Supplementary Information

Universality of Giant Seebeck Effect in Organic Small Molecules

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Additional details in the electrical and thermoelectric properties

A thermally activated behavior as in Fig. S1 was generally appeared in all of the samples. However, the activation energy was temperature dependent which appears as the variation of slope in Fig. S1(b).

**Figure S1.** Temperature dependence of the sample current in a BP thin film under a fixed bias of 50 V: (a) a linear and (b) the Arrhenius plots.

**Figure S2.** Comparison of the temperature dependences of the activation energy of conductivity, $E_a$ and Seebeck coefficient, $\alpha$, in (a) BP, (b) C$_{10}$DNTT and (c) PDI thin films. Filled and open circles denote negative and positive Seebeck coefficients, respectively.
2D-GIXD patterns

To know the orientation of the molecules against the substrate, two-dimensional grazing-incidence X-ray diffraction (2D-GIXD) patterns were obtained with some of the thin films used in this work after the electrical and thermoelectric measurements.

The 2D-GIXD measurement system was made by combining a multi-axes diffractometer and highly sensitive large-area two-dimensional detector (PILATUS 300K) at BL19B2 beamline in SPring-8. A heating-cooling stage was set on the goniometer and diffraction patterns at 300 K were recorded through the beryllium windows by exposure time of 30 seconds under steady temperature. X-ray energy was set to 12.40 keV and incidence angle to 0.12°, which satisfies the total reflection condition at organic/substrate interface.

Figure S3. 2D-GIXD patterns obtained with some of the thin films used in this work. Red and white triangles denote the major diffraction peaks indicating near perpendicular and parallel orientations of molecular planes against substrate surface.
AFM images of sapphire substrates

Even before the annealing, step-terrace structures are seen on the surface but the mean width of the terraces is small and the steps are not straight (Fig. S4(a)). After the annealing, step-terrace structures are clearly seen and the mean terrace width become nearly ten times wider than that before annealing (Fig. S4(b)).

Figure S4. AFM images of the sapphire substrates used in Fig. 5: (a) before and (b) after the thermal treatment at 1000 °C for 10 hours in oxygen atmosphere.

General for synthesis

Solvents and chemical reagents were reagent grade quality, obtained from commercial sources and used without further purification.

$^1$H NMR and $^{13}$C NMR spectra were recorded on a JEOL ECX-400P (400 MHz) spectrometer at 294 K using tetramethylsilane as an internal standard (0.00 ppm). High resolution MALDI mass spectrum was measured on a JEOL SpiralTOF™/JMS-S3000 mass spectrometer.

General for synthesis

C12-BP (C12BP) was prepared via C12-CP.
5,15-Didodecyltetrakis(bicycle[2,2,2]octadieno)porphyrin (C12-CP)

A solution of compound 1 (0.45 g, 1.5 mmol) in dehydrated CH₂Cl₂ (300 mL) was deoxygenated by bubbling of argon gas for 10 min. Tridecanal (0.40 ml, 1.1 mmol) was added to a solution of compound 1 and then the reaction system was covered with aluminum foil. Trifluoroacetic acid (3 drops) was added dropwise to the solution and the resulting mixture was stirred for 21 h at room temperature. DDQ (0.52 g, 2.3 mmol) was added to the solution and stirred for 2 h at room temperature. Then, the half amount of solvent was removed under reduced pressure. The residue was purified by alumina column chromatography (CH₂Cl₂) and recrystallization (CHCl₃/MeOH) to give C12-CP as a purple solid in 64% yield (460 mg, 0.48 mmol). ¹H NMR (400 MHz, CDCl₃, δ): 10.21 (s, 2H), 7.22–7.05 (m, 8H), 5.79–5.78 (m, 4H), 5.71–5.70 (m, 4H), 5.33–5.11 (m, 4H), 2.85–2.60 (m, 4H), 2.18–1.28 (m, 52H), 0.88 (m, 6H), –3.13 (s, 2H). ¹³C NMR spectrum was measured, but the number of peaks were insufficient due to the presence of stereoisomers: 151.14, 146.09, 141.21, 136.86, 135.74, 119.03, 95.72, 95.69, 40.09, 38.50, 36.10, 33.62, 31.93, 30.63, 30.09, 29.78, 29.76, 29.74, 29.70, 29.39, 28.08, 27.61, 27.53, 27.15, 22.70, 14.15. HRMS (MALDI): m/z [M + H]⁺ calcd for C₆₈H₈₇N₄, 959.6907; found, 959.6925.

5,15-Didodecyltetrabenzoporphyrin (C12-BP)

C12-CP (11.8 mg, 12.3 mmol) was heated at 200 °C for 1 h in a sample tube under reduced pressure to give a target compound C12-BP as a dark-purple solid in 98% yield (10.2 mg, 12.0 mmol). ¹H NMR (400 MHz, C₂D₂Cl₄, δ): 10.09–9.95 (m, 2H), 9.35–9.15 (m, 4H), 8.94–8.84 (m, 4H), 8.22–7.91 (m, 8H), 4.53–4.35 (m, 4H), 2.57–2.43 (m, 4H), 2.11–1.96 (m, 4H), 1.71–1.36 (m, 32H), 0.94–0.91 (m, 6H), –2.77 (brs, 2H). ¹³C NMR spectrum was not available due to poor solubility. HRMS (MALDI): m/z [M + H]⁺ calcd for C₆₀H₇₁N₄, 847.5642; found, 847.5673.
Figure S5. $^1$H NMR spectrum of C12-CP.

Figure S6. $^{13}$C NMR spectrum of C12-CP.
Figure S7. $^1$H NMR spectrum of C12-BP.

Reference