Electronic Supplementary Information


Fei Jia, Hao-Yi Wang, Dong-Hao Li, Liu-Pan Yang and Wei Jiang*
Department of Chemistry, South University of Science and Technology of China, Xueyuan Blvd 1088, Nanshan District, Shenzhen, 518055, P. R. China
*E-mail: jiangw@sustc.edu.cn

Table of Contents

1. Experimental Section S2
2. ^1H NMR spectra of the Complexes S3
3. Mass Spectra of the Complexes S15
4. Binding Constants Determined by ITC S21
5. Binding Constants Determined by NMR Titration S23
6. Solvent-Dependent NMR Spectra S31
7. 2D NMR Spectra of the Complexes S33
1. Experimental Section

1.1 General. All the reagents involved in this research were commercially available and used without further purification unless otherwise noted. Solvents were either employed as purchased or dried prior to use by standard laboratory procedures. $^1$H NMR, and $^1$H-$^1$H ROESY NMR spectra were recorded on Bruker Avance-400 or 600 spectrometers. All chemical shifts are reported in ppm with residual solvents or TMS (tetramethylsilane) as the internal standards. Electrospray-ionization time-of-flight high-resolution mass spectrometry (ESI-TOF-HRMS) experiments were conducted on an applied Q EXACTIVE mass spectrometry system. Molecular simulations were performed at the Semi-Empirical PM6 level of theory by using Spartan’14 (Wavefunction, Inc.). The synthesis of Oxatub[4]arene (TA4) has been reported.\(^1\)

1.2 Isothermal titration calorimetry, ITC. Titration experiments were carried out in 1,2-dichloroethane/CH$_3$CN 1 : 1 (v/v) at 25 °C on a Nano ITC LV – 190 µL (Waters GmbH, TA Instruments, Eschborn, Germany). In a typical experiment, a 190 µL solution of TA4 was placed in the sample cell at a concentration of 0.16 mM, and 50 µL of a solution of the hexafluorophosphate salt (1.0 mM in the same solvent) was in the injection syringe. The titrations consisted of 25 consecutive injections of 1.96 µL each with a 5 min interval between injections. Heats of dilution, measured by titration of the salt into the sample cell with blank solvent, were subtracted from each data set. All solutions were degassed prior to titration. The data were analysed using the instrumental internal software package and fitted with a 1:1 binding model. Errors are smaller than ±10%.

