Supporting Information

Flowerlike supramolecular architectures assembled from C_{60} equipped with a pyridine substituent

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(A) Measurements and calculation

The ¹H NMR spectra were recorded on a Bruker Biospin DRX-600 spectrometer. MALDI-TOF-MS spectra were recorded with Shimazu AXIMA-CFR Plus station. UV-vis absorption spectra in solution were recorded on Hitachi U-2900 spectrophotometer. Diffuse reflectance absorption spectra were recorded on a Shimadzu UV-2500PC UV-vis spectrometer with a diffuse reflectance accessory and barium sulfate as the reference sample. The objects obtained were characterized with SEM (S-4800, Hitachi, 10 kV), XRD (JDX-3500, JEOL), and AFM (SII E-Sweep, SPI4000 probe station, tapping mode). Small angle X-ray scattering (SAXS) patterns were measured on NANO-Viewer (Rigaku) equipped with Micro Max-007HF high intensity micro focus rotating anode X-ray generator. This generator was operated at 40 kV and 30 mA and radiated Cu K α X-ray ($\lambda = 0.154$ nm). Three beam collimation set were used to control the beam size and divergence. The diameter of each slit was 0.3 mm, 0.1 mm and 0.25 mm, respectively. The scattered X-ray on the sample passed through the vacuum chamber and collected on a two-dimensional position sensitive CCD detector. To prevent detecting direct beam, of which intensity is much stronger than that of scattered X-ray, beam stopper with 3 mm diameter was used. The distance between a sample and the detector was 38 cm. HR-cryo-TEM images were obtained with a JEOL model JEM-2100F(G5) microscope. This instrument is equipped with a liquid helium stage to keep the specimen around 4 K, and the observation was performed at an accelerating voltage of 200 kV. TEM samples were prepared by carefully scratching flowerlike objects formed on Si wafer and dispersed in EtOH. One drop of the EtOH solution of the scratched objects was deposited on a carboncoated copper grid and dried. No staining was used to observe the raw structures. Optical micrographs were taken using an Olympus BX51 microscope equipped with an MP5Mc/OL digital camera. In situ time-resolved microwave conductivity (TRMC) measurement of film sample was carried out using a X-band (9 GHz) microwave circuit at low power (approximately 3 mW) and a nanosecond laser irradiation at 355 nm with photon density of 9.1 \times 10^{15} cm⁻², on the TRMC system.^{S3} TRMC samples for all derivatives were prepared by carefully collecting objects formed on substrate and pasted on a quartz plate with double-sticky tape (the tape does not disturb any TRMC signal). The smooth film are formed by physical smoothening with a spatula and used for TRMC measurement. The smooth films of C₆₀ (MTR 99.95%) and PCBM (Aldrich, 99%) are prepared with similar manners but use the powder as received from the provider. Calculations were conducted using density functional theory method at B3LYP/6-31G* level.^{S4}

(B) Synthesis.

The fullerene C_{60} derivatives **1a-c** and **2** were synthesized by following Prato reaction^[S1] and the reported procedures ^[S2] as shown in Scheme S1.

Scheme S1 Synthesis of fullerene C_{60} derivatives 1a-c and 2



1a, ¹H NMR (600 MHz, 1:1 v/v CS₂-CDCl₃): δ = 8.653 (d, 2H, *J* = 4.8 Hz), 7.718 (br, 2H), 4.986 (d, 1H, *J* = 9.6 Hz), 4.916 (s, 1H), 4.281 (d, 1H, *J* = 9.6 Hz), 2.811 (s, 3H). MALDI-TOF-MS [dithranol] *m*/*z* calcd., C₆₈H₁₀N₂ 854.85; found, 855.03.

1b, ¹H NMR (600 MHz, 1:1 v/v CS₂-CDCl₃): $\delta = 8.992$ (br, 1H), 8.587 (d, 1H, J = 3.6 Hz), 8.152 (br, 1H), 7.365 (dd, 1H, J = 7.2 Hz, J = 4.8 Hz), 4.995 (d, 1H, J = 9.0 Hz), 4.963 (s, 1H), 4.287 (d, 1H, J = 9.0 Hz), 2.800 (s, 3H). MALDI-TOF-MS [dithranol] m/z calcd., C₆₈H₁₀N₂ 854.15; found, 855.04.

