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Synthesis of Water-Soluble Highly Two-Photon Responsive [60]Fullerene-Diphenylaminofluorene Chromophore Dyads

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We have synthesized an amphiphilic donor-acceptor type [60]fullerene-diphenylaminofluorene (DPAF) containing oligo(ethylene glycol) moieties, denoted C_{60}*-DPAF-*EG_n*. The hydrophobic* C_{60}*-DPAF moiety consisting of an electron-donating diphenylaminofluorene unit and an electron-accepting* C_{60} *cage shows large cross-sections of two-photon absorptivity (2PA) in the nanosecond region. The attachment of two hydrophilic oligo(ethylene glycol) segments on DPAF mainly increases water-solubility of the corresponding chromophoric macromolecules that enhances their potential application in biomedical treatments. Here, we present the synthesis and self-assembly study of these amphiphilic materials in aqueous solution. New* C_{60}*-DPAF-*EG_n *compounds were structurally characterized by various spectroscopic methods including,* ^{1}*H-NMR,* ^{13}*C-NMR, FT-IR, and UV spectroscopies. In the vesicle formation investigation, UV-visible absorption spectra, dynamic light scattering measurements, and transmission electron microscopy were used as primary methods for morphology characterization of molecular self-assembly behavior of these amphiphilic [60]fullerene-diphenylaminofluorene chromophore dyads.*

Keywords C_{60}, diphenylaminofluorene, poly(ethylene-glycol), amphiphilic molecule, molecular self-assembly

Introduction

Functionalization of the C_{60} cage resulted in derivatives suitable for the uses as optoelectronic materials in practical applications due to their wide range of electronically conducting, magnetic, photochemical, and electrical features (1, 2). A large variety of donor-linked fullerene conjugates have been designed, synthesized, and studied for their photoinduced electron- and energy-transfer processes, considering the unique high electron-accepting ability of [60]fullerenes (3–5). These processes make possible myriad of potential uses in photophysical and biomedical areas. Over the past decade,

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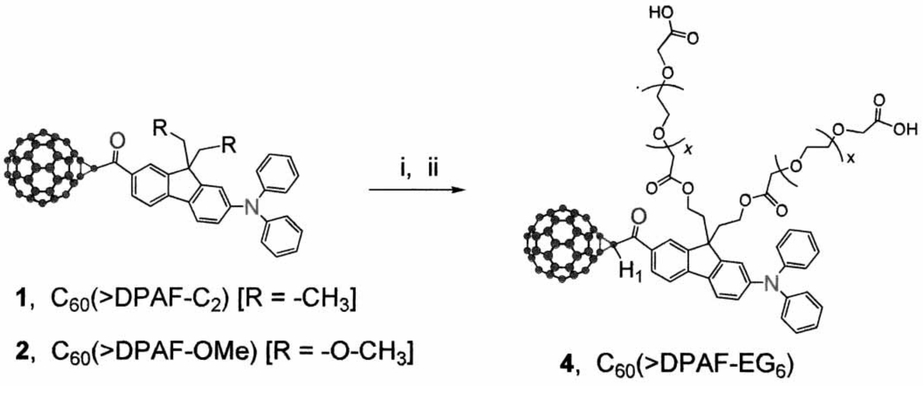
Address correspondence to Long Y. Chiang, Department of Chemistry, University of Massachusetts, Lowell, MA, USA 01854. E-mail: long_chiang@uml.edu two-photon absorption (2PA) phenomena of organic chromophore molecules have attracted considerable attention due to related promising applications, such as fluorescence imaging, data storage, microfabrication and photodynamic therapy. A number of chromophores including diphenylaminofluorene (DPAF) derivatives were investigated for the structural relationship to their multi-photon absorptivity. Relatively high 2PA cross-sections were demonstrated on some branched diphenylaminofluorene (DPAF)-derived chromophores by covalent linking with different π-acceptors in a conjugate structure (6, 7). The utility of a diphenylaminofluorene sub-unit in the design of new chromophores is the explanation for its inherently high thermal and photochemical stability and easy functionalization at 2-, 7-, and/or 9-carbon positions.

