A diquat-contained macrocyclic anion acceptor in pure water

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Supporting Information

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1. Materials and general methods

All reagents and solvents were purchased from commercial sources and used without further purification. Manipulations were performed under a normal laboratory atmosphere unless otherwise noted. The protected-bishydroxylamino linker 1.2HCl^{S1} were synthesized according to the literature procedures. Nuclear magnetic resonance (NMR) spectra were recorded at ambient temperature using Bruker AVANCE III 400/500 or Agilent DD2 600 spectrometers, with working frequencies of 400/500/600, 100/125/150 and 162/202 MHz for ¹H, ¹³C and ³¹P respectively. Chemical shifts are reported in ppm relative to the residual internal non-deuterated solvent signals (for proton NMR, D₂O: $\delta = 4.70$ ppm, DMSO-d₆: $\delta = 2.50$ ppm, CD₃CN: $\delta = 1.94$ ppm). High-resolution mass spectra (HRMS) were recorded on a Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) and ESI-Q-TOF-MS. X-ray crystallographic data were collected on a Bruker D8 Venture diffractometer. UV/Vis spectra were recorded on a Cary 300 instrument (Varian Australia Pty Ltd.).

2. Synthetic procedures



Scheme S1. Synthesis of 3.

3: [2,2'-bipyridine]-5,5'-dicarbaldehyde (1.908 g, 9 mmol) and p-Toluenesulfonic acid monohydrate (190 mg, 1 mmol) were dissolved in 100 mL of ethylene glycol. The corresponding reaction mixture was stirred at 110 °C overnight in N2 atmosphere. After the solution was cooled down to room temperature, a solution of NaHCO₃ (10 g) in water (300 mL) was added into the reaction mixture, which was used to neutralize TsOH. The aqueous reaction mixture was then extracted with DCM (300 mL) for three times. The organic solution was combined and dried with Na₂SO₄. After evaporating the solvent, a yellow oil was obtained, which was purified by column chromatography (SiO₂: ethyl acetate / light petroleum=1:1), yielding the pure **3** (950 mg, 35%). **3** was fully characterized by ¹H NMR spectroscopy (Figure S1), ¹³C NMR spectroscopy (Figure S2), and mass spectrometry (Figure S3). ¹H NMR (400 MHz, DMSO-d₆, 298 K) δ (ppm): 8.74 (d, J=1.6 Hz, 2H), 8.43 (d, J=8.0 Hz, 2H), 8.00 (q, J_1 =1.6 Hz, J_2 =8.0 Hz, 2H), 5.90 (s, 2H), 3.98–4.13 (m, 8H). ¹³C NMR (100 MHz, DMSO-*d*₆, 298 K) δ (ppm): 155.52, 147.74, 135.55, 134.13, 120.33, 100.91, 64.98. HRMS: m/z calculated for C₁₆H₁₇N₂O₄⁺ ([M + H]⁺): 301.1183; found: 301.1174. m/zcalculated for $C_{16}H_{16}N_2O_4Na$ ([M + Na]⁺): 323.1002; found: 323.0997.



Figure S1. ¹H NMR spectrum (400 MHz, DMSO-*d*₆, 298 K) of **3**.



Figure S2. ¹³C NMR spectrum (100 MHz, DMSO-*d*₆, 298 K) of **3**.



Figure S3. ESI-HRMS of **3**.



Scheme S2. Synthesis of 2²⁺·2Br⁻.

2^{2+.}2Br⁻: **3** (500 mg, 1.67 mmol) was dissolved in 1,2-dibromoethane (1 mL). The reaction mixture was stirred at 100 °C for 24 h in N₂ atmosphere, during which some solids gradually precipitated in the solution. After cooling to room temperature, the precipitates were collected by filtration and washed with CH₂Cl₂ (25 mL) for three times to yield **2**^{2+.}2Br⁻ (260 mg, 32.0%) as a white powder without further purification. The structure of **2**^{2+.}2Br⁻ was fully characterized by ¹H NMR spectroscopy (Figure S4), ¹³C NMR spectroscopy (Figure S5), and mass spectrometry (Figure S6). ¹H NMR (400 MHz, D₂O, 298 K) δ (ppm): 9.29 (d, *J*=4.0 Hz, 2H), 8.94 (d, *J*=8.0 Hz, 2H), 8.87–8.90 (q, *J*₁=4.0 Hz, *J*₂=8.0 Hz, 2H), 6.19 (s, 2H), 5.28 (s, 4H), 4.07–4.09 (m, 8H). ¹³C NMR (100 MHz, D₂O, 298 K) δ (ppm): 146.22, 145.73, 142.27, 139.69, 128.55, 98.81, 65.74, 52.56. HRMS: *m/z* calculated for C₁₈H₁₉N₂O₄⁺ ([**2** – H]⁺): 327.1339; found: 327.1347. *m/z* calculated for C₁₉H₂₃N₂O₅⁺ ([**2** + CH₃O]⁺): 359.1601; found: 359.1604.



Figure S4. ¹H NMR spectrum (400 MHz, D₂O, 298 K) of **2**²⁺·2Br⁻.



Figure S5. ¹³C NMR spectrum (100 MHz, D₂O, 298 K) of 2²⁺·2Br⁻.



Figure S6. ESI-HRMS of 2²⁺·2Br⁻.



Scheme S3. Synthesis of macrocycle 4⁴⁺.

