

Supporting Information

Photochromism in Sound-induced Alignment of a Diarylethene Supramolecular Nanofiber

Yasuhisa Hotta,^a Satomi Fukushima,^a Jin Motoyanagi^b and Akihiko Tsuda*^a

^a *Department of Chemistry, Graduate School of Science, Kobe University, 1-1 Rokkodai-cho, Nada-ku, Kobe 657-8501, Japan*

^b *Department of Chemistry and Materials Technology, Graduate School of Science and Technology, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan*

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1. Materials

Unless otherwise noted, reagents and solvents were used as received from Kishida Chemical Co., Ltd. [CHCl_3 (>99%), CH_2Cl_2 (>98%), AcOEt (>99%) and *n*-hexane (>95%)], Nakarai Tesuque, Inc. [Na_2CO_3 (>99%)], Wako Pure Chemical Industries, Ltd. [Na_2SO_4 (>99%)], Sigma-Aldrich [$\text{Pd}(\text{PPh}_3)_4$ (>99%)], Kanto Chemical Co., Inc. [THF dehydrated stabilizer free, CH_2Cl_2 dehydrated stabilizer free and 2.5M *n*-BuLi hexane solution] and Tokyo Kasei Co., Ltd. (TCI) [trimethylborate (>97%)]. Dry *n*-hexane was prepared through dehydration with Type 4A molecular sieve. For column chromatography, Wakogel C-300HG (particle size 40–60 μm , silica) was used.

2. Measurements

Absorption spectra were recorded on a JASCO V-670 UV/VIS/NIR spectrometer equipped with a JASCO ETC-717 temperature/stirring controller. ^1H and ^{13}C NMR spectra were recorded on a VARIAN model INOVA 400 spectrometer and Bruker AVANCE 500 spectrometer, where chemical shifts (δ in ppm) were determined with respect to tetramethylsilane as the internal standard. Dynamic light scattering (DLS) measurements were performed using an Otsuka model ELS-Z2 instrument. Fourier transform mass spectrometry was performed on a Thermo Fisher Scientific LTQ Orbitrap Discovery. FAB mass spectrometry was performed on a JEOL JMS-BU30 LC Mate spectrometer with 3-nitrobenzylalcohol as the matrix. Scanning electron microscopy (SEM) was performed using a JEOL JSM-7600F FE-SEM operating at 2.0 kV.

LD Spectroscopy: LD spectra were recorded on a JASCO J-820 spectropolarimeter equipped with a JASCO PTC-423L temperature controller and a custom made sound generator, composed of a function generator (NF model DF1906), an integral amplifier (DENON model PMA-390AE) and a sound speaker (AURA Sound model NS3-193-4A). The LD spectrometer was equipped with a 12 × 12 × 44 mm quartz optical cuvette, having a $\phi 10 \times$

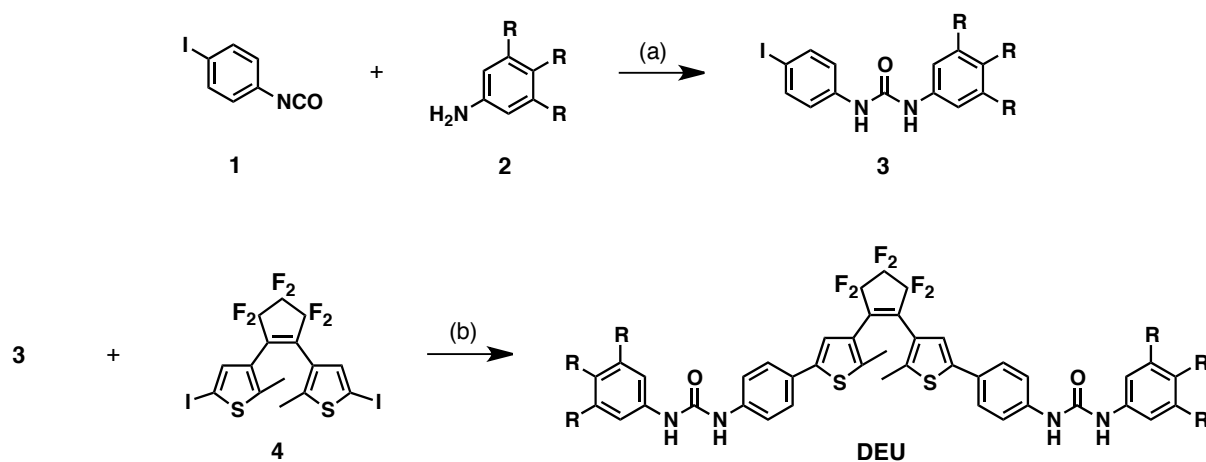
10 mm cylindrical neck (outer diameter), composed of 1 mm-thick quartz glass, which was filled with a sample solution. LD intensity is defined as $\Delta_{\text{LD}}A = A_{//} - A_{\perp}$ ($\Delta_{\text{LD}}A$ represents magnitude of LD, while $A_{//}$ and A_{\perp} denote horizontal and perpendicular absorbances, respectively). The cuvette, containing the sample solution, was fixed in the steel holder of the spectrometer. For the acoustic LD spectroscopy in this study, LD responses were monitored at a position 39 mm below the top of the optical cuvette using an 8 mm-diameter beam of linearly polarized light. Sound waves produced by a function generator from a speaker. A full range speaker, having a frequency response of ~ 15 kHz, was located 20 mm above the cuvette.

