

Electronic Supplementary Information

A novel redox-responsive pillar[6]arene-based inclusion complex with the ferrocenium guest

Wei Xia,^a Xiao-Yu Hu,^a Yong Chen,^b Chen Lin,^{*a} and Leyong Wang^{*a}

^a Key Laboratory of Mesoscopic Chemistry of MOE, Center for Multimolecular Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093 (China)

^b Department of Chemistry, State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071 (China)

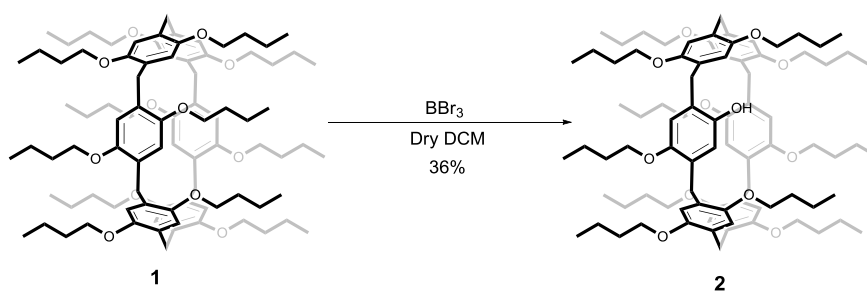
Table of Contents

| | |
|--|-----|
| 1. Materials and methods..... | S2 |
| 2. Synthesis of 2 | S3 |
| 3. Synthesis of 3 | S5 |
| 4. Stoichiometry and association constant determination for the complexation between ferrocene (Fc) and 1 | S7 |
| 5. Association constant determination for the complexation between cobaltocenium hexafluorophosphate (Cob⁺PF₆⁻) and 1 | S9 |
| 6. Fluorescent titration experiments of 3 with Cob⁺PF₆⁻ and Fc⁺PF₆⁻ , respectively..... | S11 |
| 7. 2D NOESY analysis of Cob⁺PF₆⁻ with 1 | S13 |
| 8. Cyclic voltammetry analysis of Fc with 1 | S15 |
| 9. Stability test of Fc⁺PF₆⁻ | S15 |
| 10. Quantitative stability test of Fc⁺PF₆⁻ | S16 |
| 11. LR-ESI-MS of host-guest complexes of 1 with Fc⁺ and Cob⁺ | S17 |
| 12. HR-ESI-MS of host-guest complexes of 1 with Fc⁺ and Cob⁺ | S17 |
| 13. ¹ H NMR titration spectra of 1,4-dibutoxybenzene and Cob⁺PF₆⁻ | S18 |
| 14. Optimized structure of 1 with Cob⁺ | S19 |
| 15. ¹ H NMR study about the complexation of PBP[5] with Fc and Cob⁺ , respectively..... | S22 |
| 16. Electron paramagnetic resonance (EPR) study of Fc⁺PF₆⁻ with 1 | S24 |
| 17. References..... | S24 |

1. *Materials and methods*

All reagents were commercially available and used as supplied without further purification. Ferrocenium hexafluorophosphate (Fc^+PF_6^- , Sigma Aldrich) and cobaltocenium hexafluorophosphate ($\text{Cob}^+\text{PF}_6^-$, TCI) were used in the tests of metallocenium with pillar[6]arenes. 9-(6-Bromohexyl)-carbazole was synthesized according to the published method.¹ Mono-deprotected per-butylated pillar[6]arene **2** was synthesized using a similar procedure to the reported procedure for per-ethylated pillar[6]arene.² NMR spectra were recorded with a Bruker Advance DMX 300 spectrophotometer or a Bruker Advance DMX 400 spectrophotometer with use of the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. Low-resolution electrospray ionization mass spectra (LR-ESI-MS) were obtained on Finnigan Mat TSQ 7000 instruments. High-resolution electrospray ionization mass spectra (HR-ESI-MS) were recorded on an Agilent 6210 TOF LCMS equipped with an electrospray ionization (ESI) probe. The excitation and emission spectra were recorded on a Perkin Elmer LS55 Fluorescence Spectrometer. The UV-Vis absorption spectrum was measured on a Perkin Elmer Lambda 35 UV/Vis Spectrometer. Cyclic voltammetry experiments were performed on a CHI630D electrochemical analysis system. Melting points (M.p.) were determined using a Focus X-4 apparatus (made in China) and were not corrected. The electron paramagnetic resonance (EPR) experiments were performed on a Bruker EMX-10/12 spectrophotometer at 77 K. To stabilize the ferrocenium ion, all solvents were degassed by purging argon before the addition of ferrocenium hexafluorophosphate. All solutions containing Fc^+PF_6^- were stored under argon and tested as soon as possible unless otherwise stated.

2. *Synthesis of compound 2*



Scheme S1. Synthesis of mono-deprotected pillar[6]arene (**2**).

To a solution of **1** (1.40 g, 1.0 mmol) in dry dichloromethane, BBr_3 (0.23 g, 0.085 mL, 0.90 mmol) was added in one portion under argon. The reaction was stirred at 13 °C for 8 min, and then water (50 mL) was added to quench the reaction. The organic phase was separated, washed with saturated NaHCO_3 (100 mL), brine and dried over Na_2SO_4 . After removal of the solvent under *vacuo*, the crude product was purified by silica-gel column chromatography (hexane/EtOAc = 50/1, v/v) to afford compound **2** as a sticky oil (0.490 g, 36 %). ^1H NMR (300 MHz, CDCl_3) δ (ppm): 6.85 (s, 1H, phenyl), 6.74 - 6.61 (m, 9H, phenyl), 6.48 (d, $J = 13.8$ Hz, 2H, phenyl), 3.95 - 3.54 (m, 34H, methylene), 1.79 - 1.58 (m, 20H, methylene), 1.58 - 1.13 (m, 24H, methylene), 1.02 - 0.65 (m, 33H, methyl). ^{13}C NMR (75 MHz, CDCl_3) δ (ppm): 151.56, 150.80, 150.72, 150.66, 150.63, 150.47, 148.35, 148.00, 130.39, 129.57, 128.42, 128.16, 128.01, 127.96, 127.96, 127.79, 127.56, 126.61, 124.39, 118.48, 115.72, 115.29, 115.14, 114.97, 114.91, 114.10, 113.85 (C of phenyl), 69.42, 69.13, 68.52, 68.32, 68.18 (C of $-\text{OCH}_2$), 31.99, 31.63, 31.36, 30.83, 30.24, 30.08 (C of $-\text{CH}_2-$), 19.63, 19.50, 19.39, 19.24, 14.03, 13.87 (C of methyl). HR-ESI-MS: m/z Calcd for $\text{C}_{86}\text{H}_{124}\text{O}_{12}\text{Na}$ $[\text{M}+\text{Na}]^+$: 1371.8990, found 1371.8994.

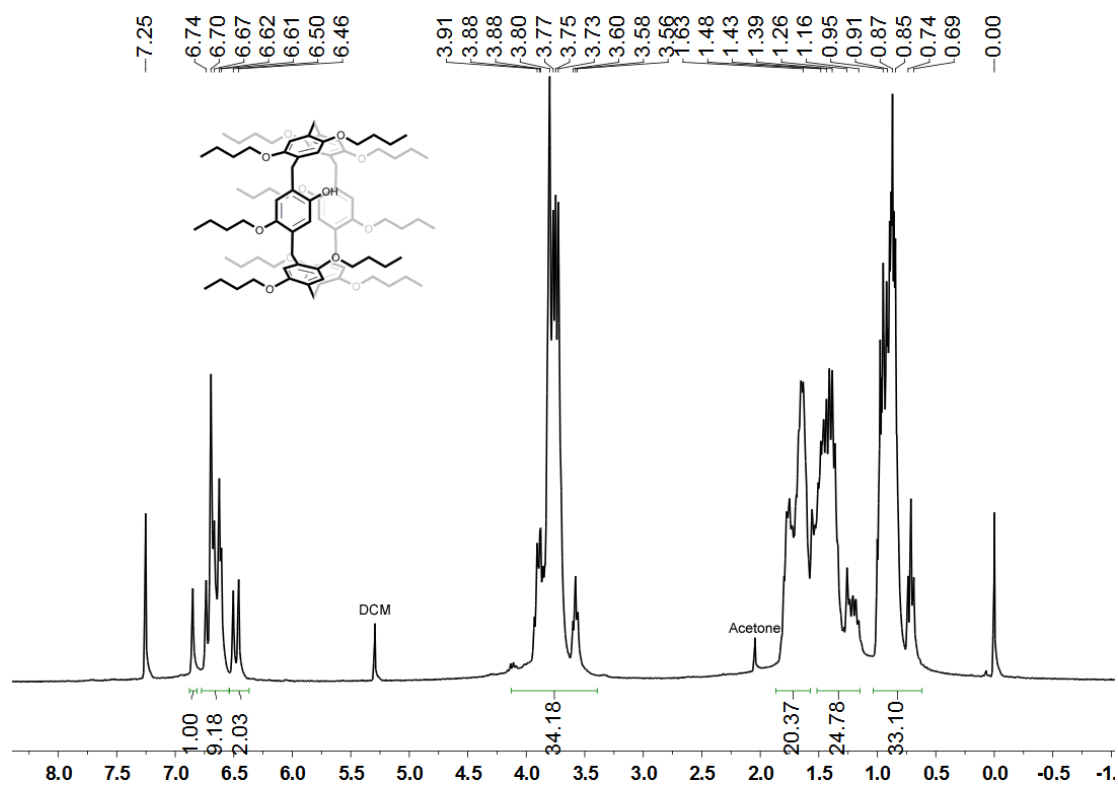


Figure S1. ¹H NMR spectrum (300 MHz, CDCl₃, 298 K) of **2**.

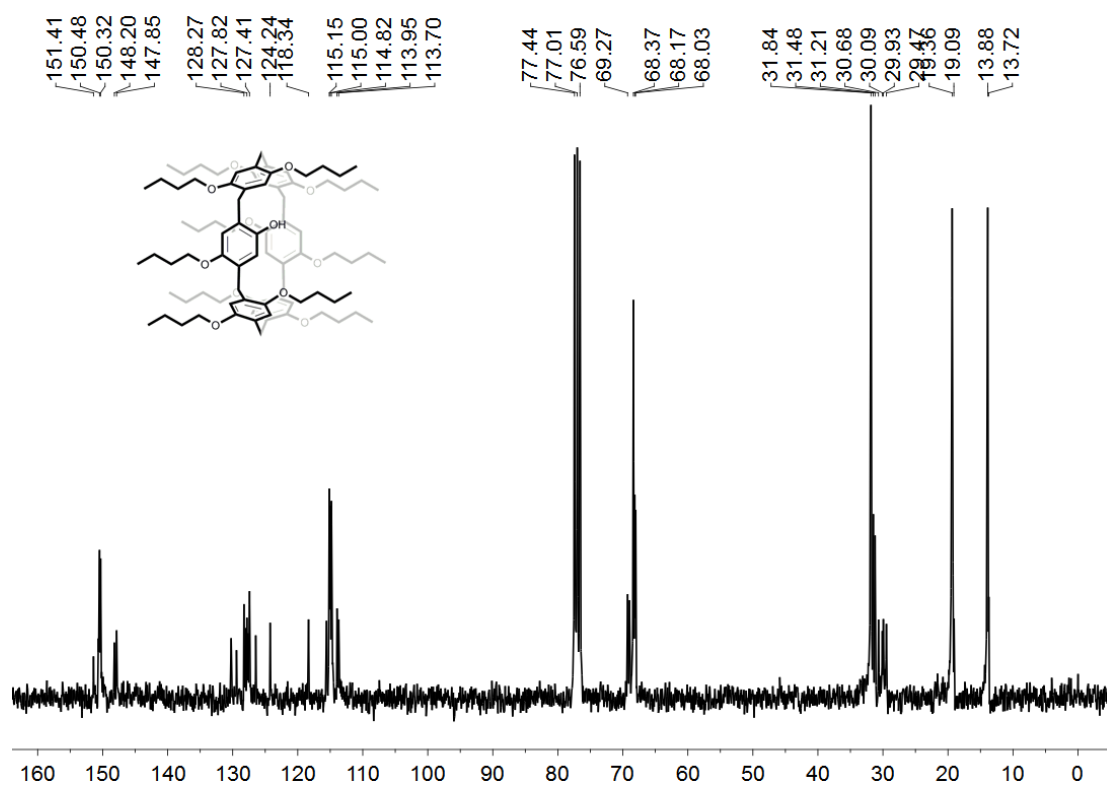
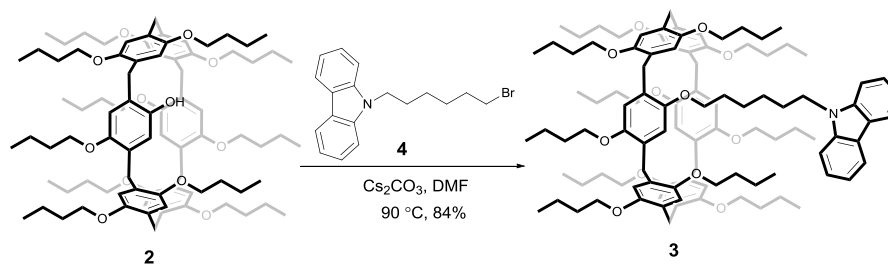


Figure S2. ¹³C NMR spectrum (75 MHz, CDCl₃, 298 K) of **2**.

