Synthesis, structure, and molecular recognition property of a [2]calix[1]biphenyl-type hybrid[3]arene

Jiong Zhou, Jie Yang, Bin Hua, Li Shao, Zhihua Zhang and Guocan Yu*

Department of Chemistry, Zhejiang University, Hangzhou 310027, P. R. China; Email: guocanyu@zju.edu.cn

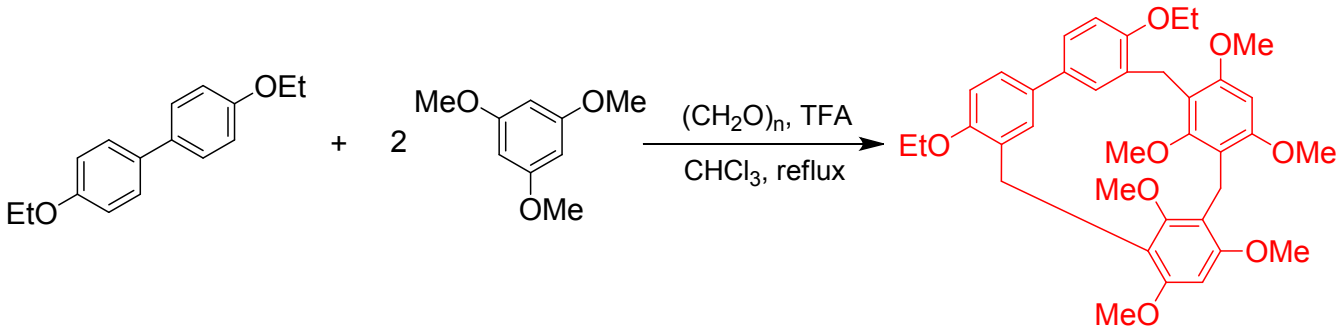
Electronic Supplementary Information (11 pages)

1. Materials and methods

All reagents were commercially available and used as supplied without further purification. Solvents were either employed as purchased or dried according to procedures described in the literature. NMR spectra were recorded with a Bruker Avance DMX 400 spectrophotometer or a Bruker Avance DMX 500 spectrophotometer with the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. Low-resolution electrospray ionization mass spectra (LRESI-MS) were obtained on a Bruker Esquire 3000 Plus spectrometer (Bruker-Franzen Analytik GmbH Bremen, Germany) equipped with an ESI interface and an ion trap analyzer. High-resolution electrospray ionization mass spectra (HRESI-MS) were obtained on a Bruker 7-Tesla FT-ICR mass spectrometer equipped with an electrospray source (Billerica, MA, USA). The melting point was collected on a SHPSIC WRS-2 automatic melting point apparatus.

*2. Synthesis of [2]Calix[1]Biphenyl-Type Hybrid[3]arene (**2C1BH3A**)*

Scheme S1. Synthetic route to [2]Calix[1]Biphenyl-Type Hybrid[3]arene (**2C1BH3A**).



4,4'-biphenol diethyl ether **1,3,5-trimethoxybenzene** **2C1BH3A**

Synthesis of **2C1BH3A**: To the solution of 4,4'-biphenol diethyl ether (2.42 g, 10.0 mmol) and 1,3,5-trimethoxybenzene (3.36 g, 20.0 mmol) in $CHCl_3$ (200 mL), paraformaldehyde (0.900 g, 30.0 mmol) and TFA (10 mL) were added. The mixture was refluxed for 30 min, and the progress was monitored by thin-layer chromatography (TLC). The mixture was cooled to room temperature, and an excess of saturated aqueous Na_2CO_3 was added to neutralize TFA. The organic phase was separated and the crude product was purified by column chromatography (petroleum ether/ CH_2Cl_2, *v*/*v* 10:1 → 3:1) to get **2C1BH3A** as a white solid (1.67 g, 25%), mp: 305.5–306.5 °C. The ^{1}H NMR spectrum of **2C1BH3A** is shown in Fig. S1. ^{1}H NMR (400 MHz, chloroform-*d*, 293 K) δ (ppm): 7.17 (d, J = 8 Hz, 2H), 6.73 (d, J = 8 Hz, 2H), 6.34 (s, 2H), 6.29 (s, 2H), 4.19–4.03 (m, 8H), 3.90 (s, 6H), 3.71 (s, 6H), 3.47 (d, J = 20 Hz, 2H), 1.45 (t, J = 4 Hz, 6H). The ^{13}C NMR spectrum of **2C1BH3A** is shown in Fig. S2. ^{13}C NMR (100 MHz, chloroform-*d*, 293 K) δ (ppm): 159.78, 157.63, 156.66, 155.70, 132.90, 129.50, 127.78, 122.74, 116.54, 112.94, 110.24, 91.62, 63.58, 61.09, 55.78, 55.53, 22.84, 16.47, 15.12. LRESIMS is shown in Fig. S3: *m*/*z* 614.7 $[M + H]^+$ (42%), 631.9 $[M + NH_4]^+$ (73%), and 672.0 $[M + H_2O + K]^+$ (100%). HRESIMS: *m*/*z* calcd for $[M + NH_4]^+$ $C_{37}H_{46}NO_8^+$, 632.3218; found 632.3215; error 0.5 ppm.

