

Inclusion complexation of cyclobis(paraquat-*p*-phenylene) with thiophene, bithiophene and terthiophene

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Abstract The inclusion complexation between the electron-poor cyclophane, i.e. cyclobis(paraquat-*p*-phenylene), and the electron-rich thiophene oligomers, i.e. thiophene, bithiophene and terthiophene, were characterized in solution and solid state. In solution, we confirmed a 1:1 complexation and that the binding strength depends on the number of the thiophene units. From the X-ray crystallographic analysis we confirmed the solid-state structure of the inclusion complex. These results indicate that charge-transfer, π - π and van der Waals interactions may contribute to the driving force of inclusion complexation.

Keywords Cyclophane · Thiophene · Inclusion complex · Host-guest chemistry · X-ray structure

Introduction

Thiophene is one of the most important functional units for the preparation of (semi)conducting materials [1]. In fact, the oligo- and polythiophenes have been extensively studied as the materials for organic field-effect transistors (FETs) [2], organic light-emitting diodes (LEDs) [3] and electrochromic

materials [4]. In recent years, the inclusion complexation has become an emerging method to functionalize the conducting polymers [5]. The insulating wire, in which the conducting polymers are wrapped with the helical polymers or macrocyclic compounds, has been prepared using polysaccharides, such as amylose [6] and cyclodextrins [7–9]. In these studies, researcher has mainly focused on the isolation of the individual conducting polymer for reducing the inter-molecular interaction between the conducting polymers. Recently, we have reported the synthesis of the thiophene donor-acceptor [2] rotaxanes [10], in which the thiophene oligomers were wrapped with the tetracationic cyclophane cyclobis(paraquat-*p*-phenylene) (**CBPQT**⁴⁺, Fig. 1). In that study, we achieved not only the isolation of the thiophene units by the encapsulation of the **CBPQT**⁴⁺ macrocycle, but also affording unique optical and electrochemical properties based on the charge-transfer (CT) interaction between the electron-rich thiophene unit and the electron-poor bipyridinium units in **CBPQT**⁴⁺. In our previous study, we used ethyleneglycol-substituted thiophene derivatives for synthesizing [2] rotaxanes. Despite extensive studies over two decades [11–18], inclusion complexation of **CBPQT**⁴⁺ with *unsubstituted* thiophene oligomers has not been reported so far. In this study, we report inclusion complexation of **CBPQT**⁴⁺ with thiophene (**1T**), bithiophene (**2T**) and terthiophene (**3T**) (Fig. 1). These inclusion complexes were characterized by UV-Vis, ¹H NMR spectra and X-ray crystallography.

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Experimental

General

CBPQT⁴⁺ · 4PF₆ was synthesized according to the literature [19]. The thiophene derivatives (**nT**, *n* = 1–3) were

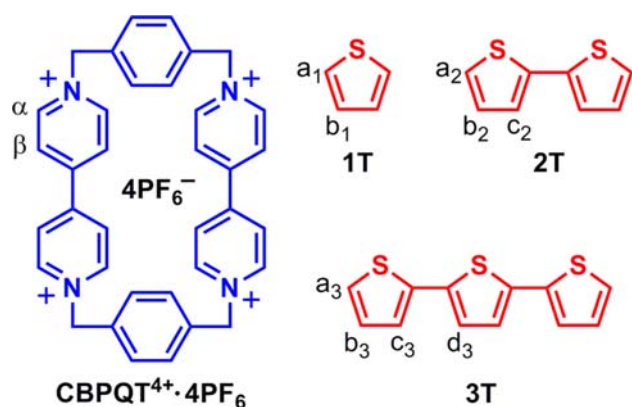


Fig. 1 Chemical structures of cyclobis(paraquat-*p*-phenylene) (**CBPQT⁴⁺·4PF₆**), thiophene (**1T**), bithiophene (**2T**), and terthiophene (**3T**). The labeling scheme for the ¹H NMR assignment is also depicted

purchased from a commercial source (TCI Co.) and used as received. UV/Vis spectra were recorded at room temperature on a UV-2550 UV-Visible spectrophotometer (Shimadzu Co.). ¹H NMR spectra were recorded at 293 K on a JNM-AL300/BZ FT NMR system (JEOL, Ltd.) with residual solvent as the internal standard.

Job plot [20]

CBPQT⁴⁺·4PF₆ and **nT** were dissolved in MeCN to be 0.01 M solutions, respectively. The solutions were mixed in different ratios with keeping the total volume to be 2 mL. These mixtures were analyzed by UV-Vis spectroscopy.