3. Synthesis of compound 3



Scheme S2. Synthesis of mono-carbazole-functionalized pillar[6]arene (3).

To a solution of 9-(6-Bromohexyl)-carbazole **4** (110 mg, 0.11 mmol) and Compound **2** (150 mg, 0.33 mmol) in dry DMF (10 mL) was added Cs₂CO₃ (289 mg, 0.89 mmol) under argon. After stirring at 90 °C for 24 h, the solvent was removed under *vacuo*. Then, water (100 mL) and dichloromethane (70 mL) were added. The organic phase was separated, washed with water (100 mL), brine and dried over Na₂SO₄. After removal of the solvent under *vacuo*, the crude product was purified by silica-gel column chromatography (hexane/EtOAc = 60/1, *v/v*) to afford Compound **3** as a white solid (150 mg, 84 %). m.p. 62-64 °C. ¹H NMR (300 MHz, acetone-*d*₆) δ (ppm): 8.13 (br d, *J* = 7.7 Hz, 2H, carbazolyl), 7.48 (t, *J* = 8.1 Hz, 2H, carbazolyl), 7.42 (td, *J* = 8.1, 1.1 Hz, 2H, carbazolyl), 7.22 - 7.16 (m, 2H, carbazolyl), 6.76 - 6.67 (m, 12H, phenyl), 4.32 (t, *J* = 7.2 Hz, 2H, N-CH₂-), 3.82 - 3.65 (m, 36H, O-CH₂- and Ph-CH₂-Ph), 1.90 - 1.57 (m, 26H, methylene), 1.52 - 1.33 (m, 26H, methylene), 0.93 - 0.82 (m, 33H, methyl). ¹³C NMR (75 MHz, CDCl₃) δ (ppm): 150.82, 150.61, 150.37 (C of phenyl), 140.57 (C of carbazolyl), 128.11, 128.09, 128.03, 128.01, 127.98, 127.93, 127.90 (C of phenyl), 125.78, 123.02, 120.52, 118.92 (C of carbazolyl), 115.32, 115.19, 115.12, 114.91 (C of phenyl), 108.76 (C of carbazolyl), 68.52, 68.41, 68.36, 68.26 (C of -OCH₂-), 43.10 (C of =N-CH₂-), 32.08, 31.99, 30.98, 30.94, 30.91, 30.86, 29.89, 29.87, 29.55, 29.15, 27.38, 26.36, 19.59 (C of -CH₂-), 14.13, 14.10, 14.07 (C of methyl). HR-ESI-MS: *m/z*. Calcd for C₁₀₄H₁₄₃NO₁₂Na [M+Na]⁺: 1622.0542, found 1622.0524.

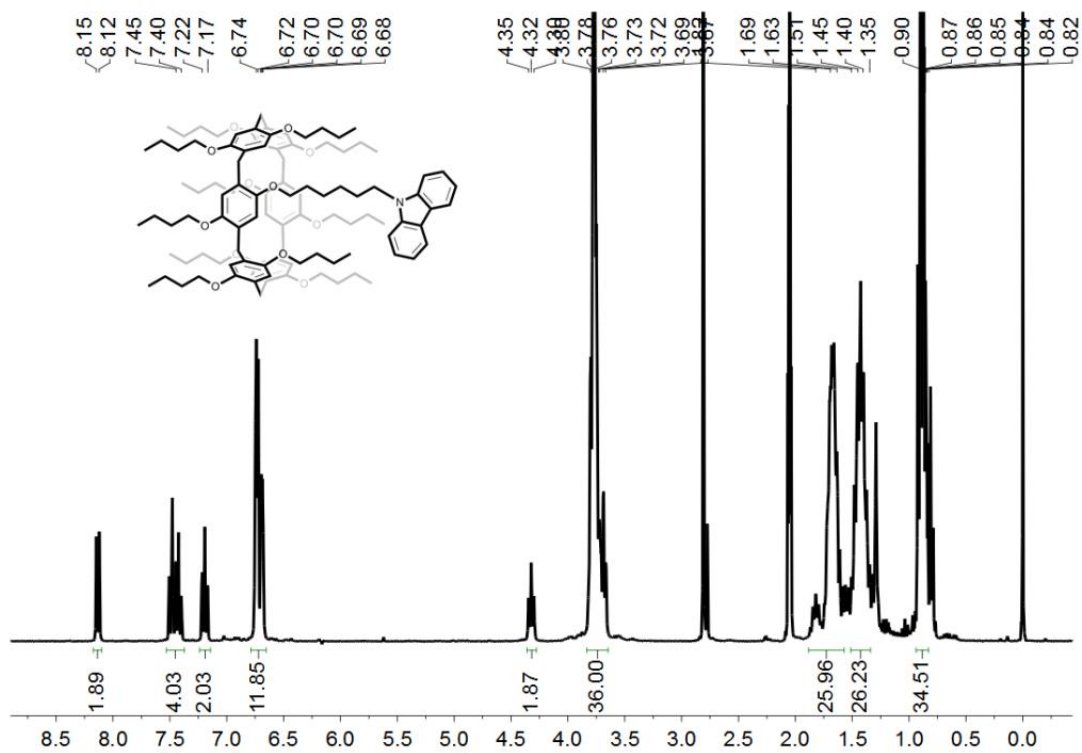


Figure S3. ¹H NMR spectrum (300 MHz, acetone-*d*₆, 298 K) of **3**.

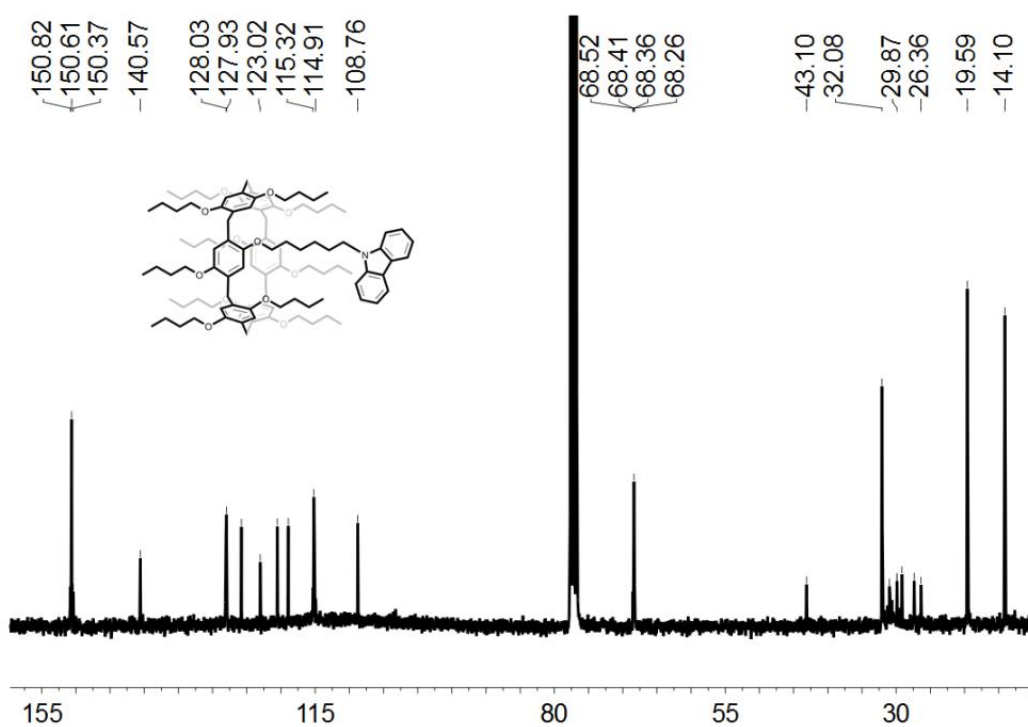


Figure S4. ¹³C NMR spectrum (75 MHz, CDCl₃, 298 K) of **3**.

4. Stoichiometry and association constant determination for the complexation between ferrocene (**Fc**) and **1**

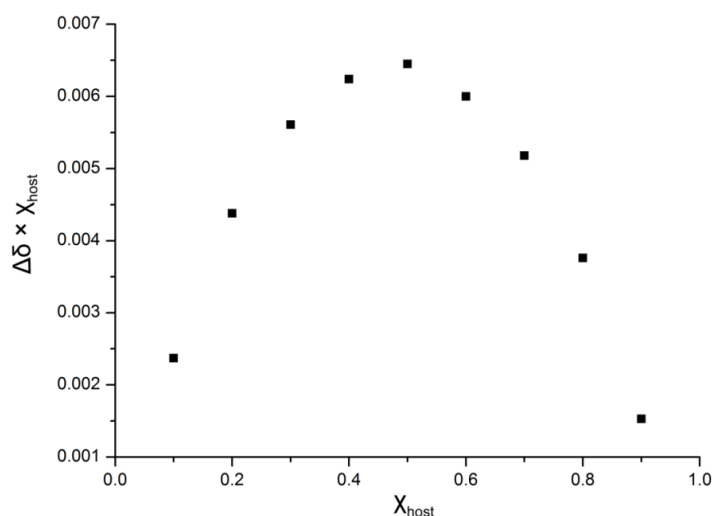


Figure S5. Job plot analysis of **1** and **Fc**.

The stoichiometry of complexation between **1** and **Fc** were determined using the method of Job plot (Figure S5). Job plot experiments were performed with a fixed total concentration ($[\text{host}] + [\text{guest}] = 10 \text{ mM}$) of the host-guest mixture in different ratios (host/guest): 10:0, 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, 1:9. And the results showing the 1:1 stoichiometry of the complexation between **1** and **Fc** in CDCl_3 by plotting the $\Delta\delta$ in chemical shift of H_A on **1** observed by ^1H NMR spectroscopy against the mole fraction of **1**.

To determine the binding constant between **Fc** and **1**, ^1H NMR titration experiments were carried out on a Bruker Advance DMX 300 spectrophotometer at 298 K with a constant concentration of **1** (4.0 mmol) and varying concentrations of **Fc** (Figure S6). The binding constant was obtained by the non-linear curve-fitting method, using the following equation:³

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

Where $\Delta\delta$ is the chemical shift change of H_A on **1**, $\Delta\delta_{\infty}$ is the chemical shift change of H_A when the host is completely complexed, $[\text{H}]_0$ is the initial concentration of **1**, and $[\text{G}]_0$ is the varying concentrations of **Fc**.

