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Terphenyl Crowns: a New Family of Receptors Containing Ethereal Canopies that Direct Potassium Cation onto Benzenoid Platforms for Cation- π Interactions

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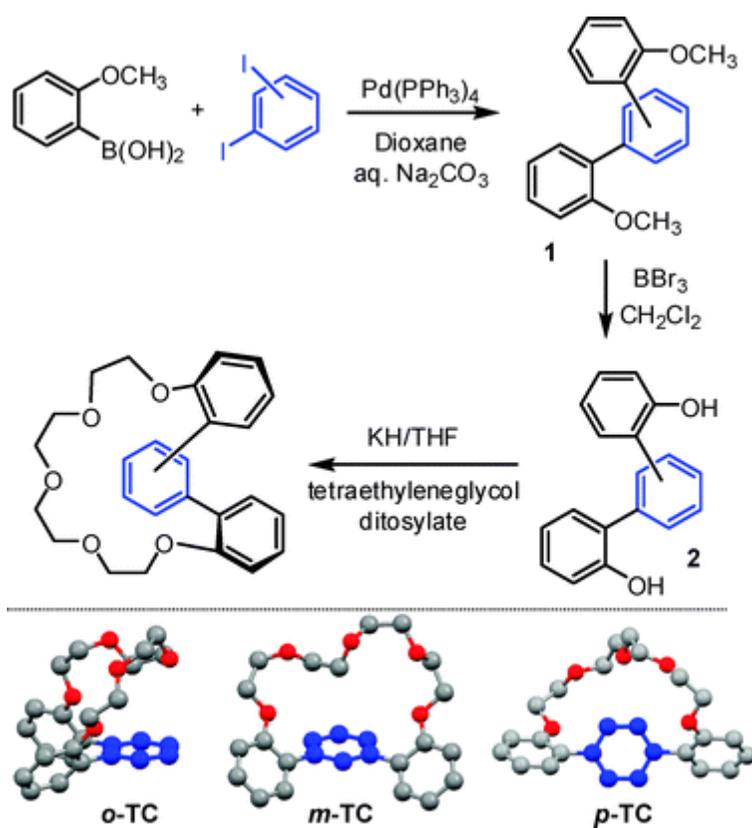
Abstract

We have synthesized three simple and versatile terphenyl crowns (TC) receptors containing ethereal canopies that direct a potassium [cation](#) for efficient cation- π interactions as established by [\$^1\text{H}\$ NMR spectroscopy](#) and by isolation and [X-ray crystallography](#) of their K^+ salts.

The noncovalent cation– π interaction has been implicated to play an important role as a stabilizing force in both biological as well as chemical assemblies.¹ These interactions have long been recognized in the gas phase and estimated for the [benzene](#)– K^+ complex to amount to ~ 16 kcal mol⁻¹.² However, the importance of cation– π interactions in biological systems is questioned due to the overwhelming need for solvation of the [cations](#) *in vivo*.³ We have recently shown that a deliberately built solvation shell (*i.e.* a hydrophilic ethereal fence) around a central [benzene ring](#) in a hexaarylbenzene derivative allows an efficient binding of a potassium [cation](#) to the (hydrophobic) π -cloud of the benzenoid ring.⁴ Moreover, it was demonstrated that such a polyaromatic system can function as an electrochemical sensor for potassium [cation](#).^{4b}

In order to probe the nature and applicability of such cation– π forces in both chemistry and biology, simple and easily modifiable scaffolds are needed which can be readily tailored for binding of different metal [cations](#) as well as hold potential to be eventually incorporated into polymeric backbones for development of new functional extractants⁵ or possibly for the preparation of conducting electrolytes for battery applications.⁶

Herein, we describe the hitherto unknown class of terphenyl crowns (**TC**) (see [Scheme 1](#)) which meet the criteria of ready availability, versatility, and possible incorporation into polymeric structures. Our interest in these receptors also stems from the fact that they possess an easily modifiable benzenoid platform as well as hydrophilic ethereal canopies which allow the positioning of the metal [cations](#) onto the aromatic platforms.



Scheme 1 A generalized synthetic scheme for *o,m,p*-terphenyl crowns and their molecular structures obtained by [X-ray crystallography](#).