¹H NMR titration [20]

The titration experiments were carried out in deuterated solvent at 293 K. The solution containing **2T** (1.3 × 10⁻¹ M) and **CBPQT⁴⁺·4PF₆** (3.2 mM) was added to a solution of **CBPQT⁴⁺·4PF₆** solution (2 mL, 3.2 mM). The concentration of the **CBPQT⁴⁺·4PF₆** remains constant during the titration process. The chemical shift during the titration was recorded using the NMR spectrometer. The molar ratio of [**nT**]/[**CBPQT⁴⁺**] was calculated from the integrals of the protons on the host and guest. From the titration result, we calculated the binding constant using a non-linear regression of Eq. 1,

$$\delta_{\text{obs}} = \delta_{\text{CBPQT}} + \frac{\Delta x}{2[\text{CBPQT}]} \left([\text{CBPQT}] + [\text{nT}] + K_a^{-1} - \sqrt{([\text{CBPQT}] + [\text{nT}] + K_a^{-1})^2 - 4[\text{CBPQT}][\text{nT}]} \right) \quad (1)$$

where δ_{CBPQT} and Δx are the chemical shift of the **CBPQT⁴⁺** proton at [**nT**] = 0 and the chemical shift

difference between the complexed and uncomplexed **CBPQT⁴⁺** species, respectively. The chemical shift change of the *p*-phenyl protons was used for curve fitting. In the cases of **1T** and **3T**, the concentrations of **CBPQT⁴⁺·4PF₆** were set to 3.5 and 1.3 mM.

X-ray crystallography

Single crystals of the inclusion complex between **CBPQT⁴⁺·4PF₆** and **2T** were prepared by vapor diffusion of *i*-Pr₂O into a MeCN solution containing equimolar amounts of **CBPQT⁴⁺·4PF₆** and **2T**. Diffraction data was collected on a Rigaku RAXIS-RAPID diffractometer using graphite-monochromated Mo K α radiation.

Crystal Data for [**CBPQT⁴⁺·4PF₆·2T·2MeCN**]: C₃₆H₃₂N₄·4PF₆·C₈H₆S₂·2MeCN, $M = 1348.89$, primitive monoclinic, $a = 10.7653(2)$, $b = 19.4889(4)$, $c = 13.8798(3)$ Å, $\beta = 109.5100(11)^\circ$, $V = 2744.85(10)$ Å³, space group P2₁/n (#14), $Z = 2$, $\rho_{\text{calcd}} = 1.632$ g cm⁻³, $\mu(\text{Mo K}\alpha) = 31.194$ cm⁻¹, $F(000) = 1364.00$, $T = 120$ K, red needle crystal, 0.18 × 0.06 × 0.03 mm, $R_1 = 0.0897$, $wR_2(F_2) = 0.2779$, goodness of fit = 1.14.

CCDC 716816 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Results and discussion

Inclusion complexation in solution

When **CBPQT⁴⁺·4PF₆** solution was added to the solutions of **2T** and **3T**, the color changes to orange and red purple, respectively, were detectable by the eye, indicating complexation (Fig. 2a) [10, 12–19]. These colors arise from the CT band between the electron-poor bipyridinium units in **CBPQT⁴⁺** and the electron-rich thiophenes [10]. Although the mixture of **CBPQT⁴⁺·4PF₆** and **1T** is almost colorless, the spectral change was detectable in the UV region. The λ_{max} of the CT band depends on the potential gap between the HOMO of **nT** and the LUMO of **CBPQT⁴⁺**. The λ_{max} of the CT band correlates well with λ_{max} of the thiophene π - π^* band (Table 1).

From the Job plot (Fig. 2b), the stoichiometry of complexation was confirmed to be 1:1 in all cases. In ¹H NMR titration experiments, we confirmed the chemical shift change of the **CBPQT⁴⁺** protons in relation to the concentration of **nT**, which implies fast exchange between the complexed and uncomplexed species on NMR timescale and we observed the weight-averaged value of the chemical shifts of complexed and uncomplexed species. Figure 3 shows the ¹H NMR spectra of (a) **2T**, (b)

Fig. 2 **a** Change in the UV-Vis spectra by changing the mixing ratio of **2T** and **CBPQT⁴⁺** · 4PF₆. Solvent: MeCN. **b** Job plot for inclusion complexation between **2T** and **CBPQT⁴⁺** · 4PF₆