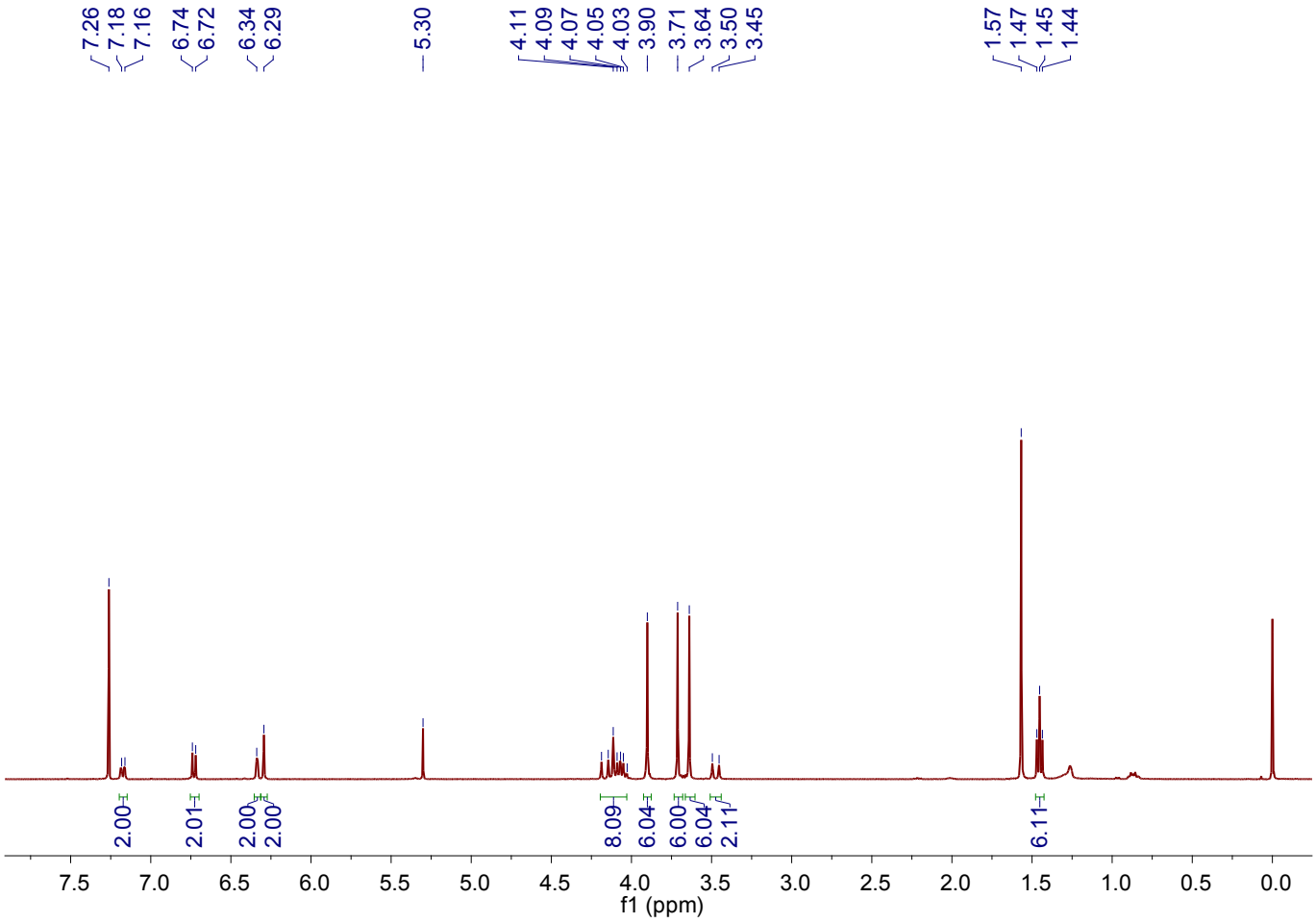


Fig. S1 ^{1}H NMR spectrum (400 MHz, chloroform-*d*, 293K) of **2C1BH3A**.

