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Synthesis and Characterization of Three Novel [60]Fullerene Derivatives toward Self-Assembled Nanoparticles through Interaction of Hydrogen Bonding

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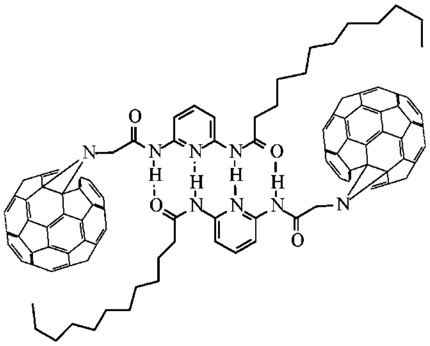
ABSTRACT



Three novel fullerene derivatives bearing a 2,6-bis(acylamino) pyridine unit as a hydrogen bonding motif displaying a dimerization tendency were synthesized and characterized by the cycloaddition reaction of alkyl azide to [60]fullerene. An SEM image of the dimerization system of compound 1 indicated spherical particles having a mean diameter of 15 nm with a rather narrow size distribution.

In the past a few years, a particular aspect in the field of organic solid-state chemistry that has gained increasing interest is the way in which molecules and ions are organized in the solid state to form novel materials with improved electrical, optical, and magnetic properties.[1] It is also fundamentally interesting to develop specific structural architectures that involve the self-assembly of molecules into well-defined supramolecules via intermolecular interactions such as hydrogen bonding and aromatic−aromatic interactions.[2] Multiple hydrogen bonding is a particularly good way to achieve the assembly of supramolecular structures because of its strength, directionality, and specificity. The 2,6-bis(acylamino)pyridine unit has been well used as a potential triple-hydrogen-bond moiety and has displayed a dimerization tendency.[3] Here we would like to report the synthesis and characterization of three novel fullerene derivatives bearing a 2,6-bis(acylamino)pyridine unit as a quadruple-hydrogen-bond motif displaying a dimerization tendency by the cycloaddition of alkyl azide with a fullerene cage.[4] We hoped that these compounds would be good candidates for constructing novel aggregates. This work is a part of our study on assembly of supramolecules based on [60]fullerenes in which we are attempting to analyze the influences of the

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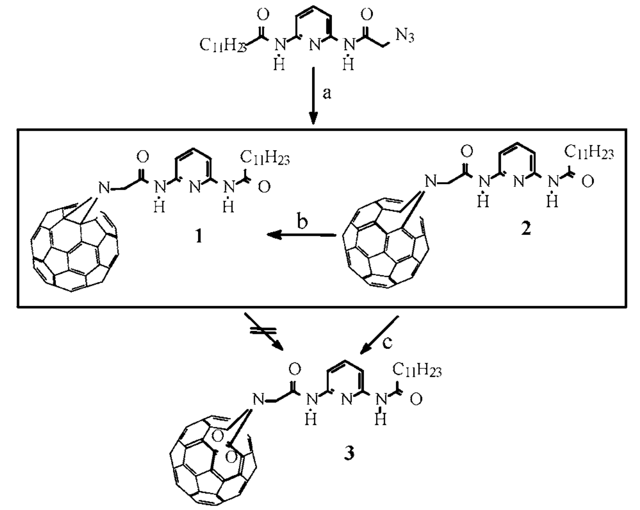
Scheme 1[a]



[a] Reaction conditions: (a) C_{60}, chlorobenzene, reflux under nitrogen, 24 h, **1** (8%) and **2** (30%), respectively; (b) *o*-dichlorobenzene, reflux under nitrogen, 36 h; (c) O_2, H•, 24 h, 57%.

different structure features on the interactions and stability of molecular aggregates.[5]

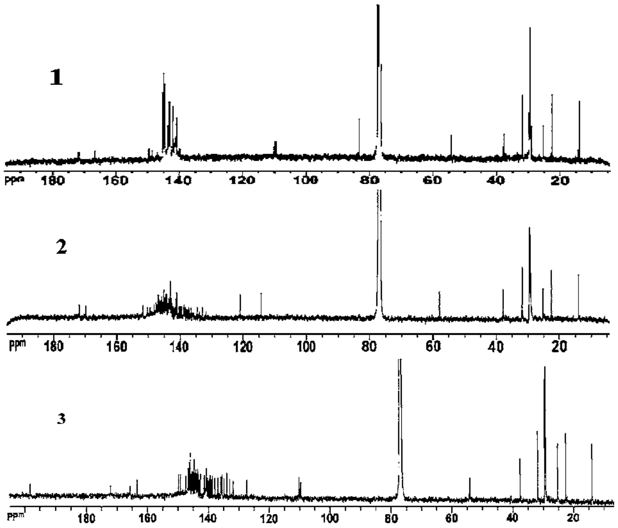


Figure 1. ^{13}C NMR spectra of compounds **1**−**3**.