Accordingly, herein we report the ready preparation of terphenyl crowns (**oo-TC**, **mm-TC** and **pp-TC**) and delineate the effective binding of potassium cation to this new class of receptors with the aid of NMR spectroscopy in solution and by X-ray crystallography in the solid state.

Syntheses of the various receptors shown above were accomplished in excellent yields by a simple three-step route (see Scheme 1). For example, a Suzuki coupling of 2-methoxyphenylboronic acid with 1,2-diiodobenzene followed by demethylation using BBr_3 afforded the bis-phenol **oo-2** in nearly quantitative yield. A solution of the bis-phenol **oo-2** in tetrahydrofuran was treated with potassium hydride followed by tetraethyleneglycol ditosylate, and the resulting mixture was refluxed for 16 h. A standard aqueous workup and chromatographic purification on alumina (using hexanes and ethyl acetate mixture as eluent) afforded pure *ortho*-terphenyl crown (**oo-TC**) in >75% yield.

Using a similar approach, **mm-TC** and **pp-TC** were obtained in 70 and 74% yields, respectively. The molecular structures of various terphenyl crowns in Scheme 1 were established by $^1\text{H}/^{13}\text{C}$ NMR spectroscopy and were further confirmed by X-ray crystallography \ddagger (see Scheme 1 and ESI \ddagger for experimental details).

The binding of potassium cation to the *para*-terphenyl crown (**pp-TC**) was initially monitored by the changes in ^1H NMR spectrum of **pp-TC** in acetone- d_6 (0.02 M) by an incremental addition of a solution of potassium perfluorotetraphenylborate (0.08 M) in acetone- d_6 (*i.e.* Fig. 1).

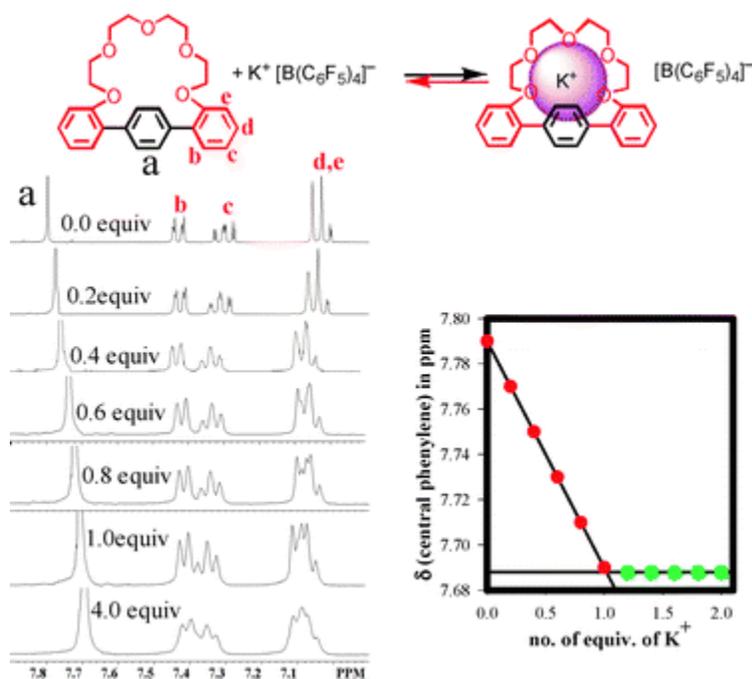


Fig. 1 Partial ^1H NMR spectra obtained upon the incremental addition of $\text{KB}(\text{C}_6\text{F}_5)_4$ to **pp-TC** in acetone- d_6 at 22 °C. The assignments of the aromatic signals in **pp-TC** are shown by letters a–e; signal “a” was chosen arbitrarily for tracking of the K^+ binding.

The incremental addition of K^+ solution led to considerable shifts of both aliphatic and aromatic signals up to the addition of 1 equiv. of K^+ as shown in Fig. 1. It is noteworthy that the ^1H NMR spectrum remained unchanged upon further addition of K^+ solution (*i.e.* beyond 1 equivalent; see Fig. 1, inset).

