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Ionic Supramolecules

Cycloparaphenylene-Based Ionic Donor–Acceptor Supramolecule: Isolation and Characterization of $Li^+@C_{60}\subset[10]CPP$**

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Abstract: *The first cycloparaphenylene (CPP)-based ionic donor–acceptor supramolecule $Li^+@C_{60}\subset[10]CPP\cdot X^-$ has been synthesized. X-ray crystallography not only confirmed the molecular structure of $Li^+@C_{60}\subset[10]CPP\cdot X^-$ but also uncovered the formation of a unique ionic crystal. The strong charge-transfer interaction between [10]CPP and $Li^+@C_{60}$, which was confirmed by electrochemical measurement and spectroscopic analyses, caused significant delocalization of the positive charge across the entire complex.*

Cycloparaphenylenes (CPPs) are ring-shaped π-conjugated molecules, which have been well-studied during the last 7 years.[1,2] As a result of significant progress in the development of synthetic procedures, [*n*]CPPs having 5–18 benzene rings ($n = 5$–18) are currently available. Since the diameters of CPPs ranging from around 0.7 to 2.4 nm can be precisely controlled according to the "*n*" values (Figure 1),[3] the concave cavities of CPPs are particularly suitable for supramolecular chemistry with spherical guests such as fullerenes.[4] Indeed, Yamago et al., Jasti et al., and our group have reported CPP–fullerene complexes, such as $C_{60}\subset[10]CPP$,[4a,b] $C_{70}\subset[10]CPP$,[4c] $C_{70}\subset[11]CPP$[4c] and $Ln@C_{82}\subset[11]CPP$.[4d,e] Especially in $La@C_{82}\subset[11]CPP$, a charge-transfer (CT) interaction was observed based on the strong electron-acceptor properties of $La@C_{82}$.[4e] Such complexes have attracted interest owing to their properties derived from intermolecular interaction and selective binding, which are a result of their unique convex–concave contact. However, complexation of CPPs with other unusual guests exhibiting specific interactions has not been reported to date.

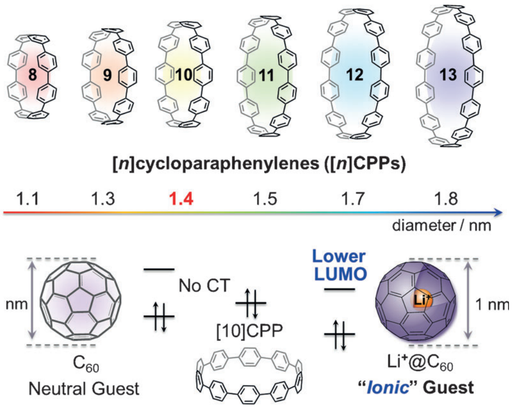

Figure 1. Top: Structures and diameters of cycloparaphenylenes ($n = 8$–13). Bottom: frontier molecular orbital energies of C_{60}, and $Li^+@C_{60}$. The diameter of the [*n*]CPPs are taken from Ref. [3].

The C_{60} with an encapsulated lithium ion ($Li^+@C_{60}$)[5] is considered as an attractive guest for complexation with [10]CPP. Despite having almost the same size as empty C_{60},[6] $Li^+@C_{60}$ has a much lower LUMO level than C_{60} (ca. 0.7 eV lower) (Figure 1). We envisioned that the drastically increased electron accepting ability of $Li^+@C_{60}$ may induce strong intermolecular CT interaction with [10]CPP. In addition, $Li^+@C_{60}$ is the only ionic fullerene consisting of a cationic $Li^+@C_{60}$ core and an external counteranion, such as PF_6^-.[7] Therefore, the resulting CPP-based complex should form an ion-pair state with the anion, representing a unique ionic supramolecule. Moreover, the positive charge of the lithium ion (Li^+) may be delocalized not only onto the C_{60} cage surface but also to the outer CPP ring. This feature is particularly attractive for a range of electrochemical applications. Although a similar convex–concave complexation of $Li^+@C_{60}$ was recently demonstrated by Isobe and co-workers using (*P*)-(12,8)-[4]cyclo-2,8-chrysenylene as a host,[8] no experimental data of the fundamental properties induced by the strong electron-acceptor cation have been collected to date.