4⁴⁺·4PF₆⁻: A 1:1 mixture of 2²⁺·2Br⁻ (100 mg, 0.20 mmol) and 1·2HCl (48.5 mg, 0.20 mmol) was dissolved in water (66 mL). Concentrated hydrochloric acid (6 mL) was added into the corresponding reaction mixtures, which was used to i) turn on the dynamic nature of oxime and ii) deprotect two formyl functional groups in $2^{2+}2Br^{-}$. The corresponding reaction mixtures were stirred at 80 °C for 12 h until the ¹H NMR no longer changed. Small amount of precipitate was observed, which might be oligomeric and polymeric byproducts of oxime condensation. After cooling down the reaction solution to room temperature, these precipitates were filtered off. NH₄⁺·PF₆⁻ (1 g) was then added into the filtrate, after which a pure vellow solid was collected by filtration and washed with water for three times, yielding the pure tetracationic macrocyclic compound $4^{4+} 4PF_6^{-}$ (159 mg, 60%). Water soluble counterparts, namely $4^{4+} \cdot 4Cl^{-}$ or $4^{4+} \cdot 4Br^{-}$, could be obtained by means of counteranion exchange in yields of 54% and 55% respectively, by adding either tetrabutylammonium chloride (TBA⁺·Cl⁻) or tetrabutylammonium bromide (TBA⁺·Br⁻) into a MeCN solution of $4^{4+} \cdot 4PF_6^{-}$, followed by collecting the corresponding precipitates. $4^{4+} \cdot 4TPB^{-}$ (TPB⁻ = tetraphenylborate) was also obtained via counteranion exchange in a yield of 50%, by adding $Na^+ \cdot TPB^-$ into a water solution of $4^{4+} \cdot 4Cl^-$.

The macrocycle 4^{4+.}4Br⁻ was fully characterized by recording the ¹H NMR spectroscopy (Figure S8), ¹³C NMR spectroscopy (Figure S12), ¹H-¹H COSY spectrum (Figure S13), HSQC spectra (Figure S14), the HMBC spectra (Figure S15)

mass spectrometry (Figure S16), as well as X-ray crystallography (Figure 3 in the main text). ¹H NMR (400 MHz, D₂O, 298 K) δ (ppm): 9.17 (s, 4H), 8.75 (d, J=8.0 Hz, 4H), 8.64 (d, J=8.0 Hz, 4H), 8.32 (s, 4H), 7.41 (s, 8H), 5.25 (s, 8H), 5.10 (s, 8H). ¹³C NMR (100 MHz, D₂O, 298 K) δ (ppm): 145.16, 144.15, 143.82, 138.68, 137.67, 135.00, 128.73, 128.03, 76.43, 52.38. HRMS: m/z calculated for C₄₄H₃₈N₈O₄²⁺ ([4 – $2H^{+}$: 371.1503; found: 371.1492; *m/z* calculated for C₄₄H₄₀Br₂N₈O₄²⁺ ([4 + 2Br]²⁺): 452.0754; found: 452.0743. m/z calculated for C₄₄H₄₀BrN₈O₄³⁺ ([4 + Br]³⁺): 274.4113; found: 274.4108; m/z calculated for C₄₄H₄₀N₈O₄⁴⁺ ([4]⁴⁺): 186.0788; found: 186.0734. The macrocycle $4^{4+}.4Cl^{-}$ was characterized by recording the ¹H NMR spectroscopy (Figure S9) and mass spectrometry (Figure S17). ¹H NMR (400 MHz, D₂O, 298 K) δ (ppm): 9.18 (s, 4H), 8.76 (d, J=8.0 Hz, 4H), 8.65 (d, J=8.0 Hz, 4H), 8.33 (s, 4H), 7.42 (s, 8H), 5.26 (s, 8H), 5.11 (s, 8H). HRMS: m/z calculated for $C_{44}H_{38}N_8O_4^{2+}$ ([4 – $2H^{2+}$): 371.1503; found: 371.1507; *m/z* calculated for $C_{44}H_{40}Cl_2N_8O_4^{2+}$ [4 + 2Cl]²⁺: 407.1269; found: 407.1273; m/z calculated for C₄₄H₄₀ClN₈O₄³⁺ ([4 + Cl]³⁺): 259.7615; found: 259.7617; m/z calculated for $C_{44}H_{39}N_8O_4^{3+}$ ([4 - H]³⁺): 247.7693; found: 247.7696; m/z calculated for C₄₄H₄₀N₈O₄⁴⁺ ([4]⁴⁺): 186.0788; found: 186.0795.

The macrocycle $4^{4+} \cdot 4PF_6^-$ was characterized by recording the ¹H NMR spectroscopy (Figure S10) and mass spectrometry (Figure S18). ¹H NMR (400 MHz, CD₃CN, 298 K) δ (ppm): 9.10 (s, 4H), 8.76 (d, *J*=8.0 Hz, 4H), 8.62 (d, *J*=8.0 Hz, 4H), 8.39 (s, 4H), 7.49 (s, 8H), 5.35 (s, 8H), 5.01 (s, 8H). HRMS: *m/z* calculated for C₄₄H₃₈N₈O₄²⁺ ([4 – 2H]²⁺): 371.1503; found: 371.1492; *m/z* calculated for C₄₄H₄₀P₂F₁₂N₈O₄²⁺ [4 + 2PF₆]²⁺: 517.1223; found: 517.1215; *m/z* calculated for C₄₄H₄₀PF₆N₈O₄³⁺ ([4 + PF₆]³⁺): 296.4266; found: 296.4253; *m/z* calculated for C₄₄H₃₉N₈O₄³⁺ ([4 - H]³⁺): 247.7693; found: 247.7696; *m/z* calculated for C₄₄H₄₀N₈O₄⁴⁺ ([4]⁴⁺): 186.0788; found: 186.0734.

The macrocycle $4^{4+.4}$ TPB⁻ was characterized by recording the ¹H NMR spectroscopy (Figure S11). ¹H NMR (400 MHz, DMSO- d_6 , 298 K) δ (ppm): 9.41 (s, 4H), 8.91 (d, *J*=4.0 Hz, 4H), 8.85 (d, *J*=4.0 Hz, 4H), 8.64 (s, 4H), 7.39 (s, 8H), 7.1–7.2 (m, 32H), 6.92 (t, 32H), 6.7–6.8 (m, 16H), 5.36 (s, 8H), 5.08 (s, 8H).



Figure S7. ¹H NMR spectra of A) S_1^{2+} (D₂O, 298 K), B) **1** and S_1^{2+} after the NMR sample was heated for 8 h (D₂O, 298 K), C) precipitations of the self-assembly reaction solutions of **1** and S_1^{2+} (DMSO- d_6 , 298K).