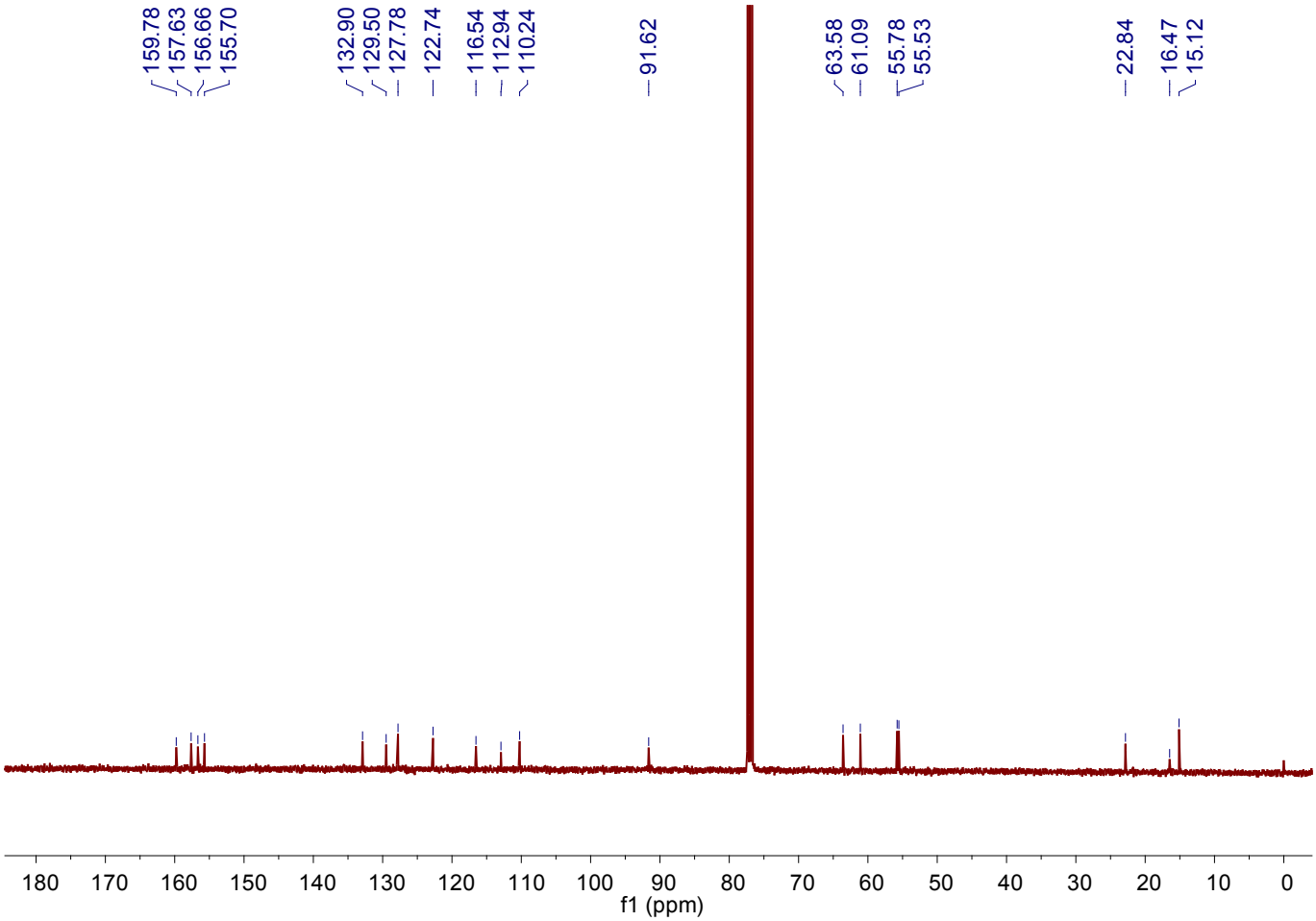


Fig. S2 ^{13}C NMR spectrum (100 MHz, chloroform-*d*, 293K) of **2C1BH3A**.