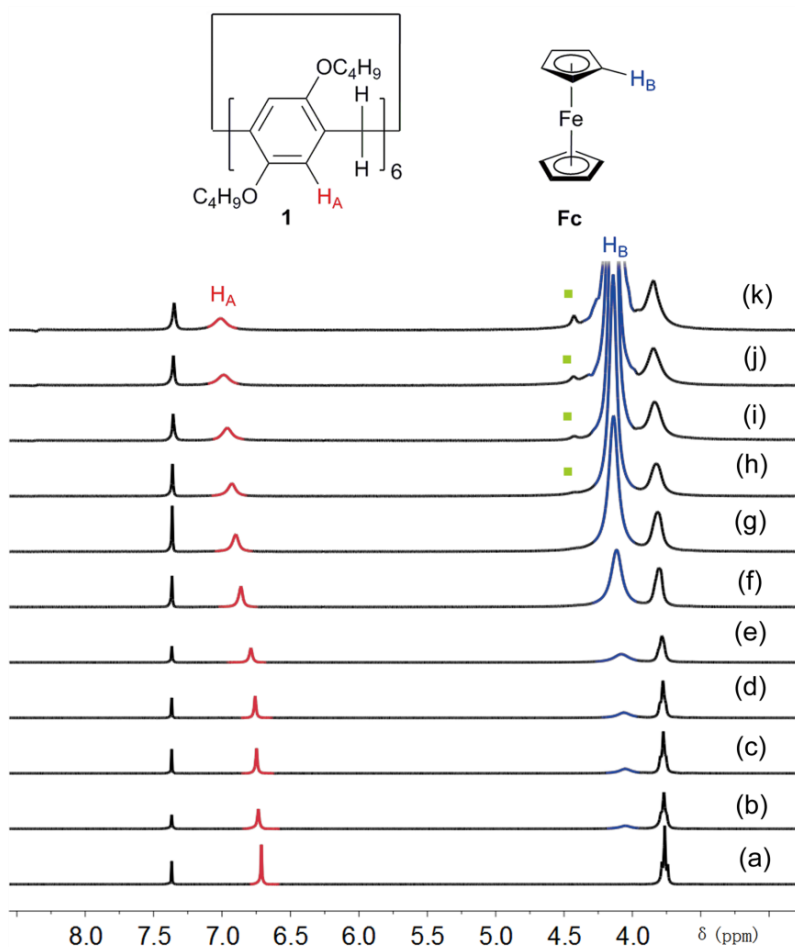


Figure S6. Partial ^1H NMR spectra ($\text{CDCl}_3/\text{CD}_3\text{CN} = 5/1$, v/v , 300 MHz, 298 K) of **1** (4.0 mM) in the presence of increasing concentrations of **Fc** (mM): (a) 0.00, (b) 4.00, (c) 6.0, (d) 8.0, (e) 16.0, (f) 40.0, (g) 60, (h) 80, (i) 120, (j) 160, (k) 240. The peaks marked with diamonds are ascribed to the spin-side-band of ferrocene.

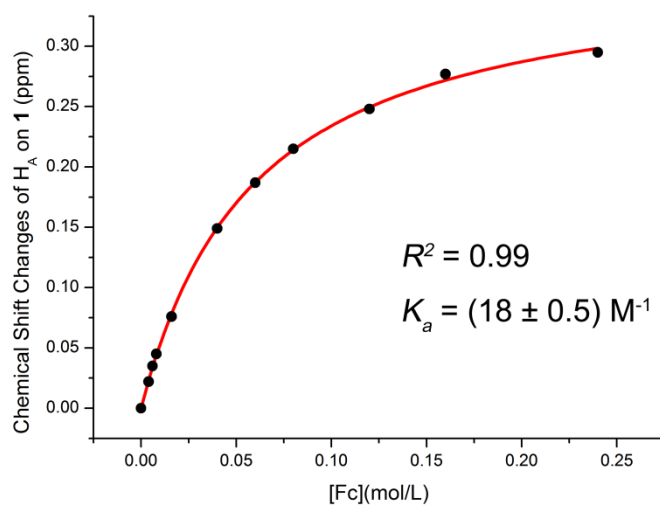


Figure S7. Fit plot for the chemical shift changes of H_A on **1** upon addition of **Fc**

5. Association constant determination for the complexation between cobaltocenium hexafluorophosphate ($\text{Cob}^+\text{PF}_6^-$) and **1**

^1H NMR titration experiments of $\text{Cob}^+\text{PF}_6^-$ with **1** were carried out on a Bruker Advance DMX 300 spectrophotometer at 298 K with a constant concentration of **1** (2.0 mM) and varying concentrations of $\text{Cob}^+\text{PF}_6^-$. The titration spectra showed that the chemical exchange of the $[\text{Cob}\subset\mathbf{1}]^+$ host-guest complex was slow on NMR time scale in a mixed solvent ($\text{CDCl}_3/\text{CD}_3\text{CN} = 5:1, v/v$), indicating the strong interaction between $\text{Cob}^+\text{PF}_6^-$ and **1**. Because the signals of the free molecules and the complexed molecules were broadened and overlapped significantly (Figure S8), an exact binding constant cannot be deduced by calculating the integrals in this mixed solvent.

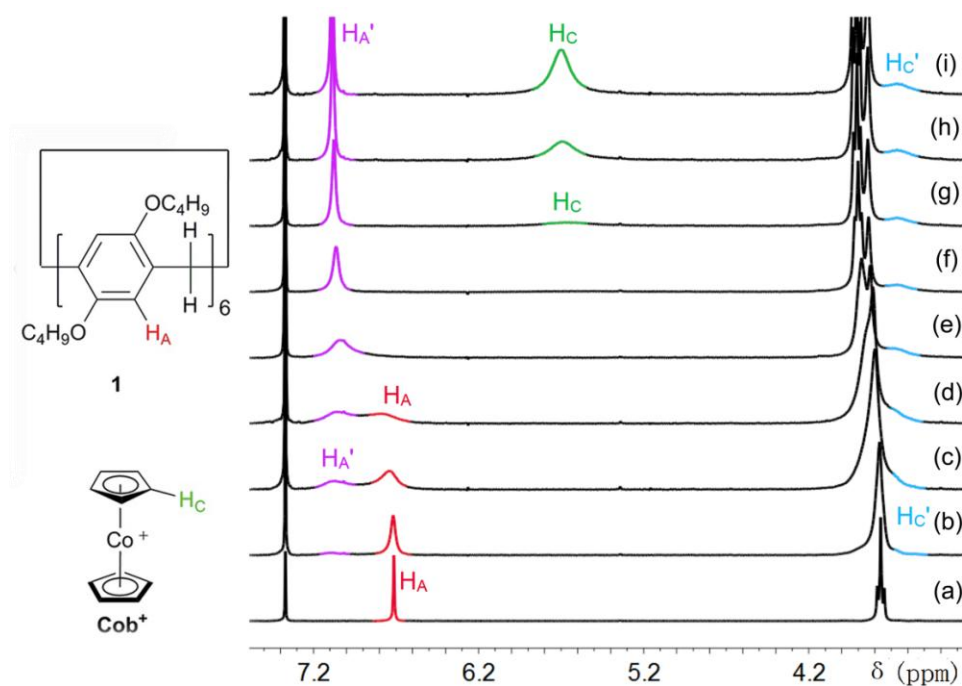


Figure S8. Partial ^1H NMR spectra (300 MHz, 298 K, $\text{CDCl}_3/\text{CD}_3\text{CN} = 5:1, v/v$) of **1** (2.0 mM) in the presence of increasing concentrations of $\text{Cob}^+\text{PF}_6^-$ (mM): (a) 0.00, (b) 0.40, (c) 1.0, (d) 1.4, (e) 2.0, (f) 3.0, (g) 4.0, (h) 6.0, (i) 8.0. H_A , H_A' , H_C , and H_C' represent for the phenyl protons on free host, the phenyl protons on complexed host, the cyclopentadienyl protons on free guest, and the cyclopentadienyl protons on complexed guest, respectively.

To avoid overlapping of the NMR signals, a mixed solvent system ($\text{CDCl}_3/\text{DMSO}-d_6 = 5:1, v/v$) was used. The chemical exchange of the $[\text{Cob}\subset\mathbf{1}]^+$

host-guest complex was also slow on NMR time scale in this mixed solvent, according to the stacked ^1H NMR titration spectra (Figure S9). A 1:1 stoichiometry of the host-guest complex could be deduced by calculating the integrals of complexed and uncomplexed species. The binding constant was obtained by the single-point method with different initial concentrations of $\text{Cob}^+\text{PF}_6^-$ (1.0 mM) and **1** (2.0 mM), using the following equation:

$$K_a = \frac{[\text{H}]_C}{[\text{H}]_F([\text{G}]_0 - [\text{H}]_C)}$$

Where $[\text{H}]_C$ is the concentration of the complexed host **1**, $[\text{H}]_F$ is the concentration of the free host **1**, $[\text{H}]_C$ and $[\text{H}]_F$ were calculated from the integral values of H_A on **1** while the total concentration of **1** is fixed, the $[\text{G}]_0$ is the concentration of the initial concentration of $\text{Cob}^+\text{PF}_6^-$. The binding constant of $\text{Cob}^+\text{PF}_6^-$ with **1** was determined to be $(3.7 \pm 1.0) \times 10^4 \text{ M}^{-1}$.

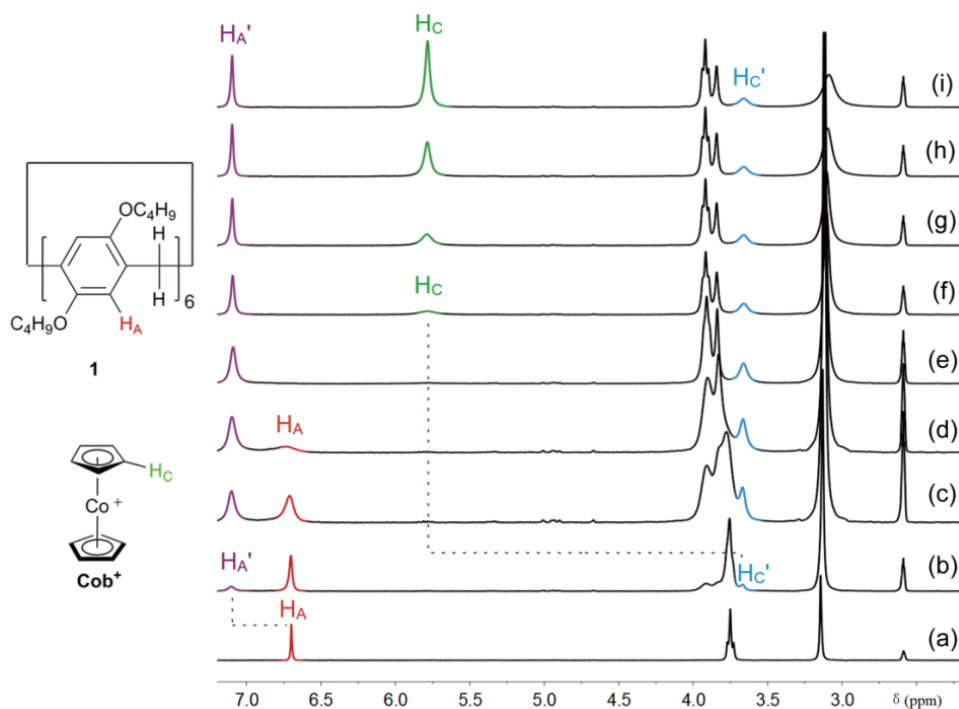


Figure S9. Partial ^1H NMR spectra (300 MHz, 298 K, $\text{CDCl}_3/\text{DMSO}-d_6 = 5:1, v/v$) of **1** (2.0 mM) in the presence of increasing concentrations of $\text{Cob}^+\text{PF}_6^-$ (mM): (a) 0.00, (b) 0.40, (c) 1.0, (d) 1.4, (e) 2.0, (f) 3.0, (g) 4.0, (h) 6.0, (i) 8.0. H_A , $\text{H}_{A'}$, H_C , and $\text{H}_{C'}$ represent for the phenyl protons on free host, the phenyl protons on complexed host, the cyclopentadienyl protons on free guest, and the cyclopentadienyl protons on complexed guest, respectively.