In order to convince of hypothesis that the high-yielding synthesis of 4^{4+} results from the templating effect of the Cl⁻ anion, we performed the condensation of a bisformylsubstituted paraquat $S_1^{2+}2Cl^-$ and 1 in water in the presence of 1M HCl, the same reaction as that for self-assembly of 4^{4+} . This reaction led to precipitation of reaction adducts, as inferred from the ¹H NMR spectrum (Figure S7B) that after condensation the reaction solution in D₂O almost contained nothing. We also dissolved the precipitates in DMSO-d₆ and recorded the ¹H NMR spectrum (Figure S7C), which indicated that these precipitates were a library of oligomeric or polymeric byproducts.

3. Characterization of macrocycles 4⁴⁺



Figure S8. ¹H NMR spectrum (400 MHz, D₂O, 298 K) of 4^{4+.}4Br⁻.



Figure S9. ¹H NMR spectrum (400 MHz, D₂O, 298 K) of $4^{4+} \cdot 4Cl^{-}$.



Figure S10. ¹H NMR spectrum (400 MHz, D_2O , 298 K) of $4^{4+.}4PF_6^{-}$.



Figure S11. ¹H NMR spectrum (400 MHz, D₂O, 298 K) of 4^{4+.}4TPB⁻.



Figure S12. ¹³C NMR spectrum (100 MHz, D_2O , 298 K) of $4^{4+.4}Br^{-.}$



Figure S13. ¹H-¹H COSY spectrum (400 MHz, D_2O , 298 K) of $4^{4+.4}Br^{-}$. Key correlation peak is labeled in the spectrum.



Figure S14. HSQC spectrum (D₂O, 298 K) of $4^{4+}\cdot 4Br^{-}$.



Figure S15. HMBC spectrum (D₂O, 298 K) of $4^{4+.}4Br^{-}$. Key correlation peaks are labeled in the spectrum.



Figure S16. ESI-HRMS of 4⁴⁺·4Br⁻.



Figure S17. High-resolution ESI-Q-TOF-mass spectrum of 4⁴⁺·4Cl⁻.



Figure S18. ESI-HRMS of $4^{4+.}4PF_6^{-.}$. Some of the signals are confirmed in Figure S17.

4. UV/Vis absorption spectra of host-guest complexes



Figure S19. Partial UV/Vis absorption spectra of $4^{4+} \cdot 4Cl^{-}$ after adding different amount of HPO₄²⁻ in H₂O at 298 K. The concentration of $4^{4+} \cdot 4Cl^{-}$ was unchanged (9.0×10⁻⁶ M) during the titration process.

UV/Vis absorption spectra of $4^{4+.4}$ Cl⁻ were recorded in water upon addition of either HPO₄²⁻ and HCO₃⁻. In the case of addition of HPO₄²⁻, an isosbestic point at 418 nm was clearly observed, indicating that only two species, namely the bound and "free" 4^{4+} , existed in the water that have absorption in the visible region. Addition of HPO₄²⁻ decreased the absorption band centered at 372 nm, while led to the appearance of a band centered at 471 nm. The latter band might result from charge-transfer from the anionic oxygen in HPO₄²⁻ to the diquat units in 4^{4+} .

UV-Vis spectroscopic studies were performed to investigate the binding behavior between 4^{4+} and HPO₄²⁻, which act as host and guest, respectively. Based on the absorbance at the charge-chansfer band (471 nm), a job plot, $\Delta A \cdot X_{guest}$ vs the X_{host} was obtained (Figure S20), in which X_{guest} represents the percentage of the molarity of the guest in the guest/host mixture, and ΔA represents the changes of the absorbance of 4^{4+} at the charge-chansfer band (471 nm). The value distribution indicates a 1:1 (host:guest) binding stoichiometry. The association constant of complex was determined by probing the charge-transfer band of the complex by UV/Vis spectroscopy and employing a titration method (Figure S19). Treatment of the collected absorbance data with a non-linear curve-fitting program (the Benesie-Hildebrand method) afforded the corresponding association constant (K_a).^{S2} The binding constant K_a of HPO₄²⁻⊂ 4^{4+} was calculated to be around 2.1(±0.1)×10³ M⁻¹ in D₂O, by using the absorption spectroscopic results (Figure S21).



Figure S20. Job-plots corresponding to the binding between $4^{4+} \cdot 4Cl^{-}$ and HPO_4^{2-} at different molarity ratio. $[4^{4+} \cdot 4Cl^{-}] + [HPO_4^{2-}] = 0.6$ mM. The value distribution indicates a 1:1 (host:guest) binding stoichiometry.



Figure S21. Plot of the changes of the absorbance intensity at $\lambda = 471$ nm (the hostguest charge transfer band) verus [HPO₄²⁻] / [4⁴⁺]. [4⁴⁺·4Cl⁻] = 9.0×10⁻⁶ M for all spectra.



Figure S22. Partial UV/Vis absorption spectra of $4^{4+.4}Cl^{-}$ after adding different amount of bicarbonate in H₂O at 298 K. The concentration of $4^{4+.4}Cl^{-}$ was unchanged (7.5×10⁻⁶ M) during the titration process.

In the case of addition of HCO_3^- , an isosbestic point at 415 nm was clearly observed, indicating that only two species, namely the bound and "free" 4^{4+} , existed in the water that have absorption in the visible region. Addition of HCO_3^- decreased the absorption band centered at 372 nm, while led to the appearance of a band centered at 471 nm. The latter band might result from charge-transfer from the anionic oxygen in HCO_3^- to the diquat units in 4^{4+} .

UV-Vis spectroscopic studies were performed to investigate the binding behavior between 4^{4+} and HCO₃⁻, which act as host and guest, respectively. Based on the absorbance at the charge-chansfer band (471 nm), a job plot, $\Delta A \cdot X_{guest}$ vs the X_{host} was obtained (Figure S23), in which X_{guest} represents the percentage of the molarity of the guest in the guest/host mixture, and ΔA represents the changes of the absorbance of 4^{4+} at the charge-chansfer band (471 nm). The value distribution indicates a 1:1 (host:guest) binding stoichiometry. The association constant of complex was determined by probing the charge-transfer band of the complex by UV/Vis spectroscopy and employing a titration method (Figure S22). Treatment of the collected absorbance data with a non-linear curve-fitting program (the Benesie-Hildebrand method) afforded the corresponding association constant (K_a).^{S2} The binding constant K_a of HCO₃⁻ \subset 4⁴⁺ was calculated to be around 3.4(±0.1)×10² M⁻¹ in D₂O, by using the absorption spectroscopic results (Figure S24).