2-Azidoacetanoylamino-6-lauroylaminopyridine was prepared as previously reported.[5] Compounds **1**−**3** were synthesized as described in Scheme 1.[6] As shown in Figure 1, there was a peak of two carbons at 83.22 ppm, and all other sp^2-C peaks of C_{60} appeared in a closed region from 149 to 140 ppm in **1**; however, no carbon atom information in the sp^3 tertiary region was evident, and all other sp^2-C peaks of C_{60} appeared in a broad region from 155 to 130 ppm in **2**, strongly indicating that **1** was a fullerene but **2** was an azafulleroid. Interestingly, reflux of fulleroid **2** in *o*-dichlorobenzene resulted in the formation of the thermodynamically more stable fullerene **1**, which was consistent with the previously reported conversion of a fulleroid to a fullerene derivative.[7] A photooxygenative reaction of **2** in dichloromethane gave a novel partial ring cleavage ketolactam fullerene derivative **3** having an 11-membered ring.[8]

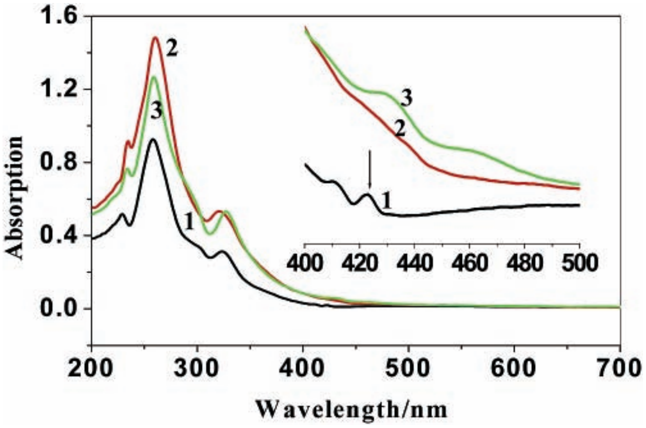


Figure 2. UV−vis absorption spectra of compounds **1**−**3** measured in CH_2Cl_2 (1.0×10^{-5} M) at room temperature. The inset shows the characteristic absorption of **1**.

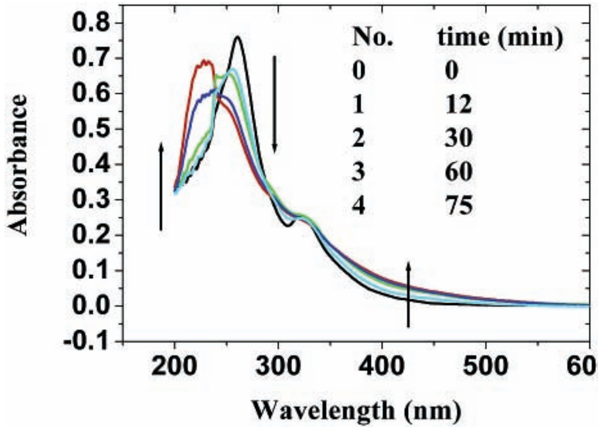


Figure 3. Time dependent UV−vis spectra in situ from the conversion of **2** to **3** in dichloromethane under irradiation. Arrows indicate the direction of spectra changes.