6. Fluorescent titration experiments of **3** with $\text{Cob}^+\text{PF}_6^-$ and Fc^+PF_6^- , respectively

The fluorescent titration experiments were carried out by measuring the emission intensity of carbazole group at 350 nm upon excitation at 330 nm. Fluorescent emission of carbazole group can be quenched by Fc^+ or Cob^+ . The binding constants were determined according to the reported method.⁴ The stoichiometry of the complexes were determined using the Job plot method based on the changes of fluorescent intensities according to the literature.⁵

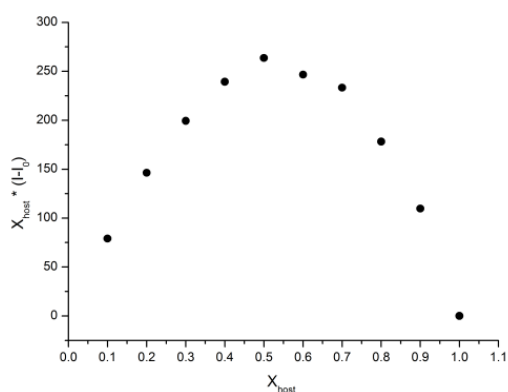


Figure S10. Job plot of **3** and $\text{Cob}^+\text{PF}_6^-$.

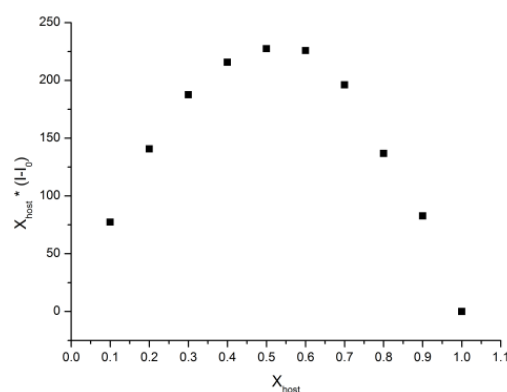


Figure S11. Job plot of **3** and Fc^+PF_6^- .

The titration experiments were performed with a constant concentration of **3** (2×10^{-5} M) and varying concentrations of ferrocenium or cobaltocenium in $\text{CHCl}_3/\text{CH}_3\text{CN}$ (5/1, v/v). Binding constants were determined by plotting changes in ratios (I/I_0) of the emission intensity at 350 nm versus the concentration of guest based on the following equation:

$$\frac{I}{I_0} = \frac{1 + aK_a C_{\text{guest}}}{1 + K_a C_{\text{guest}}}$$

Where I is the intensity of fluorescent emission at 350nm, I_0 is the fluorescent intensity of free host, “ a ” is a constant, K_a is the binding constant, and C_{guest} is the total concentration of guest.

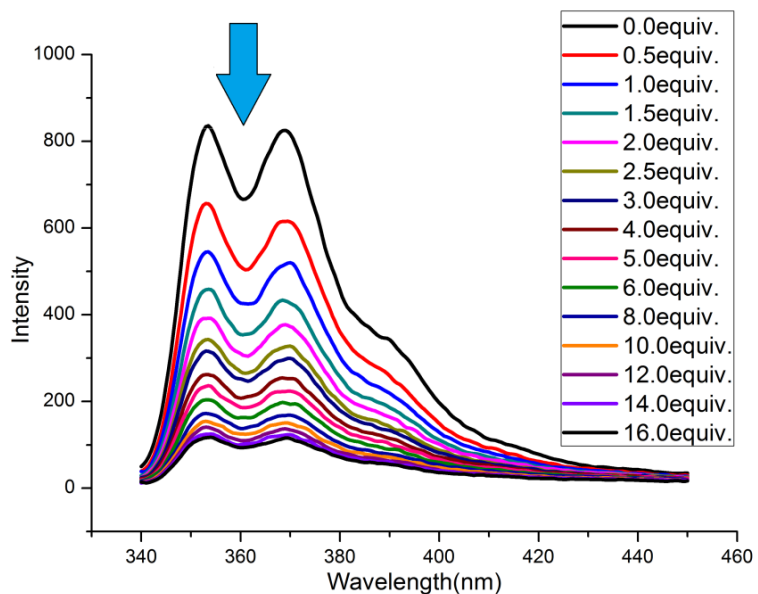


Figure S12. Fluorescent titrations of **3** (2.0×10^{-5} M) with various equivalence of $\text{Cob}^+\text{PF}_6^-$ ($\text{CHCl}_3/\text{CH}_3\text{CN} = 5/1$, v/v)

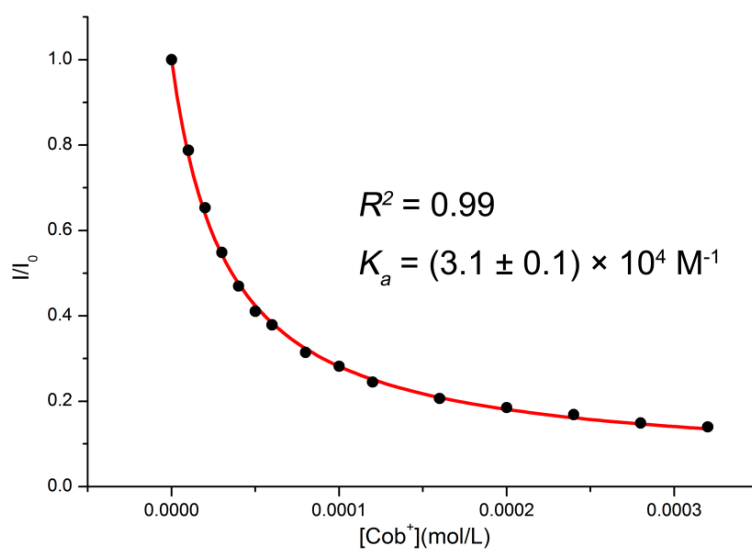


Figure S13. Fit plot for the ratio changes of the fluorescent intensities at 350 nm of **3** upon addition of $\text{Cob}^+\text{PF}_6^-$

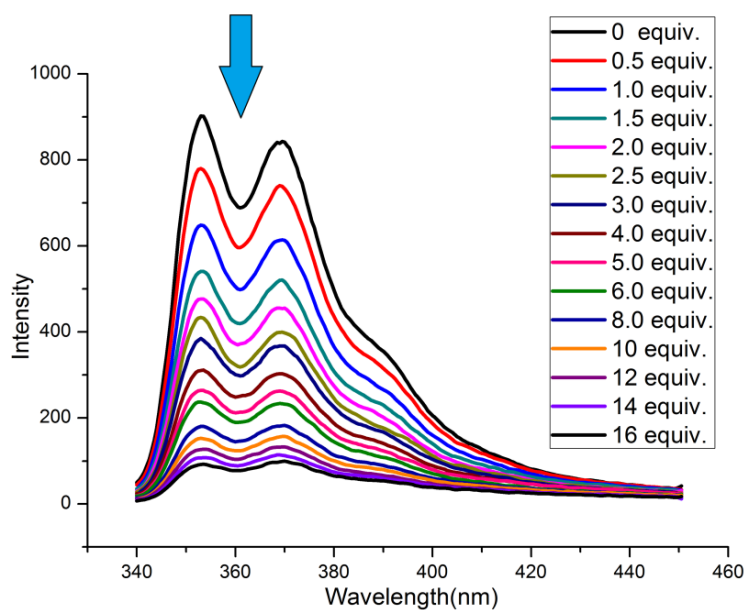


Figure S14. Fluorescent titrations of **3** (2.0×10^{-5} M) with various equivalence of Fc^+PF_6^- ($\text{CHCl}_3/\text{CH}_3\text{CN} = 5/1$, v/v)

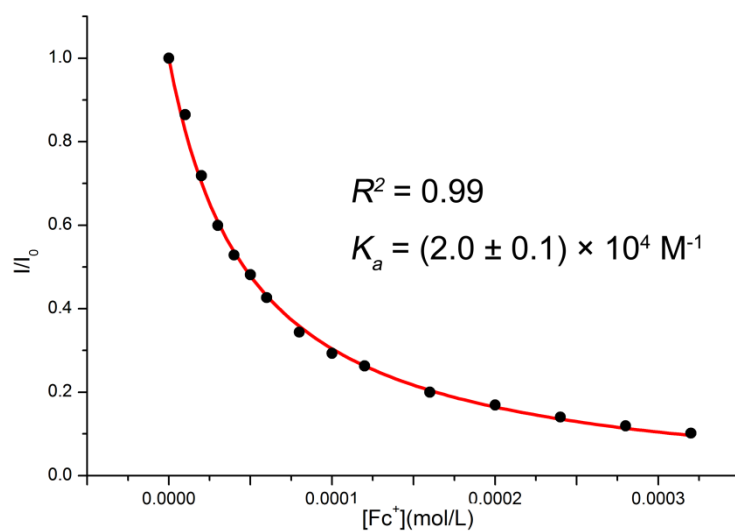


Figure S15. Fit plot for the ratio changes of the fluorescent intensities at 350 nm of **3** upon addition of Fc^+PF_6^-