Figure S23. Job-plots corresponding to the binding between $4^{4+.4}Cl^{-}$ and HCO_{3}^{-} at different molarity ratio. $[4^{4+.4}Cl^{-}] + [HCO_{3}^{-}] = 0.6$ mM. The value distribution indicates a 1:1 (host:guest) binding stoichiometry.



Figure S24. Plot of the changes of the absorbance intensity at $\lambda = 471$ nm (the hostguest charge transfer band) verus [bicarbonate] / [4⁴⁺]. [4⁴⁺·4Cl⁻] = 7.5×10⁻⁶ M for all spectra.



Figure S25. Partial UV/Vis absorption spectra of $4^{4+} \cdot 4Cl^{-}$ after adding different amount of PO₄³⁻ in H₂O at 298 K. The concentration of $4^{4+} \cdot 4Cl^{-}$ was unchanged (9.0×10⁻⁶ M) during the titration process.

UV/Vis absorption spectrum of $4^{4+} \cdot 4Cl^-$ was also recorded (Figure S25) in water upon addition of either PO₄³⁻. Addition of PO₄³⁻ decreased the absorption band centered at 372 nm, while led to the appearance of a band centered at 467 nm. This observation is similar as those in the case of HPO₄²⁻ and HCO₃⁻. The binding constant K_a of PO₄³⁻⊂ 4^{4+} was calculated to be around 9.0(±2.5)×10³ M⁻¹ in D₂O, by using the absorption spectroscopic results (Figure 26). This value is remarkably larger than that (2.1(±0.1)×10³ M⁻¹) of HPO₄²⁻⊂ 4^{4+} in the context of qualitative analysis, which could be explained by the fact that the trisanionic PO₄³⁻ undergoes larger electrostatic forces within the cavity of the ring. However, this value is quantitatively inaccurate as inferred from the large error, given that PO₄³⁻ (*pK*_{a3} = 12.7) would produce HPO₄²⁻ and OH⁻ in water when pH is around 7. The attempts to measure the K_a of PO₄³⁻⊂ 4^{4+} in a basic buffer solution (pH > 12) proven unsuccessful, because the pyridinium units in $4^{4+} \cdot 4Cl^{-}$ are a labile compound in the presence of base.



Figure S26. Plot of the changes of the absorbance intensity at λ =467 nm (the hostguest charge transfer band) verus [PO₄³⁻] / [4⁴⁺]. [4⁴⁺·4Cl⁻] = 9.0×10⁻⁶ M for all spectra.

5. Recognition for other anions in DMSO- d_6

The ability of 4^{4+} to recognize anions including Cl⁻, Br⁻, I⁻ was also justified by using ¹H NMR spectroscopy in DMSO, also due to the solubility issues. We used $4^{4+}\cdot 4\text{TPB}^-$ (TPB⁻ = tetraphenylborate) to perform anion recognition, because this couteranion is too large to reside within the ring cavity, avoiding anion binding competition. Treatment of the collected NMR data with a non-linear curve-fitting program^{S2} (the Benesie-Hildebrand method) afforded the corresponding association constant (K_a).



Figure S27. Partial ¹H NMR spectra (500 MHz, DMSO- d_6 , 298 K) of $4^{4+.4}$ TPB⁻ (1.88 mM) in the presence of different amount of TBA^{+.}Cl⁻. The key resonance of a proton in 4^{4+} are labeled with red arrows in the spectra, which undergoes downfield shifts upon addition of the guest Cl⁻. We used its downfield shifts, $\Delta\delta$, to calculate the binding constant (see Figure S28).



Figure S28. Plot of the resonance downfield shifts of labeled proton of $4^{4+} \cdot 4\text{TPB}^-$ verus [Cl⁻] / [4^{4+}]. See the assignment of labeled proton in Figure S27. [$4^{4+} \cdot 4\text{TPB}^-$] = 1.88 mM for all spectra.

The corresponding ¹H NMR spectra demonstrated (Figure S28) that the binding constants of Cl⁻ \subset 4⁴⁺ are around 2.4(±0.2)×10² M⁻¹ in DMSO-*d*₆.



Figure S29. Partial ¹H NMR spectra (500 MHz, DMSO- d_6 , 298 K) of $4^{4+.}4\text{TPB}^-$ (1.88 mM) in the presence of different amount of TBA^{+.}Br⁻. The key resonance of a proton in 4^{4+} are labeled with red arrows in the spectra, which undergoes downfield shifts upon addition of the guest Br⁻. We used its downfield shifts, $\Delta\delta$, to calculate the binding constant (see Figure S30).



Figure S30. Plot of the resonance downfield shifts of labeled proton of $4^{4+.}4\text{TPB}^-$ verus [Br⁻] / [4^{4+}]. See the assignment of labeled proton in Figure S29. [$4^{4+.}4\text{TPB}^-$] = 1.88 mM for all spectra.

The corresponding ¹H NMR spectra demonstrated (Figure S30) that the binding constants of Br⁻ \subset **4**⁴⁺ are around 2.9(±0.3)×10² M⁻¹ in DMSO-*d*₆.



Figure S31. Partial ¹H NMR spectra (500 MHz, DMSO- d_6 , 298 K) of $4^{4+.4}$ TPB⁻ (1.88 mM) in the presence of different amount of TBA^{+.}I⁻. The key resonance of a proton in 4^{4+} are labeled with red arrows in the spectra, which undergoes downfield shifts upon addition of the guest I⁻. We used its downfield shifts, $\Delta\delta$, to calculate the binding constant (see Figure S32).



Figure S32. Plot of the resonance downfield shifts of labeled proton of $4^{4+.}4\text{TPB}^-$ verus $[I^-] / [4^{4+}]$. See the assignment of labeled proton in Figure S31. $[4^{4+.}4\text{TPB}^-] = 1.88 \text{ mM}$ for all spectra.

The corresponding ¹H NMR spectra demonstrated (Figure S32) that the binding constants of I⁻ \subset 4⁴⁺ are around 2.9(±0.5)×10² M⁻¹ in DMSO-*d*₆.

