Electronic Supplementary Information for Polyurethanes synthesized using biomass-derived furan diols as sustainable triboelectric materials

June Young Jang,^{*a*‡} Youngmin Byun,^{b,c‡} Sijin You,^a Seunghun Kim,^a Dong-Min Lee,^{b,c} Sang-Woo Kim,^{b,c*} and Seung Uk Son^{a*}

^a Department of Chemistry, Sungkyunkwan University, Suwon 16419, Korea E-mail: sson@skku.edu

^b Department of Materials Science and Engineering, Yonsei University, Seoul 03722, Korea ^c Center for Human-oriented Triboelectric Energy Harvesting, Yonsei University, Seoul 03722, Korea *E-mail: kimsw1(@yonsei.ac.kr*

Experimental Section

General: ¹H and ¹³C NMR spectra were obtained using a Bruker Ascend 500 MHz spectrometer at the Chiral Material Core Facility Center of Sungkyunkwan University. IR absorption spectra were obtained using a Bruker VERTEX70 spectrometer. TGA and DSC curves were obtained using a TG/DTA7300 instrument. SEM images were obtained using JSM-7100F and JSM-7800F microscopes at the Chiral Material Core Facility Center of Sungkyunkwan University. GPC analysis was conducted using an Agilent Infinity 1260 instrument. A surface roughness (R_q) was measured using an atomic force microscope (AFM, Park Systems, NX-10). KPFM images were obtained at an EFM mode using an AFM (XE-100, Park Systems) with a scan rate of 0.5 Hz and a scan area of 5 μ m × 5 μ m. The cantilever used in this study was Multi-75EG (Budget Sensors, Pt/Cr-coated, resonance frequency of 17 kHz).

Synthetic procedures of 2,5-furan diols (FDs) and polyurethanes (PFUs)

For the synthesis of bis(2-hydroxyethyl)furan-2,5-dicarbxylate (FD-1), dimethyl furan-2,5-dicarboxylate (0.18 g, 1.0 mmol), ethylene glycol (0.12 mL, 2.2 mmol), titanium(IV) isopropoxide (10 μ L, 34 μ mol), and distilled toluene (2 mL) were added to a 20 mL pressure tube. The reaction mixture was stirred at 150 °C for 12 h. After being cooled to room temperature, the solvent was evaporated. The product was isolated by column chromatography.

For the synthesis of FD-2, the same synthetic procedures of FD-1 were applied except using 1,3-propane diol (0.16 mL, 2.2 mmol) instead of ethylene glycol. For the synthesis of FD-3, the same synthetic procedures of FD-1 were applied except using 1,5-pentane diol (0.23 mL, 2.2 mmol) instead of ethylene glycol. For the synthesis of FD-4, the same synthetic procedures of FD-1 were applied except using diethylene glycol (0.21 mL, 2.2 mmol) instead of ethylene glycol. For the synthesis of FD-5, the same synthetic procedures of FD-1 were applied except using 1,4-benzenedimethanol (0.30 g, 2.2 mmol) instead of ethylene glycol. FD-1, FD-4, and FD-5 are known compounds prepared by a different method in the literature.¹ FD-2 and FD-3 are unknown compounds. In this work, FD-1~FD-5 were fully characterized as follows.

Characterization data of FDs; **FD-1**: an isolated yield of 88%, ¹H NMR (500 MHz, DMSO-d⁶) δ = 7.46 (s, 2H), 4.95 (t, J = 5.0 Hz, 2H), 4.32 (m, 4H), 3.69 (m, 4H) ppm, ¹³C NMR (125 MHz, DMSO-d⁶) δ = 158.0, 146.7, 119.6, 67.4, 59.3 ppm, HRMS (EI): m/z calc. for C₁₀H₁₂O₇ [M]⁺ 244.0583, found, 244.0582. **FD-2**: an isolated yield of 86%, ¹H NMR (500 MHz, DMSO-d⁶) δ = 7.43 (s, 2H), 4.60 (t, J = 5.0 Hz, 2H), 4.36 (m, 4H),