Unfortunately, an accurate binding constant for the formation of $[\text{pp-TC}, \text{K}^+]$ could not be determined by [NMR](#) as it simply showed complete capture of the potassium [cation](#) and suggested that the binding constant is too large to be measured by [NMR spectroscopy](#). Moreover, both *ortho*- and *meta*-derivatives (mm-TC and pp-TC) showed a similarly efficient capture of 1 equiv. of potassium [cation](#) by $^1\text{H NMR}$ spectral titrations with $\text{K}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ in [acetone- \$d_6\$](#) (see Fig. S1 and S2 in ESI †). A comparison of the relative binding of K^+ amongst the three terphenyl crown derivatives in [Scheme 1](#) by competition experiments (using $^1\text{H NMR}$ [spectroscopy](#)) revealed that the binding efficiency of K^+ decreases in the order of $\text{oo-TC} > \text{pp-TC} > \text{mm-TC}$.

In order to ascertain that the efficiency of the binding of K^+ to various terphenyl-based receptors, in part, arises owing to the placement of K^+ onto the benzenoid platform by ethereal canopies, we obtained single crystals of $[\text{oo-TC}, \text{K}^+]\text{BPh}_4^-$ and $[\text{pp-TC}, \text{K}^+]\text{BPh}_4^-$ from mixtures of [acetonitrile](#)– CH_2Cl_2 and [acetonitrile](#)– THF , respectively, at 22 °C. Single crystals of $[\text{mm-TC}, \text{K}^+]$, suitable for [X-ray crystallography](#), were obtained only when hexafluoroarsenate (AsF_6^-) was used as the counter anion. The molecular structures of these complexes obtained by [X-ray crystallography](#) are displayed in [Fig. 2–4.5](#)

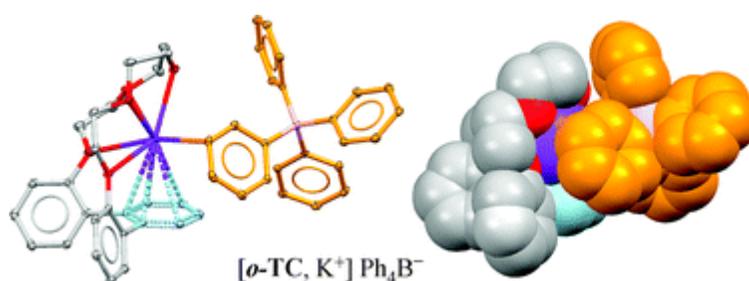


Fig. 2 The ORTEP and space-filling representations of $[\text{oo-TC}, \text{K}^+]\text{BPh}_4^-$ showing that the ethereal canopy holds the K^+ onto the central aromatic ring while a single opening is protected by a [phenyl group](#) of the BPh_4^- counter anion *via* cation– π interaction.^{8b,c} The hydrogens are omitted for the sake of clarity.

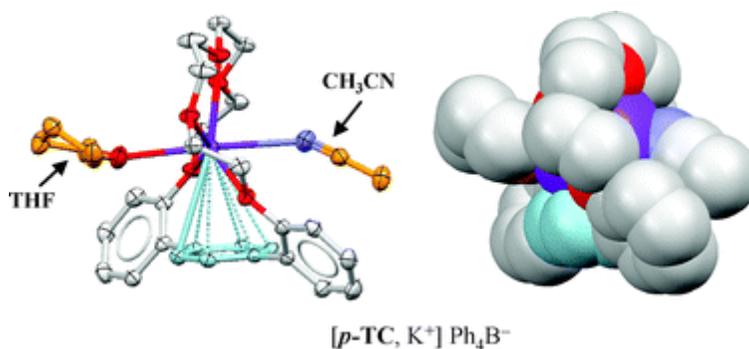


Fig. 3 The ORTEP and space-filling representations of $[\text{pp-TC}, \text{K}^+]$ showing that the ethereal canopy holds the K^+ onto the central aromatic ring while the two apical openings in the complex are plugged-in by [solvent](#) molecules. The hydrogens are omitted for the sake of clarity.

