First synthesis and aggregation behaviour of periconjugated triazoliumfullerene†

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Triazoliumfullerene was first prepared by the [3+2] cycloaddition of
in situ generated 1,3-diaza-2-azoniaallene with fullerene and was
characterized by the dispersed positive charge over the fullerene
sphere associated with periconjugation. This new type of amphi-
philic fullerene tended to form vesicles and crystalline aggregates
after the casting of THF or MeOH solutions.

Ionic fullerenes1–6 are useful compounds for medical applications
such as in antibacterial1f and anti-HIV1g agents, and also for self-
assembling nanocarbon materials2,3 owing to the presence of
amphiphilic intermolecular ionic, dipole–dipole, π–π and hydro-
phobic interactions. These ionic and highly polar fullerenes are apt
to form vesicle,1h,2,3 nanowire,1h,2,4 and nanosheet5 structures by
way of self-assembly. Their aggregation behaviors highly depend
on how the introduced ionic (hydrophilic) groups electronically
affect the nonpolar (hydrophobic) fullerene cage. Here, it is
interesting to know what kind of aggregation occurs if the ionic
charge is dispersed on the π-conjugated fullerene cage. Such
charge dispersion can be attained for the nitrogen incorporated
60π ionic azafullerene (C60N+).6 However, the extremely low
stability and intrinsic activity of reduction7 restricted its usual
application as an ionic fullerene.

This situation prompted us to design a new type of ionic
fullerene with possible conjugation; one promising candidate is
through-space periconjugation8 between the outer ionic site and
the π-conjugated fullerene cage. We have attempted the introd-
cution of a cationic 1,2,3-triazolium unit9 into the fullerene sphere,
because the possible high delocalization of positive charge on the
N1–N2–N3 linkage and the fullerene cage (Fig. 1a and b), and
the LUMO level was 0.36 eV lower than that of pyrrolidinium-
fullerene (Fig. 1d and e),1a–d,2,5a a typical ammonium fullerene.
Moreover, in the electrostatic potential (ESP) map of pyrro-
lidiniumfullerene, the positive site is apparently localized on the
pyrrolidinium moiety (blue on the ESP map in Fig. 1f) and the
fullerene sphere remains in a less charged state. By contrast, the ESP
map of triazoliumfullerene shows a considerable distribution of
positive charge over the fullerene cage with an ambiguous boundary
(Fig. 1c), whereby its dipole moment is smaller than that
of pyrrolidiniumfullerene. Therefore, triazoliumfullerene (as a salt)
is expected to behave as a unique amphiphile in contrast to
the previously employed ionic fullerenes.

Fig. 1 Comparative representation of triazoliumfullerene and pyrrolidini-
umfullerene: (a,d) molecular structure, (b,e) LUMO with its levels shown,
(c,f) electrostatic potential (ESP) maps of the electron density contours and
dipole moments with a color bar of ESP energy (kJ mol−1); i.e., blue is more
electropositive (cationic) while red is lower (relatively apolar). DFT calcu-
lations were carried out with the B3LYP/6-31G(d) level of theory.
we report the one-pot first synthesis of triazoliumfullerene (as a PF$_6$ salt), theoretical calculation of the mechanistic pathway, and preliminary DLS/SEM/TEM measurements of its self-aggregation.

To prepare triazoliumfullerene, we employed [3+2] cycloaddition$^9$ of 1,3-diaza-2-azoniaallene salt 2$^+$ with fullerene as a 2π component. The intermediate 2$^+$ was generated in situ via sequential chlorination and ionization of commercially available diphenyltriazene 1 by tert-butyl hypochlorite and the Lewis acid KPF$_6$ at $-78 \, ^\circ\text{C}$. To avoid spontaneous decomposition of the unstable intermediate 2$^+$, a one-pot reaction was carried out with C$_{60}$ at $-78 \, ^\circ\text{C}$ to give 1,3-diphenyltriazoliumfullerene salt 3$^+$-PF$_6$ (Scheme 1). The $^{13}$C-NMR measurement showed ca. 16 peaks of sp$^2$-fullerene carbons (and 4 phenyl peaks, Fig. S1 in the ESI†) and one sp$^3$ peak at 91 ppm, indicating the occurrence of C$_{60}$-based symmetric addition at the 6,6-bond of fullerene. The downfield shift of the sp$^2$ carbon is probably because of the electron-withdrawal by the conjugate positive N$_1$ and N$_2$ atoms, which is in conformity with a computational simulation (96 ppm by a GIAO/B3LYP/6-31G(d) approach with IEFPCM/DMSO, Fig. S2 in the ESI†). Unfortunately, however, such C$_{60}$ peaks gradually disappeared with the addition of D$_2$O into the NMR DMSO solution (ca. 10% v/v), while the addition of methanol-$d_4$ brought about no change in the spectra. This water degradation may be ascribed to the lower LUMO level of triazoliumfullerene (vs. water persistent pyrroldiniumfullerene), which would enhance the electrophilic activity.