Implementing similar approaches, our group reported the first highly 2PA-active diethylated C_{60}-DPAF derivative possessing a one-dimensional A-sp^3-D molecular linkage with a close coupling of the electron-accepting (A) fullerene cage and the electron-donating (D) diphenylaminofluorene moiety. Accordingly, one C_{60}-DPAF dyad 7-(1,2-dihydro-1,2-methano[60]fullerene-61-carbonyl)-9,9-diethyl-2-diphenylaminofluorene [C_{60}(>DPAF-C_2)], as shown in Scheme 1, exhibits large 2PA cross-sections ($\sigma_2' = 196 \times 10^{-48}$ cm^4-sec in nanosecond region, which is among the highest value known for many DPAF-derived 2PA molecules (8).

Fullerene derivatives are extremely hydrophobic in nature. This restrains their applicability in bio-medical areas. Several groups, including our own, have described the synthesis of amphiphilic fullerene derivatives for the enhancement of water-solubility of the C_{60} derivatives. The amphiphilic nature of the derivatives allowed their self-assemblies into different forms of micelles, vesicles, nanospheres, and nanorods in aqueous solution (9–13). Considering remarkable biocompatibility properties of poly-(ethylene glycol) (PEG), several amphiphilic C_{60} analogues consisting of poly(ethylene glycol) side-chains as hydrophilic end groups were prepared and characterized for the molecular aggregation behavior studies in aqueous medium (14, 15). Furthermore, two-photon excitation process of responsive chromophores may serve as a potential alternative treatment technique for photodynamic cancer therapy (PDT). Therefore, synthesis of amphiphilic fullerene-DPAF conjugates containing polar hydrophilic functional groups, such as carboxylic acid and poly(ethylene glycol), leading to water-soluble fullerene derivatives is in our interest in order to improve their potency in biomedical treatments.



Scheme 1. Reagents and synthetic conditons: i, **2**, BBr_3, NaI, 15-crown-5, CH_2Cl_2, $-30°C$; ii, poly(ethylene-glycol) bis(carboxymethyl) ether (M.W. 600), DCC, DMAP, $ClCH_2CH_2Cl$.

Here, we report the synthesis of oligo(ethylene glycolated) diphenylaminofluorene-[60]fullerene conjugates, namely, C_{60}(>DPAF-EG_6). Structural characterization of these new fullerenic chromophores was made by using FT-IR, ^{1}H-NMR, ^{13}C-NMR and UV-visible spectroscopies. Subsequently, we investigated the molecular self-assembly behavior of C_{60}(>DPAF-EG_6) in several dilute aqueous concentrations resulting in the formation of nano- to submicron sized spherical vesicles. These spherical vesicles were characterized using ultraviolet-visible spectroscopy (UV-Vis), dynamic light scattering measurements, and transmission electron microscopy (TEM).

Experimental

1,3-Dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP), poly(ethylene glycol) bis(carboxymethyl) ether (molecular weight 600), and anhydrous dichloroethane were purchased from Aldrich. C_{60}-methanocarbonyl-9,9-dimethoxyethan-2-diphenylaminofluorene [C_{60}(>DPAF-OMe)] **2** (Scheme 1) was prepared according to the reported procedure (8, 16) with chemical modification at C_9 group to incorporate a highly functionalizable group. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Spectrospin–250 spectrometer. Infrared spectra were recorded as KBr pellets on a Nicolet 750 series FT-IR spectrometer. UV-Vis absorption spectra were collected on a computer-controlled Perkin-Elmer UV/VIS/NIR Lambda 9 series spectrophotometer.

Light scattering experiments were performed on a Brookhaven light scattering instrument equipped with a light scattering system, a BI9000 AT digital correlator, and a photon counter with a BI-200SM research goniometer. Transmission electron microscopic (TEM) images were taken on a Philips Tecnai 20 TEM at 200 kV.