3. Experimental methods

Photo-irradiation for the sample solution was demonstrated with a 500 W xenon lamp (USHIO SPAX INC., SX-UID502XAM) equipped with a monochromator (JASCO CT-10T).

4. Synthesis

4.1. Synthetic Scheme



Scheme S1. Synthesis of **DEU**: Reagents and conditions: (a) dry CH_2Cl_2 , reflux, (b) (i) $n\text{-BuLi}$, (ii) $\text{B}(\text{OCH}_3)_3$, (iii) Na_2CO_3 , $\text{Pd}(\text{PPh}_3)_4$. R represents dodecyloxy group.

4.2. Synthetic procedures

Compounds **2** and **4** were prepared by procedures analogous to those reported previously, and unambiguously characterized by means of ^1H NMR spectroscopy.¹⁻⁶

***p*-Iodophenyl-3,4,5-[tris(dodecyloxy)]phenylurea (3):** To 20 mL of dry CH_2Cl_2 solution of **1** (361 mg, 1.44 mmol) was dropwisely added mixture of **2** (930 mg, 1.44 mmol) and triethylamine (0.5 mL). The solution was stirred for 30 min at room temperature, and evaporated to dryness. The residue was reprecipitated from THF and *n*-hexane. The residue was then subjected to silicagel chromatography with *n*-hexane as an eluent. The first colorless fraction was corrected, and evaporated under reduced pressure to leave *p*-iodophenyl-3,4,5-[tris(dodecyloxy)]phenylurea (1.21 g) as white solid in 95% yield. ^1H NMR (500 MHz, CDCl_3 , 20 °C): 7.54 (d, $J = 8.0$ Hz, 9.0H), 7.16 (br, 1H), 7.12 (d, $J = 9.0$ Hz, 2H), 6.86 (br, 1H), 6.50 (s, 2H), 3.90 (t, $J = 7.5$ Hz, 2H), 3.84 (t, $J = 6.5$ Hz, 4H), 1.72 (m, 6H), 1.46–1.36 (m, 12H), 1.26 (br, 48H), 0.88 (t, $J = 8.0$ Hz, 9H); ^{13}C NMR (125 MHz,

CDCl₃, 20 °C): 138.22, 137.94, 134.95, 133.28, 121.76, 100.97, 86.40, 73.80, 69.25, 31.96, 30.34, 29.75–29.66, 29.50, 29.40, 26.15, 22.71, 14.11; Elemental analysis: calculated for C:66.04%, H:9.39%, N:3.14% found for C:65.56%, H:9.35%, N:3.23%; FAB-MS: m/z calculated for [M+H]⁺ (C₄₉H₈₄N₂O₄) 891.55, found 891.54.

