Supplementary information

Alkyl–C₆₀ liquid electrets as deformable mechanoelectric generator

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Experimental Section

Materials

All starting materials and reagents were procured from commercial vendors (where noted) and used as obtained unless otherwise specified. All reactions were performed under an argon atmosphere. Column chromatography was performed using silica gel 60 N (spherical, neutral, particle size 40-50 μ m, Kanto Chemical Co., Inc.). C₆₀ with a purity over 99.5%, sarcosine, and anhydrous chlorobenzene were purchased from Sigma-Aldrich. Final target compounds were purified by recycling preparative high-performance liquid chromatography (HPLC) and dried under vacuum at 70 °C to remove any trace solvent. Spectroscopic grade *n*-hexane (WAKO) was used for spectroscopic studies. The matrix used for matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) was 2-(4-hydroxyphenylazo)-benzoic acid (HABA, Sigma-Aldrich).

Measurements

Recycling preparative HPLC was performed at room temperature using GPC columns (JAIGEL-1HH and 2HH, ID 20 mm, length 600 mm, exclusion limit is 1000 and 5000, respectively) on an LC-9225NEXT-Japan Analytical Industry (JAI) equipped with refractive index (RI) and ultraviolet (UV) detectors. ¹H nuclear magnetic resonance (NMR) was recorded on a JEOL ECZ-400S spectrometer using deuterated chloroform (CDCl₃) with residue solvent peaks as internal standards (δ = 7.26 ppm) at room temperature. Chemical shifts are stated in ppm, and spin-spin coupling constants (*J*) are given in Hz, while multiplicities are abbreviated by *s* (singlet), *d* (doublet), and *m* (multiplet). MALDI-TOF MS was measured by a Bruker autoflex maX. The measuring method includes Reflection Positive (RP) without matrix suppression. Fourier-transform infrared spectroscopy (FT-IR) spectra were recorded on a Thermo Scientific Nicolet iS5 spectrophotometer using the KBr method.

Thermogravimetric analysis (TGA) was executed with a TA instrument SDT Q600 under argon flow at a heating rate of 10 °C min⁻¹. Differential scanning calorimetry (DSC) was measured using Hitachi High-Tech Science DSC 7000X with liquid nitrogen or electronic cooling accessory under nitrogen flow at a scan rate of 5 °C min⁻¹. Small- and wide-angle X-ray scattering (SWAXS) measurements were executed using Anton Paar SAXSess mc² instrument with Cu K α radiation (λ = 0.154 nm). Solvent-free liquid samples were filled into the paste cell for measurements with

100 min exposure time. Rheology experiments were carried out with the help of an Anton Paar Physica MCR301 rheometer, with parallel plate geometry (10 mm and 25 mm diameter) and a measuring sample thickness of 0.25 mm. For the measurement, strain amplitude scans were first performed to determine the linear-viscoelastic region.

UV-Vis absorption features in solution and solvent-free liquid were recorded on a JASCO V-770 spectrophotometer. Solvent-free liquid samples were sandwiched between two quartz plates and measured with ISN923 60 mm ϕ integrating sphere. The flash-photolysis time-resolved microwave conductivity (FP-TRMC) experiment was performed using an X-band (9 GHz) microwave circuit at low power and a nanosecond laser irradiation at 355 nm with photon density of 1.4 x 10¹⁶ photons cm⁻². Solvent-free liquid samples were directly filmed on a quartz plate and were used for this measurement. The measurement was performed in the air at room temperature (25 °C).

Electrostatic charge measurement

The electrostatic charge of poled nylon fabrics (along with soaked liquids with a similar molar ratio of **1** (2.4 mg), **2** (3.3 mg), or **3** (3.3 mg)) were measured by Coulombmeter (NK-1001A, KASUGA Co., Ltd., Japan) equipped with Faraday cage (KQ-1400, Serial no. 22C196F) as well as Coulombmeter probe (NK-1001P). The poling parameters are applied voltage -80 kV, T = 100 °C, heating time (t_h) = 30 min, and poling time (t_p) = 90 min. The sample was kept at a hot plate at 100 °C for 10 min before poling to ensure the fabric's temperature stabilization. The negative poling was performed using a corona discharging gun (GC90PN, green Techno Co., Ltd. Japan), which was placed perpendicular to the grounded stainless-steel plate (20 cm x 20 cm). The poling temperature was controlled by a hot plate (ND-2A, AS ONE Corp., Japan). The corona discharging gun to sample distance was fixed at 20 cm.