7. 2D NOESY analysis of $\text{Cob}^+\text{PF}_6^-$ with **1**

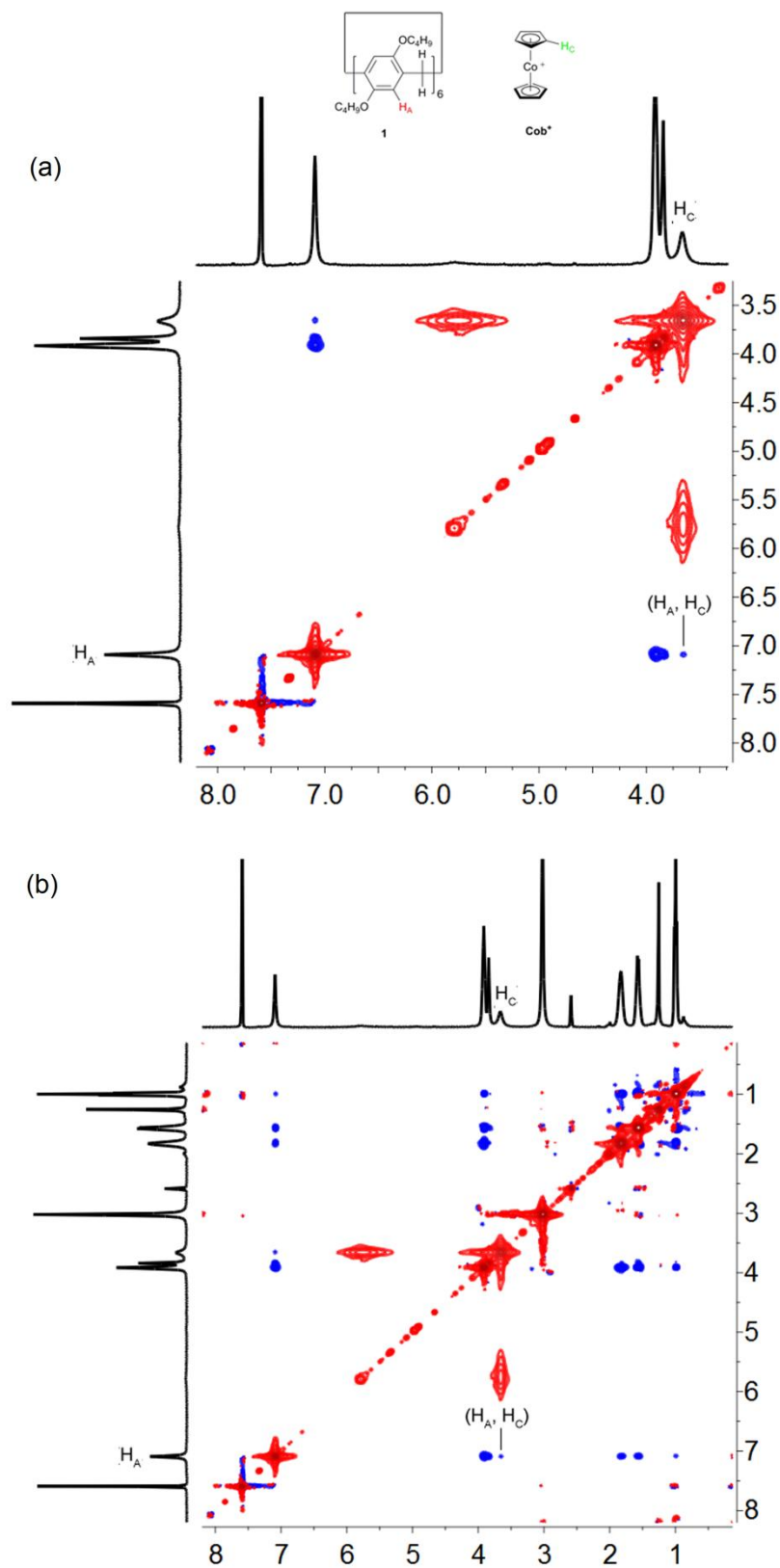


Figure S16. (a) Partial 2D NOESY (400 MHz, 298 K) spectrum of **1** with $\text{Cob}^+\text{PF}_6^-$ in $\text{CDCl}_3/\text{DMSO}-d_6$ (5/1, v/v). (b) Full 2D NOESY spectrum.

8. Cyclic voltammetry analysis of **Fc** with **1**

The cyclic voltammetry analysis were carried out in a mixed solution of chloroform and acetonitrile ($\text{CHCl}_3/\text{CH}_3\text{CN} = 5/1$, v/v) containing 0.1 M tetrabutylammonium perchlorate. A glassy carbon electrode (0.07 cm^2) was used as the working electrode; a platinum gauze electrode ($0.2 \text{ mm} \times 0.5 \text{ mm}$) was used as the counter electrode. The reference electrode used in the experiments was an Ag/Ag^+ reference electrode filled with 0.01 M AgNO_3 in acetonitrile. All solutions were purged with argon before test. The concentration of **Fc** was set to 0.5 mM in all cyclic voltammetry experiments, with increasing concentrations of **1**.

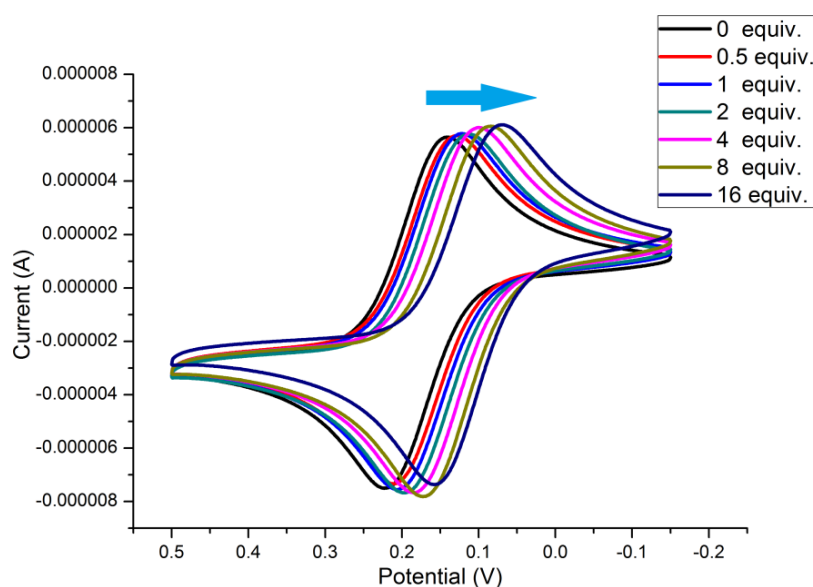


Figure S17. Stacked cyclic voltammograms of a fixed concentration of **Fc** (0.5 mM) in mixed solutions ($\text{CHCl}_3/\text{CH}_3\text{CN} = 5/1$, v/v , containing 0.1 M TBAClO_4) with increasing concentrations of **1**. From left to right: 0.0, 0.5, 1.0, 2.0, 4.0, 8.0, and 16.0 equiv.. Scan rate = 50 mV/s.

9. Stability test of Fc^+PF_6^-

The stabilities of Fc^+PF_6^- in the absence (a) and presence (b) of **1** were tested in $\text{CHCl}_3/\text{CH}_3\text{CN}$ (5/1, v/v). The solution was prepared under argon and then exposed to the air. The photos listed below showed that pillar[6]arene derivative **1** could significantly improve the stability of Fc^+PF_6^- , as a result of the formation of the inclusion complex $[\text{Fc}\subset\mathbf{1}]^+$.

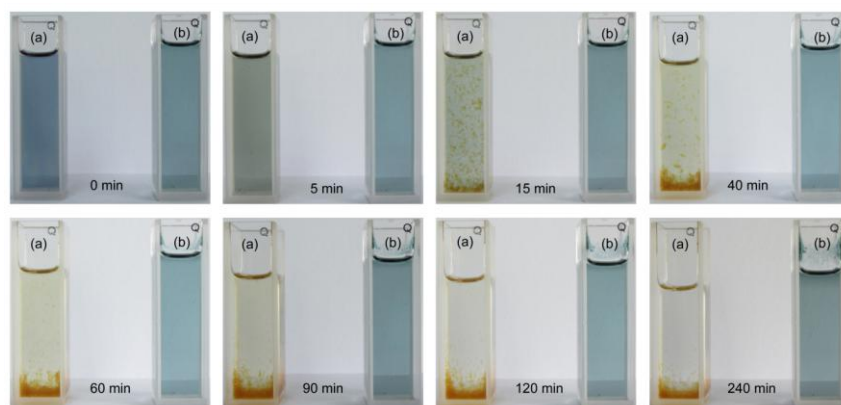


Figure S18. Stability test of Fc^+ in the absence (a) and presence (b) of **1** in $\text{CHCl}_3/\text{CH}_3\text{CN}$ (5/1, v/v). An excess amount of **1** (6.0 equiv.) was used in this test. (The volume of the solution gradually decreased due to the evaporation)

10. Quantitative stability test of Fc^+PF_6^-

A quantitative study about stabilities of Fc^+PF_6^- (4.0 mM) in the absence (a) and presence (b) of **1** (24 mM) were tested in $\text{CHCl}_3/\text{CH}_3\text{CN}$ (5/1, v/v) by using the UV-Vis spectra. The solvent was purged with argon for 30 min to remove the dissolved oxygen before use. The sample was prepared under argon atmosphere and sealed carefully. Oxygen (1 mL, gas) were added using a syringe to ensure a fixed total amount of O_2 . The stability is monitored by plotting A/A_0 versus time. Here A is the absorption of Fc^+PF_6^- at 618 nm, A_0 is the absorption of Fc^+PF_6^- at 618 nm before adding oxygen, A/A_0 represents the remaining amount of Fc^+PF_6^- , time refers to the pasting time after the injecting of oxygen.

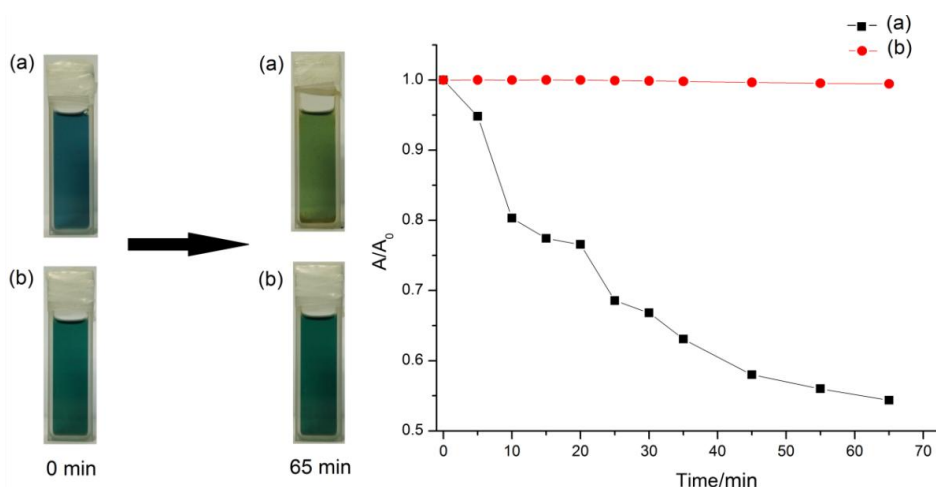


Figure S19. Stability test of Fc^+ in the absence (a) and presence (b) of **1** in $\text{CHCl}_3/\text{CH}_3\text{CN}$ (5/1, v/v). An excess amount of **1** (6.0 equiv.) was used in this test.