Herein, we report the first synthesis and characterization of a $Li^+@C_{60}\subset[10]CPP\cdot X^-$ complex (X = bis(trifluoromethanesulfonyl)imide (NTf_2) or tetrakis[3,5-bis(trifluoromethyl)-phenyl]borate (TFPB)), which is the first example of a CPP-based ionic donor–acceptor supramolecule. The strong CT interaction, significant delocalization of the positive charge, and unique ionic crystal structure of this unprecedented supramolecule were uncovered.

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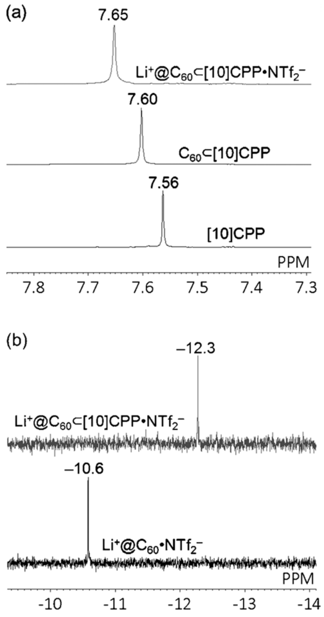


Figure 2. a) ^{1}H NMR spectra of $\mathrm{Li^+@C_{60}\subset[10]CPP{\cdot}NTf_2^-}$ (top), $\mathrm{C_{60}\subset[10]CPP}$ (middle), and pristine [10]CPP (bottom). b) ^{7}Li NMR spectra of $\mathrm{Li^+@C_{60}\subset[10]CPP{\cdot}NTf_2^-}$ (top) and pristine $\mathrm{Li^+@C_{60}{\cdot}NTf_2^-}$ (bottom). All spectra were measured in 1,1,2,2-[D$_2$]tetrachloroethane, a D$_2$O solution of LiCl was used as an external standard for ^{7}Li NMR spectroscopy.

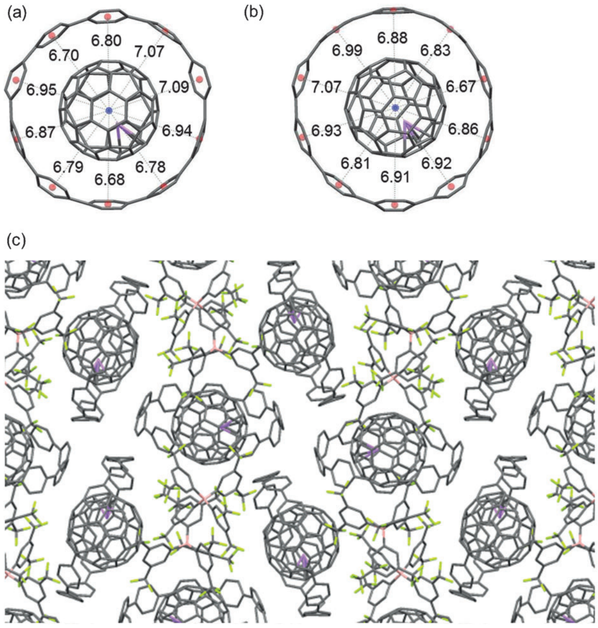


Figure 3. X-ray crystal structure of $\mathrm{Li^+@C_{60}\subset[10]CPP{\cdot}TFPB^-}$ measured at 103 K. a,b) Two crystallographically independent structures of $\mathrm{Li^+@C_{60}\subset[10]CPP}$. The numbers indicate the distances [Å] between the centroid of each $\mathrm{Li^+@C_{60}}$ and the benzene rings of [10]CPP. c) Crystal packing of $\mathrm{Li^+@C_{60}\subset[10]CPP{\cdot}\ TFPB^-}$.

