or bromide salts using our previously reported methods.\textsuperscript{[S1]} $^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker AV500 instrument. High-resolution mass spectra (HRMS) were recorded on a Bruker Daltonics, Inc. APEXIII 7.0 TESLA FTMS instrument. Melting points were obtained on an X-4 digital melting point apparatus without correction.

Synthesis of $2,2'$-EtBP$n$s

To the solution of 2,2'-diethoxybiphenyl (4.8 g, 20 mmol) in CH$_2$ClCH$_2$Cl (200 mL) was added paraformaldehyde (0.90 g, 30 mmol). Boron trifluoride diethyl etherate (5.0 ml, 40 mmol) was then added to the reaction mixture. The mixture was stirred at 25°C for 30 minutes. Then the reaction was quenched by addition of 100 mL water. The organic phase was separated and washed with saturated aqueous NaHCO$_3$, and water. The organic layer was dried over anhydrous Na$_2$SO$_4$ and concentrated. The residue was purified by column chromatography on silica gel (eluent: 10/1, v/v, Petroleum ether:ethyl acetate gradually changing to 2/1) to afford $2,2'$-EtBP$4$ (0.80 g, 16%), $2,2'$-EtBP$5$ (0.72 g, 14%), $2,2'$-EtBP$6$ (0.42 g, 8.4%), $2,2'$-EtBP$7$ (0.32 g, 6.4%), and $2,2'$-EtBP$8$ (0.30 g, 5.9%) as white solids.

$2,2'$-EtBP$4$. m.p.108–110°C. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm): 7.14–6.98 (m, 16H), 6.80 (d, $J = 8.3$ Hz, 8H), 3.91 (q, $J = 7.0$ Hz, 16H), 3.85 (s, 8H), 1.18 (t, $J = 7.0$ Hz, 24H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ (ppm): 154.8, 133.2, 132.3, 128.5, 128.3, 112.3 (C of biphenyl), 64.1 (C of methylene in ethoxy group), 40.4 (C of methylene bridge) 14.9 (C of methyl in ethoxy group). HRMS (ESI): C$_{68}$H$_{72}$O$_8$Na$^+$, calcd m/z 1039.5104; found m/z 1039.5117.

$2,2'$-EtBP$5$. m.p.86–88°C. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm): 7.10–6.98 (m, 16H), 6.80 (d, $J = 8.3$ Hz, 8H), 3.91 (q, $J = 7.0$ Hz, 16H), 3.85 (s, 8H), 1.18 (t, $J = 7.0$ Hz, 24H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ (ppm): 154.8, 133.2, 132.3, 128.5, 128.3, 112.3 (C of biphenyl), 64.1 (C of methylene in ethoxy group), 40.4 (C of methylene bridge) 14.9 (C of methyl in ethoxy group). HRMS (ESI): C$_{68}$H$_{72}$O$_8$Na$^+$, calcd m/z 1039.5104; found m/z 1039.5117.
bridge), 14.8 (C of methyl in ethoxy group). HRMS (ESI): C_{85}H_{90}O_{10}Na^+, calcd m/z 1293.6405; found m/z 1293.6234.

2,2'-EtBP6. m.p. 90–92 °C. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) (ppm): 7.08 (d, \(J = 2.2\) Hz, 12H), 7.03 (dd, \(J = 8.3, 2.2\) Hz, 12H), 6.78 (d, \(J = 8.4\) Hz, 12H), 3.85 (dd, \(J = 13.6, 6.6\) Hz, 36H), 1.12 (t, \(J = 7.0\) Hz, 36H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) (ppm): 154.6, 133.1, 132.4, 128.4, 128.0, 112.4 (C of biphenyl), 64.0 (C of methylene in ethoxy group), 40.4 (C of methylene bridge), 14.8 (C of methyl in ethoxy group). HRMS (ESI): C_{102}H_{108}O_{12}Na^+, calcd m/z 1547.7706; found m/z 1547.7764.

2,2'-EtBP7. m.p. 97–100 °C. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) (ppm): 7.09 (d, \(J = 2.2\) Hz, 14H), 7.03 (dd, \(J = 8.3, 2.2\) Hz, 14H), 6.78 (d, \(J = 8.4\) Hz, 14H), 3.85 (dd, \(J = 13.8, 6.8\) Hz, 42H), 1.12 (t, \(J = 7.0\) Hz, 42H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) (ppm): 154.6, 133.1, 132.3, 128.4, 127.9, 112.4 (C of biphenyl), 63.98 (C of methylene in ethoxy group), 40.4 (C of methylene bridge), 14.8 (C of methyl in ethoxy group). HRMS (ESI): C_{119}H_{126}O_{14}Na^+, calcd m/z 1802.9079; found m/z 1802.9056.