1,2-Bis(2-methyl-5-bis(1,4-diphenyl)bis(3-(3,4,5)tris(dodecyloxy)phenylurea)-3-yl)perfluorocyclopentene (DEU): To a dry THF solution of **3** (0.2 g, 0.32 mmol) was slowly added *n*-hexane solution of *n*-BuLi (1.55 M, 437 μL, 0.68 mmol) under Ar atmosphere at –78 °C. After stirring of the sample solution for 1 h, trimethylborate (76 μL, 0.68 mmol) was added. The sample solution was stirred for 1 h at room temperature, and then, 20% aqueous Na₂CO₃ (12 mL) and **4** (603 mg, 0.68 mmol) was added. After Ar bubbling of the sample solution for 10 min, Pd(PPh₃)₄ (18.6 mg, 16.1 μmol) was added, and the mixture was refluxed for 2 h under Ar. The sample solution was then diluted with ethyl acetate, and washed with water and brine. The organic extract was dried over Na₂SO₄, and evaporated to dryness. The residue was subjected to size-exclusion chromatography (SEC) with THF as an eluent, and silica gel chromatography with CHCl₃ as an eluent. The second blue fraction was corrected and evaporated under reduced pressure to leave **DEU** (148 mg) as blue solid in 24% yield. ¹H NMR (500 MHz, CDCl₃, 20 °C): 7.33 (d, *J* = 8.8 Hz, 4H), 7.26 (d, *J* = 8.8 Hz, 4H), 7.24 (s, 2H), 7.09 (br, 2H), 6.91 (br, 2H), 6.56 (s, 4H), 3.90 (t, *J* = 6.7 Hz, 4H), 3.89 (t, *J* = 6.5 Hz, 8H), 2.03 (s, 6H), 1.74 (m, 12H), 1.49–1.39 (m, 24H), 1.26 (br, 96H), 0.87 (t, *J* = 8.0 Hz, 18H); ¹³C NMR (125 MHz, CDCl₃, 20 °C): 153.93, 153.73, 141.19, 141.01, 138.40, 136.10, 133.43, 129.17, 126.59, 126.10, 122.74, 120.71, 101.45, 101.77, 73.93, 69.79, 32.12, 30.61, 29.97–29.27, 26.37, 22.83, 14.44, 14.18; HRMS: m/z calculated for [M+Na]⁺ (C₁₃₃H₁₇₄F₆N₄O₈S₂) 1917.2609, found 1917.2682.

5. ^1H NMR spectral changes of DEU upon photo-irradiation

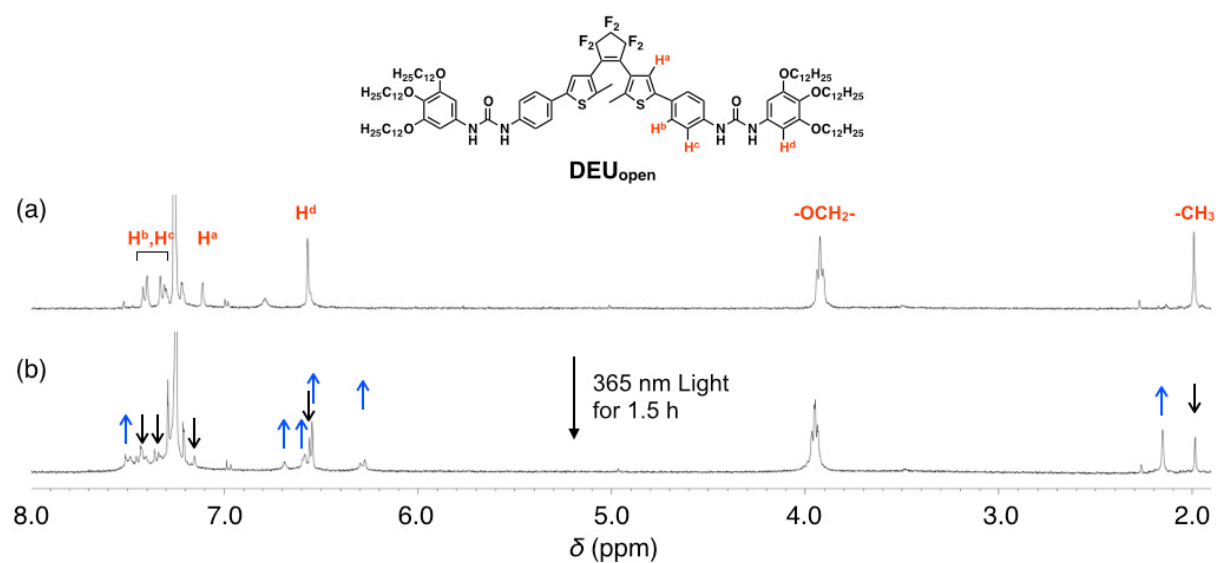


Fig. S1 ^1H NMR spectra of a mixture of DEU_{open} and $\text{DEU}_{\text{closed}}$ in CDCl_3 (a) before and (b) after photo-irradiation with 365 nm light for 1.5 h. $[\text{DEU}] = 0.6$ mM. The measurements in (a) and (b) were demonstrated at 20 and 40 °C, respectively. The ratio of DEU_{open} and $\text{DEU}_{\text{closed}}$ after the photo-irradiation is estimated to be 71 : 29 with the integral ratio of the peaks corresponding to the methyl protons attached at thiophene group.