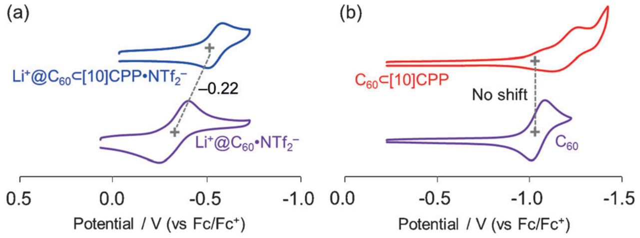
The target complex $\mathrm{Li^+@C_{60}\subset[10]CPP}$ was immediately formed by mixing [10]CPP and $\mathrm{Li^+@C_{60}{\cdot}NTf_2^-}$[9] in 1,2-dichloroethane at room temperature. The ^{1}H and ^{7} Li NMR spectra of the complex and the starting two components are shown in Figure 2. The ^{1}H NMR signal of [10]CPP and ^{7}Li-NMR signal of $\mathrm{Li^+@C_{60}}$ shifted downfield by 0.09 ppm and upfield by 1.7 ppm, respectively. Interestingly, the chemical shift change of [10]CPP upon complexation was much larger with $\mathrm{Li^+@C_{60}{\cdot}NTf_2^-}$ relative to empty $\mathrm{C_{60}}$, which clearly indicates the stronger electronic correlation between [10]CPP and $\mathrm{Li^+@C_{60}}$.

The stoichiometric analysis and the binding-constant determination for the complexation were performed by absorption titration in dichloromethane. A Job's plot[10] at 445 nm clearly showed the maximum absorption change when the ratio of [10]CPP and $\mathrm{Li^+@C_{60}}$ reached 1:1 (Figure S3 in the Supporting Information). The high-resolution ESI mass spectrum also revealed the formation of a 1:1 complex with a signal at m/z 1488.3317 assigned to the molecular ion of $\mathrm{Li^+@C_{60}\subset[10]CPP}$ ($[M]^+$, m/z calcd 1488.3319 as $\mathrm{C_{120}H_{40}Li}$). The binding constant (K_a) in dichloromethane was determined to be $4.8\times10^4(\pm 6.6\times10^3)\,\mathrm{M}^{-1}$ by absorption titration (Figure S4 and S5).[11] The K_a value was almost identical to that observed between [10]CPP and $\mathrm{C_{60}}$ in o-dichlorobenzene. To investigate the polarity dependence of the complexation, we also examined a number of different solvents. Although complexation was observed in all cases that were investigated, the high binding constant and significant overlapping of the CT absorption between $\mathrm{Li^+@C_{60}}$ and the solvent interrupted the precise determination of K_a.

The structure of $\mathrm{Li^+@C_{60}\subset[10]CPP{\cdot}X^-}$ was unambiguously confirmed by X-ray crystal structure analysis of the TFPB salt (Figure 3).[9,12,13] The change of the counteranion was crucial to obtain a single crystal of the $\mathrm{Li^+@C_{60}\subset[10]CPP}$ complex. The crystal structure of $\mathrm{Li^+@C_{60}\subset[10]CPP{\cdot}TFPB^-}$ showed a 1:1 complexation of the $\mathrm{Li^+@C_{60}}$ cation and the [10]CPP ring. The cationic complex formed an ionic crystal with TFPB$^-$. Interestingly, two crystallographically independent structures of $\mathrm{Li^+@C_{60}\subset[10]CPP}$ cations were found in the crystal structure (Figure 3a,b). In both structures, $\mathrm{Li^+@C_{60}}$ was located inside the cavity of [10]CPP with an average distance between the $\mathrm{C_{60}}$ centroid and the CPP benzene rings being 6.87 ± 0.14 Å and 6.89 ± 0.11 Å for structures (a) and (b), respectively. More interestingly, a measureable deviation between the centroids of the $\mathrm{C_{60}}$ cage and [10]CPP was observed. Thus, the centroids of each $\mathrm{C_{60}}$ cage deviates 0.74 Å for (a) or 0.89 Å for (b) from the centroids of each [10]CPP. In the simple $\mathrm{C_{60}\subset[10]CPP}$ complex, such a significantly deviated complexation was not observed (0.0 and 0.1 Å).[4a,b] Although factors underlying the discrepancy have not been well understood, the electrostatic interaction between the cationic $\mathrm{Li^+@C_{60}\subset[10]CPP}$ moiety and the counteranion as well as the unique ionic crystal packing structure may be the cause of this interesting mode of encapsulation.