Synthesis of C_{60}(>DPAF-EG_6) as C_{60}-Methanocarbonyl-9,9-dioligoethyleneglycol-2-diphenylaminofluorene

Poly(ethylene glycol) diacid (M.W. 600, 463 mg, 0.077 mmol) was taken in a 100 ml round bottom flask and stirred under reduced pressure in oil bath maintained at 80°C for 5 h. The flask was cooled to room temperature and added 1,3-dicyclohexylcarbodiimide (DCC, 160 mg, 0.077 mmol), 4-dimethylaminopyridine (DMAP, 94 mg, 0.077 mmol) and C_{60}-methanocarbonyl-9,9-diethanol-2-diphenylaminofluorene (150 mg, 0.013 mmol). Anhydrous 1,2-dichloroethane (50 ml) was then added to the reaction mixture and further stirred in an oil bath maintained at 65°C for 2 h. The reaction was terminated when a sample of the reaction mixture showed complete disappearance of the starting material on thin-layer chromatographic (TLC) plates. The reaction mixture was filtered with the filtrate liquid and subsequently dried on a rotavapor. The resulting crude products were dissolved in a solvent mixture of THF-H_2O (1 : 1, 10 ml) and dialyzed against distilled water using the dialysis membrane (MWCO 1000) to ensure complete removal of unreacted poly(ethylene glycol). The product C_{60}-methanocarbonyl-9,9-dioligoethyleneglycol-2-diphenylaminofluorene **4** was obtained as a semisolid in a 40% yield after completion of dialyses and freeze-drying.

Results and Discussion

The compound C_{60}-methanocarbonyl-9,9-dimethoxyethyl-2-diphenylaminofluorene **2** (Scheme 1) consists of a similar chromophoric structural moiety to that of highly two-photon responsive C_{60}-methanocarbonyl-9,9-diethyl-2-diphenylaminofluorene **1**, with a fluorenyl C_9 appendage that can be easily modified. A demethylation reaction of C_{60}(>DPAF-OMe) **2** was utilized as the first step synthesis towards the attachment of water-soluble functionalities on the DPAF moiety. Synthetically, the reaction was carried out by reacting **2** with BBr_3 in the presence of NaI and 15-crown-5 in methylene chloride at −30°C for a period of 1.5 h. C_{60}-methanocarbonyl-9,9-diethanol-2-diphenylaminofluorene **3** was obtained as a brown solid in 70% yield after column chromatographic purification. The product **3** showed the absence of peaks corresponding to six methyl protons at δ 3.05 in ^{1}H-NMR spectrum. Matrix-assisted laser desorption ionization (MALDI) mass spectrum showed a group of mass ion signals at m/z 1181, corresponding to the molecular mass ion of **3**, consistent with its chemical composition. In ^{1}H-NMR spectrum, α−proton to the carbonyl group appears as a singlet peak at δ 5.69. Chemical shifts of the protons at C_{10} and C_{11} of the ethanol group appeared as a multiplet peak and a triplet peak at δ 2.48−2.34 and 3.2, respectively. Chemical shift of phenyl protons at C_1, C_3, and C_4 of the fluorenyl ring moiety appeared at δ 8.47 (d, $J = 1.6$ Hz), 8.57 (dd, $J = 8$ Hz, $J = 1.6$ Hz), and 7.90 (d, $J = 8$ Hz), respectively.

Synthesis of C_{60}-methanocarbonyl-9,9-dioligoethyleneglycol-2-diphenylaminofluorene C_{60}(>DPAF-EG_6) **4** was carried out by reacting C_{60}-methanocarbonyl-9,9-diethanol-2-diphenylaminofluorene with poly(ethylene glycol) bis(carboxymethyl) ether (M.W. 600, 6.0 equiv.) in the presence of 1,3-dicyclohexylcarbodiimide and 4-dimethylaminopyridine at 80°C for a period of 5.0 h to afford the crude semi-solid products. Owing to a relatively high molecular weight of the product **4**, chromatographic separation method is not effective for the purification. Therefore, the crude products were dissolved in a solvent mixture of THF-H_2O (1 : 1) and subjected to the dialysis treatment against distilled water using a dialytic membrane (MWCO 1000) for effective removal of residual unreacted poly(ethylene glycol). The technique allows isolation of **4** as semi-solids in 40% yield. The compound **4** was found to be soluble in a variety of solvents including THF, DMSO, H_2O, and $CHCl_3$.

