

Direct Detection of the Ion Pair to Free Ions Transformation upon Complexation with an Ion Receptor in Non-Polar Solvents by using Conductometry

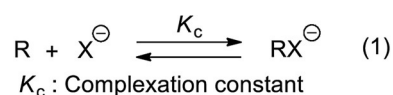
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In this study, we performed conductometry in various organic solvents to directly detect the transformation from tetrabutylammonium chloride (TBACl) ion-pair salt to the free ions through complexation with *meso*-octamethylcalix[4]pyrrole (CP), which is a well-known receptor for chloride anions. In the presence of CP, the conductivity of TBACl increases in various non-polar solvents, indicating that complexation with CP enhances the ionic dissociation of TBACl in such non-polar solvents. In other words, CP recognizes chloride as an ion-paired

salt as well as a free anion in non-polar solvents. Additionally, the TBA(CP-Cl) complex exhibited a considerably lower ion-pairing constant (K_{ip}) than TBACl in non-polar solvents, resulting in enhanced conductivity. Based on these findings, we can conclude that complexation of an anion with a hydrophobic anion receptor will be useful for creating functional and stimuli-responsive soft materials in organic solvents using coulombic forces.

1. Introduction

There has been a great deal of interest in the design and synthesis of molecular receptors for selective recognition and sensing of ionic species, owing to their importance in modern supramolecular chemistry.^[1] Ion recognition processes involving hydrogen bonding have attracted considerable attention because of their applications in chemical, biological, environmental, and medical sciences.^[2] The significant progress in molecular recognition of ion receptors has facilitated implementation of functional materials, including smart soft materials such as chemosensors, liquid crystals, molecular capsules, supramolecular gels, and artificial ion channels.^[3] Supramolecular chemistry-based prediction and control of the weak interactions between ions and receptors has attracted considerable interest for the development of such materials, and many experimental methods have been developed to measure the complexation constants, including various forms of spectroscopy and calorimetry. Most of these methods are based on the following equation [Eq. (1)]:



However, Equation (1) was developed for ionic species in aqueous solution, whereas numerous ionic complexes have been investigated in aprotic organic solvents with a low dielectric constant to preclude competitive hydrogen bonds. In such non-polar solvents, the ion receptor complexation constants markedly vary, depending on the specificity of the ionic guest and the counter cation concentrations,^[4] leading to complicated effects owing to competition by ion pairing for complexation with ionic species in non-polar solvents, which is negligible in highly polar solvents.^[5] However, such ion-pairing effects are mostly ignored in host-guest studies in non-polar solvents, except in the case of ditopic receptors directly recognizing an ion pair as the guest.^[6] Such ion-pairing effects cannot be ignored in non-polar solvents, whereas they can be ignored in highly polar solvents, including water.^[7] However, it is important to elucidate the ion-pairing effects in non-polar solvents, as many intricate supramolecular systems comprise more than two ionic species.^[8]

Nonetheless, there have been only a few studies of the ion-pairing effect in non-polar solvents. For example, Gibson and co-workers reported mathematical processing of equilibria involved in complexation paraquat^[4b] of and dibenzylammonium^[4c] salts with a crown-ether-derived receptor in non-polar solvents. They showed that ion-pairing processes are responsible for concentration-dependent fluctuations in the complexation constant.^[4,9] Although this approach has provided a deep insight into template-directing synthesis for complicated supramolecular architectures^[10] and ion-pair receptors,^[11] the reported processing relies on an approximation on a graphical plot, and does not include the ion-pairing equilibrium of the resulting ion pair. Roelens et al. investigated ion-pairing equili-

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bria by using a tripodal ureidic and pyrrolic receptor, and they proposed a general approach for estimating quantitative ion-pairing equilibria in a multi-equilibrium system.^[12] They used the non-linear least-square fitting of a ¹H NMR chemical shift upon a titration, independent from graphical approximations, and the obtained results showed that the employed ureidic and pyrrolic anion receptor recognizes chloride in an ion-paired salt, enhancing the ionic dissociation.