3.54 (m, 4H), 1.85 (m, 4H) ppm, ¹³C NMR (125 MHz, DMSO-d⁶) δ = 158.0, 146.7, 119.4, 63.1, 57.5, 31.9 ppm, HRMS (EI): m/z calc. for C₁₂H₁₆O₇ [M]⁺ 272.0896, found, 272.0891. **FD-3**: an isolated yield of 80%, ¹H NMR (500 MHz, DMSO-d⁶) δ = 7.42 (s, 2H), 4.39 (t, J = 5.1 Hz, 2H), 4.30 (m, 4H), 3.42 (m, 4H), 1.71 (m, 4H), 1.47 (m, 4H), 1.40 (m, 4H) ppm, ¹³C NMR (125 MHz, DMSO-d⁶) δ = 157.7, 146.6, 143.4, 134.1, 128.7, 127.0, 119.8, 67.1, 63.1 ppm, HRMS (EI): m/z calc. for C₁₆H₂₄O₇ [M]⁺ 328.1522, found, 328.1515. **FD-4**: an isolated yield of 75%, ¹H NMR (500 MHz, DMSO-d⁶) δ = 7.43 (s, 2H), 4.61 (t, J = 5.0 Hz, 2H), 4.42 (m, 4H), 3.73 (t, J = 4.5 Hz, 4H), 3.50 (m, 8H) ppm, ¹³C NMR (125 MHz, DMSO-d⁶) δ = 157.9, 146.6, 119.7, 72.8, 68.5, 65.0, 60.7 ppm, HRMS (EI): m/z calc. for C₁₄H₂₀O₉ [M]⁺ 332.1107, found, 332.1103. **FD-5**: an isolated yield of 65%, ¹H NMR (500 MHz, DMSO-d⁶) δ = 7.46 (s, 2H), 7.42 (d, J = 8.1 Hz, 4H), 7.35 (d, J = 8.0 Hz, 4H), 5.35 (s, 4H), 5.22 (t, J = 5.5 Hz, 2H), 4.51 (d, J = 5.4Hz, 4H) ppm, ¹³C NMR (125 MHz, DMSO-d⁶) δ = 157.9, 146.7, 119.4, 67.5, 61.0, 32.5, 28.4, 22.4 ppm, HRMS (EI): m/z calc. for C₂₂H₂₀O₇ [M]⁺ 396.1209, found, 396.1209.

For the synthesis of polyurethane using FD-1 (FPU-1), FD-1 (0.12 g, 0.50 mmol), 1,6-diisocyanatohexane (80 µL, 0.50 mmol), dibutyltin dilaurate (3.0 µL, 5.0 µmol), distilled ethyl acetate (2 mL), and distilled dimethylformamide (DMF, 2 mL) were added to a flame-dried 10 mL Schlenk flask. The reaction mixture was stirred at 80 °C for 24 h. After being cooled to room temperature, methylene chloride (5 mL) was added. After the reaction mixture was transferred to a 50 mL Falcon tube, methanol (30 mL) was added to form precipitates. The solid was isolated by centrifugation, washed with methanol (40 mL) two times, and dried under vacuum. For the synthesis of FPU-2, the same synthetic procedures of FPU-1 were applied except using FD-2 (0.14 g, 0.50 mmol) instead of FD-1. For the synthesis of FPU-3, the same synthetic procedures of FPU-4, the same synthetic procedures of FPU-1 were applied except using FD-3 (0.16 g, 0.50 mmol) instead of FD-1. For the synthesis of FPU-5, the same synthetic procedures of FPU-1 were applied of FD-1. For the synthesis of FPU-5, the same synthetic procedures of FPU-1 were applied except using FD-5 (0.20 g, 0.50 mmol) instead of FD-1.