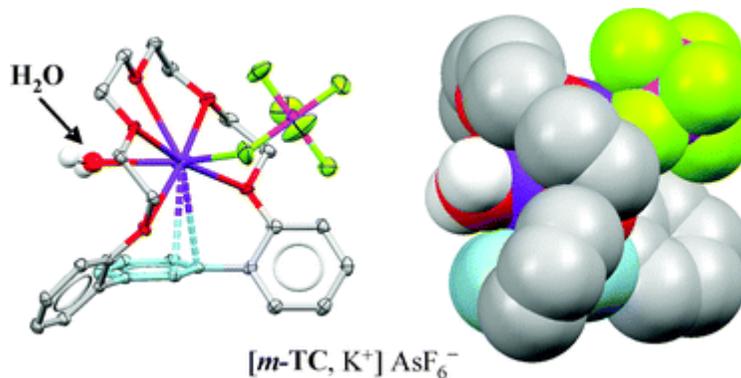


Fig. 4 The ORTEP and space-filling representations of $[mm\text{-TC}, K^+]\text{AsF}_6^-$ showing that the ethereal canopies hold the K^+ onto the central aromatic ring while the two apical openings in $mm\text{-TC}$ complex are filled in by a molecule of [water](#) and counter anion. The hydrogens are omitted for the sake of clarity.

The X-ray structure of $[oo\text{-TC}, K^+]\text{BPh}_4$ revealed that a single potassium [cation](#) is situated asymmetrically onto the central [benzene ring](#) with a distance from the mean plane of the [benzene ring](#) of 2.958 Å while coordinating to all five ethereal oxygens of the $oo\text{-TC}$ [crown](#) with the $K^+\cdots O$ distances varying in the range of 2.69–3.04 Å.^z The asymmetric (η^3) coordination of K^+ to the central [benzene ring](#) is not surprising, considering the asymmetric shape of the receptor in which two *ortho*-phenyl groups are twisted in the same direction ($\sim 75^\circ$) relative to the central [benzene ring](#) and thereby shifting the main axis of the [crown](#)-ether moiety together with the complexed K^+ away from the center of the [benzene ring](#). The asymmetric placement of K^+ onto the central [benzene ring](#) is also gauged by the $K^+\cdots C_{Ar}$ distances which vary from 3.157(1) to 3.422(2) Å.^{8a} Furthermore, one of the phenyls of the BPh_4 counter anion makes a short contact [3.317(1) Å] with the K^+ through the limited opening between the [crown ether](#) canopy and central [benzene ring](#), see [Fig. 2](#) (and [Fig. S3](#) in [ESI†](#)).^{8b,c}

In contrast, the potassium [cation](#) in $[pp\text{-TC}, K^+]\text{BPh}_4$ is almost ideally placed onto the central [benzene ring](#) for an effective η^6 coordination at a distance of 3.163 Å from the mean plane of the [benzene ring](#) with the $K^+\cdots C_{Ar}$ distances varying from 3.38 to 3.56 Å. The crown ether moiety in the $[pp\text{-TC}, K^+]$ complex makes a rigid arc over the central [benzene ring](#), as opposed to the flexible cleft in $oo\text{-TC}$, with the $K^+\cdots O$ distances varying from 2.78 to 3.31 Å. The K^+ is situated approximately in the mean plane of five ethereal oxygens which makes a $\sim 90^\circ$ dihedral angle with the plane of the [benzene ring](#) and the bridging *p*-phenyls are twisted by 56 and 60° in the same direction relative to the plane of the central [benzene ring](#). It is also noted that the $[pp\text{-TC}, K^+]\text{BPh}_4$ complex is a [solvent](#)-separated ion pair in the solid where the two apical openings in $[pp\text{-TC}, K^+]$ are coordinated (surprisingly) to two different [solvent](#) molecules, *i.e.* tetrahydrofuran and acetonitrile[§] (see [Fig. 2](#)).