6.The stability experiments of macrocycles 4⁴⁺



Figure S33. Partial ¹H NMR spectra (400 MHz, D₂O, 298 K) of $4^{4+.4}Cl^{-}$ A) before and B) after the NMR sample was heated at 80 °C for 24 h.

After the macrocycle $4^{4+.4}Cl^-$ was heated at 80 °C for 24 h, its ¹H NMR spectrum is essentially the same (Figure S33) as that before heating. The only difference is that, protons H_a and H_g disappeared. This is because these two protons are relatively acidic, on account of the electron-withdrawing effects from the pyridinium nitrogen atoms in the diquat. The acidic protons thus undergo hydrogen-deuterium exchange in D₂O.



Figure S34. Partial ¹H NMR spectra (400 MHz, CD₃CN,298 K) of $4^{4+}\cdot 4PF_6^-$ A) before and B) after the NMR sample was heated at 80°C for 24 h.

After the macrocycle $4^{4+} \cdot 4PF_6^-$ was heated at 80 °C for 24 h, its ¹H NMR spectrum is essentially the same (Figure S34) as that before heating, indicating that the ring is a kinetically inert compound that does not undergo appreciable decomposition on the laboratory timescale.

7. X-ray Crystallography

 $1.4^{4+.4}Cl^{-}$

1.1) Methods

Single crystals of $4^{4+.4}Cl^{-}$ suitable for X-ray crystallography, were grown by slow vapor diffusion of acetone into aqueous solution of $4^{4+.4}Cl^{-}$ over the course of days.

1.2) Crystal data

 $C_{44}H_{40}N_8O_4$ ·(Cl)₄, M = 886.64, triclinic, space group *P-1*, a = 10.5445(18) Å, b = 14.095(2) Å, c = 17.622(3) Å, $a = 89.490(12)^\circ$, $\beta = 79.110(11)^\circ$, $\gamma = 84.227(13)^\circ$, V = 2558.8(7) Å³, Z = 2, T = 170 K, μ (GaK α) = 1.608 mm⁻¹, *Dcalc* = 1.151 g/mm³, 28278 reflections measured (9.238° $\leq 2\Theta \leq 111.164^\circ$), 9697 unique ($R_{int} = 0.2064$, $R_{sigma} = 0.2731$) which were used in all calculations. The final R_I was 0.1609 (I $\geq 2\sigma$ (I)) and wR_2 was 0.4500 (all data). CCDC number: 1908955.

1.3) Refinement details

Data were collected at 170 K on a Bruker D8 Venture Diffractometer equipped with a GaKα IµS source and MX optic. Using Olex2,^{S3} the structure was solved with the XS^{S4} structure solution program using Directed Method and refined with the SHELXL^{S5} refinement package using Least Squares minimisation. Due to the weak diffraction, the enhanced rigid-bond restraint (SHELXL keyword RIGU) was applied on the whole structure. The hydrogen atoms on carbon were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms). For the solvent treatment details, the solvent masking procedure as implemented in Olex2 was used to remove the electronic contribution of solvent molecules from the refinement.

1.4) Solid-state (super) structures



Figure S35. Different crystallographic views of 4⁴⁺·4Cl⁻.

2. $4^{4+} \cdot 4PF_6^{-}$

2.1) Methods

Single crystals of $4^{4+}\cdot 4PF_6^-$ suitable for X-ray crystallography, were grown by slow vapor diffusion of ethyl ether into MeCN solution of $4^{2+}\cdot 4PF_6^-$ over the course of days.

2.2) Crystal data

 $C_{44}H_{40}N_8O_4 \cdot (C_2H_3N)_1 \cdot (PF_6)_4$ (*M* =1365.77 g/mol): triclinic, space group P-1 (no. 2), *a* = 11.6025(11) Å, *b* = 16.878(2) Å, *c* = 17.2459(18) Å, *a* = 115.767(7)°, *β* = 91.170(8)°, γ = 91.512(7)°, *V* = 3038.5(6) Å³, *Z* = 2, *T* = 170.01 K, μ (GaK α) = 1.459 mm⁻¹, *Dcalc* = 1.493 g/cm³, 33945 reflections measured (8.49° ≤ 2 Θ ≤ 110.612°), 11498 unique (R_{int} = 0.1747, R_{sigma} = 0.2280) which were used in all calculations. The final R_1 was 0.1467 (I > 2 σ (I)) and *w* R_2 was 0.3903 (all data). CCDC number: 1908956.

2.3) Refinement details

Data were collected at 170 K on a Bruker D8 Venture Diffractometer equipped with a GaK α I μ S source and MX optic. Using Olex2, the structure was solved with the SHELXT^{S6} structure solution program using Intrinsic Phasing and refined with the SHELXL refinement package using Least Squares minimisation. The hydrogen atoms on carbon were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms).

2.4) Solid-state (super) structures



Figure S36. Different crystallographic views of $4^{4+.}4PF_6^{-.}$

3. TsO[−] ⊂4⁴⁺

3.1) Methods

Single crystals of $TsO^- \subset 4^{4+}$ suitable for X-ray crystallography, were grown by slow vapor diffusion of ethyl ether into MeCN solution of $4^{2+}\cdot 4PF_6^-$ and TsOH over the course of days.

3.2) Crystal data

C₇H₇O₃S·C₄₄H₄₀N₈O₄·(PF₆)₃ (*M*=1350.93 g/mol): orthorhombic, space group Cmcm (no. 63), *a* = 17.4113(5) Å, *b* = 33.6611(11) Å, *c* = 20.8777(6) Å, *V* = 12236.1(6) Å³, *Z* = 8, *T* = 169.99 K, µ(GaKα) = 1.433 mm⁻¹, *Dcalc* = 1.467 g/cm³, 38555 reflections measured (5.868° ≤ 2Θ ≤ 110.016°), 6161 unique (R_{int} = 0.1249, R_{sigma} = 0.0894) which were used in all calculations. The final R_1 was 0.1307 (I > 2σ(I)) and *wR*₂ was 0.4193 (all data). CCDC number: 1908957.