Characterization data of FPUs; FPU-1: an isolated yield of 85%, ¹H NMR (500 MHz, DMSO-d⁶) δ = 7.39 (s, 2H), 7.23 (s, 2H), 4.45 (s, 4H), 4.24 (s, 4H), 2.91 (s, 4H), 1.33 (s, 4H), 1.18 (s, 4H) ppm, ¹³C NMR (125 MHz, DMSO-d⁶) δ = 157.7, 156.3, 146.5, 119.8, 64.4, 62.0, 40.6, 29.7, 26.4 ppm. FPU-2: an isolated yield of 80%, ¹H NMR (500 MHz, DMSO-d⁶) δ = 7.41 (s, 2H), 7.09 (s, 2H), 4.33 (s, 4H), 4.05 (s, 4H), 2.93 (s, 4H), 1.97 (s, 4H), 1.34 (s, 4H), 1.20 (s, 4H) ppm, ¹³C NMR (125 MHz, DMSO-d⁶) δ = 157.8, 156.6, 146.6, 119.6, 62.8, 60.7, 40.6, 29.8, 28.5, 26.4 ppm. FPU-3: an isolated yield of 75%, ¹H NMR (500 MHz, DMSO-d⁶) δ = 7.37 (s, 2H), 7.00 (s, 2H), 4.28 (s, 4H), 3.91 (s, 4H), 2.91 (s, 4H), 1.71 (m, 4H), 1.56 (s, 4H), 1.40 (s, 4H), 1.33 (s, 4H), 1.18 (s, 4H) ppm, ¹³C NMR (125 MHz, DMSO-d⁶) δ = 157.9, 156.8, 146.6, 119.4, 65.6, 63.8, 40.6, 29.8, 28.8, 28.2, 28.1, 22.3 ppm. FPU-4: an isolated yield of 80%, ¹H NMR (500 MHz, DMSO-d⁶) δ = 7.41 (s, 2H), 7.13 (s, 2H), 4.40 (s, 4H), 4.04 (s, 4H), 3.72 (s, 4H), 3.61 (s, 4H), 2.91 (s, 4H), 1.33 (s, 4H), 1.20 (s, 4H) ppm, ¹³C NMR (125 MHz, DMSO-d⁶) δ = 157.8, 156.6, 146.5, 119.7, 69.4, 68.4, 64.9, 63.3, 40.6, 29.8, 26.4 ppm. FPU-5: an isolated yield of 60%, ¹H NMR (500 MHz, DMSO-d⁶) δ = 7.43 (d, J = 6.3 Hz, 6H), 7.34 (d, J = 6.2 Hz, 4H), 7.21 (s, 2H), 5.33 (s, 4H), 4.99 (s, 4H), 2.94 (s, 4H), 1.36 (s, 4H), 1.21 (s, 4H) ppm, ¹³C NMR (125 MHz, DMSO-d⁶) δ = 157.7, 156.5, 146.6, 138.1, 135.3, 128.8, 128.3, 119.8, 668.8, 65.2, 40.7, 29.8, 26.4 ppm.

Preparation procedures of FPU/PET films

For the fabrication of FPU/PET films, FPU (40 mg) and DMF (0.40 mL) were added to a 10 mL vial. The solution was stirred at 100 °C for 1 h. After being cooled to room temperature, the solution was dropped on the PET fabric (Toray Advance Materials Korea Inc., a fiber diameter of 13.8 μ m, a film thickness of 0.1 mm, area of 2 cm × 2 cm). After drying at room temperature for 1 day, FPU/PET films were obtained.

Triboelectric energy harvesting studies of FPU/PET films

Triboelectric performance of FPU/PET films was studied using a pushing tester (JIPT-120, JUNIL Tech Co.). FPU-3/PET and FPU-4/PET films were cut into pieces with area of 2 cm \times 2 cm. The films were attached on the printed circuit board (PCB, area of 3 cm \times 3 cm, a PR-4 glassy epoxy film) using a carbon tape (area of 2 cm \times 2 cm) and used tribopositive materials. A perfluoroalkoxy alkanes (PFA, Alphafion) film was cut into pieces with area of 2 cm \times 2 cm.² The PFA film was attached on a Cu electrode of a pushing tester using a carbon tape, and used as tribonegative materials. The Au electrode of PCB with FPU/PET films was connected to a pushing tester. The output voltages were investigated using an oscilloscope (DPO 3052, Tektronix). The pushing force was scanned in the range of 0.5~2.5 kgf. The pushing frequency was scanned in the range of 0.23~2.73 Hz. The RH was scanning in the range of 30~80%. The stability of triboelectric energy harvesting of a FPU-4/PET film was investigated through durability tests for 30000 cycles.