6. Photochromism of DEU in absorption spectroscopy

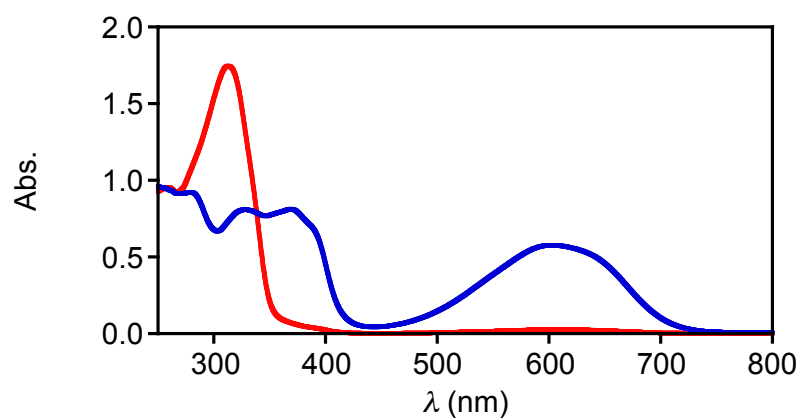


Fig. S2 Absorption spectra of **DEU** in CHCl_3 at 20 °C with the concentration of $[\text{DEU}] = 2.2 \times 10^{-5}$ M before and after photo-irradiation with 365 nm light (red and blue curve, respectively).

7. DLS profiles of a *n*-hexane solution of DEU before and after UV-irradiation

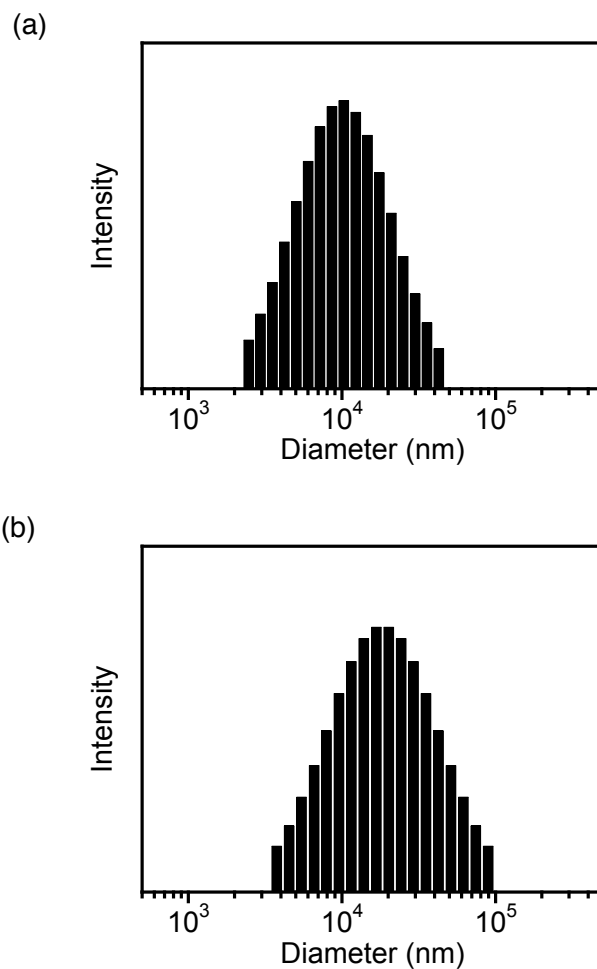


Fig. S3 DLS histogram profiles of a *n*-hexane solution containing self-assembled **DEU** with the concentration of 2.2×10^{-5} M at 20 °C (a) before and (b) after photo-irradiation with 365 nm light. The sample solution was prepared upon 130-fold dilution of a CHCl_3 solution of **DEU**_{open}. Average diameter: 5777.4 nm for (a) and 9047.5 nm for (b).

8. Estimation of the open/closed ratio of DEU after photoisomerization in *n*-hexane

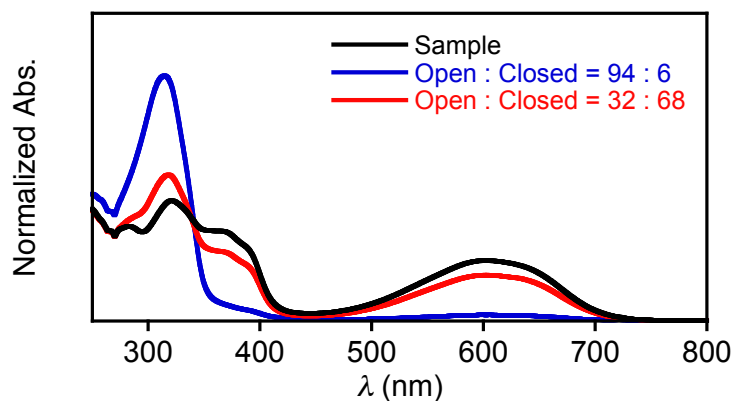


Fig. S4 Absorption spectrum of a chloroform solution of **DEU** (black curve), prepared after photo-irradiation of **DEU_{open}** (2.2×10^{-5} M) with 365 nm light (500 W xenon lamp) for 20 min in *n*-hexane, in comparisons with those of reference samples containing mixtures of **DEU_{open}** and **DEU_{closed}** with the ratio of 94 : 6 (blue curve) and 32 : 68 (red curve). Absorbances are normalized at 338.8 nm, an isosbestic point observed in the photoisomerization between open and closed form. With these reference spectra, the ratio of open and closed forms is estimated to be 7 : 93.