11. LR-ESI-MS of host-guest complexes of **1** with Fc^+ and Cob^+

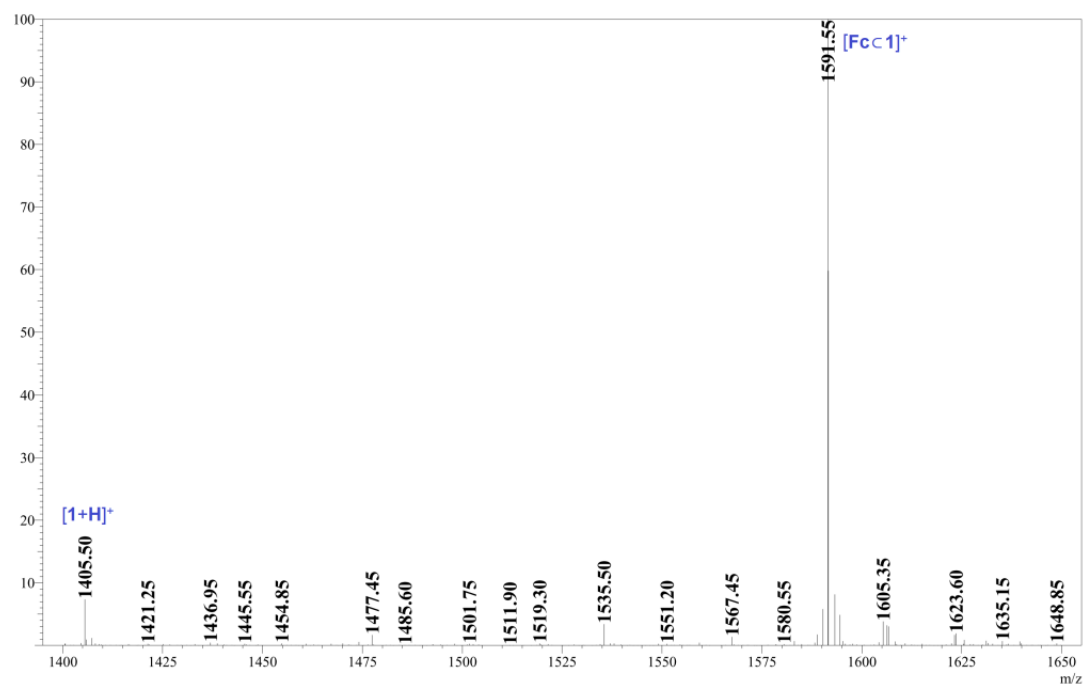


Figure S20. ESI-MS of an equimolar solution of Fc^+PF_6^- and **1**

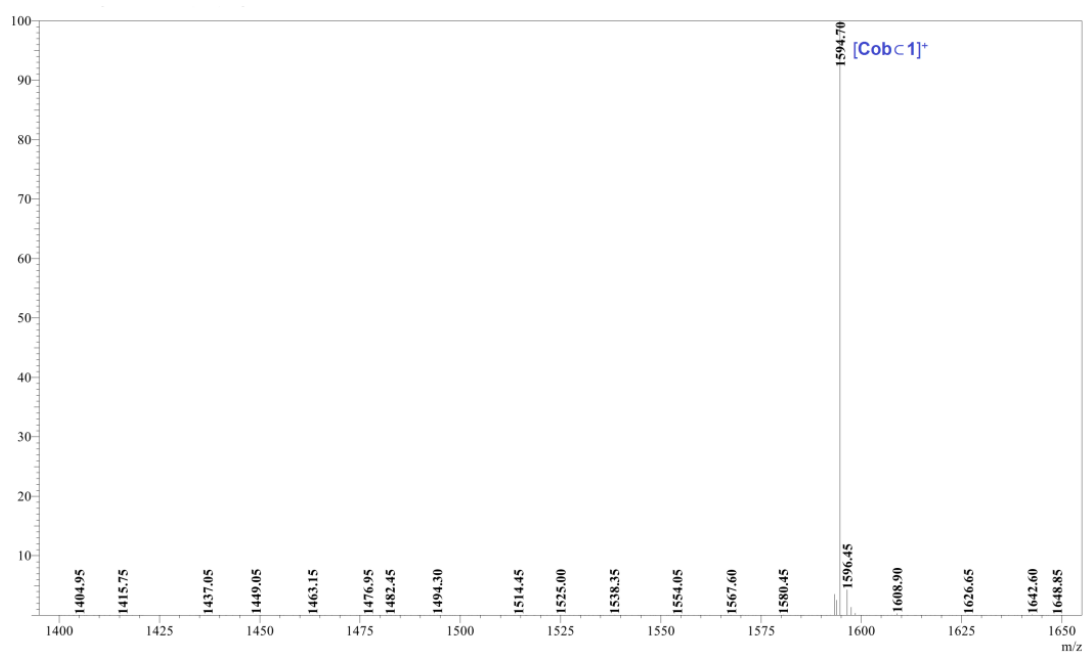


Figure S21. ESI-MS of an equimolar solution of $\text{Cob}^+\text{PF}_6^-$ and **1**

12. HR-ESI-MS of host-guest complexes of **1** with Fc^+ and Cob^+

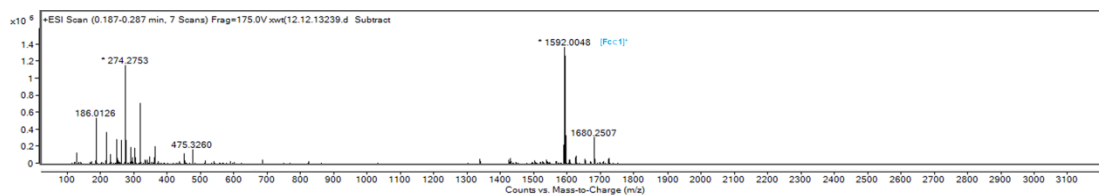


Figure S22. HR-ESI-MS of an equimolar solution of Fc^+PF_6^- and **1**

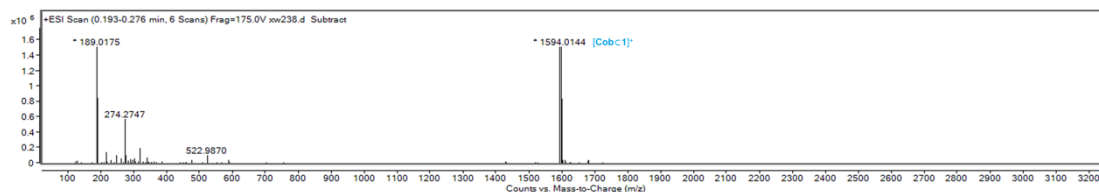


Figure S23. HR-ESI-MS of an equimolar solution of $\text{Cob}^+\text{PF}_6^-$ and **1**

13. ^1H NMR titration spectra of 1,4-dibutoxybenzene and $\text{Cob}^+\text{PF}_6^-$

The ^1H NMR titration experiments of 1,4-dibutoxybenzene and $\text{Cob}^+\text{PF}_6^-$ were performed with a constant concentration of 1,4-dibutoxybenzene and varying concentrations of $\text{Cob}^+\text{PF}_6^-$ in mixed solvents ($\text{CDCl}_3/\text{DMSO}-d_6 = 5:1, v/v$). The stacked ^1H NMR spectra suggested that $\text{Cob}^+\text{PF}_6^-$ has no obvious interactions with 1,4-dibutoxybenzene.

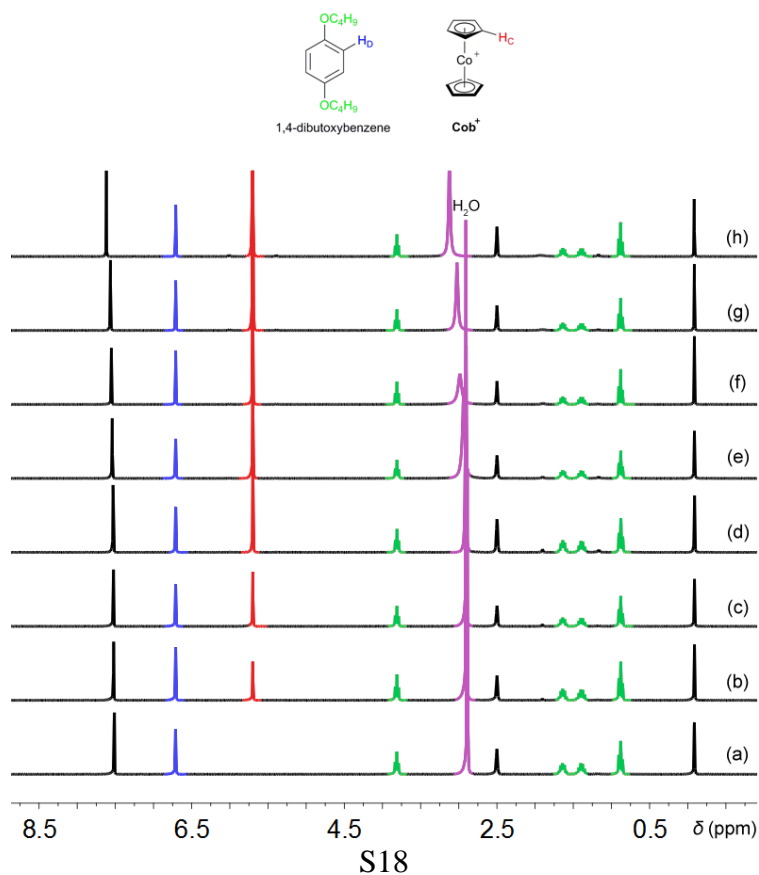


Figure S24. ^1H NMR spectra (300 MHz, $\text{CDCl}_3/\text{DMSO-}d_6 = 5:1$, v/v , 298 K) of 1,4-dibutoxybenzene (3.0 mM) in the presence of increasing amounts of $\text{Cob}^+\text{PF}_6^-$ (mM): (a) 0.0, (b) 1.5, (c) 3.0, (d) 4.5, (e) 6.0, (f) 9.0, (g) 12, (h) 24. Peaks corresponding to phenyl group, cyclopentadienyl group, butoxyl group, and water were colored with blue, red, green, and purple, respectively.

14. Optimized structure of **1** with Cob^+

Using the density functional theory (DFT) method, the inclusion structure $[\text{Cob}\text{C}1]^+$ were optimized. The geometry optimizations were carried out in gas phase, at the B3LYP/6-31G level by employing the Gaussian09 program.⁶ Figure S25 shows the geometry of the optimized structure, while Table 1 shows the coordinates of $[\text{Cob}\text{C}1]^+$.

Table S1. coordinates of the optimized structure of $[\text{Cob}\text{C}1]^+$

| No. | X | Y | Z | No. | X | Y | Z |
|-----|-----------|-----------|-----------|------|-----------|-----------|-----------|
| C1 | -0.522288 | -3.727917 | 3.495162 | H129 | -5.197775 | 4.685828 | -1.118467 |
| C2 | -0.388966 | -2.646632 | 4.373629 | H130 | -5.61242 | 0.494818 | -4.377972 |
| C3 | 0.867399 | -2.099333 | 4.667404 | H131 | -5.068878 | -4.059215 | -2.367023 |
| C4 | 1.99802 | -2.657767 | 4.040694 | H132 | -4.233254 | 3.989667 | 3.993957 |
| C5 | 1.865934 | -3.75436 | 3.177695 | C133 | 1.699634 | 0.218616 | 0.903799 |
| C6 | 0.608849 | -4.312879 | 2.897286 | C134 | 1.683703 | -1.129078 | 0.405657 |
| H7 | -1.254268 | -2.205874 | 4.85165 | C135 | 1.455344 | -1.076188 | -1.0114 |
| H8 | 2.732572 | -4.205183 | 2.710669 | C136 | 1.328122 | 0.303738 | -1.389939 |
| C9 | 1.002008 | -0.961321 | 5.667297 | C137 | 1.479398 | 1.104569 | -0.206354 |
| H10 | 1.973857 | -1.047164 | 6.160029 | H138 | 1.828689 | 0.510894 | 1.935205 |
| H11 | 0.226242 | -1.078834 | 6.429626 | H139 | 1.795487 | -2.025148 | 0.996792 |
| C12 | 0.883218 | 0.435623 | 5.076616 | H140 | 1.372353 | -1.925133 | -1.672649 |
| C13 | 2.02801 | 1.150917 | 4.690788 | H141 | 1.133417 | 0.670183 | -2.386251 |
| C14 | -0.365604 | 1.070408 | 4.947424 | H142 | 1.414901 | 2.180975 | -0.156051 |
| C15 | 1.938326 | 2.468853 | 4.221402 | C143 | -1.579097 | -0.185184 | 1.481301 |
| H16 | 2.986221 | 0.655126 | 4.783166 | C144 | -1.759862 | 0.923829 | 0.585296 |
| C17 | -0.454896 | 2.390934 | 4.493071 | C145 | -1.656592 | -1.39487 | 0.710751 |
| C18 | 0.690165 | 3.115925 | 4.138785 | H146 | -1.399991 | -0.124471 | 2.544194 |
| H19 | -1.412169 | 2.88936 | 4.406661 | C147 | -1.951723 | 0.398367 | -0.739183 |
| C20 | 0.480733 | -5.535183 | 2.000618 | H148 | -1.729156 | 1.968231 | 0.855845 |
| H21 | 1.397484 | -6.124869 | 2.08336 | C149 | -1.887727 | -1.035266 | -0.660659 |
| H22 | -0.349011 | -6.147073 | 2.36546 | H150 | -1.541581 | -2.397752 | 1.092993 |
| C23 | 0.240424 | -5.219716 | 0.532123 | H151 | -2.088032 | 0.97788 | -1.639856 |
| C24 | 1.316111 | -5.060054 | -0.361696 | H152 | -1.971434 | -1.722226 | -1.489314 |