The UV−vis spectra of compounds **1**−**3** are shown in Figure 2. Note that there was a weak peak at ca. 423 nm in the absorption spectrum of compound **1**, which has a [6,6]-closed fullerene structure. However, a similar absorption band was not observed in the spectrum of compound **2**, which has a [5,6]-open fulleroid structure. This weak band was a characteristic absorption observed for the fullerenes but not for the fulleroids.[7,9] As shown in the time-dependent UV−vis spectra changes observed in situ from the irradition on compound **2** in dichlomethane (Figure 3),

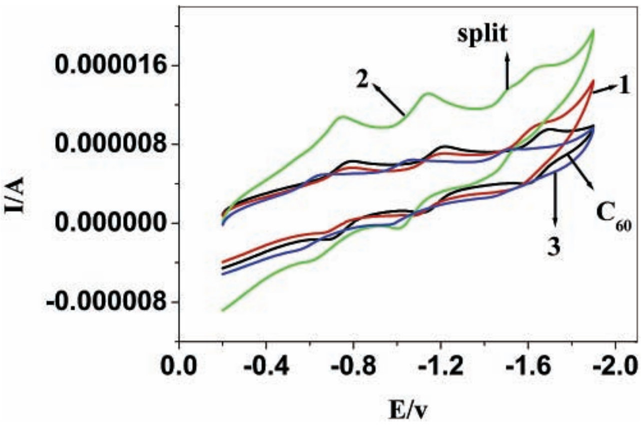


Figure 4. Cyclic voltammograms of the compounds **1**−**3** and [60]-fullerene. CV experiments were performed at room temperature in dichloromethane solutions containing 0.1 M TBAPF$_6$ as a supporting electrolyte and with a platinum disk 3 mm in diameter as the working electrode. The counter electrode was a Pt plate, and an Ag wire was used as the reference electrode. The scan rate was 100 mV/s.

there clearly wasa depiction of the conversion from **2** to **3**.

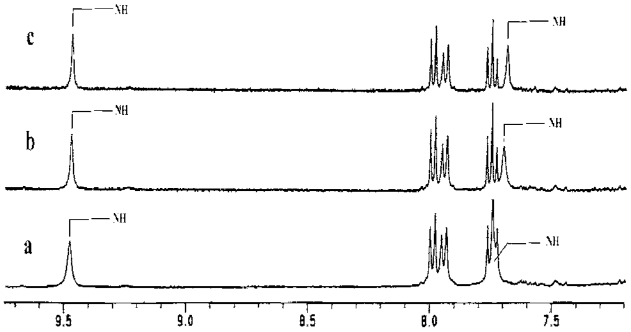


Figure 5. Chemical shifts of amidic hydrogens at different concentrations of compound **1** in *d*-CHCl$_2$CHCl$_2$ ((a) 30 mmol/L, (b) 10 mmol/L, (c) 5 mmol/L).

From the cyclic voltammogram experiments, three reversible oxidation and reduction waves of **1**−**3** in deoxygenated CH$_2$Cl$_2$ were found (Figure 4). These values were cathodically shifted relative to those of C$_{60}$, correlated to the one-electron reduction steps of the C$_{60}$ moiety. The typical sequential electron transfer series was clearly observed for three reduction steps, with a relatively constant separation of ca. 0.45 V between the waves. And more interestingly, there was a split peak in the reduction process between the second and the third waves. The same phenomenon was encountered by Francisco Arias et al.,[10] who attributed it to a chemical step that involved the isomerization of the fulleroid into the corresponding fullerene polyanion as first suggested by Eirmann et al.[7] But conversion of fulleroid **2** to fullerene **1** required more energy because **2** was rather stable. And we did not find the diagnostic UV absorption at 423 nm after the cyclic voltametry experiment, which indicated that little conversion of **2** to **1** happened.

In certain solvents, the strength of a single hydrogen bond is related to the hydrogen bond acidity of the donor group and basicity of the acceptor group involved. In complexes held together by multiple hydrogen bonds, additional factors influence the stability of the complex. Jorgensen and coworkers[11] have shown that the particular arrangement of donor (D) and acceptor (A) groups in an array of hydrogen bonds has a strong influence on complex stability. Our evidence for the formation of the complexes by hydrogen

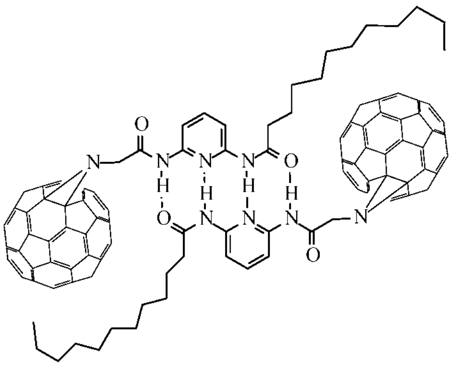


Figure 6. Proposed dimer geometry of compound **1** with a quadruple hydrogen bond.

