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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 amphiphilic fullerene tended to form vesicles and crystalline aggregates after the casting of THF or MeOH solutions.

Ionic fullerenes[1–6] are useful compounds for medical applications such as in antibacterial[1f] and anti-HIV[1g] agents, and also for self-assembling nanocarbon materials[2,3] owing to the presence of amphiphilic intermolecular ionic, dipole–dipole, π–π and hydrophobic interactions. These ionic and highly polar fullerenes are apt to form vesicle,[1h,2,3] nanowire,[1h,2,4] and nanosheet[5] 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 ($C_{59}N^+$).[6] However, the extremely low stability and intrinsic activity of reduction[7] 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 periconjugation[8] between the outer ionic site and the π-conjugated fullerene cage. We have attempted the introduction of a cationic 1,2,3-triazolium unit[9] into the fullerene sphere, because the possible high delocalization of positive charge on the N_1–N_2–N_3 linkage will allow direct electron withdrawal as well as possible periconjugation with the adjacent fullerene *cis*-1 π-orbital. By DFT calculations,[10] it was found that the LUMO of the triazoliumfullerene was delocalized both on the cationic

N_1–N_2–N_3 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 pyrrolidiniumfullerene, 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. In this communication,
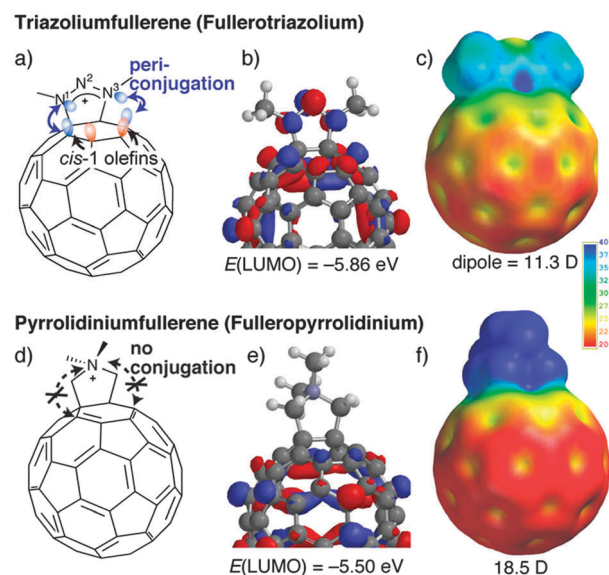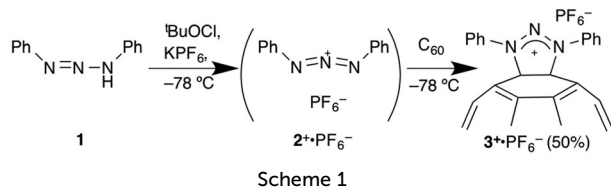

Fig. 1 Comparative representation of triazoliumfullerene and pyrrolidiniumfullerene: (a,d) molecular structure, (b,e) LUMO with its levels shown, (c,f) electrostatic potential (ESP) maps of the electron density contours and dipole moments with a color bar of ESP energy (kJ mol⁻¹); *i.e.*, blue is more electropositive (cationic) while red is lower (relatively apolar). DFT calculations were carried out with the B3LYP/6-31G(d) level of theory.

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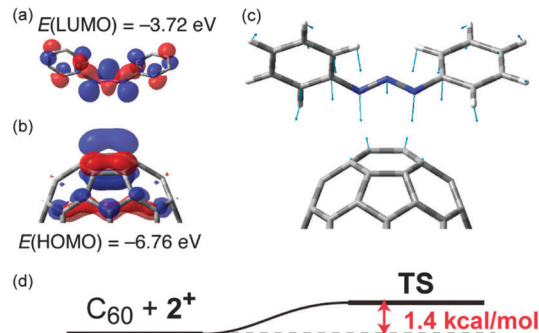
Scheme 1

Fig. 2 (a) LUMO of 2^+ (hydrogen omitted), (b) HOMO (in part) of C_{60}, (c) transition state (TS) geometry and the vibrational vectors of imaginary frequency ($\nu_i = -102.3$ cm^{-1}), and (d) energy diagram (ZPE corrected) of the reaction. These calculations were carried out with the BHandHLYP/6-31G(d) level of theory with solvent parameters (IEFPCM, toluene).[13]

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$_6$[11] at -78 °C. To avoid spontaneous decomposition of the unstable intermediate 2^+, a one-pot reaction was carried out with C_{60} at -78 °C to give 1,3-diphenyltriazoliumfullerene salt $3^+ \cdot$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_{2v} symmetric addition at the 6,6-bond of fullerene. The downfield shift of the sp^3 carbon is probably because of the electron-withdrawal by the conjunct 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_{2v} 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 pyrrolidiniumfullerene), 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,N*-dimethylpyrrolidiniumfullerene[1b,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,[9d,13] it is unclear whether this is also the case for the highly conjugated and strained alkenes like fullerenes. As indicated by DFT calculations[10] (BHandHLYP/6-31G(d) with IEFPCM (toluene)),[13] the unusually low LUMO level (-3.72 eV) of 2^+ is suitable for orbital interaction with the symmetry allowed HOMO (-6.76 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 (2.3963 and 2.3965 Å). Moreover, the calculation for the product 3^+ (Fig. S4 in the ESI†) showed a *ca.* 1.0 eV lower HOMO level (-7.79 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 (1×10^{-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
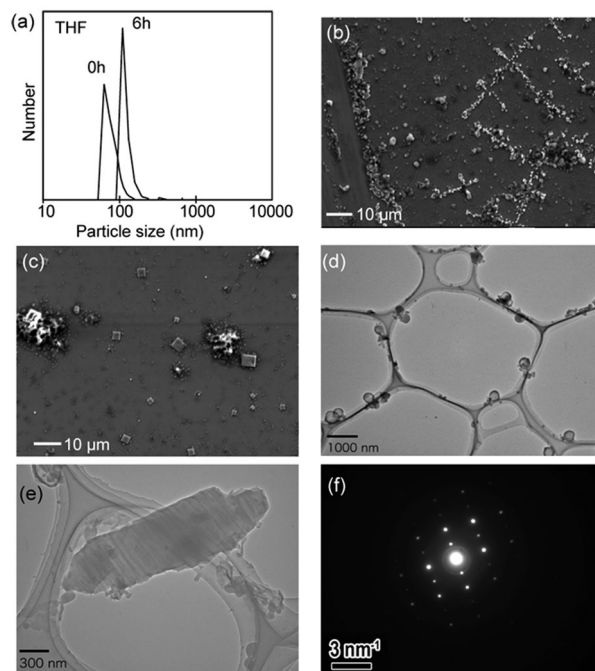

Fig. 3 Aggregation behaviour of $3^+ \cdot$PF$_6^-$ salt. (a) DLS measurement in THF solution. SEM image after casting (b) THF solution or (c) MeOH solution. (d) Vesicle and (e) microcrystal TEM images and (f) diffraction pattern after casting MeOH solution on a carbon/Cu microgrid.

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 fullerenes 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 substituents and counteranions), we consider that the moderate amphiphilicity of 3^+ 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,[1i] 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 aryl-substituents.

In conclusion, we first prepared triazoliumfullerene by a one-pot reaction of in situ generated 1,3-diaza-2-azoniaallene with C_{60} 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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