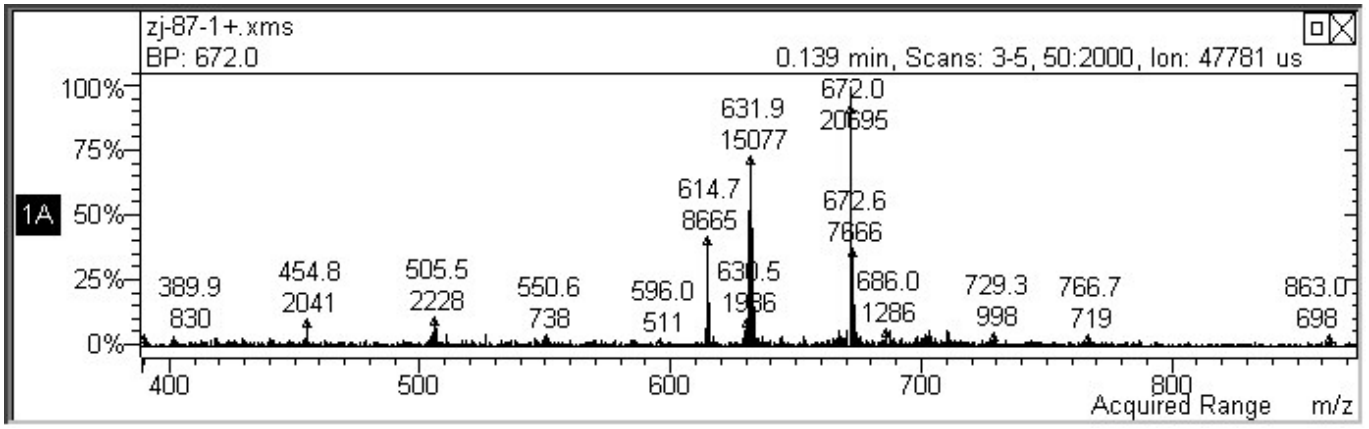
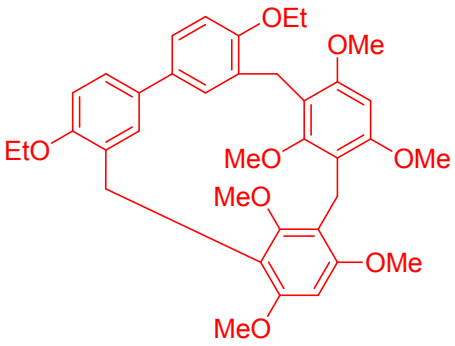


Fig. S3 Electrospray ionization mass spectrum of **2C1BH3A**. Assignment of main peaks: *m*/*z* 614.7 $[M + H]^+$, 631.9 $[M + NH_4]^+$, and 672.0 $[M + H_2O + K]^+$.

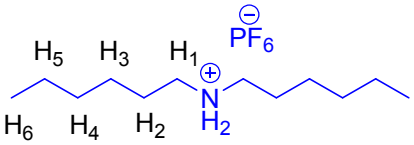
3. X-ray crystal data of ***2C1BH3A***

Crystallographic data: colorless, $C_{38}H_{43}Cl_3O_8$, *FW* 734.07, monoclinic, space group *C*2/*c*, a = 28.1180(13), b = 14.1732(6), c = 19.5603(11) Å, α = 90.00°, β = 106.288(5)°, γ = 90.00°, V = 7482.4(6) Å^3, Z = 8, D_c = 1.303 g cm^{-3}, T = 170 K, μ = 0.295 mm^{-1}, 14054 measured reflections, 6833 independent reflections, 450 parameters, 0 restraints, $F(000)$ = 3088, R_1 = 0.0987, wR_2 = 0.1430 (all data), R_1 = 0.0536, wR_2 = 0.1224 [$I > 2\sigma(I)$], max. residual density 0.457 e•Å^{-3}, and goodness-of-fit (F^2) = 1.020. CCDC 1431824.