9. DLS profile of self-assembled $\text{DEU}_{\text{closed}}$ in *n*-hexane

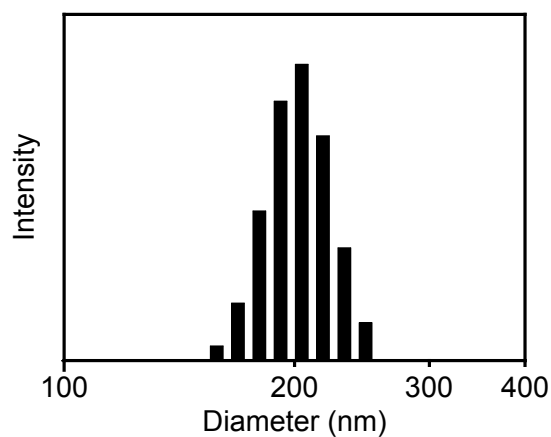


Fig. S5 A DLS histogram profile of a *n*-hexane solution containing self-assembled $\text{DEU}_{\text{closed}}$ with the concentration of 2.2×10^{-5} M at 20 °C. The sample solution was prepared upon 130-fold dilution of a CHCl_3 solution of $\text{DEU}_{\text{closed}}$. Average diameter: 200.0 nm.

10. LD spectroscopies of the DEU supramolecular nanofibres without sound-irradiation

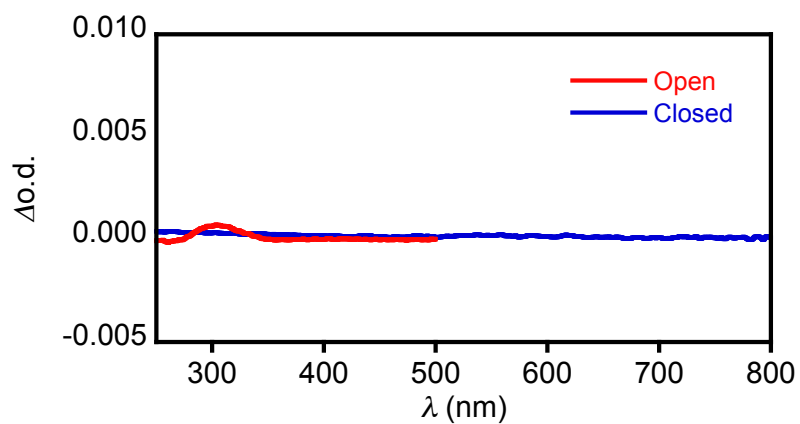


Fig. S6 LD spectra of the **DEU** supramolecular nanofibres without sound-irradiation before and after photo-irradiation with 365 nm and 580 nm light (red and blue curves, respectively), Solvent; *n*-hexane, $[\text{DEU}] = 2.2 \times 10^{-5}$ M, temperature; 20 °C.