Structure of the product C_{60}(>DPAF-EG_6) was fully characterized by various spectroscopic methods including ^{1}H-NMR, ^{13}C-NMR, FT-IR and UV-visible spectroscopies. ^{1}H-NMR spectrum of **4** showed no change of proton peaks in the aromatic region at δ 7.0−8.6, whereas the aliphatic proton peak corresponding to the chemical shift of the α-proton to carbonyl group appears at δ 5.72 for both derivatives **3** and **4**. This clearly indicated the attachment of oligo(ethylene glycol) chains to the hydroxyl functional groups of diphenylaminofluorene moiety. Also, disappearance of the triplet peak at δ 3.20 corresponding to methylene protons of C_{11} and an additional peak at δ 4.33 for methylene protons next to the ester functionality indicated the attachment of oligo(ethylene glycol) chain to C_{60}-DPAF moiety. Additional structural confirmations were made by ^{13}C-NMR spectrum. Presence of a carbonyl carbon signal at δ 189.7 and a total of 29 carbon signals distributed in a range of δ 137−149 indicated a C_2 symmetry for 58 sp^2 carbons of the fullerene cage that provides evidence for the monoadduct structure of **3** and **4**. The presence of several peaks at δ 172.2 and 170.4 in the spectrum of **4** indicated the existence of acid and ester carbonyl carbons. A strong carbon signal at δ 70.9 corresponds to the chemical shift of methylene carbons of oligo(ethylene glycol) moiety. Presence of oligo(ethylene glycol) moiety in the structure of **4** was also seen in the FT-IR spectrum (Figure 1c), which showed an optical absorption profile superimposed with the combination of the IR profiles of poly(ethylene glycol) bis(carboxymethyl) ether (Figure 1a) and C_{60}(>DPAF-OH) (Figure 1b). Poly(ethylene glycol) gave the strongest symmetrical ether stretching band (–C–O–C–) at 1109 cm^{-1}. In Figure 1c, a strong band centered at 1746 cm^{-1}, corresponding to the absorption of C=O functional

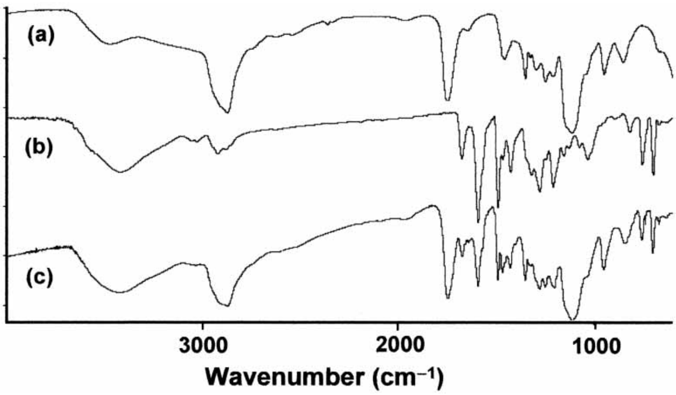


Figure 1. FT-IR spectra of (a) poly(ethylene glycol) bis(carboxymethyl) ether, (b) C_{60}(>DPAF-OH) **3**, and (c) C_{60}(>DPAF-EG$_6$) **4**.

groups indicated the presence of ester and acid moieties that is consistent with the chemical conversion of hydroxyl groups of C_{60}(>DPAF-OH) to the corresponding ester in **4**. Characteristic optical stretching absorption of the carbonyl group, that bridges fluorene and fullerene moieties of **4**, was also detected at 1670 cm^{-1}. Other significant IR bands include fullerenyl signals appearing at 750, 695 and 534 cm^{-1}.

Optical absorption of **3** gave three major bands at 259 ($\varepsilon = 1.3 \times 10^5$), 324 ($\varepsilon = 4.5 \times 10^4$), and 408 nm ($\varepsilon = 3.7 \times 10^4$ L/mol/cm). Similarly, the compound **4** displayed closely related three absorption bands at 256 ($\varepsilon = 1.1 \times 10^5$), 322 ($5.1 \times 10^4$), and 409 nm ($\varepsilon = 3.5 \times 10^4$ L/mol/cm) in their UV-vis spectra, as shown in Figure 2A. The former two bands approximately match those of the model compounds C_{60}(>COPh) and C_{60}[>$(CO_2Et)_2$] mainly contain an optically active fullerene moiety that confirms these absorption bands being attributed to the C_{60} cage. The latter band fits well with the main optical absorption of 7-bromoacetyl-9,9-diethanol-2-diphenylaminofluorene (DPAF-OH) centered at 405 nm ($\varepsilon = 2.9 \times 10^4$ L/mol/cm) that is attributed to the corresponding diphenylaminofluorene moiety. Nearly absorptive superimposition of **3** and **4** in Figure 2A with the combined spectra of two independent chromophores, containing either the fullerene cage or diphenylaminofluorene, revealed no ground-state interaction between these two moieties present in the molecule **4** in chloroform at the concentration of 2.0×10^{-5} M.