*4. [1]H NMR spectroscopy investigation of **2C1BH3A⊃G***



2C1BH3A



G

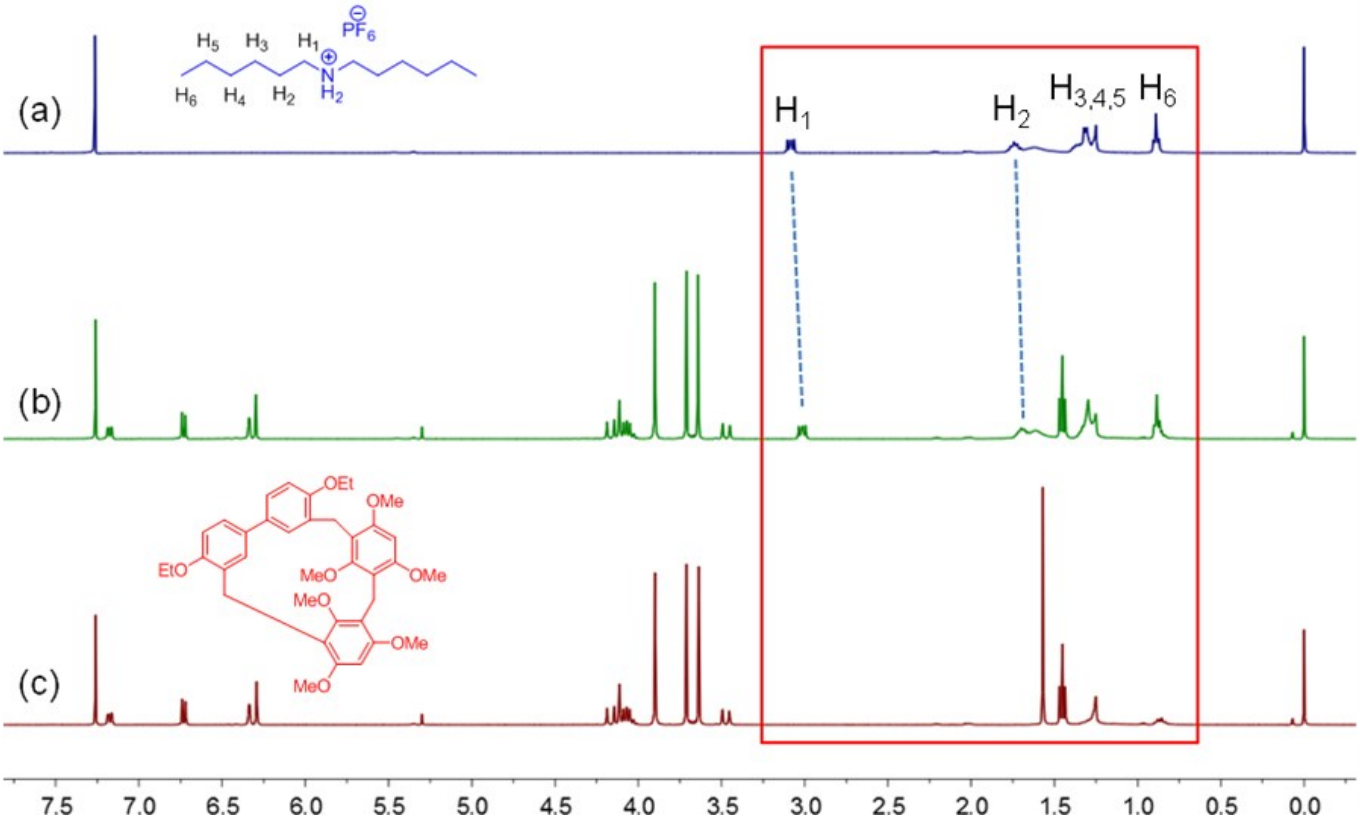


Fig. S4 Partial [1]H NMR spectra (400 MHz, chloroform-*d*, 293K): (a) **G** (5.00 mM); (b) **G** (5.00 mM) and **2C1BH3A** (10.0 mM); (c) **2C1BH3A** (10.0 mM).