Although ¹H NMR spectroscopy is widely used to detect host-guest interactions in various organic solvents, it has many inherent limitations in estimating the complexation of a receptor with ionic guest. Especially in non-polar solvents, the ionic guest would be mostly ion paired at the high concentration required for ¹H NMR spectroscopy, and ¹H NMR chemical shifts appear at the averaged position between paired and dissociated ionic species.^[13] Although spectroscopy can be used to determine if an ion receptor binds an ionic guest, it is very difficult to recognize ionic dissociation of the guest, because such methods usually focus on changes in the receptor rather than the guest.

Calix[4]pyrroles are neutral selective anion-binding receptors,^[6a,14] and widely used in many applications including electron-transfer systems,^[15] chemosensors,^[16] solid supports in liquid column chromatography,^[17] and extractants.^[3d] Calix[4]pyrrole has also been shown to act as a ditopic receptor for certain solid-state salts.^[18] Upon complexation with an anion, the calix[4]pyrrole scaffold adopts a cone-shaped conformation, in which pyrrolic NH groups are directed toward the rim and form hydrogen bonds with the anion on one face of the macrocycle. The nature of the solvents and counter cations generally governs the complexation of calix[4]pyrrole with chloride salts. The complexation constants of calix[4]pyrrole with tetraethylammonium chloride (TEACl) and tetrabutylammonium chloride (TBACl) are on the order of 10⁴ and 10² M⁻¹, respectively, in dichloromethane.^[19] This marked difference in the complexation constant suggests the existence of an ion-pairing effect, which is important to understand the mechanism of complexation in organic solvents. The mechanism underlying this ion-pairing effect remains unclear despite a lot of research on anion recognition of calix[4]pyrroles.^[20]

In this study, we used conductometry to elucidate the ion-pairing tendency in non-polar solvents, as conductometry is not subject to limitations regarding salt concentrations and readily allows detection of free ions derived from ion-paired salts through conductivity changes. This allows the detection of complexation between an ion and a receptor even at high dilution, which is ideal for investigating changes in ionic species. As shown in Figure 1, in the *meso*-octamethylcalix[4]pyrrole (CP)-TBACl system, four equilibria in organic solvents should be considered, especially in non-polar solvents with dielectric constant (ϵ) lower than 10. However, the difference in ion-pairing constant (K_{ip} , thus K_{ip1} and K_{ip2}) is usually ignored,^[5] whereas ionic guests for CP are normally ion paired in non-polar solvents, especially at the high concentration required for ¹H NMR spectroscopy. On the other hand, as the CP-Cl complex anion is larger than the bare chloride anion, the ion-pairing constant between the TBA cation and CP-Cl complex

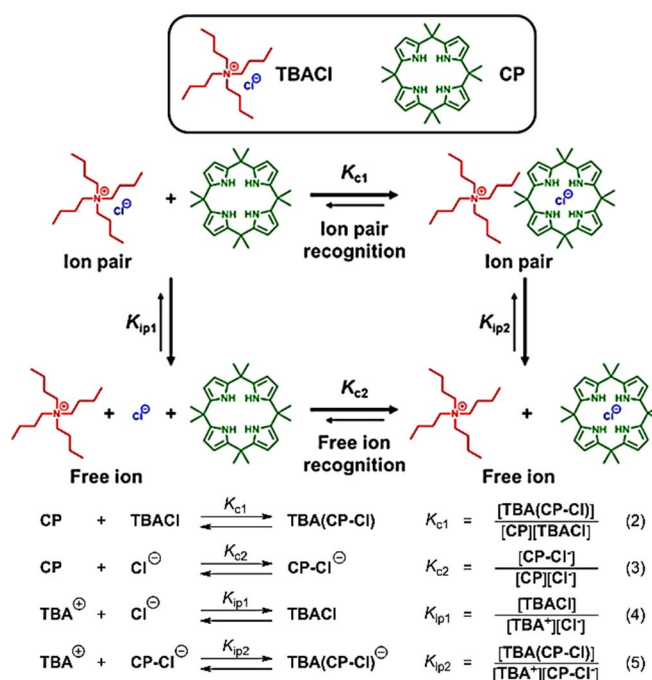


Figure 1. Complexation and ion-pairing equilibria of ion receptor (CP) and ionic guest (TBACl) in organic solvents: complexation of CP with ion-paired TBACl [Eq. (2)], complexation of CP with the free chloride anion [Eq. (3)], ion pairing between the TBA cation and chloride anion [Eq. (4)], and ion pairing between the TBA cation and CP-Cl complex anion [Eq. (5)].