3.3) Refinement details

Data were collected at 170 K on a Bruker D8 Venture Diffractometer equipped with a GaK α IµS source and MX optic. Using Olex2, the structure was solved with the SHELXT structure solution program using Intrinsic Phasing and refined with the SHELXL refinement package using Least Squares minimisation. Due to the weak diffraction, the enhanced rigid-bond restraint (SHELXL keyword RIGU) was applied on the guest molecule (tosylate). The hydrogen atoms on carbon were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms). A large portion of the unit cell was composed of disordered solvent molecules. Most of this region was composed of very diffuse electron density from which recognizable solvent molecules could be derived. These solvent molecules were hopelessly scrambled. The contributions to the scattering factors due to these solvent molecules were removed by use of the utility SQUEEZE.⁸⁷

3.4) Solid-state (super) structures



Figure S37. Different crystallographic views of $4^{4+.}4PF_6^{-.}$

8. IGM analysis of weak interactions between the host and guests



Figure S38. Visual presentation of the possible interactions between chloride ion and bipyridine ring in the subject using IGM Analysis with isovalue being set to 0.0075.



Figure S39. Visual presentation of interactions between hexafluorophosphate anion and bipyridine ring in the subject using IGM analysis with isovalue being set to 0.0075.



Figure S40. Visual presentation of the possible interactions between *para*-Toluenesulfonate anion and bipyridine ring in the subject using IGM Analysis with isovalue being set to 0.0075.



Figure S41. Weak interactions in complex $2Cl^{-} \subseteq 4^{4+}$, $2PF_{6}^{-} \subseteq 4^{4+}$ and $TsO^{-} \subseteq 4^{4+}$.

To gain visualization of the possible weak interactions between the host and the guests, DFT calculations have been performed using Gaussian 16 software package.^{S8} Geometry optimizations were carried out with M06-2X^{S9} functional and the 6-31G(d) basis set with the self-consistent reaction field (SCRF) using SMD^{S10} model under acetonitrile to simulate solvent environment. During geometry optimization, only coordinates of hydrogen atoms were optimized and coordinates of other heavy atoms are fixed. The coordinates of heavy atoms are taken from corresponding crystal structures.

Based on the optimized structures, Multiwfn^{S11} software package was used then to qualitatively study weak interactions in the system. IGM^{S12} analysis based on promolecular density was selected. VMD^{S13} visualization software is used to give diagrams for IGM analysis. Isovalue parameters were adjusted individually for clarity. In Figures S38–S40, carbon atoms are presented as grey balls. Blue, red and white balls stand for nitrogen, oxygen and hydrogen atoms respectively. Green atoms stand for chloride ion in Figure S38. Phosphorus atoms are presented as lime balls and green balls stand for fluorine atoms in Figure S39. Yellow atom stands for sulfur atom in Figure S40. IGM analysis shows that there are multiple types of interactions between host and hexafluorophosphate anion and *para*-Toluenesulfonate anion. The green ovals represent the favorable interactions between 2,2'-bipyridine rings and corresponding anions in the pocket. (Figures S38–S40). Based on the geometries of 2,2'-bipyridine motif and anions, these interactions (Figure S41) may include C–H…F and C–H…O hydrogen bonding interactions, anion– π interactions, C–H… π interactions and π – π stacking.

Optimized Structure for $2Cl^{-} \subset 4^{4+}$ (Figure S38)

Charge: 2

Spin Multiplicity: 1

Cl	1.47698000	0.05683100	-1.26253800
Cl	-3.05032100	-0.17040400	-1.45447000
0	-6.65598600	-3.43636400	0.89127200
0	-7.11343500	3.18234100	0.70478300
0	6.90321600	3.49640600	-0.44700600
0	7.31723500	-3.24946100	-0.45085400
Ν	-5.32492200	-3.35250200	0.38242400
Ν	-5.76099700	3.10012000	0.33413800
Ν	5.56080700	3.30353400	0.18993200
Ν	6.02330600	-3.14390100	0.11943100
Ν	-1.70242600	3.20716300	-0.34788900
Ν	0.98652900	3.48573300	-0.91846900
Ν	-1.23787900	-3.18949600	-0.33981800
Ν	1.44355700	-3.44585000	-0.87217400
С	-7.56041300	-3.20721300	-0.20884400
Н	-8.51257000	-3.64495800	0.09448900
Н	-7.17784800	-3.68985700	-1.10988000
С	-7.71443800	-1.62473300	-0.40587800
		S57	

С	-8.79631900	-0.94544400	0.25416300	
Н	-9.55133100	-1.52170600	0.78142500	
С	-8.86302400	0.46469300	0.22192700	
Н	-9.67502000	0.97937000	0.72771700	
С	-7.87496500	1.19034400	-0.43195100	
С	-6.88981500	0.59744600	-1.10457700	
Н	-6.13195400	1.15723100	-1.64333800	
С	-6.78937700	-0.89881600	-1.08954200	
Н	-5.95215500	-1.36327600	-1.60215300	
С	-7.96385800	2.69416700	-0.37027600	
Н	-7.65152500	3.16983100	-1.30453100	
Н	-8.96213000	3.03635200	-0.09414700	
С	-5.00131800	3.35746800	1.41143200	
Н	-5.40148600	3.55938600	2.40055300	
С	-3.56412700	3.33649900	1.11049800	
С	-3.13306500	3.11325400	-0.16164500	
Н	-3.71984900	2.92939000	-1.04918200	
С	-2.66971600	3.54822800	2.19422900	
Н	-3.05830200	3.71616100	3.19186300	
С	-1.42085300	3.53296900	1.92051100	
Н	-0.72025000	3.69648600	2.73696100	
С	-0.84247300	3.34781700	0.68893000	
С	0.60337300	3.33894500	0.34770500	
С	1.52236600	3.19460100	1.30451400	
Н	1.19259900	3.07482500	2.33051200	
С	2.92147900	3.19518500	1.07098400	
Н	3.65902700	3.09855200	1.85628900	
С	3.27401800	3.29710500	-0.32143400	
C	2.40496200	3.46821400 \$58	-1.31700000	