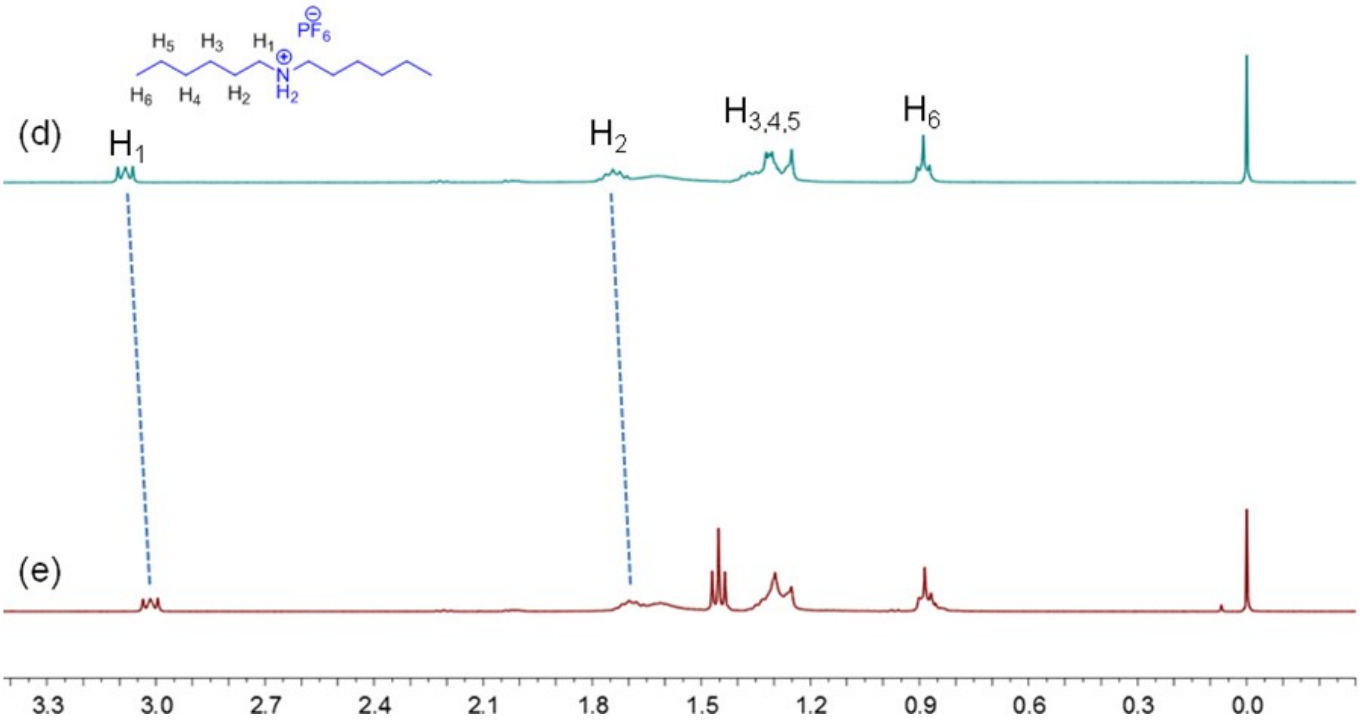


Fig. S5 Partial ^{1}H NMR spectra (400 MHz, chloroform-*d*, 293K): (d) **G** (5.00 mM); (e) **G** (5.00 mM) and **2C1BH3A** (10.0 mM).

*5. Association constant and stoichiometry determination for the complexation between **2C1BH3A** and **G***

To determine the association constant and stoichiometry for the complexation between **2C1BH3A** and **G**, ^{1}H NMR titration was done with solutions which had a constant concentration of the guest **G** (5.00 mM) and varying concentrations of the host **2C1BH3A**. By a non-linear curve-fitting method, the association constant (K_a) of **2C1BH3A⊃G** was determined. By a mole ratio plot, 1:1 stoichiometry was obtained for the complexation between **2C1BH3A** and **G**.

The non-linear curve-fitting was based on the equation:[S1]

$$\Delta\delta = (\Delta\delta_\infty/[G]_0)\ (0.5[H]_0 + 0.5([G]_0+1/K_a) - (0.5\ ([H]_0^2 + (2[H]_0\ (1/K_a - [G]_0)) + (1/K_a + [G]_0)^2)^{0.5})) \quad \text{(Eq. S1)}$$

Where $\Delta\delta$ is the chemical shift change of H_1 on **G**, $\Delta\delta_\infty$ is the chemical shift change of H_1 when the guest **G** is completely complexed, $[H]_0$ is the initial concentration of the host **2C1BH3A**, and $[G]_0$ is the fixed initial concentration of the guest **G**.