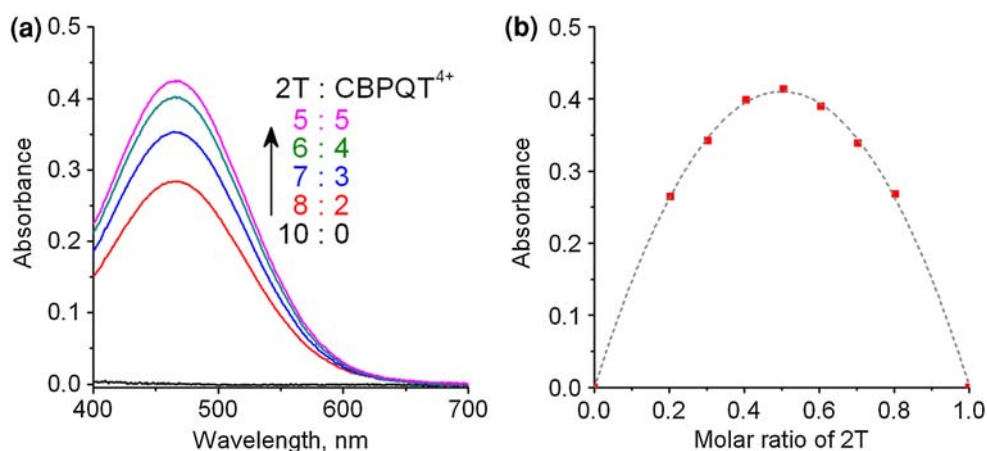


Table 1 Maximum absorption wavelength (λ_{\max}) in UV-Vis spectra for π - π^* and CT bands and association constants of inclusion complex in CD₃CN at 293 K (K_a)

Guest	λ_{\max} (nm) π - π^* band ^a	λ_{\max} (nm) CT band ^b	K_a (M ⁻¹)
1T	230	<400 ^c	30
2T	302	467	100
3T	352	507	180

^a π - π^* transition band of the thiophene derivatives

^b Charge-transfer band of inclusion complex

^c λ_{\max} is less than 400 nm

CT band overlaps the absorption band of **CBPQT⁴⁺** · 4PF₆

CBPQT⁴⁺ · 4PF₆ and (c) 9:1 mixture of **2T** and **CBPQT⁴⁺** · 4PF₆. The chemical shift of the β and *p*-phenylene protons of **CBPQT⁴⁺** strongly affected in the presence of **2T**, while the chemical shift of the α and CH₂ protons on **CBPQT⁴⁺** did not. This result suggests that the aromatic plane of the thiophene derivative is inserted in a parallel fashion between two bipyridinium aromatic planes [10, 12–19]. In this configuration, the β and *p*-phenylene protons are strongly affected by the shielding and deshielding effects of the thiophene ring, respectively.

From the chemical shift change of the *p*-phenylene protons in relation to the concentration of the thiophene compounds, we calculated the association constants (Fig. 4). Table 1 summarizes the association constants for inclusion complexation between the **CBPQT⁴⁺** · 4PF₆ and **nT** in CD₃CN. The obtained K_a values for **nT** are much smaller than those observed for the diethyleneglycol-substituted thiophenes ($K_a = 10^3$ M⁻¹ order) [10]. The strong binding of the diethyleneglycol substituted thiophenes is attributable to the electrostatic interaction of the ether oxygen atoms to the cationic cyclophane and the hydrogen bonds of the ether oxygen atoms to the α -hydrogen atoms of **CBPQT⁴⁺** [10]. Therefore, the diethyleneglycol substitution of the thiophenes is of great

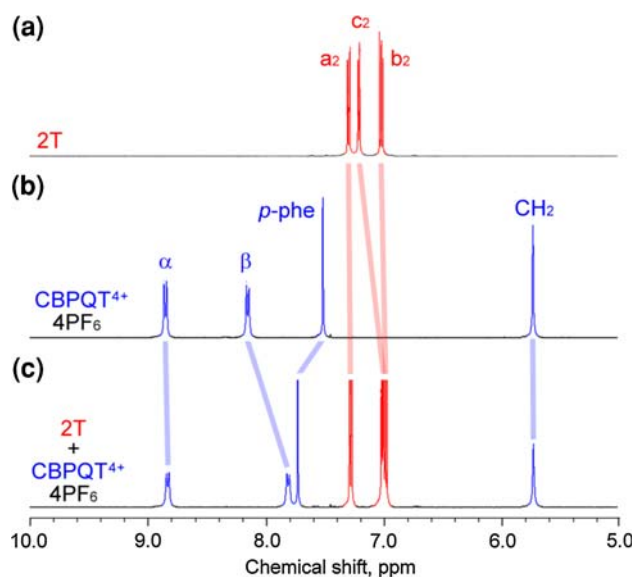


Fig. 3 ¹H NMR spectra of **a** **2T**, **b** **CBPQT⁴⁺** · 4PF₆ and **c** 9:1 mixture of **2T** and **CBPQT⁴⁺** · 4PF₆. Conditions: CD₃CN, 300 MHz, 293 K

importance to enhance the stability of the inclusion complex [19]. The binding strength depends on the number of the thiophene units (Table 1). The inclusion complex between **CBPQT⁴⁺** · 4PF₆ and the longer **nT** has the smaller CT band gap (Table 1), which may induce stronger CT interaction.