The enhancement of the electron accepting ability of 3$^+$ was also confirmed by cyclic voltammetry (Fig. S3, ESI†). The higher reducing potential of 3$^+$ (vs. N$_2$/dimethylpyrroldiniumfullerene$^{16,2}$) is ascribed to the lower LUMO level due to the periconjugation. The irreversibility of the first peak may indicate the instability of the reduced intermediate. This higher electron accepting ability would lead to intensified n-type semiconductibility and π-soft Lewis acidity.$^{12}$ Moreover, 3$^+$ seems to be a potential candidate for photoinduced electron-transfer materials if some donating counteranions or substituents are introduced.

Although the [3+2] cycloaddition of 1,3-diaza-2-azoniaallene salt with small alkenes was reported to proceed via a concerted pathway,$^{6d,11}$ it is unclear whether this is also the case for the highly conjugated and strained alkenes like fullerene. As indicated by DFT calculations$^{10}$ (BHandHLYP/6-31G(d) with IEFPCM (toluene)),$^{13}$ the unusually low LUMO level ($-3.72 \, \text{eV}$) of 2$^+$ is suitable for orbital interaction with the symmetry allowed HOMO ($-6.76 \, \text{eV}$) of C$_{60}$ (Fig. 2a and b). TS calculations clarified a concerted transition state with the extremely small activation energy of 1.4 kcal mol$^{-1}$ (Fig. 2c and d) and almost equivalent C$_{60}$–N distances (2.9636 and 2.9665 Å). Moreover, the calculation for the product 3$^+$ (Fig. S4 in the ESI†) showed a ca. 1.0 eV lower HOMO level ($-7.79 \, \text{eV}$) than that of C$_{60}$, explaining the absence of bisadducts of 2$^+$.$^{14}$ These theoretical results imply that the present [3+2] reaction of 2$^+$ proceeds via a concerted process like 1,3-dipolar cycloaddition, although such HOMO controlled reactions of C$_{60}$ are very rare on account of the inherent low LUMO level of fullerene.$^{15}$

The self-assembly of triazoliumfullerene was assessed by dynamic light scattering (DLS) and scanning and transmission electron microscopy (SEM and TEM). The solvation of its PF$_6$ salt in THF showed slight aggregation ($1 \times 10^{-5}$ M, ca. 100 nm particle size, Fig. 3a). After casting of the solution on a Si-plate and evaporation, SEM images indicated both spherical and nanocrystalline self-assemblies (Fig. 3b and Fig. S5a, ESI†). For the solution with methanol, the ratio of nanocrystals/vesicles...
seems to increase [Fig. 3c]. By TEM analysis, these spherical aggregates seem to be 100–300 nm vesicles with hollow centers [Fig. 3d and Fig. S5b, ESI†], although the present experiments cannot unambiguously certify bilayer formation. Such vesicles have often been observed in ionic fullerenes.2,3 Interestingly, TEM also showed micrometer-scale crystals (Fig. 3e) with a clear diffraction pattern (Fig. 3f). Such microcrystals were occasionally observed in non-ionic supramolecular fullerene with semi-conductivity.16 Crystalline triazoliumfullerene can be useful for electron-transport materials with lower LUMO levels, although the configurational control of counteranions is required to inhibit the possible carrier-trapping.

Although the quantitative evaluation of periconjugative effects requires further experiments (e.g., with varying substrates and counteranions), we consider that the moderate amphiphilicity of C60 with a small dipole moment (≈11 D) and highly delocalized positive charge would be responsible for the simultaneous formation of vesicles and microcrystals. While pyrrolidiniumfullerene with a larger dipole (≈18 D) preferably aggregates in an antiparallel manner to form bilayers,4 the smaller dipole of triazoliumfullerene can exhibit another type of aggregation mode. In this case, the enhanced π-acceptor ability caused by the delocalized positive charge on the fullerene sphere may promote crystalline aggregation with the aid of counteranions as well as the ary-substituents.

In conclusion, we first prepared triazoliumfullerene by a one-pot reaction of in situ generated 1,3-diaza-2-azoniaallene with C60 and confirmed the periconjugative delocalization of positive charge into the fullerene cage. This compound is expected to exhibit vesicle/crystalline self-assembly due to its moderate amphiphilic interactions and highly delocalized positive charge.

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Notes and references


10 In this paper, all DFT calculations were carried out with Spartan08 or Gaussian 09. Full citations are shown in the ESL1.

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15 However, the use of a large excess of 1 and KPF6 gave inseparable byproducts, e.g., bi- and multi-adducts or products due to the decomposition of the labile intermediate 2.


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