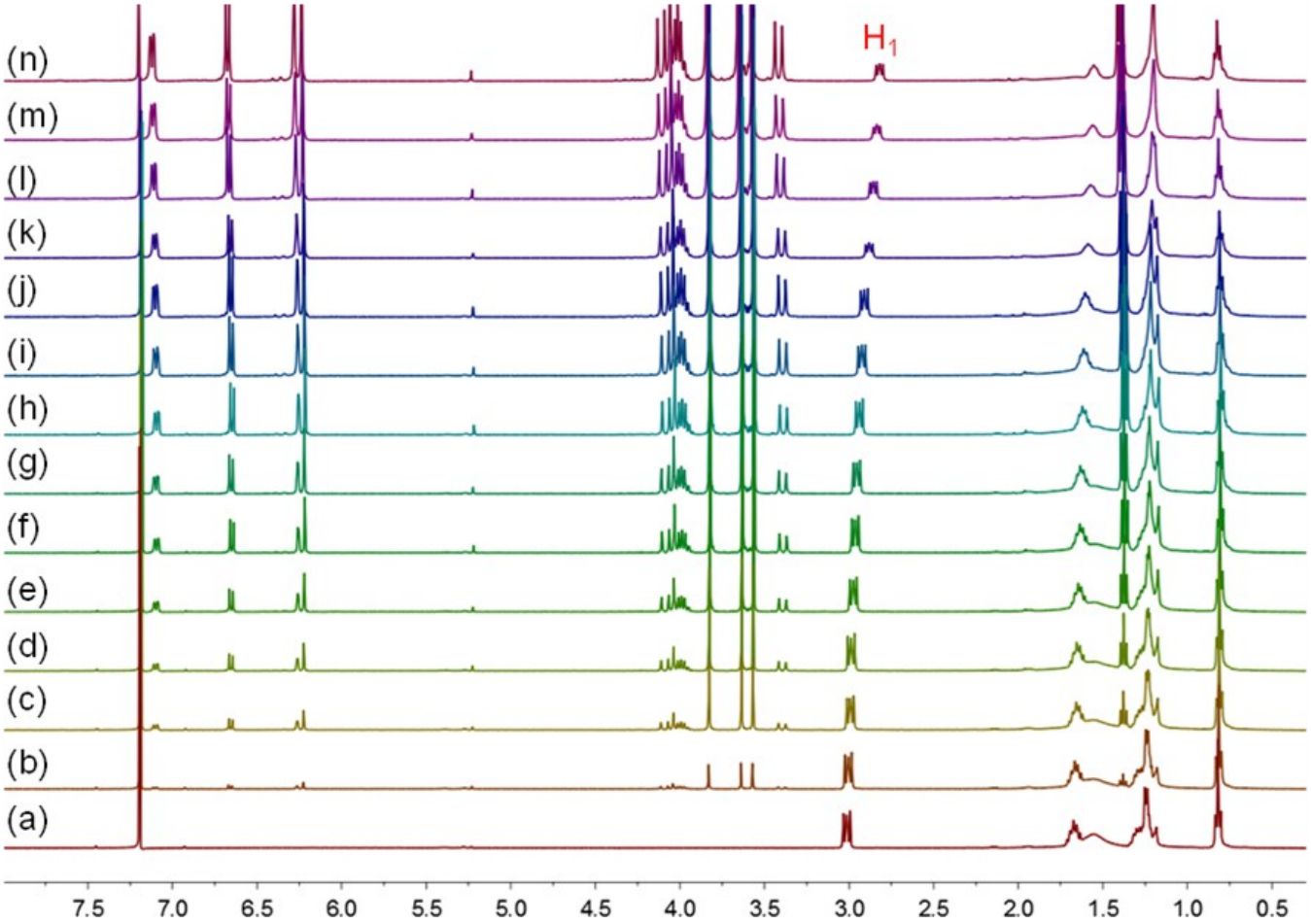


Fig. S6 Partial ^{1}H NMR spectra (400 MHz, chloroform-*d*, 293K) of **G** at a concentration of 5.00 mM upon addition of **2C1BH3A**: (a) 0.00 mM; (b) 0.778 mM; (c) 1.678 mM; (d) 2.03 mM; (e) 2.94 mM; (f) 3.76 mM; (g) 4.67 mM; (h) 5.71 mM; (i) 7.54 mM; (j) 9.12 mM; (k) 12.3 mM; (l) 15.5 mM; (m) 18.3 mM; (n) 20.6 mM.