2,2'-EtBP8. m.p. 92–95 °C. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) (ppm): 7.10 (d, \(J = 2.2\) Hz, 16H), 7.03 (dd, \(J = 8.4, 2.2\) Hz, 16H), 6.78 (d, \(J = 8.4\) Hz, 16H), 3.86 (dd, \(J = 13.9, 6.9\) Hz, 48H), 1.12 (t, \(J = 7.0\) Hz, 48H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) (ppm): 154.6, 133.1, 132.4, 128.4, 128.0, 112.4 (C of biphenyl), 64.0 (C of methylene in ethoxy group), 40.4 (C of methylene bridge), 14.8 (C of methyl in ethoxy group). HRMS (ESI): C_{136}H_{144}O_{16}NH_{4}^+, calcd m/z 2052.0832; found m/z 2052.0833.
Copies of $^1$H NMR and $^{13}$C NMR spectra of the new macrocycles.

**Figure S1.** $^1$H NMR spectrum (500 MHz) of 2,2'-EtBP4 in CDCl$_3$

**Figure S2.** $^{13}$C NMR spectrum (125 MHz) of 2,2'-EtBP4 in CDCl$_3$
Figure S3. $^1$H NMR spectrum (500 MHz) of 2,2'-EtBP$_5$ in CDCl$_3$

Figure S4. $^{13}$C NMR spectrum (125 MHz) of 2,2'-EtBP$_5$ in CDCl$_3$
Figure S5. $^1$H NMR spectrum (500 MHz) of 2,2’-EtBP in CDCl$_3$.

Figure S6. $^{13}$C NMR spectrum (125 MHz) of 2,2’-EtBP in CDCl$_3$. 
Figure S7. $^1$H NMR spectrum (500 MHz) of 2,2’-EtBP7 in CDCl$_3$.

Figure S8. $^{13}$C NMR spectrum (125 MHz) of 2,2’-EtBP7 in CDCl$_3$. 
Figure S9. $^1$H NMR spectrum (500 MHz) of 2,2'-EtBP8 in CDCl$_3$.

Figure S10. $^{13}$C NMR spectrum (125 MHz) of 2,2'-EtBP8 in CDCl$_3$. 
VT $^1$H NMR spectra of 2,2’-EtBP4 and 2,2’-EtBP8.

Figure S11. VT $^1$H NMR spectra of 2,2’-EtBP4 in toluene-$d_8$ in the temperature range from –60 °C to 100 °C.
Figure S12. VT $^1$H NMR spectra of 2,2'-EtBP in toluene-$d_8$ in the temperature range from −60 °C to 100 °C.
Additional $^1$H NMR spectra of host-guest mixture.

![Additional $^1$H NMR spectra of host-guest mixture.](image)

**Figure S13.** $^1$H NMR spectra (500 MHz, 298 K) of $2^+$ (2.0 mM) in CD$_2$Cl$_2$ in the absence (A) and presence of ~1.0 equiv. of 2,2'-EtBP4 (B), 2,2'-EtBP5 (C), 2,2'-EtBP6 (D), 2,2'-EtBP7 (E), and 2,2'-EtBP8 (F).
Figure S14. $^1$H NMR spectra (500 MHz, 298 K) of $3^{2+}$ (2.0 mM) in CD$_2$Cl$_2$ in the absence (A) and presence of ~1.0 equiv. of 2,2’-EtBP4 (B), 2,2’-EtBP5 (C), 2,2’-EtBP6 (D), 2,2’-EtBP7 (E), and 2,2’-EtBP8 (F).
Figure S15. $^1$H NMR spectra (500 MHz, 298 K) of $4^{2+}$ (2.0 mM) in CD$_2$Cl$_2$ in the absence (A) and presence of ~1.0 equiv. of 2,2’-EtBP4 (B), 2,2’-EtBP5 (C), 2,2’-EtBP6 (D), 2,2’-EtBP7 (E), and 2,2’-EtBP8 (F).
Molar ratio plots and determination of $K_a$.