2. $^1$H NMR spectra of the Complexes

Fig. S1 $^1$H NMR spectra (400 MHz, CD$_2$Cl$_2$:CD$_3$CN=1:1, 2.0 mM, 298 K) of (a) Guest 1-PF$_6$, (c) TA4 and (b) their equimolar mixture. In the host-guest mixture, the protons of the guest shifted upfield, while the protons of TA4 becomes slightly broadened and undergo downfield shift, suggesting the formation of the complex between 1-PF$_6$ and TA4.
Fig. S2 $^1$H NMR spectra (400 MHz, CD$_2$Cl$_2$:CD$_3$CN=1:1, 2.0 mM, 298 K) of (a) Guest 2-PF$_6$, (c) TA4, and (b) their equimolar mixture. In the host-guest mixture, the protons of the guest shifted upfield, while the protons of TA4 becomes broadened and undergo downfield shift, suggesting the formation of the complex between 2-PF$_6$ and TA4.
Fig. S3 $^1$H NMR spectra (400 MHz, CD$_2$Cl$_2$:CD$_3$CN=1:1, 2.0 mM, 298 K) of (a) Guest 3-PF$_6$, (c) TA4 and (b) their equimolar mixture. In the host-guest mixture, the protons of the guest became broadened and rolled into the baseline, while the protons of TA4 shifted downfield, suggesting the complexation between 3-PF$_6$ and TA4.
Fig. S4 $^1$H NMR spectra (400 MHz, CD$_2$Cl$_2$:CD$_3$CN=1:1, 2.0 mM, 298 K) of (a) Guest 4-PF$_6$, (c) TA4 and (b) their equimolar mixture. The protons of the guest disappeared into the baseline, while all the protons of TA4 shifted downfield, suggesting the complexation between 4-PF$_6$ and TA4.
Fig. S5 $^1$H NMR spectra (400 MHz, CD$_2$Cl$_2$:CD$_3$CN=1:1, 2.0 mM, 298 K) of (a) Guest 5-PF$_6$, (c) TA4 and (b) their equimolar mixture. The protons of the guest disappeared into the baseline, while all the protons of TA4 shifted downfield, indicating the complexation between 5-PF$_6$ and TA4.
Fig. S6 $^1$H NMR spectra (400 MHz, CD$_2$Cl$_2$:CD$_3$CN=1:1, 2.0 mM, 298 K) of (a) Guest 6-PF$_6$, (c) TA4 and (b) their equimolar mixture. The protons of the guest shifted upfield, while all the protons of TA4 became broadened and shifted downfield, suggesting the complexation between 6-PF$_6$ and TA4.
**Fig. S7** $^1$H NMR spectra (400 MHz, CD$_2$Cl$_2$:CD$_3$CN=1:1, 2.0 mM, 298 K) of (a) Guest 7-PF$_6$, (c) TA4 and (b) their equimolar mixture. The protons of the guest became significantly broadened and rolled into the baseline, while all the protons of TA4 shifted downfield, suggesting the complexation between 7-PF$_6$ and TA4.
Fig. S8 $^1$H NMR spectra (400 MHz, CD$_2$Cl$_2$:CD$_3$CN=1:1, 2.0 mM, 298 K) of (a) Guest 8-PF$_6$, (c) TA4 and (b) their equimolar mixture. The protons of the guest became significantly broadened and rolled into the baseline, while the protons of TA4 shifted downfield, suggesting the complexation between 8-PF$_6$ and TA4.
Fig. S9 $^1$H NMR spectra (400 MHz, CD$_2$Cl$_2$;CD$_3$CN=1:1, 2.0 mM, 298 K) of (a) Guest 9-PF$_6$, (c) TA4 and (b) their equimolar mixture. The protons of the guest shifted upfield and became broadened, while the protons of TA4 shifted downfield, suggesting the complexation between 9-PF$_6$ and TA4.
**Fig. S10** $^1$H NMR spectra (400 MHz, CD$_2$Cl$_2$:CD$_3$CN=1:1, 2.0 mM, 298 K) of (a) Guest 10-2PF$_6$, (c) TA4 and (b) their equimolar mixture. The protons of guest shifted upfield and became broadened, while all the protons of TA4 shifted downfield, suggesting the complexation between 10-2PF$_6$ and TA4.
Fig. S11 ¹H NMR spectra (400 MHz, CD₂Cl₂:CD₃CN=1:1, 2.0 mM, 298 K) of (a) Guest 11-2PF₆, (c) TA4 (b) their equimolar mixture. The protons of the guest shifted upfield and became broadened, while all the protons of TA4 shifted downfield, suggesting the complexation between 11-2PF₆ and TA4. (d) molecular models to show the cavity size of four conformers and the size of guest 11-2PF₆. In view of the NMR result and molecular model, guest 11-2PF₆ may be shallowly encapsulated in the cavity of TA4.
Fig. S12 $^1$H NMR spectra (400 MHz, CD$_2$Cl$_2$:CD$_3$CN=1:1, 2.0 mM, 298 K) of (a) Guest 12-2PF$_6$, (c) TA4 and (b) their equimolar mixture. The protons of the guest shifted upfield, and the protons of TA4 did not move, suggesting that TA4 cannot complex with 12-2PF$_6$. The guest probably sits at the entrance of TA4; (d) molecular models to show the cavity size of four conformers and the size of guest 12-2PF$_6$. Obviously, guest 12-2PF$_6$ is too large to even fit the largest cavity (conformer IV). The observed downfield shift of the guests’ protons may result from the interactions of 12-2PF$_6$ with the outside surface of TA4.
3. Mass spectra of the Complexes

**Fig. S13** ESI mass spectrum of 1-PF$_6@$TA4. The result indicates 1-PF$_6$ and TA4 form a 1:1 complex.

**Fig. S14** ESI mass spectrum of 2-PF$_6@$TA4. The result indicates 2-PF$_6$ and TA4 form a 1:1 complex.
**Fig. S15** ESI mass spectrum of 3-PF$_6$@TA4. The result indicates 3-PF$_6$ and TA4 form a 1:1 complex.

**Fig. S16** ESI mass spectrum of 4-PF$_6$@TA4. The result indicates 4-PF$_6$ and TA4 form a 1:1 complex.
Fig. S17 ESI mass spectrum of 5-PF₆@TA4. The result indicates 5-PF₆ and TA4 form a 1:1 complex.

Fig. S18 ESI mass spectrum of 6-PF₆@TA4. The result indicates 6-PF₆ and TA4 form a 1:1 complex.
**Fig. S19** ESI mass spectrum of **7-PF₆@TA4**. The result indicates 7-PF₆ and TA4 form a 1:1 complex.