The X-ray structure of $[mm\text{-TC}, K^+]\text{AsF}_6^-$ complex showed that K^+ is coordinated by all five oxygens of the [crown-ether](#) canopy with the $K^+\cdots O$ distances varying in the range of 2.74–3.14 Å. The potassium [cation](#) sits asymmetrically onto the central [benzene ring](#) with ideal η^2 coordination with the shortest $K^+\cdots C$ distances of 3.239 and 3.238 Å to the central [benzene ring](#) (see [Fig. 4](#)). The $K^+\cdots C$ distances to other four carbons of the central [benzene ring](#) vary from 3.298 to 3.346 Å. Furthermore, the nucleophilic AsF_6^- and a [water](#) molecule also make short $F\cdots K^+$ (2.704 Å) and $O\cdots K^+$ (2.637 Å) contacts *via* the two apical openings in the $[mm\text{-TC}, K^+]\text{AsF}_6^-$ complex.⁹

The X-ray crystallographic analyses of the K^+ complexes in [Fig. 2–4](#) shows that going from $oo\text{-TC}$ to $mm\text{-TC}$ to $pp\text{-TC}$ complex leads to a progressive stretching of the ethereal canopies. As such the stretching of the

ethereal canopies affects the $K^+ \cdots Ar$ coordination which varies from asymmetric to symmetric coordination going from **oo-TC** to **mm-TC** to **pp-TC**. Furthermore the structural analysis provides important clues as to the potential of the terphenyl crowns for the development of a whole new family of [crown](#) receptors for practical applications. For example, incorporation of electro/photo-active groups either at the site of single opening in the [**oo-TC**, K^+] complex or at the site of a pair of apical openings in [**mm-TC**, K^+] and [**pp-TC**, K^+] complexes should lead to the next-generation of sensing scaffolds for various metal ions using electrochemical/optical techniques.

In summary, we have designed and synthesized simple terphenyl-based receptors containing (polar) ethereal canopies that direct a potassium [cation](#) to the central [benzene ring](#) for cation- π interaction—a phenomenon that is well established in the gas phase² and is known to play an important role in the stabilization of tertiary structures of various [proteins](#).¹⁰

We are actively exploring the potential of this new family of [crowns](#) for the preparation of functional devices for potential applications in emerging areas ranging from molecular electronics and nanotechnology¹¹ to solar energy storage.¹²

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Notes and references

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7. According to the Cambridge Structural Database, the $K^+ \cdots O$ distances in various potassium/crown complexes have a median value of ~ 2.85 Å.
8. Note that the closest $K^+ \cdots C_{Ar}$ distance of 3.156 Å in [**oo-TC**, K^+] complex is much shorter than the $K^+ \cdots C_{Ar}$ distance of 3.38 Å in a K^+ /[toluene](#) complex, see: (a) B. T. King, B. C. Noll and J. Michl, *Collect. Czech. Chem. Commun.*, 1999, **64**, 1001 ; (b) G. W. Gokel, L. J. Barbour, R. Ferdani and J. Hu, *Acc. Chem. Res.*, 2002, **35**, 878 ; (c) Q. Q. Munro and N. Pearson, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2003, **59**, m407 .
9. The X-ray structure analysis of the [**mm-TC**, K^+] AsF_6^- complex showed that there were two symmetrically independent molecules with one of them containing a coordinated water molecule with only 32% population. The inclusion of a coordinated water molecule in the cleft between the ethereal arc and aromatic ring does not change the K^+ coordination to aromatic ring but does alter the cleft angle slightly, *i.e.* a 58° opening in the non-aqueous complex vs. 67° in the aqueous one, suggesting a significant stability of the η^2 -coordination of the K^+ similar to that found for various Ag^+ analogs.

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Footnotes

† Electronic supplementary information (ESI) available: Synthetic details of various compounds and [NMR spectra](#). CCDC 738411–738416. For ESI and [crystallographic data](#) in CIF or other electronic format see DOI: [10.1039/b912796h](https://doi.org/10.1039/b912796h)

