

Redox Control of the Binding Modes of an Organic Receptor

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1. Introduction

1-1. Mechanically interlocked molecules (MIMs)

- Molecular recognition events on the redox potential are a fundamental theme of biological relevant processes. e.g) Enzyme co-factor recognition
- In order to understand the recognition phenomena, the control of noncovalent bonding interaction in supramolecular assemblies has been studied.

⇒ Study of mechanically interlocked molecules (MIMs) e.g) catenanes and rotaxanes

1-2. Previous Work

1) CBPQT⁴⁺ (cyclobis(paraquat-*p*-phenylene)), “blue-box”

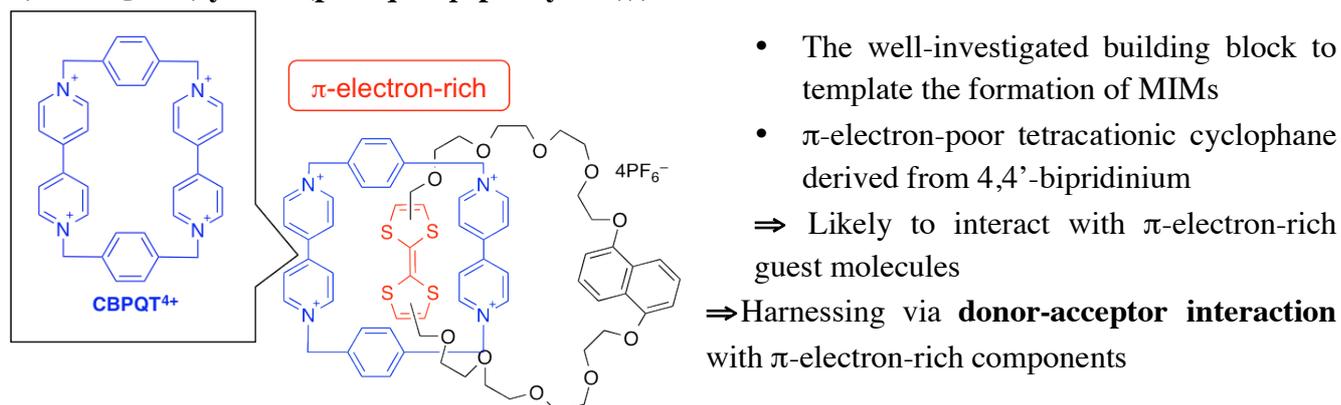


Figure 1. CBPQT⁴⁺ as π-electron-deficient components for MIMs¹

2) CBPQT²⁽⁺⁺⁾, as components showing radical-pairing interactions

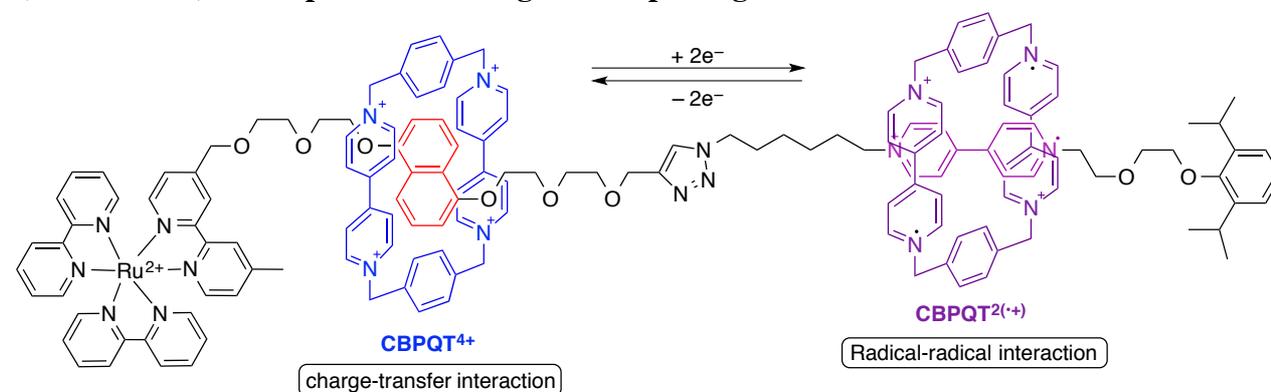
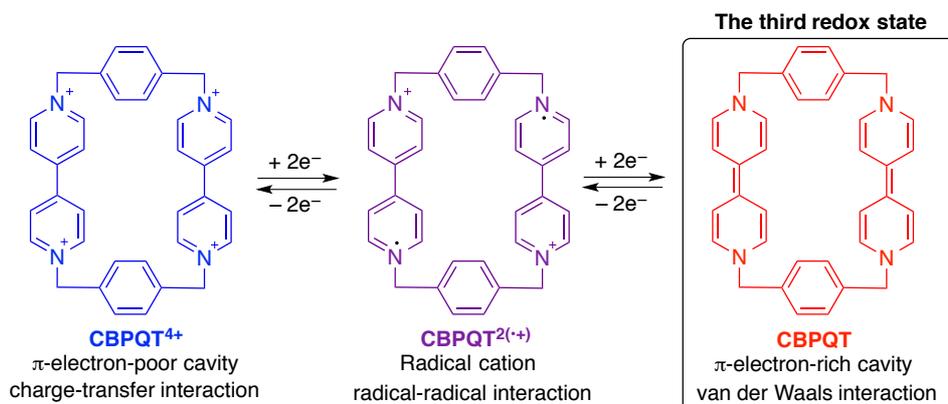


Figure 2. Shuttle-like mechanical interlocked system using CBPQT in different redox states.²

- Reduction of CBPQT⁴⁺ afforded biradical cation specie, CBPQT²⁽⁺⁺⁾.
- CBPQT²⁽⁺⁺⁾ tends to interact with monoradical cation unit via radical-radical interaction.

⇒ **CBPQT** in different redox states affords different interaction between host and guest molecules.

1-3. This Work



- The fully reduced state of **CBPQT** was expected to possess the new property of host-guest interaction because of its π-electron-rich cavity.
- The property of the neutral **CBPQT** as host molecule has not been investigated.

⇒ Investigation of the neutral **CBPQT**, as the third redox state

- Formation and isolation of fully reduced neutral **CBPQT** and investigation of its electronic configuration
- Formation of host-guest intramolecular interactions using **CBPQT** as host molecule and investigation of the preference of guest molecule via DFT calculation

2. Results and Discussion

2-1. The difference of UV-Vis and ESR spectra depending on the amount of reductant