11. LD responses of the self-assembled DEU upon sound-irradiation

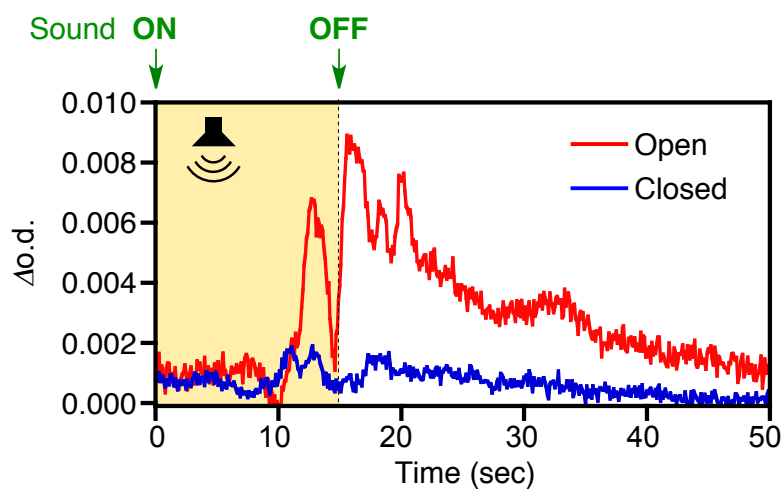
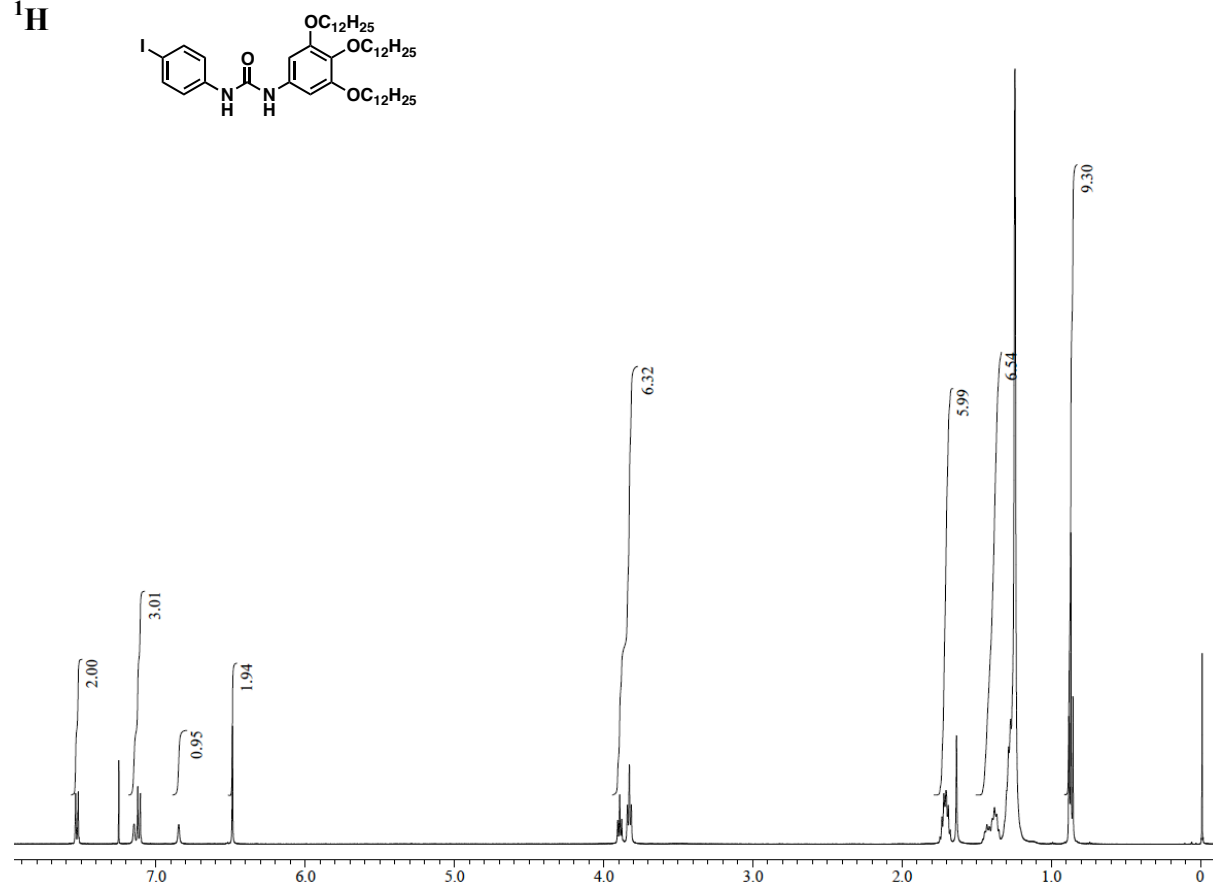