Although the thermal ellipsoid of the Li$^+$ was large in the crystal, even at 103 K, it was found that the Li$^+$ ion locates somewhat closer to the CPP ring rather than the counteranion (TFPB). We presume that the electrostatic attractive force between Li$^+$ and TFPB$^-$ is much weaker than that observed in general ion pairs because of the delocalized positive charge on the $\mathrm{C_{60}}$ cage and the distance shielding by the cage.[7] In addition, owing to the inhibited thermal motion of Li$^+$ at low temperature (103 K), the LUMO of $\mathrm{Li^+@C_{60}}$ might be slightly localized at the Li$^+$-bound $\mathrm{C_{60}}$ surface.[14] Thus, the observed positional relationship between [10]CPP and Li^{+} maximizes the overlapping of the HOMO of CPP and the LUMO of Li^{+}@C$_{60}$, thereby stabilizing the complex by a CT interaction.[15]

To shed light on the electronic interaction between [10]CPP and Li^{+}@C$_{60}$, along with the electrochemical stability of the ionic supramolecule, the redox properties of Li^{+}@C$_{60}$⊂[10]CPP·X^{-} were investigated by cyclic voltammetry (Figure 4). The complexation with [10]CPP rendered Li^{+}@C$_{60}$ harder to reduce with respect to free Li^{+}@C$_{60}$·NTf$_2^{-}$ (0.22 V difference), whereas C$_{60}$⊂[10]CPP showed the same reduction potential as pristine C$_{60}$. The presence of CPP-to-Li^{+}@C$_{60}$ charge transfer should contribute to the increase in electron density at the Li^{+}@C$_{60}$ cage. However, the oxidation potential of Li^{+}@C$_{60}$⊂[10]CPP was found to be little different to that of pristine [10]CPP (0.02 V difference), which does not appear to reflect the effect of charge transfer from [10]CPP to Li^{+}@C$_{60}$. A possible reason for this seemingly counterintuitive phenomena is that the electrostatic repulsion between the oxidized [10]CPP ([10]CPP$^{\cdot+}$) and cationic Li^{+}@C$_{60}$ induces the deformation of Li^{+}@C$_{60}$⊂[10]CPP, thereby reducing the complexation effect.



(c)

Sample	E_1^{Ox} / V	$E1^{\mathrm{Red}}$ / V	Shift / vs Free molecule	
			Ox	Red
Li^{+}@C$_{60}$⊂ [10]CPP•NTf$_2^{-}$	+0.73	–0.54	–0.02	–0.22
C$_{60}$⊂[10]CPP	–[a]	–1.10	–	0
[10]CPP	+0.75	–[a]		
Li^{+}@C$_{60}$•NTf$_2^{-}$	–[a]	–0.32		
C$_{60}$	–[a]	–1.10		

Figure 4. Reduction potentials of a) Li^{+}@C$_{60}$⊂[10]CPP·NTf$_2^{-}$ (blue), Li^{+}@C$_{60}$·NTf$_2^{-}$ (purple), and b) C$_{60}$⊂[10]CPP (red), and C$_{60}$ (purple) in CH$_2$Cl$_2$ containing 50 mM of TBA^{+}NTf$_2^{-}$. For the oxidation wave of Li^{+}@C$_{60}$⊂[10]CPP·NTf$_2^{-}$, see Supporting Information. The oxidation/reduction potentials are summarized in (c). [a] The oxidation or reduction wave could not be observed under the conditions employed.