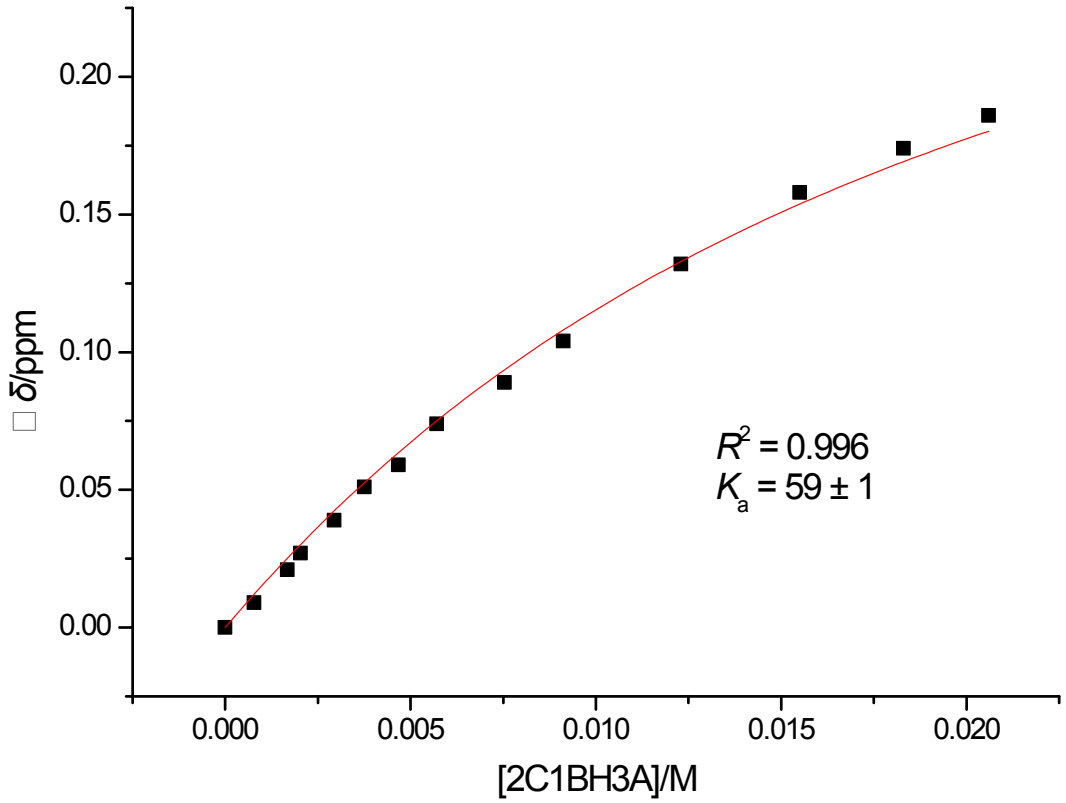


Fig. S7 The chemical shift changes of H_1 on **G** upon addition of **2C1BH3A**. The red solid line was obtained from the non-linear curve-fitting using Eq. S1.

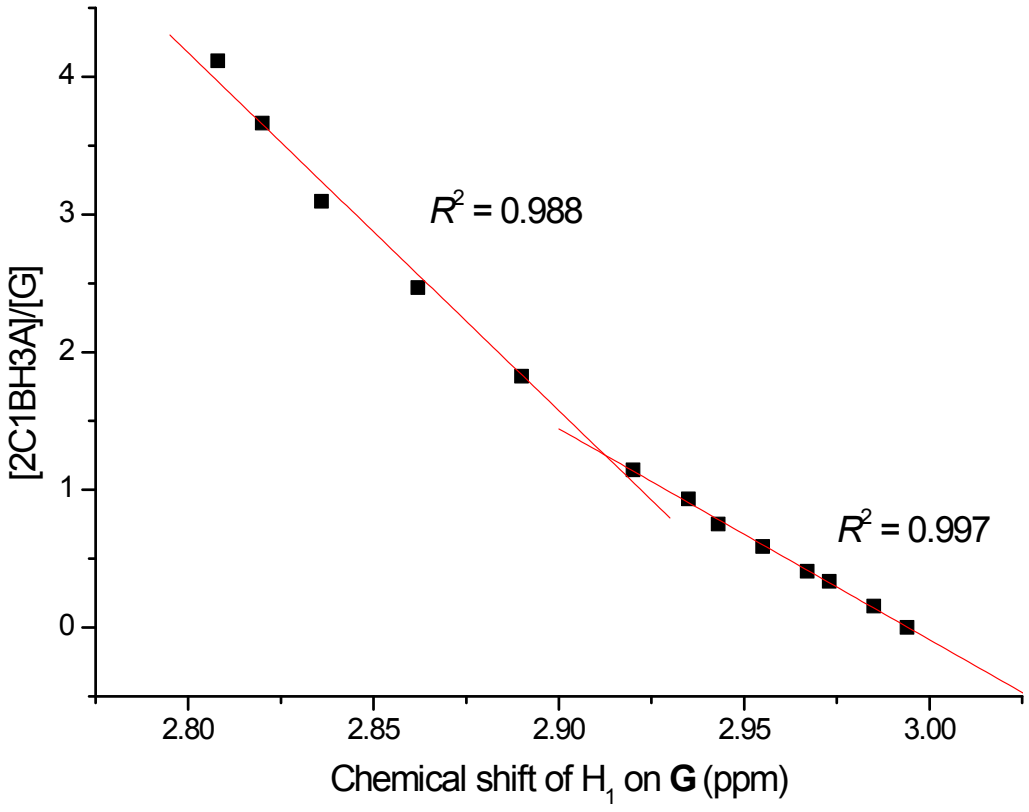


Fig. S8 Mole ratio plot for **2C1BH3A** and **G**, indicating a 1:1 stoichiometry.

References:

S1. (a) K. A. Connors, *Binding Constants, The Measurement of Molecular Complex Stability*, Wiley, New York, 1987; (b) P. R. Ashton, R. Ballardini, V. Balzani, M. Belohradsky, M. T. Gandolfi, D. Philp, L. Prodi, F. M. Raymo, M. V. Reddington, N. Spencer, J. F. Stoddart, M. Venturi and D. J. Williams, *J. Am. Chem. Soc*., 1996, **118**, 4931−4951; (c) Y. Inoue, K. Yamamoto, T. Wada, S. Everitt, X.-M. Gao, Z.-J. Hou, L.-H. Tong, S.-K. Jiang and H.-M. Wu, *J. Chem. Soc., Perkin Trans. 2*, 1998, 1807−1816.