Fabrication of mechanoelectric generators

Deformable electrodes were fabricated on polyurethane (Breath Roll[®] BR15, Nitto Co., Ltd., Japan, 13 μ m thickness) by applying silver-plated nylon fibers (AGposs[®], Mitsufuji Co., Ltd., Japan, fiber length = 3 mm) and a terminal was connected with a Cu tape. The typical resistance of the electrode was < 5 Ω . For the fabrication of the deformable

electret device, polyurethane transparent film (3M Tegaderm[™] Roll, 16002JP, 24 µm thickness) was used as a base layer, masking layer as well as sealing layer. A similar molar ratio of alkylated liquids (1 (2.3 mg), 2 (3.2 mg), or 3 (3.1 mg)) were soaked in nylon fabrics (*Nytal* NY5-HC, Sefar Inc., Switzerland with open eyes of 5 μ , size 2 cm x 3 cm). The weight of fabricated MEGs is <1 g. The poling parameters are an applied voltage -80 kV, 100 °C of bottom substrate temperature, heating time (t_h) = 30 min, and poling time $(t_p) = 90 \text{ min}$, *i.e.*, the sample was maintained at 100 °C for heating time (t_h) then the hot plate was switched off and allowed to cool naturally till room temperature. Then, the sample was kept at a hot plate at 100 °C for 10 min before poling to ensure the fabric's temperature stabilization. The open circuit voltage (V_{oc}) of mechanoelectric generators (MEGs) was recorded on an oscilloscope (MT-775, MotherTool Co., Ltd., Japan) equipped with a probe with an input impedance of 1 M Ω . The bottom electrode of MEGs was connected to the probe, and the top electrode was grounded. For output voltage measurement, deformable devices were hit by DOCTORAIR Exagun Hot & Cool / REG-03 instrument with variable frequency (18, 32, and 53 Hz) by keeping < 6 mm distance from the device. The common circular piezoelectric buzzer surface mount was procured from muRata (made in Thailand) RS part number 747-4691 and manufacturer part number 7BB-35-3L0 with size of 35 mm (diameter) x 0.53 mm (height).

Synthesis and characterization

The synthesis of precursor 2,5-bis(2-dodecylhexadecyloxy)benzaldehyde was performed as reported in the literature.¹ Alkylated-C₆₀ with mono (**1**) and regioisomeric bis-adduct (**2**) were synthesized and purified according to reported literature for similar C₆₀ derivatives with different branched alkyl chains.² The detailed modified synthetic procedure is as follows.

Synthesis of alkylated-C₆₀ compounds



Scheme S1. Synthetic route for alkylated C₆₀ (1 and 2).

 C_{60} (0.54 g, 0.75 mmol) and sarcosine (0.221 g, 2.48 mmol) were taken to a two-neck amber flask. Air in the flask was removed by repeating vacuum-argon cycles, then 450 mL anhydrous chlorobenzene was mixed, and the mixture was heated at around 80 °C to dissolve C_{60} completely. Then pre-dissolved, 0.56 mmol of 2,5-bis(2dodecylhexadecyloxy)benzaldehyde in 50 mL anhydrous chlorobenzene was added via a syringe and refluxed the mixture for 16-18 h. After that reaction was stopped, the crude mixture was let to reach ambient temperature; the mixture was filtered to remove unreacted sarcosine, and the chlorobenzene was evaporated under a vacuum. The crude mixture was first passed through silica gel column chromatography (SiCC) using CHCl₃ as an eluent to remove the unreacted C_{60} . Next, the collected solution was concentrated using a rotatory evaporator. The crude was then subjected to open GPC (Bio-Beads ® S-X1 Beads, 200-400 mesh) using toluene as an eluent affording mono (**1**) as well as regioisomeric bis-adducts (**2**) of alkylated C_{60} compounds. Next, both fractions containing **1** and **2** were purified separately by HPLC and SiCC using the CHCl₃–n-hexane mixture as eluent. The yields were 69% and 25% for **1** and **2**, respectively, based on C₆₀ conversion.



Figure S1. ¹H NMR (400 MHz, CDCl₃, r.t.) of 1.



Figure S2. ¹H NMR (400 MHz, CDCl₃, r.t.) of **2**.

1: ¹H NMR (400 MHz, CDCl₃, r.t.) *δ* 7.57 (d, *J* = 4 Hz, *m*-coupled 1H, a-H), 6.86-6.83 (m, 2H, b-H), 5.52 (s, 1H, c-H), 4.98 (d, *J* = 8 Hz, 1H, d-H), 4.28 (d, *J* = 8 Hz, 1H, d-H), 3.89-3.70 (m, 4H, e-H), 2.81 (s, 3H, f-H), 1.74–1.72 (m, 1H, g-H), 1.59 (m, 1H, g-H), 1.41-1.25 (m, 96H, h-H), 0.92-0.85 (m, 12H, i-H).