anion (K_{ip2}) should be lower than that between TBA and the bare chloride anion (K_{ip1}).^[5] Therefore, the measurable molar conductivity of TBACl should increase after complexation of TBACl with CP, because of the transformation of the ion pair to free ions. The increase in amount of ionic species in the solution will readily cause a conductivity increase.^[21] In other words, only in the case that CP recognizes ion-paired TBACl to freshly generate ionic species [Eq. (2)], should the conductivity of TBACl solution increase. In contrast, the molar conductivity should decrease when CP recognizes the free chloride anion, because it converts the free anion to a complex anion [Eq. (3)], resulting in an increase in the size and a decrease in the mobility. That is, an increase in conductivity after CP addition in organic solvents indicates transformation of TBACl from ion pair to free ions. At present, conductometry is the only method that can directly determine the concentration of free ions or ion pairs.

2. Results and Discussion

2.1. Conductivity of TBACl in THF with CP Addition

Conductometric titrations of TBACl with CP were carried out at different concentrations (10⁻³–1 mM) in tetrahydrofuran (THF, dielectric constant: $\epsilon = 7.6$, Figure 2). The molar conductivity (Λ_m) increases with increasing [CP] and reaches saturation at a stoichiometry of 1:1, suggesting the formation of a 1:1 complex in THF. As a result of electrolyte dissociation, the concentration of ionic species generally determines the con-

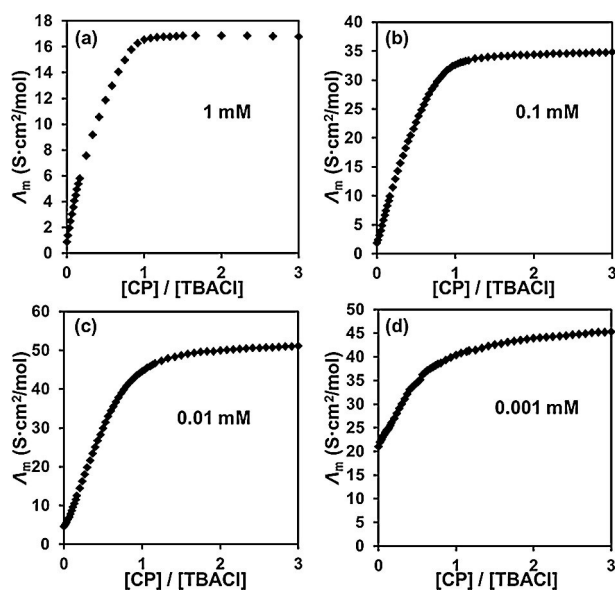


Figure 2. Conductometric titration curves of a) 0.001 mM, b) 0.01 mM, c) 0.1 mM, and d) 1 mM TBACl solution with CP addition (in THF, at 298.15 K).

ductivity of the solution.^[22] An enlarged ionic species after the complexation decreases the ionic mobility, which in turn results in a decrease in the molar conductivity.^[23] From this point of view, the increase in molar conductivity with CP addition in THF in Figure 2 indicates a higher conductivity of the CP–Cl complex anion than non-ionic species; thus, CP promotes ion-pair dissociation.^[21] That is, CP recognizes the chloride as an ion-paired salt as well as a free anion. Compared to other techniques, conductometry can detect the complexation of CP with chloride in THF even under highly dilute conditions (ca. 10^{-6} M).

The diffusion coefficients of TBACl before and after complexation with CP in $[D_8]THF$ (5.0 mM, Figure S1) were determined by using diffusion-ordered spectroscopy (DOSY) NMR to confirm the decrease in the mobility after complexation. As shown in Table 1, the diffusion coefficient (D) of TBACl with CP is apparently lower than TBACl or CP alone.