UV-visible absorption spectra of C_{60}(>DPAF-PEG$_6$) at the concentration of 1.0×10^{-5} M in chloroform and water are shown in Figure 4B. Interestingly, in a water medium, these absorption peaks displayed a slight red shift to 260, 327, and 417 nm, respectively, with broadened bands with less intensity. These characteristic features may reveal molecular aggregation of C_{60}(>DPAF-EG$_6$) in water.

Molecular self assembly behavior of amphiphilic C_{60}(>DPAF-EG$_6$) was investigated in aqueous solution. During the solution preparation, a small quantity of the compound was first dissolved in THF–DMSO (1 : 1, 2.4% by volume of whole aqueous solution). This was used to enhance the solubility of **4** in water. Further dilution of the master solution of C_{60}(>DPAF-EG$_6$) to various concentrations ranging from 3.0×10^{-4} M down to 1.0×10^{-6} M was prepared by the addition of the corresponding quantity of water. These solutions were used for the studies under transmission electron microscopy (TEM) and dynamic light scattering (DLS) measurements to investigate molecular

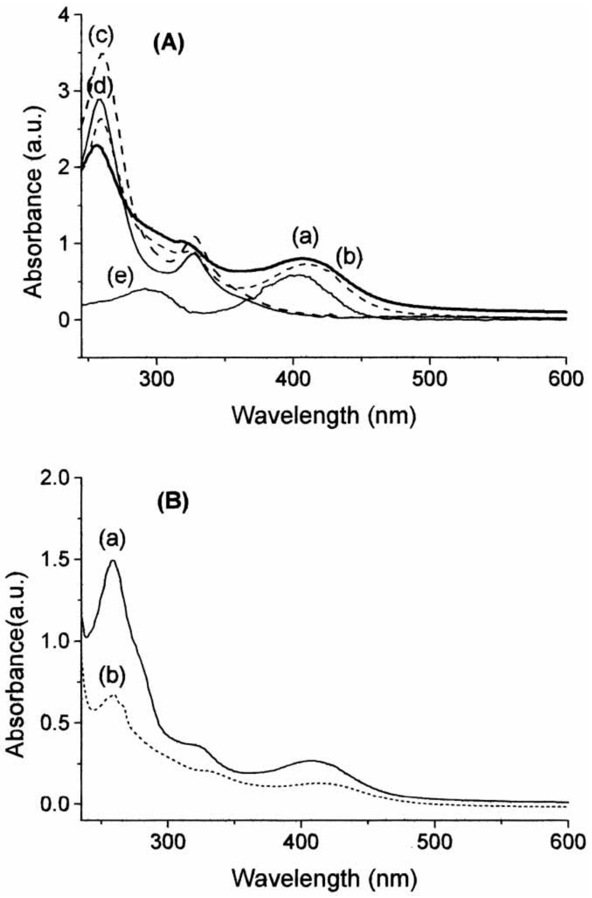


Figure 2. (A) UV-Vis spectra of (a) C_{60}(>DPAF-OH) **3**, (b) C_{60}(>DPAF-EG$_6$) **4**, (c) C_{60}(>COPh), (d) C_{60}[>(CO$_2$Et)$_2$] and (e) DPAF-OH in chloroform at a concentration of 2.0×10^{-5} M; (B) UV-vis absorption spectra of C_{60}(>DPAF-EG$_6$) in (a) chloroform and (b) water at the concentration of 1.0×10^{-5} M.

assembly characteristics and the distribution of average effective diameter of aggregates formed, respectively.

In DLS, a distinct relationship between the concentration and the sphere size was found, where the effective diameter of the sphere increases with the increase of concentration. A maximum average effective sphere diameter of 300 ± 50 nm based on more than 3 repeat trial runs was obtained as shown in Figure 3, perhaps, due to the effect of membrane filtration (a pore size of 0.45 μm). A slight scattering of the DLS data among different repeated experiments indicated that the sphere size might depend on the procedure of sample preparation and subsequent treatments of the solution. However, the sphere-size distributions at all concentrations agree well with those observed in TEM micrographs.