In the present host-guest systems, chemical exchange is fast on the NMR time scale. To determine the association constants ($K_a$), $^1$H NMR titrations were performed in CD$_2$Cl$_2$ with solutions which had a constant concentration of 2,2’-EtBP$n$ host and varying concentrations of guest. Assuming 1 : 1 binding stoichiometry between 2,2’-EtBP$n$s and these guests, the $K_a$ values could be calculated by analyzing the sequential changes in chemical shift changes of 2,2’-EtBP$n$ host that occurred with changes in guest concentration by using the nonlinear curve-fitting method from the following equation$^{[S2]}$:

$$A = (A_\infty/[H]_0) (0.5[G]_0 + 0.5([H]_0+1/K_a)−(0.5 ([G]_0)^2+(2[G]_0(1/K_a − [H]_0)) + (1/K_a + [H]_0)^2) ^{0.5})$$

Where $A$ is the chemical shift change of aromatic protons on 2,2’-EtBP$n$ host at [G]$_0$, $A_\infty$ is the chemical shift change when the host is completely complexed, [H]$_0$ is the fixed initial concentration of the 2,2’-EtBP$n$ host, and [G]$_0$ is the initial concentration of guest.

For each host–guest pair examined, the plot of $\Delta \delta$ as a function of [G]$_0$ gave an excellent fit (Figure S16~S20), verifying the validity of the 1:1 binding stoichiometry assumed. Additionally, mole ratio plots were also made (Figure S21~25); they proved consistent with the proposed 1 : 1 host–guest binding stoichiometry.
Figure S16. The non-linear curve-fitting (NMR titrations) for the complexation of 2,2'‐EtBP4 (2.0 × 10⁻⁴ mol/L) with and guest 1⁺ in CD₂Cl₂ at 298 K.

Figure S17. The non-linear curve-fitting (NMR titrations) for the complexation of 2,2'‐EtBP5 (2.0 × 10⁻⁴ mol/L) with and guest 1⁺ in CD₂Cl₂ at 298 K.
Figure S18. The non-linear curve-fitting (NMR titrations) for the complexation of 2,2’-EtBP6 (2.0 × 10^{-4} mol/L) with and guest 1+ in CD_{2}Cl_{2} at 298 K.

Figure S19. The non-linear curve-fitting (NMR titrations) for the complexation of 2,2’-EtBP7 (2.0 × 10^{-4} mol/L) with and guest 1+ in CD_{2}Cl_{2} at 298 K.
**Figure S20.** The non-linear curve-fitting (NMR titrations) for the complexation of 2,2’-EtBP8 (2.0 × 10^{-4} mol/L) with and guest 1⁺ in CD₂Cl₂ at 298 K.

**Figure S21.** Mole ratio plot for 2,2’-EtBP4 and 1⁺ from ¹H NMR (500 MHz, 298 K) experiments, wherein 2,2’-EtBP4 (at a fixed concentration) in CD₂Cl₂ was treated different molar equivalents of 1⁺. The results are consistent with a 1 : 1 binding stoichiometry.
Figure S22. Mole ratio plot for 2,2'-EtBP5 and 1+ from ¹H NMR (500 MHz, 298 K) experiments, wherein 2,2'-EtBP5 (at a fixed concentration) in CD₂Cl₂ was treated different molar equivalents of 1+. The results are consistent with a 1 : 1 binding stoichiometry.

Figure S23. Mole ratio plot for 2,2'-EtBP6 and 1+ from ¹H NMR (500 MHz, 298 K) experiments, wherein 2,2'-EtBP6 (at a fixed concentration) in CD₂Cl₂ was treated different molar equivalents of 1+. The results are consistent with a 1 : 1 binding stoichiometry.
Figure S24. Mole ratio plot for 2,2'-EtBP7 and 1+ from 1H NMR (500 MHz, 298 K) experiments, wherein 2,2'-EtBP7 (at a fixed concentration) in CD2Cl2 was treated different molar equivalents of 1+. The results are consistent with a 1 : 1 binding stoichiometry.

Figure S25. Mole ratio plot for 2,2'-EtBP8 and 1+ from 1H NMR (500 MHz, 298 K) experiments, wherein 2,2'-EtBP8 (at a fixed concentration) in CD2Cl2 was treated different molar equivalents of 1+. The results are consistent with a 1 : 1 binding stoichiometry.
References.