Н	2.59936400	3.59083700	-2.37453200
С	-0.03886400	3.69507600	-1.98637200
Н	-0.27900100	4.76298800	-1.99633900
Н	0.42378700	3.42260300	-2.93505900
С	-1.17118200	2.86550100	-1.71390100
Н	-0.93101800	1.79534900	-1.68996500
Н	-1.97443600	3.03937600	-2.42929200
С	4.64439300	3.36669900	-0.74323800
Н	4.90380100	3.49568100	-1.79286700
С	7.81281400	3.09142400	0.52022900
Н	7.53279600	3.46415300	1.51256500
Н	8.76299900	3.57387800	0.25146400
С	7.92363500	1.66548800	0.47909300
С	8.39997000	0.89098900	1.51479500
Н	8.70422200	1.41246300	2.42439700
С	8.51025100	-0.38049400	1.48462000
Н	8.90106600	-0.85528700	2.39045800
С	8.15249800	-1.21814200	0.49491300
С	7.70562100	-0.51485300	-0.65821700
Н	7.40719200	-1.04277400	-1.55879100
С	7.58151700	0.90548100	-0.62125400
Н	7.19883400	1.39128300	-1.51514700
С	8.30105300	-2.74773400	0.46736800
Н	9.25940400	-3.05445600	0.04302900
Н	8.17112000	-3.19178100	1.45873500
С	5.13124200	-3.37117100	-0.74276100
Н	5.35958400	-3.59231600	-1.78608100
С	3.77552800	-3.31629300	-0.30411200
С	3.39868900	-3.14479400	1.02996300
		S59	

Н	4.10894800	-3.01920600	1.83793000
С	1.95805400	-3.10747800	1.30351500
Н	1.68671100	-2.94379400	2.33706100
С	1.09165000	-3.23579800	0.39423400
С	2.79155100	-3.54425900	-1.13805500
Н	2.99173800	-3.76023900	-2.18472400
С	-0.38073700	-3.28372700	0.66685200
С	-0.82659600	-3.32045900	2.01125300
Н	-0.13757900	-3.39146700	2.83888300
C	-2.22110500	-3.34241100	2.22956300
Н	-2.59367300	-3.40013500	3.24780800
С	-3.09930500	-3.28432500	1.18262600
С	-2.62679500	-3.21977500	-0.08829500
Н	-3.24291000	-3.15826500	-0.97562100
С	-0.75788500	-2.97919900	-1.62809300
Н	-0.58363600	-1.89821800	-1.73970500
Н	-1.52198900	-3.26498900	-2.35164900
С	0.47934100	-3.72353800	-1.90803200
Н	0.31250800	-4.80590800	-1.93006600
Н	0.89279200	-3.40277900	-2.86351300
С	-4.53598700	-3.36592000	1.43655700
Н	-4.91784500	-3.41710200	2.45301000

Optimized Structure for $2PF_6^- \subset 4^{4+}$ (Figure S39)

Charge: 2

Spin Multiplicity: 1

Р	2.41011900	0.07264300	-0.23399700
F	2.77980800	-0.93913100	-1.29372200
F	3.15671800	-0.69476900	0.77105600
		S60	

F	3.43536500	1.06599500	-0.73248700
F	1.75912200	1.13264700	0.72268800
F	1.51970100	0.78601700	-1.31811100
F	1.28321400	-0.88227900	0.18916700
Р	-2.46094000	-0.40053600	-1.15113100
F	-3.39922300	-0.89890100	0.03545700
F	-1.46067000	-1.48573500	-0.75999900
F	-1.51200300	0.11078200	-2.31409700
F	-1.76494300	0.58987400	-0.16946600
F	-3.48343200	0.73013500	-1.53728600
F	-3.26658700	-1.32783600	-2.10621000
0	-6.96776700	3.63057000	-0.05917800
0	6.90654800	3.56104300	0.14598800
0	7.07055500	-3.26575600	0.60747000
0	-6.87731300	-3.50291400	0.25598100
Ν	-5.58549000	3.46291500	-0.15698700
Ν	-1.41707700	3.65360000	-0.09498800
Ν	1.40170600	3.96827900	-0.09089500
Ν	5.54312100	3.53900400	-0.05677500
Ν	5.68433500	-3.30486800	0.34581100
Ν	1.63669000	-3.76570700	-0.00369700
Ν	-1.10644900	-4.36295300	-0.23473900
Ν	-5.56803100	-3.36114800	0.77366200
С	-5.00910200	4.01997500	0.83344700
Н	-5.56447000	4.50487700	1.63581900
С	-3.53807200	3.99573300	0.91524000
С	-2.91377400	4.46581300	2.03194200
Н	-3.49728900	4.81666200	2.87757000
С	-1.52048100	4.48476200	2.10323000
		S61	

Н	-1.03095800	4.86387800	2.99042000	
С	-0.78490900	4.06778400	1.02830600	
С	-2.75545500	3.62097800	-0.18836500	
Н	-3.17692600	3.27906900	-1.12661900	
С	-0.58527800	3.21411300	-1.26007000	
Н	-0.32558800	2.16550800	-1.09343500	
Н	-1.19435300	3.30901900	-2.15822500	
С	0.60477200	4.07054600	-1.35248400	
Н	0.35673900	5.12672200	-1.48725500	
Н	1.24110600	3.73532300	-2.17201600	
С	2.72014500	3.92570300	-0.09439800	
Н	3.18495000	3.92007300	-1.07558400	
С	3.46762000	3.89467700	1.04323600	
С	2.76521400	3.91139000	2.25260600	
Н	3.31404400	3.87550900	3.18891700	
С	1.36266600	3.97677400	2.28411700	
Н	0.83154600	3.96484300	3.22576000	
С	0.69321500	4.01185800	1.07396800	
С	4.90429100	3.83270900	1.05181700	
Н	5.43843600	4.00782400	1.98439400	
С	7.52591700	2.99333200	-1.00490000	
Н	8.53426200	3.41636100	-1.01161900	
Н	6.99039900	3.32671900	-1.89709500	
С	7.58968500	1.47491700	-0.93621500	
С	8.57774800	0.84516900	-0.22241200	
Н	9.33954000	1.44327700	0.27336800	
С	8.59698700	-0.53751700	-0.08205800	
Н	9.39112100	-1.01154400	0.48957200	
C	7.68580700	-1.28793300 S62	-0.73996300	