Table 1. Diffusion coefficients (D) in $[D_8]THF$ (5.0 mM) determined by DOSY NMR.	
	D [$\times 10^{-10}$ m ² s ⁻¹]
TBACl + CP (1.0 equiv)	3.35
TBACl	6.97
CP	6.45

2.2. Determination of the Ion-Pairing Constants (K_{ip1} and K_{ip2}) and Complexation Constants (K_{c1} and K_{c2}) in THF

As shown in Figure 3, conductometry at different salt concentrations was performed to determine the ion-pairing constant (K_{ip}) of TBACl and TBA(CP–Cl) with different ratios of CP in THF. A marked increase in molar conductivity was observed

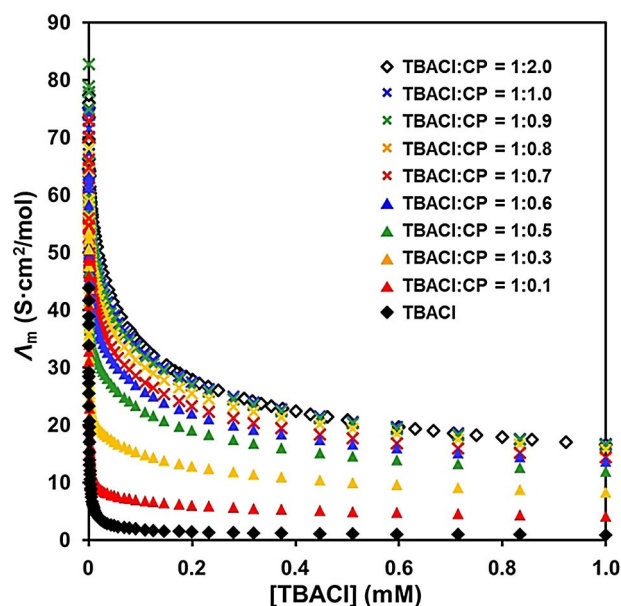


Figure 3. Molar conductivity (Λ_m) of TBACl with various amount of CP (in THF, at 298.15 K).

with decreasing TBACl concentration, meaning that both TBACl and TBA(CP–Cl) behave as weak electrolytes in THF. With increasing CP concentration, the molar conductivity of TBACl increases over the whole concentration range considered. Log–log plots of molar conductivity versus concentration of TBACl also demonstrated gradual changes of slope from TBACl with increasing CP concentration, whereas TBACl showed a slope of -0.5 , which is typical for a simple weak electrolyte (Figure S2). Thus, ionic dissociation of TBACl in THF was significantly triggered by complexation with CP. Next, we determined the limiting molar conductivity (Λ_m^∞) and ion-pairing constants (K_{ip}) of TBACl ($\Lambda_m^\infty = 108$ S cm² mol⁻¹, $K_{ip1} = 3.9 \times 10^7$ M⁻¹, determined from conductometry of TBACl in THF) and TBA(CP–Cl) ($\Lambda_m^\infty = 58$ S cm² mol⁻¹, $K_{ip2} = 1.95 \times 10^4$ M⁻¹, determined by conductometry of TBACl with 2 equiv of CP in THF), along with the complexation constants (K_{c1} and K_{c2}). As a result, the molar conductivity of TBA(CP–Cl) with 2 equivalents of CP (TBACl/CP = 1:2) is almost the same as that with 1 equivalent of CP (TBACl/CP = 1:1), resulting in comparable ion-pairing constants (K_{ip2} , Table 2). Therefore, CP forms the TBA(CP–Cl) complex over the total considered concentration range, and we fixed K_{ip2} at 1.95×10^4 M⁻¹ (i.e. the value with 2 equiv of CP).

¹H NMR titration was performed with 5.0 mM TBACl to determine the complexation constant (K_{c1}) of CP with the chloride anion in THF. As shown in Figure 4, the pyrrole β -proton

Table 2. Ion-pairing constants (K_{ip}) of TBACl with CP in THF.	
[TBACl]/[CP]	K_{ip} [M ⁻¹]
1:1	1.80×10^4
1:2	1.95×10^4