UV/Vis-NIR spectra also showed specific absorption derived from the electronic interaction between [10]CPP and Li^{+}@C$_{60}$ (Figure 5). The new broadened absorption observed at around 350 nm and the NIR region can be ascribed to the CT band in the ionic complex.[16] Although C$_{60}$⊂[10]CPP also showed characteristic absorption at around 360 nm, the CT interaction between [10]CPP and C$_{60}$ was much less pronounced owing to the lower electron acceptor character of empty C$_{60}$ compared to Li^{+}@C$_{60}$.

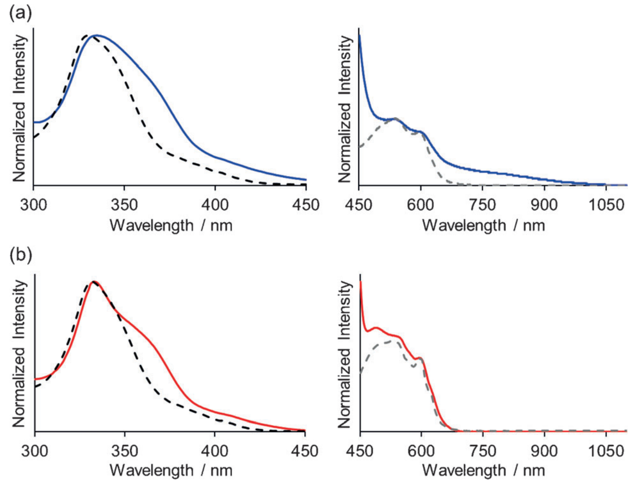


Figure 5. UV/Vis-NIR absorption spectra of a) Li^{+}@C$_{60}$⊂[10]CPP·NTf$_2^{-}$ (blue line) and b) C$_{60}$⊂[10]CPP (red line) measured in CH$_2$Cl$_2$ at room temperature. The black dotted lines are the sum of the absorption of each host and guest, and the gray dotted lines are the absorption of each fullerene guest.

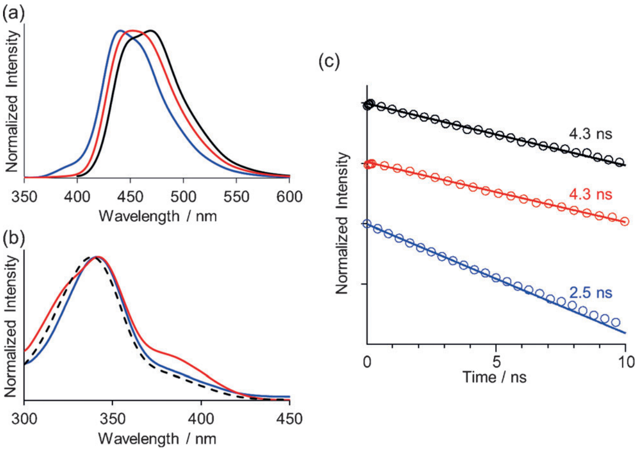


Figure 6. a) Photoluminescence spectra, b) photoluminescence excitation spectra, and c) photoluminescence decay curves of Li^{+}@C$_{60}$⊂[10]CPP·NTf$_2^{-}$ (blue), C$_{60}$⊂[10]CPP (red), and pristine [10]CPP (black) measured in CH$_2$Cl$_2$ at room temperature. The plotted data in (c) are offset for clarity.