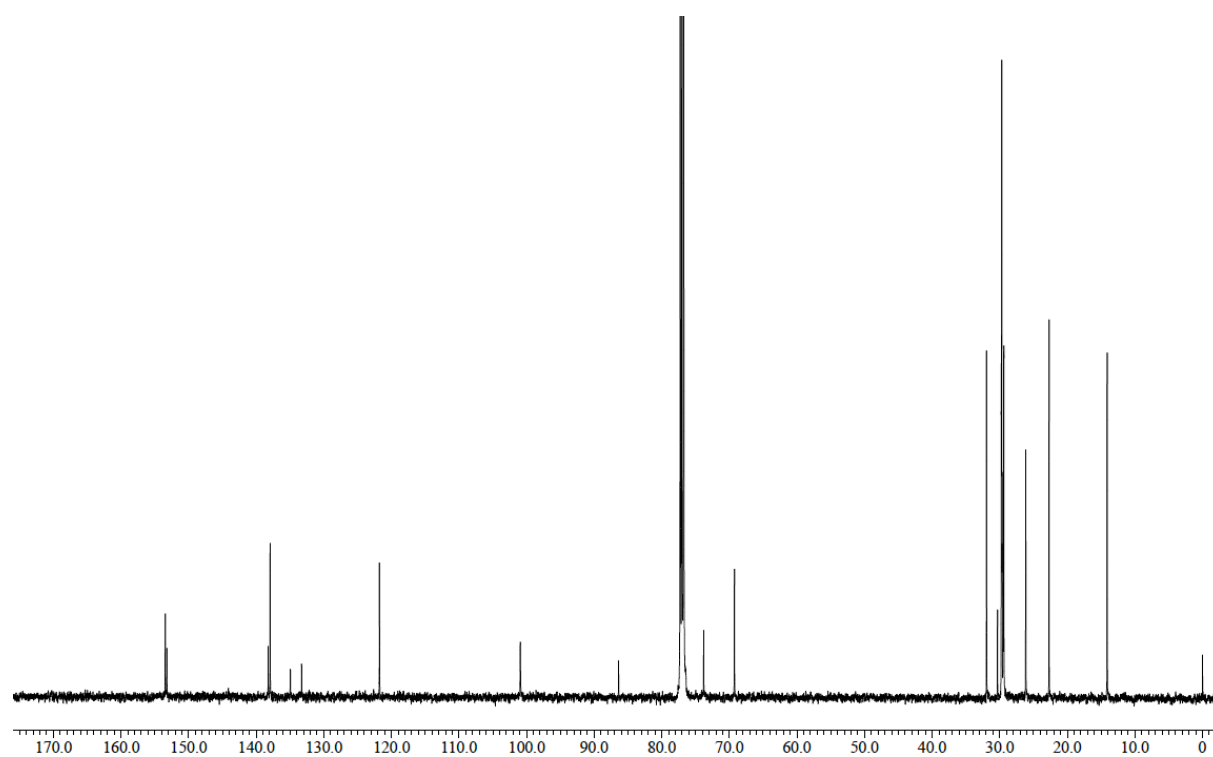
Fig. S7 Time course LD intensity profiles of self-assembled DEU_{open} (red curve) and $\text{DEU}_{\text{closed}}$ (blue curve) in *n*-hexane upon exposure to 120 Hz sound for 15 sec. The LD intensity was monitored at 304 nm at 20 °C. $[\text{DEU}] = 3.3 \times 10^{-5}$ M.