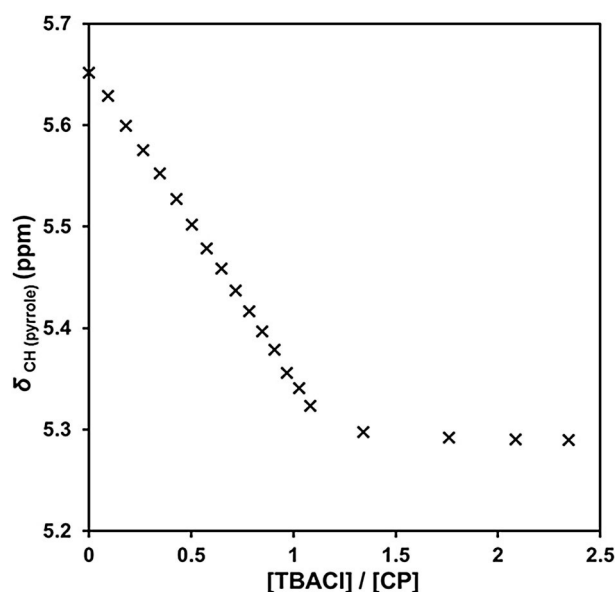


Figure 4. ^1H NMR signal shift of the CP β -proton with addition of TBACl (5.0 mM) in $[\text{D}_8]\text{THF}$.

shows a significant upfield shift upon titration of TBACl, which corresponds to the formation of a hydrogen bond between CP and the chloride anion. The observed shift indicates that the complexation constant of CP (K_{c1}) in $[\text{D}_8]\text{THF}$ is $3.40 \times 10^3 \text{ M}^{-1}$. Determined from $K_{ip1} = 3.9 \times 10^7 \text{ M}^{-1}$, TBACl completely exists as an ion-paired salt in THF and the degree of dissociation (α) was calculated to be lower than 0.0001% under these conditions (i.e. $[\text{TBACl}] = 5.0 \text{ mM}$). Therefore, the calculated complexation constant predominantly represents complexation of CP with the ion-paired salt of TBACl (K_{c1}). The following equation [Eq. (6)] gives a complexation constant of CP with the free chloride anion (K_{c2}), which is calculated to be $6.80 \times 10^6 \text{ M}^{-1}$.

$$K_{c2} = (K_{c1} \times K_{ip1}) / K_{ip2} \quad (6)$$

Table 3 summarizes the complexation and ion-pairing constants. In THF, CP has a higher complexation ability with free chloride anions than that with ion-paired TBACl ($K_{c1} < K_{c2}$), and the TBA(CP-Cl) complex has a higher dissociative ability than TBACl ($K_{ip2} < K_{ip1}$).

Complexation and ion-pairing constant	Value [M^{-1}]
K_{c1}	3.40×10^3
K_{c2}	6.80×10^6
K_{ip1}	3.90×10^7
K_{ip2}	1.95×10^4

2.3. Solvent Dependence of the Conductivity Change with CP Addition

As shown in Figure 5, we investigated the molar conductivity of TBACl in various organic solvents (0.1 mM) with CP addition. In chloroform ($\epsilon = 4.8$), although CP acts as a receptor for TBACl, the conductivity remains low and constant even after excess CP addition (Figure 5a).^[24] This fact indicates complete