The steady-state and time-resolved photoluminescence (PL) measurements of Li^{+}@C$_{60}$⊂[10]CPP·NTf$_2^{-}$, C$_{60}$⊂[10]CPP, and pristine [10]CPP provided further insight into the intermolecular interaction in Li^{+}@C$_{60}$⊂[10]CPP·NTf$_2^{-}$ (Figure 6). All the PL bands were observed in the same wavelength region between 350 and 600 nm, which indicates that PL processes are attributed to [10]CPP in all samples (Figure 6 a). To confirm this rationale, we performed photoluminescence excitation (PLE) measurements, and the results are shown in Figure 6 b. Indeed, the PLE spectra of Li^{+}@C$_{60}$⊂[10]CPP·NTf$_2^{-}$ and C$_{60}$⊂[10]CPP were similar to the absorption spectrum of pristine [10]CPP. It should also be noted that the PL spectra of Li^{+}@C$_{60}$⊂[10]CPP·NTf$_2^{-}$ and C$_{60}$⊂[10]CPP showed blue shifts compared to that of [10]CPP (Figure 6 a). The complexation is expected to significantly inhibit the structure relaxation of excited [10]CPP, as the C$_{60}$ cages precisely fill the inner space of the [10]CPP ring.

Despite displaying similar PL and PLE spectra, Li^{+}@C$_{60}$⊂[10]CPP·NTf$_2^{-}$ showed distinctive PL decay behavior (Figure 6c). The PL decays of all samples are shown as a single exponential function. Both [10]CPP and $C_{60}\subset$[10]CPP showed an almost identical PL lifetime of 4.3 ns, whereas $Li^+@C_{60}\subset$[10]CPP·NTf_2^- displayed a much shorter PL lifetime of 2.5 ns. Thus, it became clear that 1) the presence of empty C_{60} has negligible impact on the PL process of [10]CPP, but 2) the lithium cation inside the C_{60} cage can trigger an additional nonradiative decay channel. We assume that the appearance of a new decay channel may be due to the CT interaction and/or the strong electron acceptance by $Li^+@C_{60}$.

From these findings, we reveal the specific ionic property of the complex arising from the positive charge distribution. The schematic image is shown in Figure 7. It has already been reported that the positive charge of $Li^+@C_{60}$ is mainly distributed on Li^+ but is also delocalized on the C_{60} surface; thus the appropriate description might be "$Li^+@C_{60}{}^{\delta+}$". What we discovered during this study is that, by making a complex with [10]CPP, the positive charge of the lithium cation can be further delocalized to the outer CPP ring, mainly because of to the strong CPP-to-$Li^+@C_{60}$ charge transfer. Such fine charge distribution attenuates the electrostatic force, making the encapsulated Li^+ more unconfined in the C_{60} cage.[17] Accordingly, this unique ionic compound can be considered promising as an unusual electrolyte, dielectric substance, and for single-molecular memories in the field of organic devices.

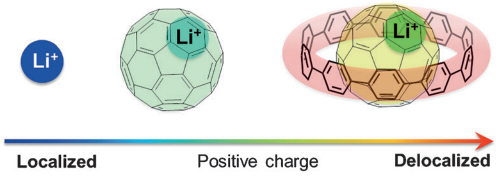


Figure 7. The change in positive-charge delocalization of Li^+, $Li^+@C_{60}$, and $Li^+@C_{60}\subset$[10]CPP complex.

The $Li^+@C_{60}\subset$[10]CPP complex is also interesting in terms of "structuralization" of the cation. Through the encapsulation with C_{60} and complexation with CPP, the spherical "isotropic" lithium cation has now been transformed into a three-dimensional "anisotropic" cation, similar to carbocations and related organo-modified cations. The acquirement of "structural" information should have numerous applications, such as use as a new type of cation-based organocatalyst and a component of new supramolecular structures.

In summary, we have successfully synthesized and characterized $Li^+@C_{60}\subset$[10]CPP·X^-, as a new type of ionic supramolecule. The strong charge-transfer interaction between [10]CPP and $Li^+@C_{60}$, which was confirmed by electrochemical measurement and spectroscopic analyses, caused significant delocalization of the positive charge to the entire complex. Having uncovered the basic structural and optoelectronic properties of $Li^+@C_{60}\subset$[10]CPP·X^-, we are now in a position to fully utilize these unique ionic supramolecular nanocarbons for various applications.

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