| | | | | | | | |
|-----|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| C25 | -1.062505 | -5.105147 | 0.025523 | Co15 3 | -0.118594 | -0.191302 | 0.008652 |
| C26 | 1.084169 | -4.827629 | -1.723375 | H154 | 3.263478 | 1.992905 | -6.921395 |
| C27 | -1.293509 | -4.847979 | -1.331415 | H155 | 3.805996 | -4.306066 | -5.346711 |
| H28 | -1.885217 | -5.225017 | 0.718895 | H156 | 5.484056 | -1.916229 | 5.656206 |
| C29 | -0.219166 | -4.724237 | -2.232237 | H157 | 3.874592 | 6.753425 | -2.262076 |
| H30 | 1.906421 | -4.725715 | -2.419934 | H158 | -3.858288 | -0.819212 | 5.473929 |
| C31 | -0.46233 | -4.525622 | -3.720654 | H159 | -4.270325 | -4.717031 | 2.500583 |
| H32 | -1.377808 | -5.056674 | -3.995521 | C160 | -5.067369 | 0.609245 | 6.578011 |
| H33 | 0.367846 | -4.978023 | -4.270338 | H161 | -4.911807 | 1.413044 | 7.311658 |
| C34 | 0.578373 | 4.568668 | 3.703516 | H162 | -5.512067 | 1.082812 | 5.690007 |
| H35 | 1.514677 | 5.077392 | 3.945519 | C163 | -5.711061 | 5.459577 | 3.376561 |
| H36 | -0.22248 | 5.042737 | 4.278004 | H164 | -5.723199 | 6.49059 | 2.995041 |
| C37 | 0.2877 | 4.760559 | 2.223843 | H165 | -6.160498 | 4.834056 | 2.590931 |
| C38 | -1.032534 | 4.832559 | 1.740681 | C166 | -6.790396 | 4.58922 | -2.595345 |
| C39 | 1.336836 | 4.904028 | 1.30464 | H167 | -6.910285 | 4.756709 | -3.675335 |
| C40 | -1.283813 | 5.070023 | 0.383346 | H168 | -7.035516 | 3.5315 | -2.417427 |
| C41 | 1.085809 | 5.137924 | -0.053535 | C169 | -6.981634 | -1.081596 | -4.9853 |
| H42 | 2.350045 | 4.840988 | 1.681901 | H170 | -6.979489 | -1.942999 | -5.668669 |
| C43 | -0.235037 | 5.23823 | -0.531553 | H171 | -7.123515 | -1.49026 | -3.973563 |
| H44 | -2.296933 | 5.14091 | 0.007375 | C172 | -6.245139 | -5.53325 | -1.28584 |
| C45 | -0.596076 | -3.075075 | -4.15985 | H173 | -6.122728 | -6.562067 | -0.918064 |
| C46 | 0.534628 | -2.318137 | -4.518795 | H174 | -6.408316 | -4.904546 | -0.397781 |
| C47 | -1.855801 | -2.464377 | -4.255815 | C175 | -5.343949 | -4.694314 | 4.389918 |
| C48 | 0.397465 | -1.00824 | -4.993011 | H176 | -5.129626 | -4.886599 | 5.450902 |
| C49 | -1.992214 | -1.146099 | -4.71158 | H177 | -5.653281 | -3.640462 | 4.322903 |
| H50 | -2.721964 | -3.049401 | -3.973604 | H178 | 4.269231 | -3.549772 | -3.821687 |
| C51 | -0.862888 | -0.404831 | -5.107488 | H179 | 3.846444 | 1.06417 | -5.539689 |
| H52 | 1.260894 | -0.427254 | -5.290463 | H180 | 4.258379 | 5.045942 | -2.479219 |
| C53 | -0.524196 | 5.552888 | -1.990468 | H181 | 5.255633 | 4.009542 | 2.647286 |
| H54 | -1.457416 | 6.118753 | -2.047576 | H182 | 5.594306 | -0.939683 | 4.191535 |
| H55 | 0.280057 | 6.18652 | -2.374535 | H183 | 5.10067 | -4.78443 | 0.877242 |
| C56 | -1.00142 | 0.996917 | -5.681202 | C184 | 5.40063 | -2.838579 | -5.535719 |
| H57 | -1.979168 | 1.078395 | -6.162501 | H185 | 5.677537 | -1.873864 | -5.084861 |
| H58 | -0.234363 | 1.133703 | -6.448939 | H186 | 5.224449 | -2.642149 | -6.602968 |
| C59 | -0.645849 | 4.329554 | -2.88527 | C187 | 6.566781 | -3.828061 | -5.383953 |
| C60 | 0.489074 | 3.776188 | -3.493016 | H188 | 7.478456 | -3.441945 | -5.852386 |
| C61 | -1.896545 | 3.739343 | -3.150559 | H189 | 6.78827 | -4.018749 | -4.326249 |
| C62 | 0.386529 | 2.685256 | -4.364095 | H190 | 6.330439 | -4.790132 | -5.854187 |
| H63 | 1.448259 | 4.226103 | -3.270332 | C191 | 6.250149 | -5.79796 | -0.664754 |
| C64 | -2.000518 | 2.656018 | -4.033742 | H192 | 6.432816 | -4.895762 | -1.267594 |
| C65 | -0.867106 | 2.120904 | -4.665337 | H193 | 6.106492 | -6.622125 | -1.378159 |
| H66 | -2.96233 | 2.215874 | -4.266921 | C194 | 7.481041 | -6.087868 | 0.208588 |

| | | | | | | | |
|------|-----------|-----------|-----------|------|-----------|-----------|-----------|
| O67 | -2.580068 | -4.705766 | -1.873413 | H195 | 8.380107 | -6.216661 | -0.403624 |
| O68 | 2.601077 | -5.159062 | 0.189962 | H196 | 7.669317 | -5.267167 | 0.912119 |
| O69 | -3.229442 | -0.497149 | -4.81876 | H197 | 7.341059 | -7.004277 | 0.794429 |
| O70 | 1.779801 | -2.950889 | -4.377303 | C198 | 6.991596 | -2.604515 | 4.247516 |
| O71 | 1.502741 | 2.100858 | -4.984587 | H199 | 7.115454 | -2.676756 | 3.156604 |
| O72 | -3.001251 | 4.307358 | -2.502387 | H200 | 7.015067 | -3.634884 | 4.630318 |
| O73 | 2.106328 | 5.298245 | -1.001944 | C201 | 8.164966 | -1.811205 | 4.844117 |
| O74 | -2.056232 | 4.66541 | 2.686575 | H202 | 9.124514 | -2.282039 | 4.604689 |
| O75 | 3.052897 | 3.219623 | 3.827862 | H203 | 8.188031 | -0.786017 | 4.453857 |
| O76 | -1.498048 | 0.311877 | 5.29176 | H204 | 8.084976 | -1.751044 | 5.936195 |
| O77 | 3.230179 | -2.065259 | 4.344708 | C205 | 6.845715 | 3.390783 | 3.994802 |
| O78 | -1.767626 | -4.28415 | 3.158349 | H206 | 7.070406 | 2.450294 | 3.469777 |
| C79 | 4.392533 | 2.71898 | 4.130046 | H207 | 6.96914 | 3.183024 | 5.067383 |
| H80 | 4.572613 | 1.787179 | 3.575097 | C208 | 7.852029 | 4.469845 | 3.564669 |
| H81 | 4.465584 | 2.49963 | 5.203745 | H209 | 8.881284 | 4.157031 | 3.771024 |
| C82 | -2.744642 | 1.011961 | 5.612837 | H210 | 7.773736 | 4.677512 | 2.490183 |
| H83 | -3.161977 | 1.460098 | 4.700442 | H211 | 7.674422 | 5.410177 | 4.100306 |
| H84 | -2.531561 | 1.818844 | 6.32609 | C212 | 5.786604 | 6.161923 | -1.409881 |
| C85 | 3.473973 | 5.537039 | -0.541169 | H213 | 6.214632 | 5.288581 | -0.895671 |
| H86 | 3.858403 | 4.636923 | -0.040952 | H214 | 5.835779 | 6.996081 | -0.695399 |
| H87 | 3.474057 | 6.361058 | 0.184682 | C215 | 6.63763 | 6.496787 | -2.645217 |
| C88 | -3.412678 | 5.094448 | 2.343837 | H216 | 7.678816 | 6.694011 | -2.368143 |
| H89 | -3.822815 | 4.437379 | 1.563825 | H217 | 6.633113 | 5.668135 | -3.364404 |
| H90 | -3.379651 | 6.118136 | 1.947972 | H218 | 6.253402 | 7.386493 | -3.158372 |
| C91 | 2.763982 | 2.842886 | -5.015284 | C219 | 5.094483 | 2.771133 | -6.041433 |
| H92 | 3.172507 | 2.918945 | -3.997872 | H220 | 5.532551 | 2.883909 | -5.038426 |
| H93 | 2.577488 | 3.858762 | -5.387971 | H221 | 4.962431 | 3.788236 | -6.437309 |
| C94 | -4.347881 | 3.959569 | -2.952222 | C222 | 6.069505 | 1.995155 | -6.941059 |
| H95 | -4.544879 | 2.898042 | -2.744631 | H223 | 6.249146 | 0.98558 | -6.550497 |
| H96 | -4.421399 | 4.117362 | -4.036584 | H224 | 5.671592 | 1.893835 | -7.957926 |
| C97 | 2.949472 | -2.363893 | -5.031372 | H225 | 7.03678 | 2.504439 | -7.009761 |
| H98 | 3.195763 | -1.404988 | -4.554002 | H226 | -5.066884 | 5.90052 | -2.390261 |
| H99 | 2.716699 | -2.172766 | -6.087332 | H227 | -5.465206 | 0.034807 | -6.074057 |
| C100 | -4.457142 | -1.283741 | -4.715059 | H228 | -4.776351 | -5.721646 | -2.879073 |
| H101 | -4.559164 | -1.675915 | -3.692988 | H229 | -3.734037 | -5.951276 | 3.641062 |
| H102 | -4.403138 | -2.135748 | -5.406016 | H230 | -3.244736 | -0.463179 | 7.089074 |
| C103 | 3.74817 | -5.318291 | -0.702858 | H231 | -3.790778 | 5.652467 | 4.3808 |
| H104 | 3.893209 | -4.397218 | -1.285061 | C232 | -7.779946 | 5.479998 | -1.827627 |
| H105 | 3.552266 | -6.140875 | -1.40355 | H233 | -8.81329 | 5.274439 | -2.127155 |
| C106 | -3.732811 | -5.154848 | -1.092273 | H234 | -7.704953 | 5.313003 | -0.745838 |
| H107 | -3.860858 | -4.504313 | -0.215578 | H235 | -7.58185 | 6.54205 | -2.016047 |
| H108 | -3.554524 | -6.178746 | -0.737926 | C236 | -6.567217 | 5.375854 | 4.650091 |
| C109 | 4.463967 | -2.751275 | 3.96426 | H237 | -7.596723 | 5.69638 | 4.457455 |

| | | | | | | | |
|------|-----------|-----------|-----------|------|-----------|-----------|-----------|
| H110 | 4.543718 | -2.787244 | 2.868432 | H238 | -6.602444 | 4.34943 | 5.036113 |
| H111 | 4.438297 | -3.782407 | 4.341491 | H239 | -6.159754 | 6.016402 | 5.441475 |
| C112 | -2.922953 | -3.999506 | 4.011789 | C240 | -6.049202 | -0.424253 | 7.152546 |
| H113 | -3.2029 | -2.941474 | 3.911782 | H241 | -7.006756 | 0.039885 | 7.411982 |
| H114 | -2.653422 | -4.186472 | 5.059583 | H242 | -6.249561 | -1.223952 | 6.428389 |
| C115 | 4.099761 | -3.352654 | -4.889361 | H243 | -5.645638 | -0.888847 | 8.060219 |
| C116 | 5.386024 | 3.79788 | 3.717491 | C244 | -6.499905 | -5.596789 | 3.930221 |
| C117 | 4.314337 | 5.879286 | -1.765228 | H245 | -7.399759 | -5.425249 | 4.530645 |
| C118 | 3.719917 | 2.08454 | -5.927574 | H246 | -6.756103 | -5.406852 | 2.88033 |
| C119 | 5.624495 | -1.971069 | 4.569094 | H247 | -6.233279 | -6.656513 | 4.022415 |
| C120 | 4.96579 | -5.610351 | 0.165096 | C248 | -7.479617 | -5.460655 | -2.19858 |
| C121 | -5.325498 | 4.85156 | -2.197129 | H249 | -8.383437 | -5.782199 | -1.670013 |
| C122 | -5.620628 | -0.363902 | -5.063427 | H250 | -7.646791 | -4.437009 | -2.556617 |
| C123 | -4.954492 | -5.088759 | -2.000342 | H251 | -7.35792 | -6.105911 | -3.07688 |
| C124 | -4.061532 | -4.906721 | 3.562646 | C252 | -8.158698 | -0.1571 | -5.333943 |
| C125 | -3.707631 | -0.010677 | 6.202766 | H253 | -8.207815 | 0.697346 | -4.647404 |
| C126 | -4.253213 | 5.019954 | 3.612388 | H254 | -8.060535 | 0.238107 | -6.35217 |
| H127 | 5.146412 | 4.723535 | 4.256197 | H255 | -9.1134 | -0.690576 | -5.273065 |
| H128 | 4.768431 | -6.512449 | 0.758231 | | | | |