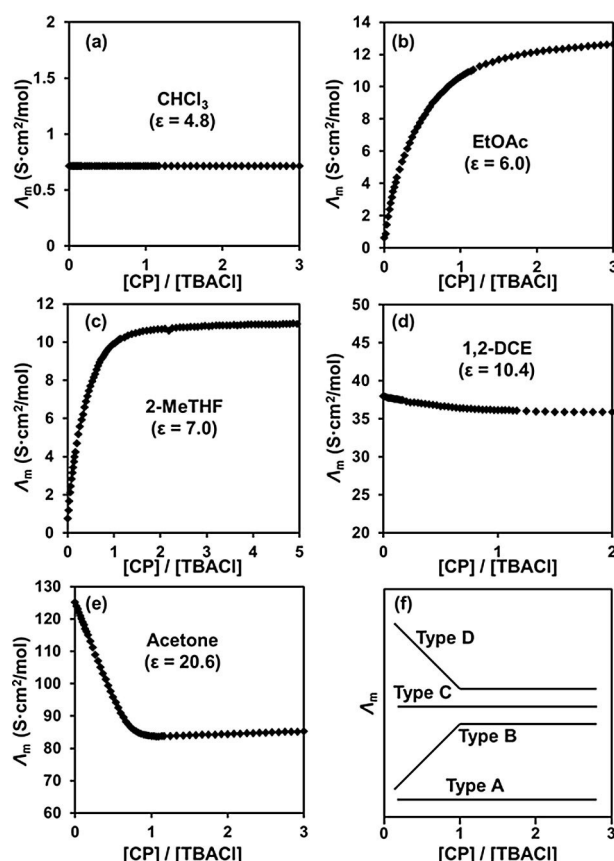


Figure 5. Conductometric titration curves of TBACl (0.1 mM) with CP addition at 298.15 K in a) CHCl_3 ($\epsilon = 4.8$), b) EtOAc ($\epsilon = 6.0$), c) 2-MeTHF ($\epsilon = 7.0$), d) 1,2-dichloroethane (1,2-DCE, $\epsilon = 10.4$), e) acetone ($\epsilon = 20.6$), and a summary of the conductometric titration curves.

suppression of TBACl dissociation even after complexation [TBA(CP-Cl)], owing to the low polarity of chloroform. That is, CP recognizes ion-paired TBACl with no apparent increase in ionic dissociation, and thus conductivity. In other non-polar solvents, the molar conductivity of TBACl solution increases with CP addition, including butyl acetate (BuOAc, $\epsilon = 5.0$), chlorobenzene ($\epsilon = 5.6$), tetrahydropyran (THP, $\epsilon = 5.6$), ethyl acetate (EtOAc, $\epsilon = 6.0$), methyl acetate (MeOAc, $\epsilon = 6.7$), 2-methyltetrahydrofuran (2-MeTHF, $\epsilon = 7.0$), THF ($\epsilon = 7.6$), trifluoromethylbenzene ($\epsilon = 9.0$), and *o*-dichlorobenzene ($\epsilon = 9.9$) (Figures 5b, 5c, 2b, and S3), owing to their slightly polar character compared to chloroform, and the molar conductivity was saturated at a CP/TBACl ratio of approximately 1:1, indicating the formation of a 1:1 complex. In these solvents, TBACl originally forms a tightly bound ion-paired salt, owing to the low dielec-

tric constant. Hence, ion-paired **TBACl** dissociation by complexation is enhanced with **CP** addition, as determined from the increase in the conductivity. In 1,2-dichloroethane (1,2-DCE, $\epsilon = 10.4$), the molar conductivity marginally decreases with **CP** addition (Figure 5d). **CP** forms the **CP-Cl** complex anion, because the complexation constant (K_c) of **CP** with **TBACl** in 1,2-DCE is $1.5 \times 10^4 \text{ M}^{-1}$.^[19] The balance between the increase in ionic species and the decrease in mobility, owing to the larger size of **CP-Cl** complex anion, resulted in a marginal change in molar conductivity. In the relatively polar solvent acetone ($\epsilon = 20.6$), the molar conductivity decreases with increasing **CP** concentration (Figure 5e). **TBACl** shows 50 and 97% ionic dissociation in 0.1 mM 1,2-DCE and acetone, respectively, as determined by the Fuoss–Kraus equation.^[5] As **TBACl** itself is almost fully dissociated in acetone, the ionic species does not decrease even after **CP** addition. Therefore, **CP** addition is associated with a decrease in the molar conductivity, owing to an increase in the size of the **CP-Cl** complex anion compared to the free chloride anion,^[25] and the enhancement of ion-paired **TBACl** dissociation associated with **CP** addition is negligible in acetone because of the high original degree of dissociation (97%). In 1,2-DCE, complexation with **CP** changes both the dissociation and mobility of the anion species, because of the moderate original degree of dissociation of **TBACl** in 1,2-DCE (50%). Accordingly, there is only a slight change in the conductivity in 1,2-DCE in contrast to acetone. From these observations, the conductometric titration curves can be classified into four types (Figure 5f): type A (chloroform), type B (EtOAc, THF, etc.), type C (1,2-DCE), and type D (acetone).