The protons on the thiophene unit were also affected in the presence of **CBPQT⁴⁺** · 4PF₆. Figure 5 summarizes the chemical shift changes of the thiophene protons in the presence of **CBPQT⁴⁺** · 4PF₆. All of the peaks of the thiophene protons showed up-field shift after adding **CBPQT⁴⁺** · 4PF₆. These chemical shift changes arise from the shielding effect on the sandwiched thiophene unit by two bipyridinium units. The protons at the central part of the (oligo)thiophene backbone shift more significantly in all cases. This result suggests that the central part of the thiophene backbone resides in the cavity of **CBPQT⁴⁺** · 4PF₆.

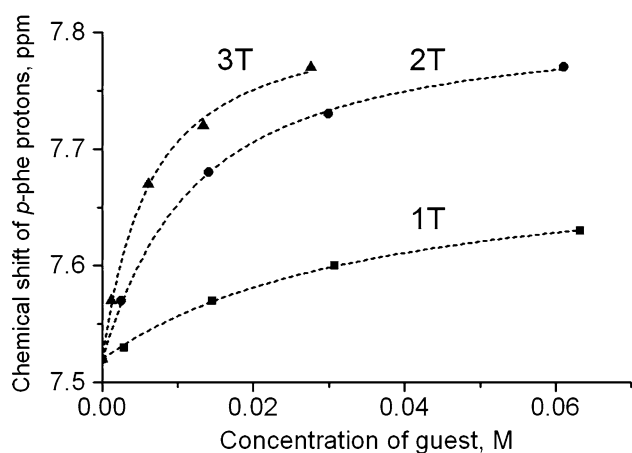


Fig. 4 ^1H NMR titration results for inclusion complexation of $\text{CBPQT}^{4+} \cdot 4\text{PF}_6$ with thiophene (solid square), bithiophene (solid circle) and terthiophene (solid triangle). The concentrations of $\text{CBPQT}^{4+} \cdot 4\text{PF}_6$ for the titration of **1T**, **2T** and **3T** are 3.5 mM, 3.2 mM, and 1.3 mM, respectively

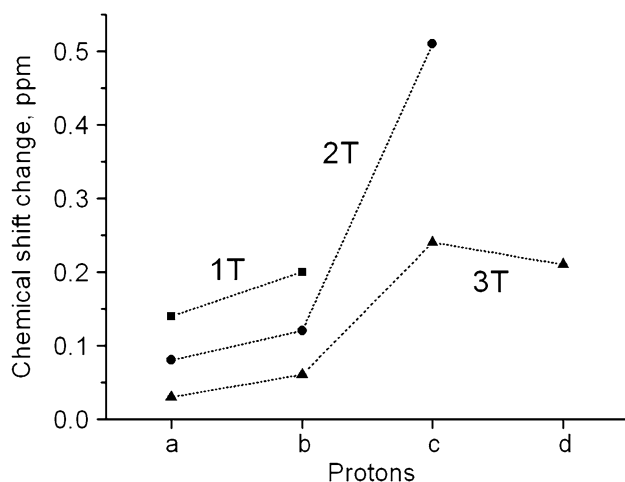


Fig. 5 Chemical shift changes of the thiophene protons in the presence of $\text{CBPQT}^{4+} \cdot 4\text{PF}_6$. Concentrations of **nT** and $\text{CBPQT}^{4+} \cdot 4\text{PF}_6$: 2.9 and 3.5 mM for **1T** (solid square), 2.6 and 3.2 mM for **2T** (solid circle), 1.2 mM and 1.3 mM for **3T** (solid triangle)

Inclusion complexation in solid state

The solid state structure of the inclusion complex between $\text{CBPQT}^{4+} \cdot 4\text{PF}_6$ and **2T** was characterized by X-ray crystallography (Fig. 6). **2T**, in which the sulfur atoms possess an anti orientation, is inserted centrosymmetrically through the center of the CBPQT^{4+} macrocycle. While the bipyridinium units are distorted from the normal planar geometries (dihedral angle between two pyridinium ring mean planes: 21°), the π -system in the bithiophene is completely planarized (dihedral angle between two thiophene ring mean planes: 0°). The tilt angle of the central C–C vector between two thiophene rings relative to the