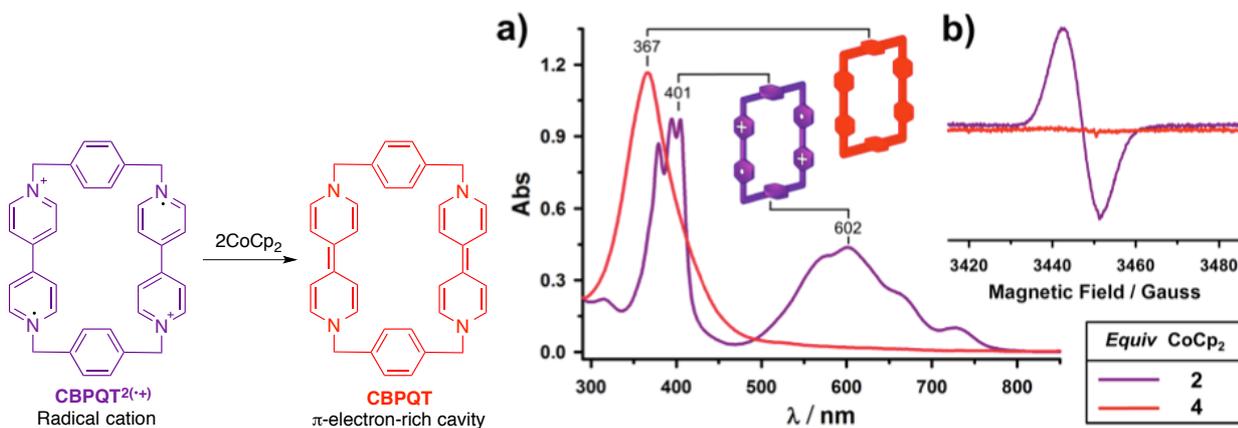


Figure 3. a) UV-Vis spectra and b) ESR spectra of **CBPQT** with different amount of reductant (The both of them were those in acetonitrile.)

- The strong reductant, **CoCp₂**, with different equivalent was added to the **CBPQT⁴⁺**.
- With 4 equivalent of **CoCp₂**, the peak particular to biradical **CBPQT^{2(•+)}** disappeared and a new peak appeared in UV-Vis spectra.
- In the ESR spectra, the peak, which is the evidence for existence of radical species, such as **CBPQT^{2(•+)}**, was also quenched with 4 equivalent of **CoCp₂**.

⇒ Electronically neutral and nonradical **CBPQT**, “red box” was generated.

2-2. X-ray analysis of neutral **CBPQT** in the solid-state structure.

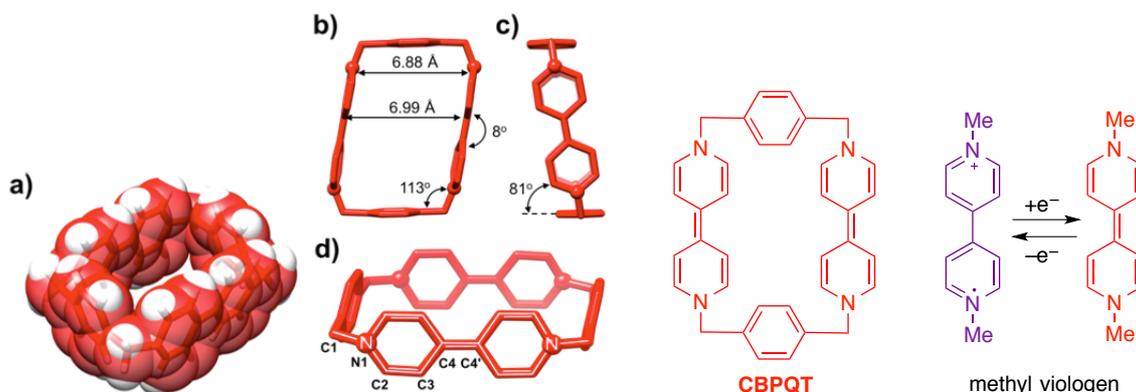


Figure 4. Solid-state structure of the neutral **CBPQT** obtained from single-crystal X-ray crystallography

- Single crystal of the neutral **CBPQT** was obtained by vapor diffusion, following reduction by 4 equivalent of CoCp_2 under Ar atmosphere.
- The each bond length of 1,4-bipyridine was similar to that of fully reduced methyl viologen.

⇒ The obtained crystal was composed of totally reduced **CBPQT**.

2-3. Investigation of the π -electron-rich cavity of **CBPQT** as a new guest

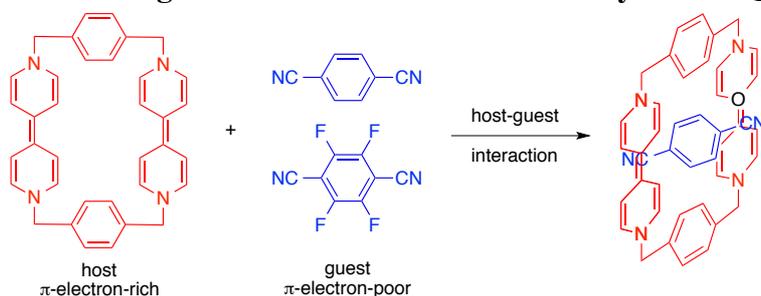


Figure 5. Formation of complex of **CBPQT** and π -electron-poor molecules

- To investigate the property of neutral **CBPQT** as π -electron-rich host molecule, 1,4-dicyanobenzene (DCB) and 1,4-dicyanotetrafluorobenzene (DCFB) were introduced as π -electron poor guest molecule.