Fabrication procedures of spring-assisted TENGs of FPU/PET and PFA films

Spring-assisted TENGs consisted of two acrylic plates with triboelectric materials and four supporting springs. Each acrylic plate was prepared by attaching an acrylic plate with area of 4 cm × 4 cm (thickness of 1 mm) to the center of another acrylic plate with area of 7 cm × 7 cm. Aluminum tapes with area of 4 cm × 6 cm were attached to the acrylic plates. The Al electrodes were connected to wires using conductive tapes. FPU-3/PET, FPU-4/PET, and PFA films with area of 4 cm × 4 cm were attached to aluminum electrodes using carbon tapes. Four springs were placed at the corners of two acrylic plates. The FPU-3/PET or FPU-4/PET films on the Al/acrylic plate was used as a tribopositive material. The PFA film on the Al/acrylic plate was used as a tribopositive material.

Studies of the power densities of the spring-assisted TENGs with FPU-4/PET and PFA films

Two electrodes of the spring-assisted TENGs with FPU-4/PET and PFA films were connected to a current amplifier (FEMTO, DLPCA-200) and an oscilloscope (Tektronix, DPO3052). To apply a consistent force of 2 kgf, a pushing tester (Z-Tech, ZPS-100) was used. The operating range of the pushing machine was adjusted to ensure that the triboactive surfaces of the TENGs contacted each other. While the resistances (ABCO, EPX series) were scanned in the range of 10 k Ω to 1 G Ω , the current outputs generated by the TENGs were investigated using an oscilloscope at RH 50%.

Application of the spring-assisted TENGs of FPU-4/PET and PFA films to operate electronic devices

To charge aluminium electrolytic capacitors (Samyoung Electronics, MHA series), the spring-assisted TENG with FPU-4/PET and PFA films was connected to a circuit consisting of a full-wave bridge recitifier (Vishay,

EPXMPGPM). To compare charging rates, capacitors with capacitances of 1, 4.7, 10, and 33 μ F were used. A pushing force of 2 kgf was applied using a pushing tester (Z-Tech, ZPS-100) at RH 50%. The charging rate was evaluated by monitoring the voltage increase over time for each capacitor using an electrometer (Keithley 6514).

To turn on the green LED bulbs (Photron, PV525-5A5D-NNISLA-Z), a full-wave bridge rectifier and 79 green LEDs were assembled on a breadboard (Coms, EPXRTHCG). Two electrodes of the spring-assisted TENG were connected to the breadboard. A pushing force of 2 kgf was applied using a pushing tester (Z-Tech, ZPS-100) to generate output currents sufficient to turn on the 79 green LED bulbs at RH 50%.

To operate a hygrometer (Asung, 1047246), a battery was removed, leaving only the power supply terminals. Two electrodes of the spring-assisted TENG were connected to a circuit comprising a rectifier and 33 μ F capacitor. A pushing force of 2 kgf was applied to the spring-assisted TENG using a pushing tester (Z-Tech, ZPS-100) at RH 50%. After the capacitor was charged to ~6 V, it was connected to the hygrometer and then, the operation of the hygrometer was checked.

Reference

- 1. J. Y. Jang, G. M. Lee, J. D. Lee and S. U. Son, J. Mater. Chem. A, 2023, 11, 23772-23778.
- R. Hinchet, H.-J. Yoon, H. Ryu, M.-K. Kim, E.-K. Choi, D.-S. Kim and S. W. Kim, *Science*, 2019, 365, 491-494.









90 80 f1 (ppm)





Fig. S2 ¹H and ¹³C NMR spectra of FPU-1~FPU-5.













Fig. S3 TGA curves of FPU-1~FPU-5.



Fig. S4 SEM images (side views) of (a) PET, (b) FPU-3/PET, and (c) FPU-4/PET films. (d) IR spectra of PET, FPU-3, FPU-3/PET, FPU-4, and FPU-4/PET.