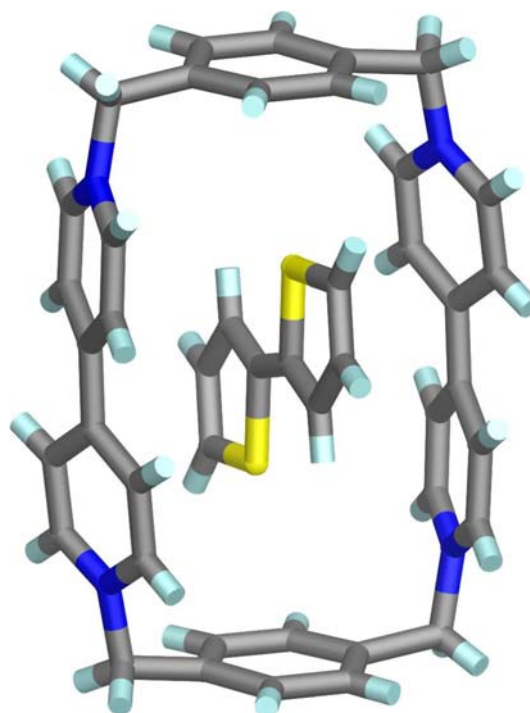


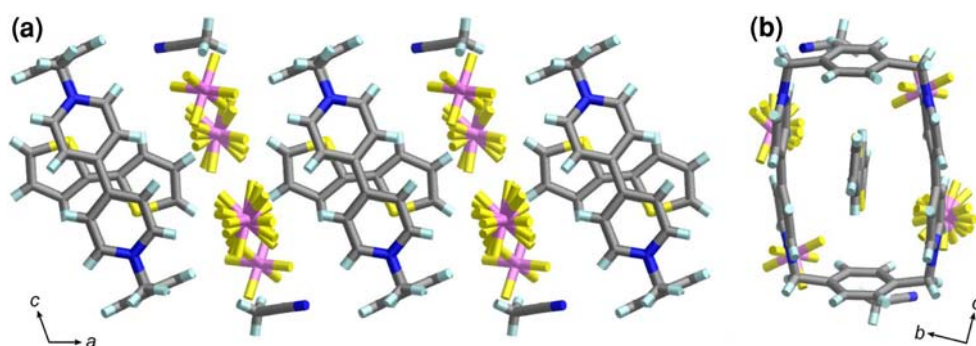
Fig. 6 X-ray crystallographic structure of the inclusion complex between **2T** and $\text{CBPQT}^{4+} \cdot 4\text{PF}_6$. The solvent molecules and the counter ions are omitted for clarity

bipyridinium $\text{N}^+ - \text{N}^+$ vector is 75° . The dihedral angles of the mean planes of the *p*-phenylene and the bipyridinium units with respect to the mean plane of the bithiophene are 5° and 90° , respectively. These results are in good agreement with the molecular orientation deduced from the ^1H NMR results. The distance between the centers of the bithiophene and bipyridinium units is 3.4 \AA , which is suitable for π - π and van der Waals interactions [19]. The inclusion complexes form continuous stacks in the crystallographic *a* direction with no hindrance of the central channel by either the MeCN molecule or PF_6 counter ions (Fig. 7). The bithiophene molecules have their long axes almost perfectly aligned along their direction with a separation of 4.8 \AA between the terminal thiophene carbon atoms in adjacently located bithiophene molecules. The sulfur atom of each thiophene ring is positioned approximately midway between the directly opposite β carbon atoms of the bipyridinium units at a mean distance of 3.6 \AA . These results are comparable to the results obtained from the X-ray structure of the inclusion complex between $\text{CBPQT}^{4+} \cdot 4\text{PF}_6$ and the tetrathiafulvalene [14].

Conclusion

We confirmed that the cyclophane $\text{CBPQT}^{4+} \cdot 4\text{PF}_6$ forms the inclusion complex with thiophene, bithiophene

Fig. 7 **a** A part of the continuous stacks of $2T \cdot CBPQT^{4+} \cdot 4PF_6 \cdot 2MeCN$. **b** Same structure of **(a)** viewed from another direction



and terthiophene. The driving forces for inclusion complexation are considered to be charge-transfer, π - π , and van der Waals interactions. These results afford important directions towards more complex architecture based on the host-guest pairs of $CBPQT^{4+}$ and the thiophene derivatives.

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