Dark black viscous liquid.

MALDI-TOF-MS (HABA matrix, reflection positive): calculated for M⁺ 1669.96; obtained 1670.1

FTIR (KBr method): *v*_{asym} (CH₂) 2922.6 cm⁻¹; *v*_{sym} (CH₂) 2851.7 cm⁻¹

2: Dark black viscous liquid.

MALDI-TOF-MS (HABA matrix, reflection positive): calculated for M⁺ 2619.91; obtained 2620.6

FTIR (KBr method): *v*_{asym} (CH₂) 2923.1 cm⁻¹; *v*_{sym} (CH₂) 2852.2 cm⁻¹



Figure S3. MALDI-TOF-MS (matrix: HABA, RP) of 1.



Figure S4. MALDI-TOF-MS (matrix: HABA, RP) of 2.

Supplementary Figures



Figure S5. TGA graphs of solvent-free **1** and **2** at a heating rate of 10 °C min⁻¹ from 25 °C to 700 °C under argon flow.



Figure S6. DSC thermogram of solvent-free **1** and **2** at a scan rate of 5 $^{\circ}$ C min⁻¹ from -100 $^{\circ}$ C to 150 $^{\circ}$ C under nitrogen flow.



Figure S7. Complex viscosity ($|\eta^*|$) of **1** (a) and **2** (b) as a function of angular frequency (ω) with strain amplitude (γ) of 0.01 (red), 0.05 (blue), 0.10 (pink), and 0.25 (navy) at 25 °C.



Figure S8. Zero shear viscosity (η_0) of **1** (a) and complex viscosity ($|\eta^*|$) of **2** (b) as a function of angular frequency (ω) at various temperatures with 25% strain amplitude.



Figure S9. UV-Vis absorption spectrum of **1** (a) and **2** (b) in *n*-hexane solution with varying concentrations. Insets show the expanded region from 630-730 or 740 nm.



Figure S10. Normalized UV-Vis absorption spectrum of **1** (a) and **2** (b) in *n*-hexane solution (10 μ M) as well as neat liquid samples sandwiched between two quartz plates at room temperature. The inset shows an expanded region (650-800 nm) used for normalization.



Figure S11. Comparison of Flash-photolysis time-resolved microwave conductivity (FP-TRMC) profiles of **1** and **2** recorded at 23 °C upon excitation with a 355 nm laser pulse. $\phi \Sigma \mu_{max}$ is transient photoconductivity, ϕ represents the quantum efficiency of the charge carrier generation, and $\Sigma \mu$ is the sum of the nanometer-scale charge carrier mobilities. The photoconductivity maximum ($\phi \Sigma \mu_{max}$) values observed for **1** and **2** were 1.8 x 10⁻⁵ cm² V⁻¹ s⁻¹ and 1.4 x 10⁻⁵ cm² V⁻¹ s⁻¹, respectively.



Figure S12 (a) Schematic drawing shows an experimental setup for corona charging. (b) An output voltage measurement setup.



Figure S13. The ball-dropping experiment measured the output voltage using a wooden ball. The weight of the wooden ball is 1.54 g, and the dropping height is 20 cm. (a 10 cm tube was taken for the photo instead 20 cm tube).



Figure S14. To understand the output waveform of Exagun, we used commercially available circular piezoelectric buzzer surface mount and measured the V_{oc} under continuous vibration at 53 Hz. The negative signal in output waveform shows its negative polarity.



Figure S15. Open circuit voltage (V_{oc}) characteristics of fabricated mechano-electric generators of (a) **1**–MEG, (b) **2**–MEG, (c) **3**–MEG, and (d) **Blank**–MEG under continuous vibration at different frequencies (18, 32, and 53 Hz).



Figure S16. Open circuit voltage (V_{oc}) characteristics of fabricated mechano-electric generators a) **1**–MEG; b) **2**–MEG; c) **3**–MEG, and d) **Blank**–MEG under continuous vibration at 53 Hz, after 65 days of their fabrication.

References

- 1. X. Zheng, K. Nagura, T. Takaya, K. Hashi and T. Nakanishi, *Chem. Eur. J.*, 2023, DOI: 10.1002/chem.202203775.
- 2. H. Li, S. S. Babu, S. T. Turner, D. Neher, M. J. Hollamby, T. Seki, S. Yagai, Y. Deguchi, H. Möhwald and T. Nakanishi, *J. Mater. Chem. C*, 2013, **1**, 1943—1951.