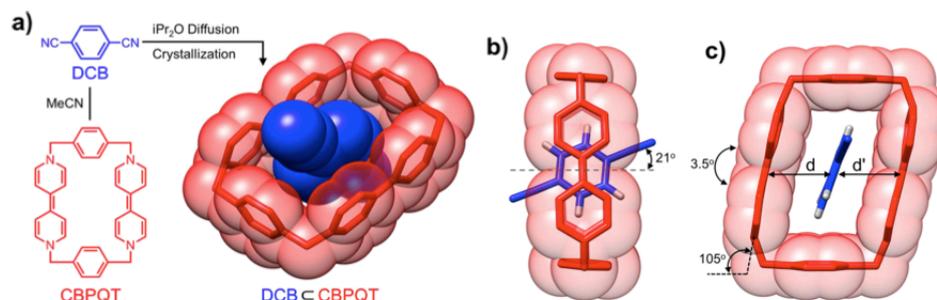


Figure 6. Solid-state structure of the complex of **CBPQT** and **DCB** obtained from single-crystal X-ray crystallography

- Single crystal of complex of **CBPQT** and **DCB** showed the clear evidence for the ability of the neutral **CBPQT** to form 1:1 inclusion complexes with **DCB**.
- The distance between the guest and the two bipyridine units, are 3.45 Å and 3.47 Å.
⇒ Typical distance of π -stacking interactions

2-4. Calculation of the enthalpies of complexation

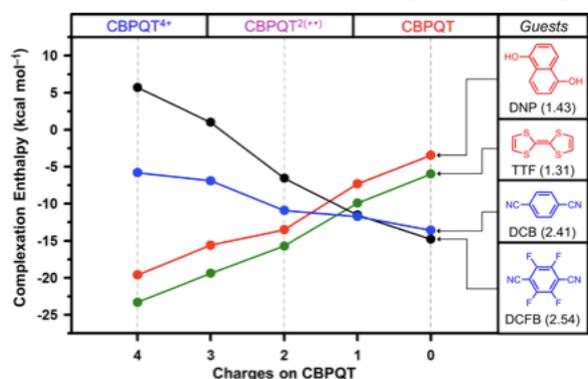


Figure 7. Plot of the complexation enthalpies derived from DFT calculation (M06/6-311++G**//M06/6-31G*) (The value under the guests' structure means calculated Mulliken electronegativities.)

- The enthalpies of complexation between π -electron-poor guest and host **CBPQT** became lower as **CBPQT**'s reduction promoted.

⇒ Altering oxidation state of **CBPQT** changed preference of π -system guest molecule.

3. Conclusion

- The structural, optical, and quantum mechanical studies of **CBPQT**, the totally reduced form, were conducted.
- The merely reduction of **CBPQT**⁴⁺ afforded the different preference to the guest molecules and the new property as host molecules for π -electron-poor guest molecules.

⇒ The possibility for switching the preference for guest molecule by reproducible redox reaction and utilizing the property for a new MIMs

4. Reference

1. V. Balzani, J. F. Stoddart, M. Venturi, and D. J. Williams *et al.*, *Angew. Chem., Int. Ed.*, **1998**, *37*, 333–337.
2. J. Sauvage, and J. F. Stoddart *et al.*, *Angew. Chem., Int. Ed.*, **2011**, *50*, 6782–6788.