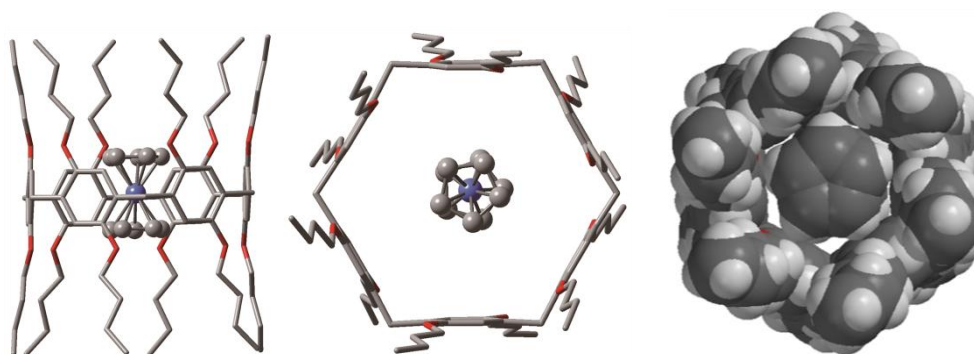


Figure S25. Side (left) and top (middle) views of the optimized geometry of $[\text{Cob-1}]^+$ (B3LYP/6-31G). Hydrogen atoms were omitted for clarity; (right) top view of the optimized geometry (space filling)

15. ^1H NMR study about the complexation of **PBP[5]** with **Fc** and **Cob⁺**, respectively

The interactions of per-butylated pillar[5]arene (**PBP[5]**) with **Fc** or **Cob⁺PF₆⁻** was studied by ^1H NMR titrations with a constant concentration of **PBP[5]** (2.0 mM) and increasing amounts of **Fc** or **Cob⁺** in mixed solvent system ($\text{CDCl}_3/\text{CD}_3\text{CN} = 5/1$, v/v). The unchanged chemical shift (Figure S26-S27) indicated that **PBP[5]** has no binding with either **Fc** or **Cob⁺**. It is probably because the cavity of **P5** is too small for **Fc** or **Cob⁺**.

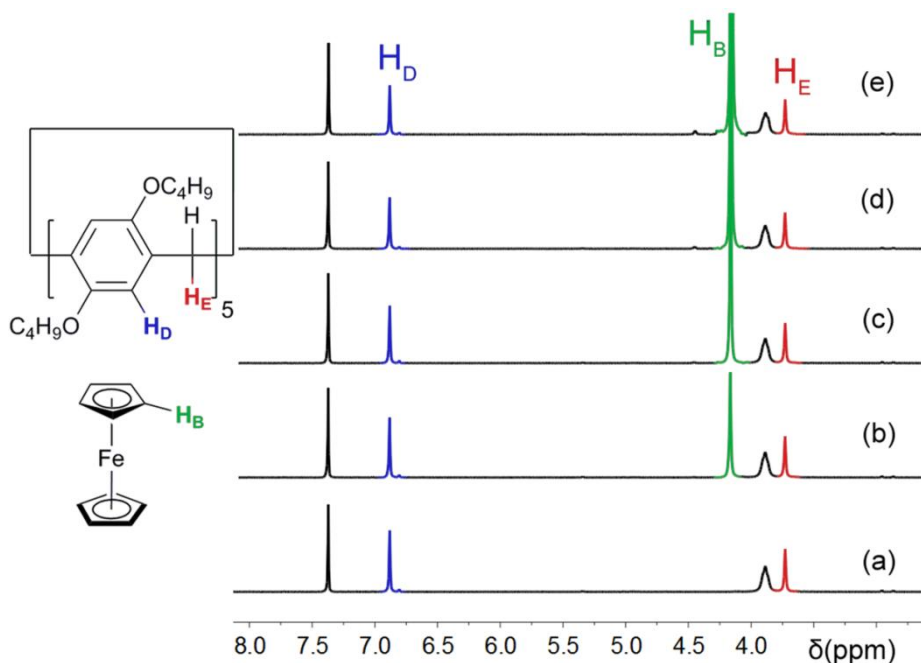


Figure S26. ¹H NMR spectra (300 MHz, CDCl₃/CD₃CN = 5:1, v/v, 298 K) of **PBP[5]** (2.0 mM) in the presence of increasing amounts of **Fe** (mM): (a) 0.0, (b) 4.0, (c) 8.0, (d) 20, (e) 40. Peaks corresponding to phenyl groups, cyclopentadienyl groups, and bridging methylene groups were colored with blue, green, and red, respectively.

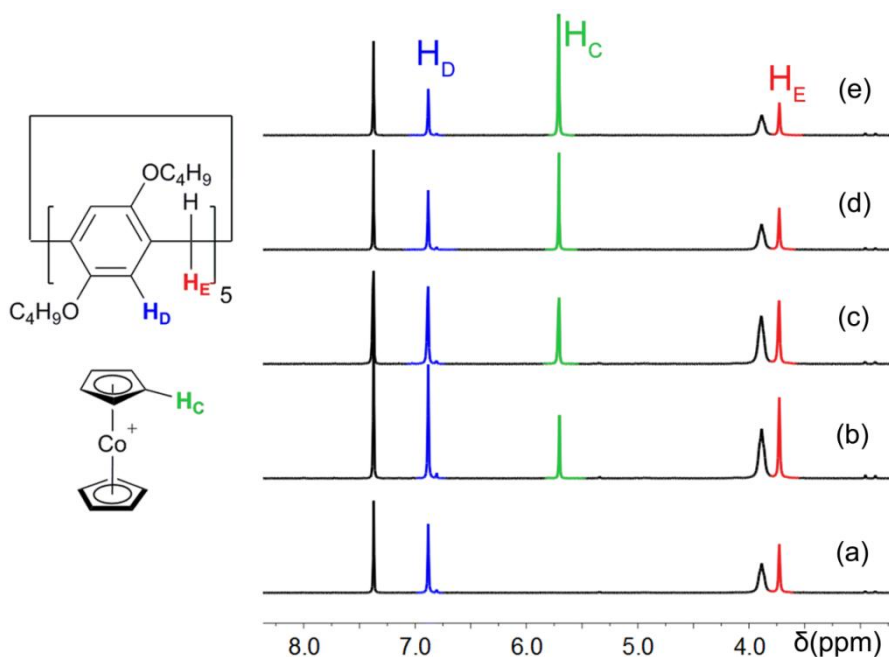


Figure S27. ¹H NMR spectra (300 MHz, CDCl₃/CD₃CN = 5:1, v/v, 298 K) of **PBP[5]** (2.0 mM) in the presence of increasing amounts of **Cob⁺PF₆⁻** (mM): (a) 0.0, (b) 1.0, (c) 2.0, (d) 3.0, (e) 8.0. Peaks corresponding to phenyl groups, cyclopentadienyl groups, and bridging methylene groups were colored with blue, green, and red, respectively.

16. Electron paramagnetic resonance (EPR) study of Fc^+PF_6^- with **1**

Since no EPR signal in solution was observed at room temperature, the EPR studies were tried at 77 K. It was found that the EPR signal of Fc^+ in solid state was observed, but the EPR signal of Fc^+ in the presence of **1** was very weak and asymmetry.

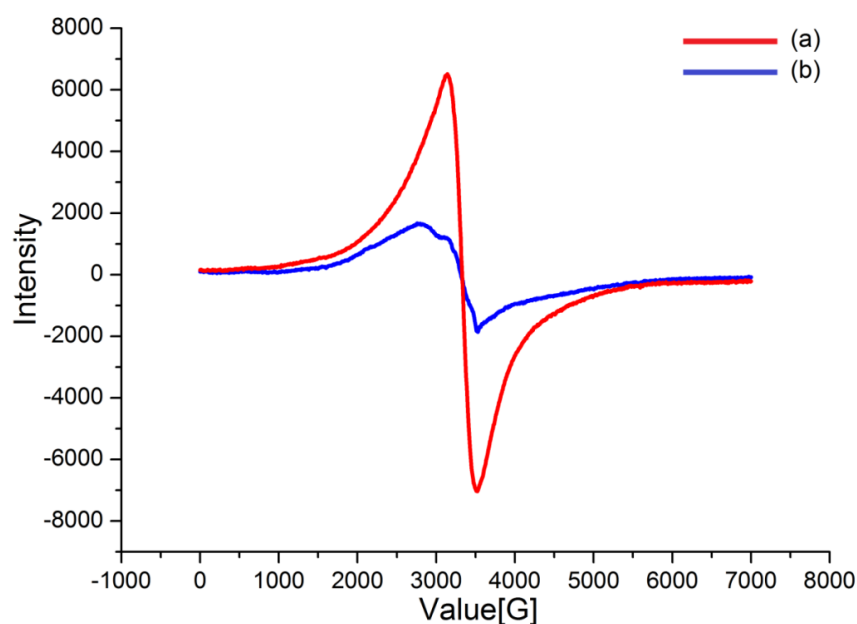


Figure S28. EPR spectra of Fc^+ in solid state (a) and in the presence of **1** (b) in solution at 77 K. In (b), an excess amount of **1** (2.0 eq) was used while the concentration of Fc^+PF_6^- was 0.1 M.

17. References

- S1. J. Liu and Q. Pei, *Macromolecules*, 2010, **43**, 9608-9612.
- S2. T. Ogoshi, H. Kayama, D. Yamafuji, T. Aoki and T.-a. Yamagishi, *Chem. Sci.*, 2012, **3**, 3221-3226.
- S3. (a) 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; (b) P. R. Ashton, R. Ballardini, V. Balzani, M. Bělohradský, 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.

- S4. T. Ogoshi, S. Kanai, S. Fujinami, T.-a. Yamagishi and Y. Nakamoto, *J. Am. Chem. Soc.*, 2008, **130**, 5022-5023.
- S5. N. L. Strutt, H. Zhang, M. A. Giesener, J. Lei and J. F. Stoddart, *Chem. Commun.*, 2012, **48**, 1647-1649.
- S6. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox. Gaussian 09, Revision B.01; Gaussian, Inc., Wallingford CT, 2010.