**Fig. S20** ESI mass spectrum of **8-PF₆@TA4**. The result indicates 8-PF₆ and TA4 form a 1:1 complex.
**Fig. S21** ESI mass spectrum of 9-PF₆@TA4. The result indicates 9-PF₆ and TA4 form a 1:1 complex.

**Fig. S22** ESI mass spectrum of 10-2PF₆@TA4. The result indicates 10-2PF₆ and TA4 form a 1:1 complex.
Fig. S23 ESI mass spectrum of 11-2PF₆@TA4. The result indicates 11-2PF₆ and TA4 form a 1:1 complex.
4. Binding Constants Determined by ITC

**Fig. S24** Titration plots (heat flow versus time and heat versus guest/host ratio) obtained from ITC experiments of TA4 with 1-PF$_6$ in the 1:1 mixture of 1,2-dichloroethane and CH$_3$CN.

**Fig. S25** Titration plots (heat flow versus time and heat versus guest/host ratio) obtained from ITC experiments of TA4 with 2-PF$_6$ in the 1:1 mixture of 1,2-dichloroethane and CH$_3$CN.
**Fig. S26** Titration plots (heat flow versus time and heat versus guest/host ratio) obtained from ITC experiments of TA4 with 5-PF$_6$ in the 1:1 mixture of 1,2-dichloroethane and CH$_3$CN.

**Fig. S27** Titration plots (heat flow versus time and heat versus guest/host ratio) obtained from ITC experiments of TA4 with 6-PF$_6$ in the 1:1 mixture of 1,2-dichloroethane and CH$_3$CN.
5. Binding Constants Determined by Titration

**Fig. S28** Job’s plot obtained by plotting the chemical shift change ($\Delta\delta$) of the Host’s proton ($a+b$) in $^1$H NMR spectra by varying the ratio of the host and the guest against the mole fraction of TA4. The total concentration of the host and the guest is fixed: $[\text{Host}] + [\text{Guest}] = 2.0$ mM. This experiment supports the 1:1 binding stoichiometry between 3-PF$_6$ and TA4 in the 1:1 mixture of CD$_2$Cl$_2$ and CD$_3$CN.

**Fig. S29** Job’s plot obtained by plotting the chemical shift change ($\Delta\delta$) of the Host’s proton $c$ in $^1$H NMR spectra by varying the ratio of the host and the guest against the mole fraction of Host TA4. The total concentration of the host and the guest is fixed: $[\text{Host}] + [\text{Guest}] = 2.0$ mM. This experiment supports the 1:1 binding stoichiometry between 9-PF$_6$ and TA4 in the 1:1 mixture of CD$_2$Cl$_2$ and CD$_3$CN.
**Fig. S30** Partial $^1$H NMR spectra (400 MHz, CD$_2$Cl$_2$:CD$_3$CN=1:1, 298 K) of TA4 (0.5 mM) titrated by 3-PF$_6$. From bottom to top, the concentrations of 3-PF$_6$ are in the range of 0–30.0 mM. Protons ($a+b$) of TA4 were monitored for the calculation of binding constants. This is the same for all the following experiments, unless otherwise noted. Nonlinear curve-fitting method$^2$ used here has been reported.

**Fig. S31** Non-linear curve-fitting for the complexation between TA4 and 3-PF$_6$ in the 1:1 mixture of CD$_2$Cl$_2$ and CD$_3$CN at 298 K.

---

**Fig. S32** Partial $^1$H NMR spectra (400 MHz, CD$_2$Cl$_2$:CD$_3$CN=1:1, 298 K) of TA4 (0.5 mM) titrated by 4-PF$_6$. From bottom to top, the concentrations of 4-PF$_6$ are in the range of 0~35.0 mM.

**Fig. S33** Non-linear curve-fitting for the complexation between TA4 and 4-PF$_6$ in the 1:1 mixture of CD$_2$Cl$_2$ and CD$_3$CN at 298 K.
**Fig. S34** Partial $^1$H NMR spectra (400 MHz, CD$_2$Cl$_2$:CD$_3$CN=1:1, 298 K) of TA4 (0.5 mM) titrated by 7-PF$_6$. From bottom to top, the concentrations of 7-PF$_6$ are in the range of 0~10.0 mM.

**Fig. S35** Non-linear curve-fitting for the complexation between TA4 and 7-PF$_6$ in the 1:1 mixture of CD$_2$Cl$_2$ and CD$_3$CN at 298 K.
**Fig. S36** Partial $^1$H NMR spectra (400 MHz, CD$_2$Cl$_2$:CD$_3$CN=1:1, 298 K) of TA4 (0.5 mM) titrated by 8-PF$_6$. From bottom to top, the concentrations of 8-PF$_6$ are in the range of 0~30.0 mM.