4000 3500 3000 2500 2000 1500 1000 Wavenumber / cm⁻¹ Fig. S5 Tensile tests of PET, FPU-3/PET, and FPU-4/PET films.



Materials	Max. Strain (%)	Max. Strength (Mpa)	Young's Modulus (GPa)
PET	4.07	2.95	0.20
FPU-3/PET	8.74	9.16	0.39
FPU-4/PET	6.56	10.88	0.58

Fig. S6 (a) Output current densities of PET, FPU-3/PET, and FPU-4/PET films (conditions: an area of 2 cm × 2 cm, a pushing force of 2 kgf, a pushing frequency of 0.73 Hz, RH 50%, PFA as a tribonegative material).
(b) A pushing frequency, (c) a pushing force, and (d) relative humidity dependent triboelectric output currents of a FPU-4/PET film.



Entry	Tribopositive Materials	Tribonegative Materials	V_{p-p}	P _{max}	Year	Ref
			(V)	(mW/cm^2)		
1	Silk Fibroin	PET	268	0.194	2016	S1
2	Hosta Leaf	PMMA	230	0.0045	2018	S2
3	Porous Chitosan	PI	60.6	0.233	2018	S3
4	Cellulose Paper	PCL/GO	120	0.00725	2019	S4
5	Silk Fibroin	Mxene-PVA	~225	0.109	2019	S5
6	Silk Composite	PTFE	52.8	0.037	2020	S6
7	Fish Gelatin	PTFE/PDMS	130	0.0458	2020	S7
8	White Sugar	PTFE	95.68	0.0034	2020	S 8
9	Cellulose Aerogel	PTFE	65	0.0127	2020	S9
10	Wheat Straw	FEP	250	0.0404	2021	S10
11	Sea Grass	PET	258	0.07042	2021	S11
12	Starch/Laver	PCL	50	0.648	2021	S12
13	Pectin	PI	300	2.0	2022	S13
14	Polydopamine/Cellulose	FEP	205	0.04875	2022	S14
15	Wood	FEP	198	0.01197	2023	S15
16	Lignin/PCL	PTFE	93	0.0157	2023	S16
17	Silkworm Cocoon	PDMS	126	0.0216	2023	S17
18	Lignin/PVA/EPCH	PTFE	65	0.01354	2024	S18
19	Keratin/Chitosan	PTFE	322	1.44	2024	S19
20	PEI-GO Chitosan	PTFE	222	0.0407	2024	S20

Table S1 Triboelectric performance of biomass-derived natural polymers recently reported in the literature.

PET: poly(ethylene terephthalate), PMMA: poly(methyl methacrylate), PI: polyimide, PCL: poly(caprolactone), PVA: poly(vinyl alcohol), PTFE: poly(tetrafluoroethylene), PDMS: polydimethylsiloxane, PVDF: poly(vinylidene fluoride), FEP: fluorinated ethylene propylene, EPCH: epichlorohydrin, PEI: polyethylenimine, GO: graphene oxide.

S1 X. -S. Zhang, J. Brugger and B. Kim, Nano Energy, 2016, 20, 37-47.

