Self-assembly of a new C_{60} compound with L-glutamid-derived lipid unit: formation of organogels and hierarchically structured spherical particles

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1. Synthesis and characterization

**Materials.** 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC-HCl) were purchased from Acros. Triphenylphosphine, diethyl azodicarboxylate (DEAD) and 4-(Dimethylamino)pyridine (DMAP) were purchased from Alfa Aesar. \(N_1^1, N_5^5\)-didodecyl-L-glutamide, 1-(3-carboxypropyl)-1-phenyl[6,6]C\(61\) (compound 3) and 9,10-bis(1,3-dithiol-2-ylidene)-2-hydroxymethyl-9,10-dihydroanthracene (compound 4) were prepared according to literatures.\(^S1\)\(^S2\) All other reagents and solvents (standard grade) were used as received unless otherwise stated.

**Characterization techniques.** Melting point was measured with a BÜCHI B-540 microscope apparatus. TOF-MS spectra were determined with a BEFLEX III spectrometer. HRMS data were determined with an FTICR-APEX instrument.

**References**

(S1). \(N_1^1, N_5^5\)-didodecyl-L-glutamide was prepared according to the reported synthetic procedures: V. Gopal, T. K. Prasad, N. M. Rao, M. Takafuji, M. M. Rahman and H. Ihara, *Bioconjugate Chem.*, 2006, 17, 1530.

(S2). Compound 2 was prepared according to the reported synthetic procedures: (a) F. Wudl, M. L. Kaplan, E. J. Hufnagel and E. W. Southwick, *J. Org. Chem.*, 1974, 39, 3608; (b) S. González and N. Martín, *J. Org. Chem.*, 2003, 68, 779.
$^1$H-and $^{13}$C-NMR spectra of LMWG 1
$^1$H-and $^{13}$C-NMR spectra of compound 2
2. TEM images of the xerogel of LMWG 1 and that of LMWG 1 and compound 2 from toluene

Figure S1. (a, b) TEM images of the xerogel of LMWG 1 from toluene at macro- and nano-scale; (c, d) TEM images of the xerogel of LMWG 1 and compound 2 (1.0 eq. vs. LMWG 1) from toluene at macro- and nano-scale.
3. XRD patterns of the xerogels and the precipitates of LMWG 1 from DMSO

![XRD patterns](image)

Figure S2. XRD patterns of the xerogels (left) formed with LMWG 1 (a) and the mixture of LMWG 1 and compound 2 (1.0 eq. vs. LMWG 1) (b) from toluene; XRD patterns of the precipitates (right) prepared with LMWG 1 from DMSO using a 20 °C-water bath (c) and a hot-oil bath (d).
4. Transient absorption measurements for LMWG 1 and compound 2

Figure S3. **Top**: Differential absorption spectra obtained upon femtosecond flash photolysis (440 nm) of LMWG 1 and compound 2 (LMWG 1: 1.0 mM; compound 2: 1.0 mM) in toluene with time delays of 0.9 and 16.4 ps at room temperature; **Bottom**: decay profile for the absorption at 683 nm.\(^a\)

\(^a\) A Ti:sapphire femtosecond laser system provided laser pulses for the femtosecond transient absorption measurements.
absorption measurements. A regenerative amplifier (Spitfire, Spectra Physics) seeded with a mode-locked Ti:sapphire laser (Tsunami, Spectra Physics) delivered laser pulses at 800 nm (120 fs, 1 kHz), which were then divided into two components by using a 9:1 beam splitter. The major component was sent to an optical parametric amplifier (OPA-800CF, Spectra Physics) to generate the pump pulses (440 nm, 130 fs, 1 kHz). The minor component was further attenuated and focused into a 3-mm sapphire plate to generate the probe pulses. A band-pass filter (SPF-750, CVI) was inserted into the probe beam to select visible probe (540–700 nm). The time delay between the pump and probe beams were regulated through a computer-controlled motorized translation stage in the probe beam. A magic-angle scheme was adopted in the pump-probe measurement. The temporal resolution between the pump and the probe pulses was determined to be ~150 fs (FWHM). The transmitted light was detected by a CMOS linear image sensor (S8377-512Q, Hamamatsu). The excitation pulsed energy was 0.2 μJ/pulse as measured at the rotating sample cell (optical path length 1 mm). A typical absorbance of ~0.4 at the excitation wavelength was used. The stability of the solutions was spectrophotometrically checked before and after each experiment. Differential absorption spectra upon femtosecond flash photolysis at 390 nm were also tested.
5. Photographs of water contact angles at different surfaces

Figure S4. (a) The photograph of a water droplet on the surface of xerogel of LMWG 1 from toluene (contact angle of 142.0°); (b) the photograph of a water droplet on the surface of the spherical particles formed with LMWG 1 after cooling its hot solution in DMSO in a 20 °C-water bath (contact angle of 139.1°). [a]

[a] The contact angles were measured on a contact angle system (OCA20, Dataphysics, Germany) at ambient temperature. Water droplets with a volume of 4 μL were carefully dropped onto the samples. The average contact angles values were obtained by measuring five different positions of the same sample.