‡ *Crystal structure data for pp-TC* [$C_{26}H_{28}O_5$] (raj1v): $M = 420.48$, monoclinic, $P2_1/n$, $a = 13.048(5)$, $b = 9.487(3)$, $c = 17.671(6)$ Å, $\beta = 97.031(5)^\circ$, $Z = 4$, $V = 2170.9(13)$ Å³, $D_c = 1.287$ Mg m⁻³, $T = 100$ K, 24585 reflections measured, 6832 unique reflections, $R_{int} = 0.0463$, 281 parameters refined, $R(all) = 0.1310$, $wR(all) = 0.2779$, $S = 1.067$. *Crystal structure data for mm-TC* [$C_{26}H_{28}O_5$] (raj4b): $M = 420.48$, triclinic, $P\bar{1}$, $a = 8.8435(5)$, $b = 19.9062(10)$, $c = 26.7874(14)$ Å, $\alpha = 111.253(2)$, $\beta = 98.337(2)$, $\gamma = 93.101(2)^\circ$, $Z = 8$, $V = 4319.3(4)$ Å³, $D_c = 1.293$ Mg m⁻³, $T = 100$ K, 35 410 reflections measured, 12 685 unique reflections, $R_{int} = 0.0247$, 1119 parameters refined, $R(all) = 0.0417$, $wR(all) = 0.1105$, $S = 1.044$. *Crystal structure data for oo-TC* [$C_{26}H_{28}O_5$] (raj4d): $M = 420.48$, triclinic, $P\bar{1}$, $a = 9.2824(2)$, $b = 10.4418(2)$, $c = 11.6456(2)$ Å, $\alpha = 90.9020(10)$, $\beta = 98.7730(10)$, $\gamma = 102.9340(10)^\circ$, $Z = 2$, $V = 1085.78(4)$ Å³, $D_c = 1.286$ Mg m⁻³, $T = 100$ K, 8959 reflections measured, 3184 unique reflections, $R_{int} = 0.0164$, 393 parameters refined, $R(all) = 0.0281$, $wR(all) = 0.0684$, $S = 0.992$. *Crystal structure data for [pp-TC, K⁺]-BPh₄* [$C_{26}H_{28}O_5 \cdot KBPh_4 \cdot THF \cdot CH_3CN$] (raj3ya): $M = 891.95$, triclinic, $P\bar{1}$, $a = 10.7324(2)$, $b = 113.8365(3)$, $c = 17.2011(4)$ Å, $\alpha = 77.8290(10)$, $\beta = 89.3530(10)$, $\gamma = 77.0660(10)^\circ$, $Z = 2$, $V = 2431.85(9)$ Å³, $D_c = 1.218$ Mg m⁻³, $T = 100$ K, 20552 reflections measured, 7178 unique reflections, $R_{int} = 0.0141$, 843 parameters refined, $R(all) = 0.0319$, $wR(all) = 0.0869$, $S = 1.016$. *Crystal structure data for [mm-TC, K⁺]-AsF₆* [$C_{26}H_{28}O_5 \cdot KAsF_6 \cdot xH_2O$] (raj9qa): $M = 651.10$, triclinic, $P\bar{1}$, $a = 10.0564(3)$, $b = 15.2834(4)$, $c = 18.9578(5)$ Å, $\alpha = 103.571(1)$, $\beta = 103.485(2)$, $\gamma = 91.093(1)^\circ$, $Z = 4$, $V = 2745.89(13)$ Å³, $D_c = 1.575$ Mg m⁻³, $T = 100$ K, 8874 reflections measured, 6702 unique reflections, $R_{int} = 0.0164$, 393 parameters refined, $R(all) = 0.0589$, $wR(all) = 0.1603$, $S = 1.039$. *Crystal structure data for [oo-TC, K⁺]-BPh₄* [$C_{26}H_{28}O_5 \cdot KBPh_4$] (raj3sa): $M = 778.79$, monoclinic, $P2_1/c$, $a = 13.1774(5)$, $b = 15.6866(6)$, $c = 19.6322(7)$ Å, $\beta = 94.300(2)^\circ$, $Z = 4$, $V = 4046.7(3)$ Å³, $D_c = 1.278$ Mg m⁻³, $T = 100$ K, 25942 reflections measured, 6139 unique reflections, $R_{int} = 0.0180$, 716 parameters refined, $R(all) = 0.0284$, $wR(all) = 0.0774$, $S = 1.009$.

§ For a discussion of the bent $K^+ \cdots NC-Me$ interaction in the [pp-TC, K⁺] complex, see Fig. S4 and S5 in the ESI.†