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(6) Selected data for **1**: ^{1}H NMR, δ [ppm]: 9.70 (s, 1H), 7.8−8.08 (m, 4H), 4.58 (S, 2H), 2.43 (t, 2H, $J = 7.0$ Hz), 1.76 (m, 2H), 1.25 (m, 16H), 0.88 (t, 3H, $J = 7.0$ Hz).^{13}CNMR, δ [ppm]: 171.68, 166.60, 149.65, 148.40, 146.87, 145.21, 144.90, 144.72, 144.55, 143.78, 143.39, 143.26, 143.12, 142.99, 142.85, 142.19, 142.07, 141.72, 141.48, 141.42, 141.32, 141.07, 140.97, 139.90, 110.07, 109.58, 83.22, 54.34, 37.82, 31.81, 29.60, 29.51, 29.37, 29.27, 29.23, 29.01, 25.28, 22.60, 14.04. FT-IR (KBr), ν [cm^{-1}]: 3423 (b, s), 1295, 1243 (m), 1697. Calcd for $C_{79}H_{30}N_4O_2$ (M$^+$), *m*/*z* = 1066.24; found, 1067.1947 (M + H$^+$). Selected data for **2**: ^{1}H NMR, δ [ppm]: 8.42 (d, 1H, $J = 8$ Hz), 8.05 (s, 1H), 7.98 (t, 1H, $J = 8$ Hz), 7.36 (d, 1H, $J = 8$ Hz), 5.21 (d, 1H, $J = 16$ Hz), 4.96 (d, 1H, $J = 16$ Hz), 2.43 (t, 2H, $J = 8.0$ Hz), 1.69 (m, 2H), 1.25 (m, 16H), 0.87 (t, 3H, $J = 7.0$ Hz).^{13}CNMR, δ [ppm]: 171.85, 169.82, 151.65, 150.26, 149.41, 148.10, 147.66, 147.16, 147.08, 146.80, 146.65, 146.51, 146.23, 146.02, 145.89, 145.78, 145.46, 145.23, 145.12, 144.73, 144.54, 144.33.144.24, 143.70, 143.63, 143.49, 143.44, 143.20, 143.03, 142.87, 142.78, 142.68, 142.27, 141.32, 141.11, 141.01, 140.40, 139.95, 139.55, 138.79, 138.43, 138.12, 137.28, 137.21, 136.50, 136.02, 135.83, 134.56, 133.89, 132.98, 131.82, 120.98, 114.38, 57.98, 37.82, 31.82, 29.61, 29.52, 29.37, 29.28, 29.24, 29.08, 25.25, 22.60, 14.05. FT-IR (KBr), ν [cm^{-1}]: 3423 (b, s), 1301 (m), 1718, 1696 (s), 1579, 1522, 799, 527. MALDI-TOF MS: calcd for $^{12}C_{79}H_{30}N_4O_2$ (M$^+$), *m*/*z* = 1066.24; found, 1066.1025 (M $^+$). Selected data for **3**: ^{1}H NMR (CDCl$_3$, 400 MHz), δ [ppm]: 9.39 (s, 1H), 8.38 (s, 1H), 7.95 (d, 1H), 7.82 (m, 1H), 7.65 (m, 1H), 6.51 (d, $J = 15.2$, 1H), 5.52 (d, $J = 15.2$, 1H), 2.47 (t, 2H), 1.71 (m, 2H), 1.62 (m, 2H), 1.25 (m, 14H), 0.89 (t, $J = 6.8$, 3H). ^{13}C NMR (CDCl$_3$, 600 MHz), δ [ppm]: 198.22, 172.16, 165.81, 163.35, 149.80, 149.14, 147.47, 147.34, 146.81, 146.67, 146.58, 146.42, 146.27, 146.09146.02, 145.92, 145.84, 145.69, 145.40, 145.27, 145.15, 144.92, 144.68, 144.50, 144.29, 144.17, 144.10, 144.02, 143.96, 143.83, 143.68, 143.62, 143.56, 143.38, 143.34, 142.99, 142.60, 141.41, 141.22, 140.71, 140.67, 140.42, 139.99, 139.62, 139.35, 138.97, 138.64, 137.87, 136.77, 135.86, 135.70, 135.51, 134.86, 133.97, 133.91, 132.95, 131.95, 131.86, 127.28, 110.20, 109.65, 54.17, 37.66, 31.79, 29.53, 29.42, 29.35, 29.22, 25.28, 22.56, 13.97. FT-IR (KBr), ν [cm^{-1}]: 3416 (b, s), 1293, 1243 (m), 1725 (s), 1696 (s), 1686 (s), 1585, 1507, 800, 523. MALDI-TOF MS: Calcd for $^{12}C_{79}H_{30}N_4O_4$ (M$^+$), *m*/*z* = 1098.23; found, 1099.7548 (M + H$^+$).