- S2 Y. Jie, X. Jia, J. Zou, Y. Chen, N. Wang, Z. L. Wang and X. Cao, Adv. Energ Mater., 2018, 8, 1703133.
- S3 Q. Zheng, L. Fang, H. Guo, K. Yang, Z. Cai, M. A. B. Meador and S. Gong, Adv. Funct. Mater., 2018, 28, 1706365.
- S4 S. Parandeh, M. Kharaziha and F. Karimzadeh, Nano Energy, 2019, 59, 412-421.
- S5 C. Jiang, C. Wu, X. Li, Y. Yao, L. Lan, F. Zhao, Z. Ye, Y. Ying and J. Ping, Nano Energy, 2019, 59, 268-276.
- S6 H. -Y. Mi, H. Li, X. Jing, P. He, P. -Y. Feng, X. Tao, Y. Liu, C. Liu and C. Shen, Ind. Eng. Chem. Res., 2020, 9, 12399-12408.
- S7 Y. Han, Y. Han, X. Zhang, L. Li, C. Zhang, J. Liu, G. Lu, H. -D. Yu and W. Huang, ACS Appl. Mater. Interfaces, 2020, 12, 16442-16450.
- S8 H. Liu, H. Wang, Y. Fan, Y. Lyu and Z. Liu, Solid State Electron., 2020, 175, 107920
- S9 L. Zhang, Y. Liao, Y. -C. Wang, S. Zhang, W. Yang, X. Pan and Z. L. Wang, Adv. Funct. Mater., 2020, 30, 2001763.
- S10 P. Ma, H. Zhu, H. Lu, Y. Zeng, N. Zheng, Z. L. Wang and X. Cao, Nano Energy, 2021, 86, 106032.
- S11 Q. M. Saqib, M. Y. Chougale, M. U. Khan, R. A. Shaukat, J. Kim, J. Bae, H. W. Lee, J. -I. Park, M. S. Kim and B. G. Lee, *Nano Energy*, 2021, **89**, 106458.
- S12 G. Khandelwal, N. P. M. J. Raj, N. R. Alluri and S. -J. Kim, ACS Sustainable Chem. Eng., 2021, 9, 9011-9017.
- S13 H. Patnam, S. A. Graham, P. Manchi, M. V. Paranjape and J. S. Yu, Nanoscale, 2022, 14, 13236-13247.
- S14 Q. Zhu, T. Wang, Y. Wei, X. Sun, S. Zhang, X. Wang and L. Luo, Cellulose, 2022, 29, 8733-8747.
- S15 B. Tang, Z.-P. Deng, J. -M. Wu, Y. -Y. Zhao, Q. -W. Tan, F. Song, X. -L. Wang and Y. -Z. Wang, J. Mater. Chem. A, 2023, 11, 26716-26726.
- S16 H. Jo, D. Park, M. Joo, D. Choi, J. Kang, J. -M. Ha, K. H. Kim, K. H. Kim and S. An, *EcoMat*, 2023, 5 e12413.
- S17 Q. Wang, B. Xu, J. Huang and D. Tan, ACS Appl. Mater. Interfaces, 2023, 15, 9182-9192.
- S18 S. A. Khan, M. A. Ahmed, M. M. Baig, M. M. Rehman, Y. Yang, S. G. Lee, J. W. Choi and W. Y. Kim, Chem. Eng. J., 2024, 485, 149660.
- S19 K. G. Motora, C. -M. Wu, C. R. M. Jose and G. M. Rani, Adv. Funct. Mater., 2024, 34, 2315069.
- S20 S. S., A. M. Chandran, S. Varun, M. V. P. Kumar and P. K. S. Mural, ACS Appl. Electron. Mater., 2024, 6, 887-900.

Entry	Tribopositive Materials	Tribonegative Materials	V_{p-p}	\mathbf{P}_{max}	Year	Ref
			(V)	(mW/cm ²)		
1	Waste PET Bottle	PVDF	67.7	0.547	2021	S21
2	Waste PP	Mylar	200	0.007116	2021	S22
3	Nylon Bag	PVC	36	0.0153	2021	S23
4	Waste PS	PTFE	~250	0.405	2022	S24

Table S2 Triboelectric performance of recycled petroleum-based polymers recently reported in the literature.

PET: poly(ethylene terephthalate), PVDF: poly(vinylidene fluoride), PP: Poly(propylene), PVC: poly(vinyl chloride), PS: poly(styrene), PTFE: poly(tetrafluoroethylene).

S21 S. Roy, P. K. Maji and K. -L. Goh, Chem. Eng. J., 2021, 413, 127409.

S22 H. Varghese and A. Chandran, ACS Appl. Mater. Interfaces, 2021, 13, 51132-51140.

S23 X. Feng, Q. Li and K. Wang, ACS Appl. Mater. Interfaces, 2021, 13, 400-410.

S24 S. M. Nawaz, M. Saha, N. Sepay and A. Mallik, Nano Energy, 2022, 104, 107902.