С	6.65750400	-0.69741900	-1.43764000
Н	5.90487900	-1.30109400	-1.93709400
С	6.62405900	0.73492800	-1.56218200
Н	5.82651000	1.21157000	-2.12429400
С	7.75093100	-2.80209200	-0.67234700
Н	8.77232100	-3.16793400	-0.56144900
Н	7.24695400	-3.29097800	-1.50597100
С	5.05290300	-3.53982300	1.42111800
Н	5.53554900	-3.65366500	2.39048800
С	3.60822100	-3.64157300	1.31625000
С	2.95428700	-3.66606000	0.10529900
Н	3.49927500	-3.61816400	-0.83128000
С	2.79287400	-3.71963200	2.45553300
Н	3.24989900	-3.71891100	3.44028900
С	1.41676300	-3.79085900	2.34526400
Н	0.81290000	-3.85771200	3.24226200
С	0.83226000	-3.81505500	1.13150200
С	-0.60912600	-3.88562300	0.92990100
С	-1.51967300	-3.48277300	1.90718400
Н	-1.16490000	-3.07904400	2.84684600
С	-2.87600000	-3.56485100	1.64911900
Н	-3.58782500	-3.23513000	2.39834900
С	-3.33997800	-4.04869300	0.41192000
С	-2.41444000	-4.46989300	-0.47227800
Н	-2.68115000	-4.87244600	-1.44428100
С	-0.10683300	-4.75589400	-1.29780700
Н	0.25464700	-5.75650100	-1.04771800
Н	-0.63909900	-4.77973000	-2.24739700
С	0.99022300	-3.75566400	-1.33327900
		S63	

Н	1.73566800	-4.03239600	-2.07725900
Н	0.63090500	-2.73800700	-1.51133400
С	-4.75948100	-4.08853800	0.08261300
Н	-5.09801900	-4.66852400	-0.77536500
С	-7.73259000	-2.57106000	0.88179200
Н	-7.46374800	-2.50166800	1.94290100
Н	-8.72928200	-3.02138800	0.82836100
С	-7.74358400	-1.22256600	0.26194000
С	-8.84618100	-0.38022000	0.45322800
Н	-9.70378100	-0.76288600	1.00439600
С	-8.86654900	0.98536300	0.00968800
Н	-9.71371500	1.63357800	0.20478400
С	-7.74154100	1.40843700	-0.69120900
С	-6.67684300	0.56420400	-0.94584800
Н	-5.81911500	0.93063900	-1.50072000
С	-6.68591200	-0.74485600	-0.47686600
Н	-5.82203500	-1.37180500	-0.67571700
С	-7.64114900	2.89768600	-1.06640900
Н	-7.12744500	3.03830400	-2.02288900
Н	-8.63388700	3.35003500	-1.11884900

Optimized Structure for TsO⁻ \subset **4**⁴⁺ (Figure S40)

Charge: 3

Spin Multiplicity: 1

S	-0.60603600	0.00000100	1.68808400
0	-1.06487800	-1.17687700	2.33599600
0	-1.06488600	1.17687500	2.33599800
0	-1.19059400	0.00000000	0.27979800
С	1.19208000	0.00000700	1.59621700
		S64	

С	1.84887400	0.00000800	2.86720600
Н	1.29607200	0.00090000	3.79940600
С	3.20729800	0.00001300	2.78575800
Н	3.77986000	0.00142400	3.71361000
С	3.87732900	0.00001600	1.63994400
С	3.19442500	0.00001500	0.41513300
Н	3.75598400	0.00208400	-0.51622700
С	1.82063300	0.00001000	0.42668900
Н	1.24411700	0.00086100	-0.49657300
С	5.33089400	0.00002200	1.61651300
Н	5.73123700	-0.91051300	1.15104300
Н	5.76216700	0.07020000	2.61946400
Н	5.72991300	0.83474200	1.02603800
0	6.55306400	-3.33936000	-0.59491000
0	6.55304100	3.33941600	-0.59490400
0	-7.11046600	-3.40934900	-0.34801300
0	-7.11048900	3.40930800	-0.34800700
Ν	5.16403200	-3.26504100	-0.63216600
Ν	5.16401000	3.26508600	-0.63216100
Ν	1.08115300	-3.47425000	-0.40613300
Ν	1.08112900	3.47426700	-0.40612700
Ν	-1.71628200	-3.22727600	-0.30418800
Ν	-1.71630500	3.22727300	-0.30418300
Ν	-5.76982600	-3.33105200	-0.45796200
Ν	-5.76984900	3.33102200	-0.45795600
С	4.66398400	-3.41244000	0.50305800
С	4.66396000	3.41248000	0.50306400
Н	5.26410000	-3.54465300	1.40471700
Н	5.26418200	3.54301700	1.40491300
		S65	

С	3.20814900	-3.42747700	0.62745000
С	3.20812500	3.42750700	0.62745600
С	2.57089900	-3.50598000	1.84691400
С	2.57087400	3.50600400	1.84692000
Н	3.16668900	-3.51628100	2.75569000
Н	3.16666300	3.51627500	2.75569300
С	1.22072600	-3.54753200	1.93484500
С	1.22070100	3.54754600	1.93485100
Н	0.73268900	-3.55685600	2.90147400
Н	0.73266500	3.55686700	2.90148000
С	0.45175600	-3.56632400	0.78305400
С	0.45173100	3.56633400	0.78306000
С	2.41069700	-3.39825000	-0.50365400
С	2.41067300	3.39827600	-0.50364800
Н	2.81760900	-3.33723700	-1.50676100
Н	2.81757700	3.33728900	-1.50676000
С	-1.01191700	-3.64232300	0.80674600
С	-1.01194300	3.64232400	0.80675200
С	-1.72419500	-4.08597800	1.89347100
С	-1.72422400	4.08597100	1.89347800
Н	-1.19533100	-4.45091300	2.76502500
Н	-1.19536200	4.45090700	2.76503300
С	-3.11011400	-4.06427000	1.89217400
С	-3.11014300	4.06425400	1.89218100
Н	-3.65705900	-4.40846500	2.76413600
Н	-3.65709000	4.40844400	2.76414400
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Н	-5.82957000	-1.25788700	-2.86171900	
Н	-5.82956300	1.25786200	-2.86169000	

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