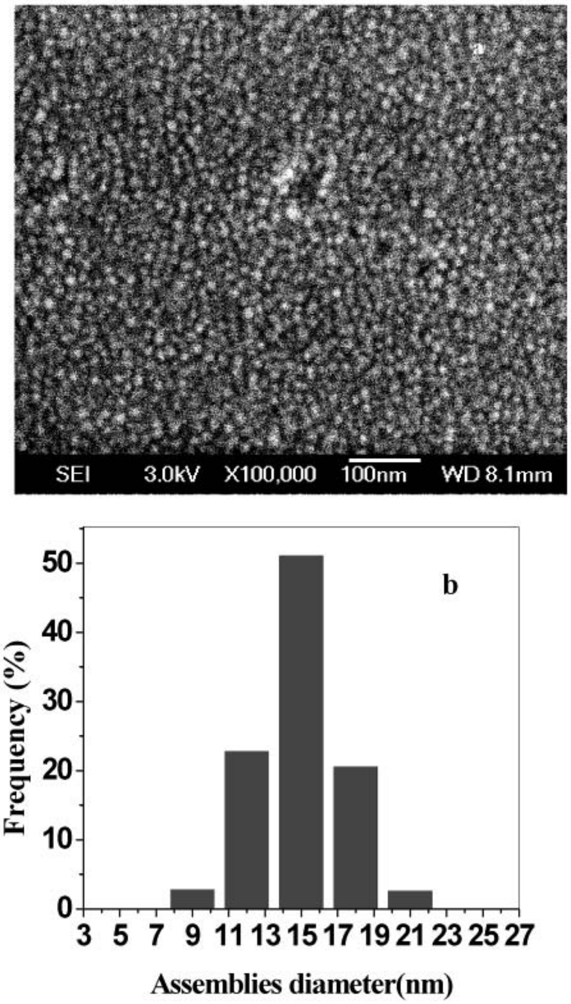

Figure 7. SEM image and size distribution histogram of dimerization system of compound **1** in dichloromethane (10^{-5} M).

bond self-assembly came from ^{1}H NMR spectroscopic studies (Figure 5). The ^{1}H NMR spectra showed a slight upfield shift of the amidic proton signals as the concentration of compound **1** in $CDCl_2CDCl_2$ decreased. This observation was consistent with four ADAD hydrogen bonds in the noncovalent C_{60}-dimer system. In **1**−**3**, due to the existence of the C_{60} moiety, the carbonyl of acetylamino preferentially showed a cis conformation. Thus, a quadruple-hydrogen-bond motif formed as ADAD arrays (Figure 6).

Figure 7 shows an SEM image of a dilute dispersion of the dimerization system of **1** in dichloromethane. As the image shows, the dimerization system consists of spherical particles having a mean diameter of 15 nm. The corresponding histogram (Figure 7b) reveals that the particle size distribution was rather narrow and exhibited the features of a log-normal distribution.

In conclusion, three novel fullerene cycloadducts containing a 2,6-bis(acylamino) pyridine unit as quadruple-hydrogen-bond motif displaying a dimerization tendency were synthesized and characterized. ^{1}H NMR spectra confirmed the dimerization. An SEM image of **1** also indicated the dimerization and indicated that π−• interactions of fullerene cages may have resulted in nanoscale aggregations.

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Supporting Information Available: Experimental details and characterization of compounds **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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