1c, ¹H NMR (600 MHz, 1:1 v/v CS₂-CDCl₃): δ = 8.619 (d, 1H, *J* = 4.8 Hz), 7.963 (d, 1H, *J* = 7.8 Hz), 7.798-7.770 (m, 1H), 7.243-7.222 (m, 1H), 5.180 (s, 1H), 4.980 (d, 1H, *J* = 9.6 Hz), 4.321 (d, 1H, *J* = 9.6 Hz), 2.852 (s, 3H). MALDI-TOF-MS [dithranol] *m*/*z* calcd., C₆₈H₁₀N₂ 854.15; found, 853.91.

2, ¹H NMR (600 MHz, 1:1 v/v CS₂-CDCl₃): δ (ppm) = 7.767 (br, 2H), 7.391 (t, 2H, J = 7.8 Hz), 7.319-7.292 (m, 1H), 4.968 (d, 1H, J = 9.0 Hz), 4.916 (s, 1H), 4.257 (d, 1H, J = 9.0 Hz), 2.801 (s, 3H). MALDI-TOF-MS [dithranol] m/z calcd., C₆₉H₁₁N 853.87; found, 853.81.

(C) Additional data.



Fig. S1 SEM images of flowerlike assemblies of **1a** obtained from a 1:1 mixture of chloroform and 2-(R)-butanol (a), 2-propanol (b), ethanol (c) and methanol (d).



Fig. S2 XRD patterns of flowerlike objects **1a** on Si wafer and a Si wafer itself. The peaks from Si wafer are indicated by asterisks (*).



Fig. S3 SAXS pattern of flowerlike objects of **1a**. Inset image is two dimensional (2D) image obtained by SAXS measurement



Fig. S4 Magnified cryo-TEM image of flowerlike assemblies of 1a.



Fig. S5 SEM (top) and AFM (bottom) images of platelike intermediate assemblies of 1a. fabricated on Si wafer by rapid dried from a solution of a 1:1 mixture of chloroform and 2-(*S*)-butanol.

Fig. S6 Absorption spectra change of C_{60} solution in pyridine with aged time.

Fig. S7 Diffuse reflectance absorption spectra of cast films of **1a** and **2** measured on a quartz plate. The absorption in the region 440–550 nm show broad and structureless bands that prevent the observation of clear difference between **1a** and **2** as observed in chloroform solution and the confirmation of the CT interaction in solid state.

Fig. S8 TRMC kinetics of C_{60} derivatives (1a–c, 2) employed in this work.

Fig. S9 TRMC kinetics (up) and SEM image (bottom) of pristine C_{60} microcrystals.

Compounds	Transient photoconductivity	Half-lifetime
	$(\phi \Sigma \mu, 10^{-4} \mathrm{cm}^2/\mathrm{V} \cdot \mathrm{s})$	(ns)
1a	1.4	160
1b	0.86	120
1c	1.2	260
2	0.79	120
C ₆₀	3.2	50
РСВМ	0.67	-

Table S1 The TRMC results of all compounds employed in this work.

Reference

[S1] M. Maggini, G. Scorrano and M. Prato, J. Am. Chem. Soc., 1993, 115, 9798-9799.

[S2] F. D'Souza, G. R. Deviprasad, M. E. Zandler, V. T. Hoang, A. Klykov, M.

VanStipdonk, A. Perera, M. E. El-Khouly, M. Fujitsuka and O. Ito, J. Phys. Chem. A, 2002, 106, 3243–3252.

[S3] (a) A. Saeki, S. Seki, T. Takenobu, Y. Iwasa and S. Tagawa, *Adv. Mater.* 2008, 20, 920–923; (b) A. Saeki, S. Seki, T. Sunagawa, K. Ushida and S. Tagawa, *Philos. Mag.* 2006, 86, 1261–1276. (c) A. Saeki, S. Seki, S. Koizumi and S. Tagawa, *J. Photochem. Photobio. A*, 2007, 186, 158–165.

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