Transmission electron micrographs of **4** taken at the concentration of 3.0×10^{-4} M in water are shown in Figure 4. TEM images displayed spherical aggregates in an average diameter of 200–400 nm. The size of these spheres falls within the range of fullerene

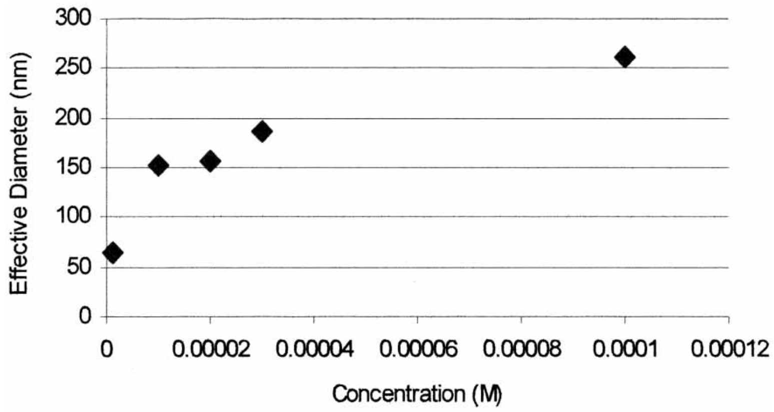


Figure 3. Dynamic light scattering data of C_{60}(>DPAF-EG_6)-derived vesicles showing distribution of effective sphere diameters in water (average of three trials) at concentrations of $1.0 = \times 10^{-6}$ M to 3.0×10^{-4} M.

vesicles reported that typically reaches from 50 nm to 5.0 μm. Also, the size of spherical vesicles increases with an increase in concentration. This observation is consistent with that concluded in dynamic light scattering measurements.

Conclusion

Amphiphilic two-photon absorptive oligo(ethylene glycolated) diphenylamino-fluorene[60]fullerene conjugate C_{60}(>DPAF-EG_6) was synthesized by esterification of

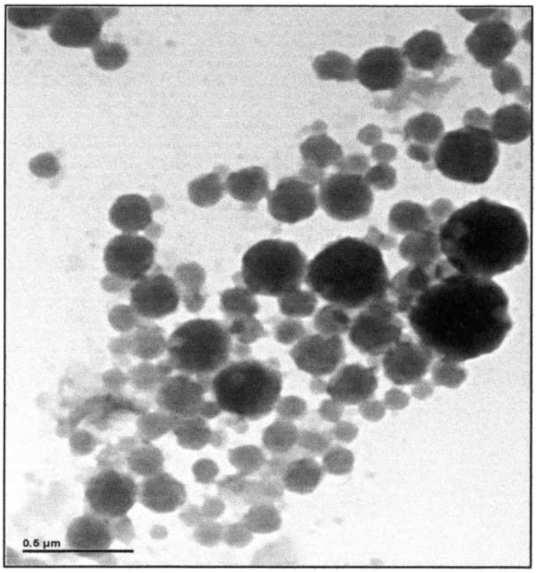


Figure 4. Transmission electron micrographs of the vesicles derived from the dilute solution of C_{60}(>DPAF-EG_6) prepared at the concentration of 3.0×10^{-4} M in water.

hydroxy terminated C_{60}-DPAF moieties with acid-terminated poly(ethylene glycol) chains. Structural characterization of these new fullerenyl chromophores was made by various spectroscopic methods. Molecular aggregation behavior of $C_{60}(>\text{DPAF-EG}_6)$ in dilute aqueous solutions was investigated. That led to observation of molecular self-assembly phenomena of $C_{60}(>\text{DPAF-EG}_6)$ in H_2O showing many nano- to submicron-sized spherical vesicle formations, in a diameter of 200–400 nm, in TEM photographs, using the aqueous solution concentration of 1.0×10^{-4} M to 3.0×10^{-4} M. Some of these displayed vesicle images, prepared at a low concentration of 2.0×10^{-5} M, with a sharp broken edge revealed a constitute bilayer membrane structure. Arrangement of a bilayer structure is reasonable based on geometric packing considerations and strong intermolecular hydrophobic interactions of C_{60}-DPAF moeity. These vesicles based on bilayer-membrane structures may serve as an alternative to lipid membranes and liposome vesicles.

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