The relationship between the dielectric constant and the conductivity was investigated by using a mixed solvent to determine the mechanism underlying the change in the conductivity associated with complexation of **TBACl** with **CP**. The dielectric constant (ϵ) of the mixed solvent was defined by using the following equation [Eq. (7)]:

$$\epsilon = \epsilon_A \varphi_A + \epsilon_B \varphi_B \quad (7)$$

where ϵ_n and φ_n are the dielectric constant and volume fraction of pure solvent, respectively. We measured the molar conductivity of **TBACl** solution in a mixture of 0.11:0.89 (v/v) acetone/EtOAc with **CP** addition. The mixing fraction was chosen to achieve the same dielectric constant as that of THF ($\epsilon = 7.6$). As shown in Figure 6, after **CP** addition, the conductivity clearly increases, which is the same as in THF. Thus, the dielectric constant of the surrounding solvent mainly dominates the conductivity of the ion pair solution.

3. Conclusions

We have shown that conductivity changes directly detect the complexation of **TBACl** with **CP** in a wide range of organic solvents, indicating that ionic dissociation of **TBACl** in these solvents is affected by its complexation with **CP**. For example, the molar conductivity of **TBACl** in THF is enhanced after complexation with **CP**, owing to the increased concentration of ionic

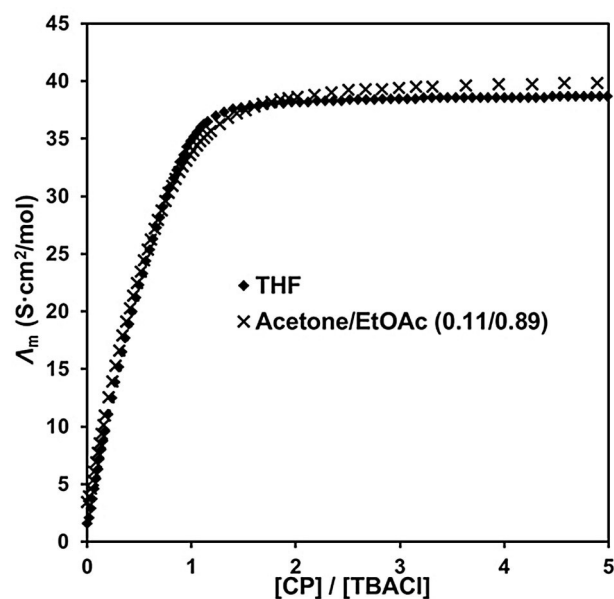


Figure 6. Conductivity change of **TBACl** (0.1 mM) with **CP** addition in THF (squares) and acetone/EtOAc (v/v = 0.11:0.89) (diamonds).

species. These facts indicate the capability of **CP** to recognize a chloride as an ion-paired salt as well as a free anion, especially in non-polar solvents. Additionally, the complexation constant of **CP** with a free chloride anion is higher than that with an ion-paired salt of **TBACl** ($K_{c1} < K_{c2}$). In non-polar solvents, the **TBA(CP-Cl)** complex has a lower ion-pairing constant than **TBACl** ($K_{ip1} < K_{ip2}$), owing to its increased size. The results of the present study indicate that complexation or encapsulation of hydrophobic bulky ion receptors with ionic species^[26] can be applied to the molecular design of novel functional soft materials in non-polar solvents by using coulombic forces.^[23a, 27, 28]

Experimental Section

Materials

All reagents were obtained from a commercial source (Wako Chemicals and Tokyo Chemical Industry) and used without further purification.

Measurements

The ^1H (500 MHz) NMR measurements were performed with a Bruker Biospin AVANCE DRX500 using 0.05% tetramethylsilane as the internal standard. The DOSY NMR measurements were performed with a JEOL JNM-ECP400 spectrometer at the Creative Research Institution, Hokkaido University. Conductometry was performed with a TOA DKK CM-30G conductivity meter.

Conductometry

Conductivity titrations were carried out by adding **TBACl** + **CP** solution to **TBACl** solution to keep the **TBACl** concentration constant. The two solutions contained the same concentration of **TBACl**. Concentration dependence of molar conductivity was performed

by gradually adding a pure solvent to TBACl or TBACl + CP solution.

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: anions · host-guest systems · molecular recognition · receptors · supramolecular chemistry

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