**Fig. S37** Non-linear curve-fitting for the complexation between TA4 and 8-PF$_6$ in the 1:1 mixture of CD$_2$Cl$_2$ and CD$_3$CN at 298 K.
**Fig. S38** Partial $^1$H NMR spectra (400 MHz, CD$_2$Cl$_2$:CD$_3$CN=1:1, 298 K) of TA4 (0.5 mM) titrated by 9-PF$_6$. From bottom to top, the concentrations of 9-PF$_6$ are in the range of 0–35.0 mM. The chemical shifts of proton c of TA4 were monitored for the calculation of binding constants.

**Fig. S39** Non-linear curve-fitting for the complexation between TA4 and 9-PF$_6$ in the 1:1 mixture of CD$_2$Cl$_2$ and CD$_3$CN at 298 K.
**Fig. S40** Partial $^1$H NMR spectra (400 MHz, CD$_2$Cl$_2$:CD$_3$CN=1:1, 298 K) of TA4 (0.5 mM) titrated by 10-2PF$_6$. From bottom to top, the concentrations of 10-2PF$_6$ are in the range of 0–8.0 mM.

**Fig. S41** Non-linear curve-fitting for the complexation between TA4 and 10-2PF$_6$ in the 1:1 mixture of CD$_2$Cl$_2$ and CD$_3$CN at 298 K.
Fig. S42 Partial $^1$H NMR spectra (400 MHz, CD$_2$Cl$_2$:CD$_3$CN=1:1, 298 K) of TA4 (0.5 mM) titrated by 11-2PF$_6$. From bottom to top, the concentrations of 11-2PF$_6$ are in the range of 0–3.5 mM.

Fig. S43 Non-linear curve-fitting for the complexation between TA4 and 11-2PF$_6$ in the 1:1 mixture of CD$_2$Cl$_2$ and CD$_3$CN at 298 K.
6. Solvent-Dependent NMR Spectra

Fig. S44 $^1$H NMR spectra (400 MHz, 2.0 mM, 298 K) of the equimolar mixture of 1-PF$_6$@TA4 in the (a) 5:1 or (b) 1:1 mixture of CD$_2$Cl$_2$ and CD$_3$CN.

Fig. S45 $^1$H NMR spectra (400 MHz, 2.0 mM, 298 K) of the equimolar mixture of 2-PF$_6$@TA4 in the (a) 5:1 or (b) 1:1 mixture of CD$_2$Cl$_2$ and CD$_3$CN.
Fig. S46 $^1$H NMR spectra (400 MHz, 2.0 mM, 298 K) of the equimolar mixture of 5-PF$_6$@TA4 in the (a) 5:1 or (b) 1:1 mixture of CD$_2$Cl$_2$ and CD$_3$CN.

Fig. S47 $^1$H NMR spectra (400 MHz, 2.0 mM, 298 K) of the equimolar mixture of 6-PF$_6$@TA4 in the (a) 10:1, (b) 5:1, (c) 2:1 or (d) 1:1 mixture of CD$_2$Cl$_2$ and CD$_3$CN.
7. 2D NMR Spectra of the Complexes

Fig. S48 $^1$H,$^1$H-ROESY NMR spectra (600 MHz, CD$_2$Cl$_2$:CD$_3$CN=1:1, 6.0 mM,) of 1-PF$_6$@TA4 at -20°C. This result supports that TA4 in this complex predominantly exists as conformation I.
Fig. S49 $^1$H,$^1$H-ROESY NMR spectra (600 MHz, CD$_2$Cl$_2$:CD$_3$CN=1:1, 6.0 mM,) of 2-PF$_6$@TA4 at -20°C. This result supports that TA4 in this complex predominantly exists as conformation IV.
Fig. S50 $^1$H,$^1$H-ROESY NMR spectra (600 MHz, CD$_2$Cl$_2$:CD$_3$CN=1:1, 6.0 mM,) of 5-PF$_6$@TA4 at -20°C. This result supports that TA4 in this complex predominantly exists as conformation IV.
Fig. S51 $^1$H,$^1$H-ROESY NMR spectra (600 MHz, CD$_2$Cl$_2$:CD$_3$CN=1:1, 6.0 mM,) of 6-PF$_6$@TA4 at -20°C. This result supports that TA4 in this complex predominantly exists as conformation IV.