12. ^1H and ^{13}C NMR spectra and ESI-FT-MS

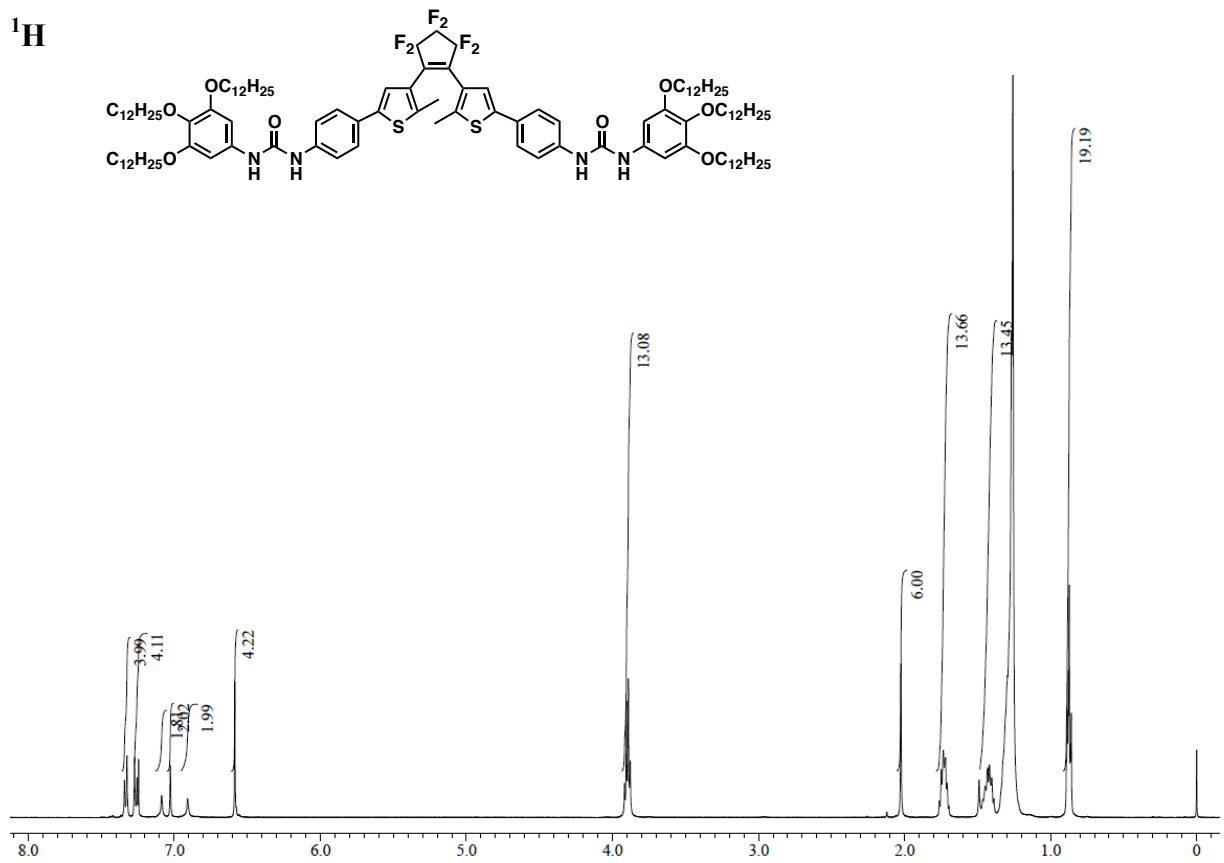
^1H



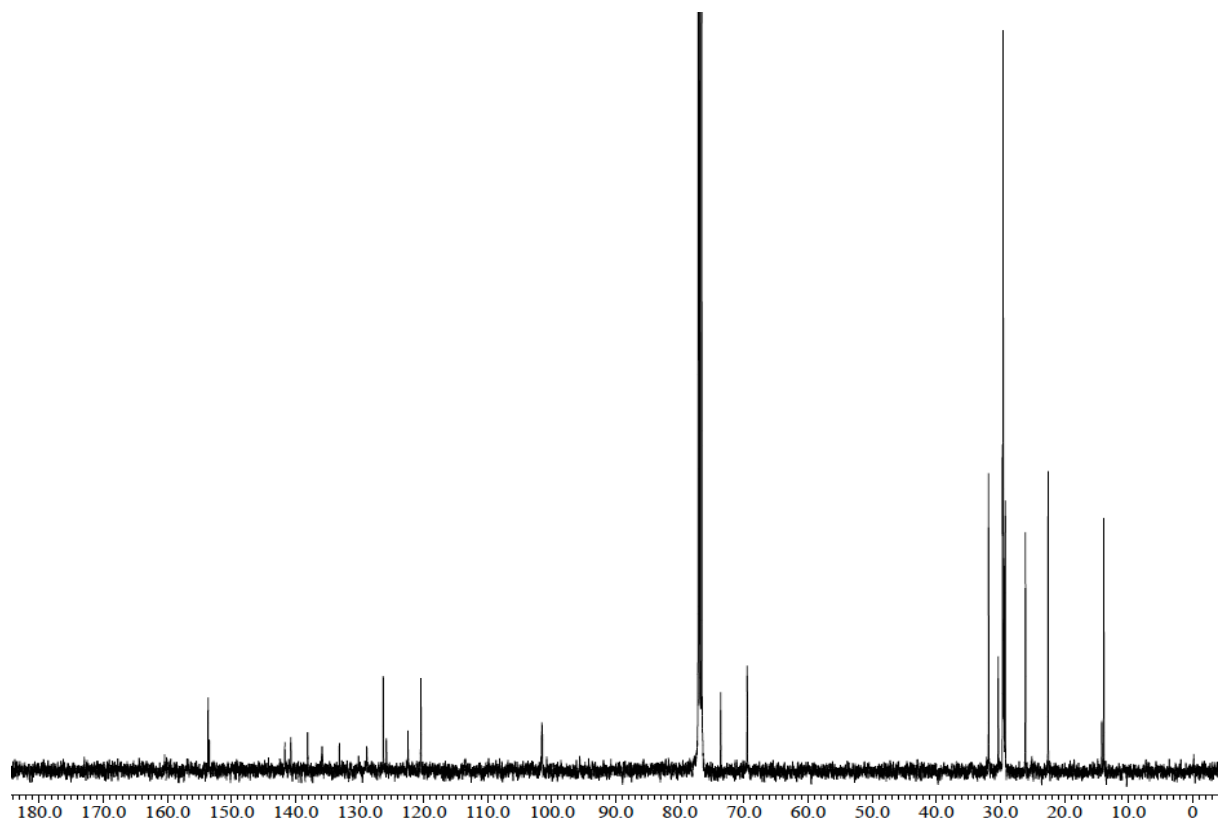
^{13}C



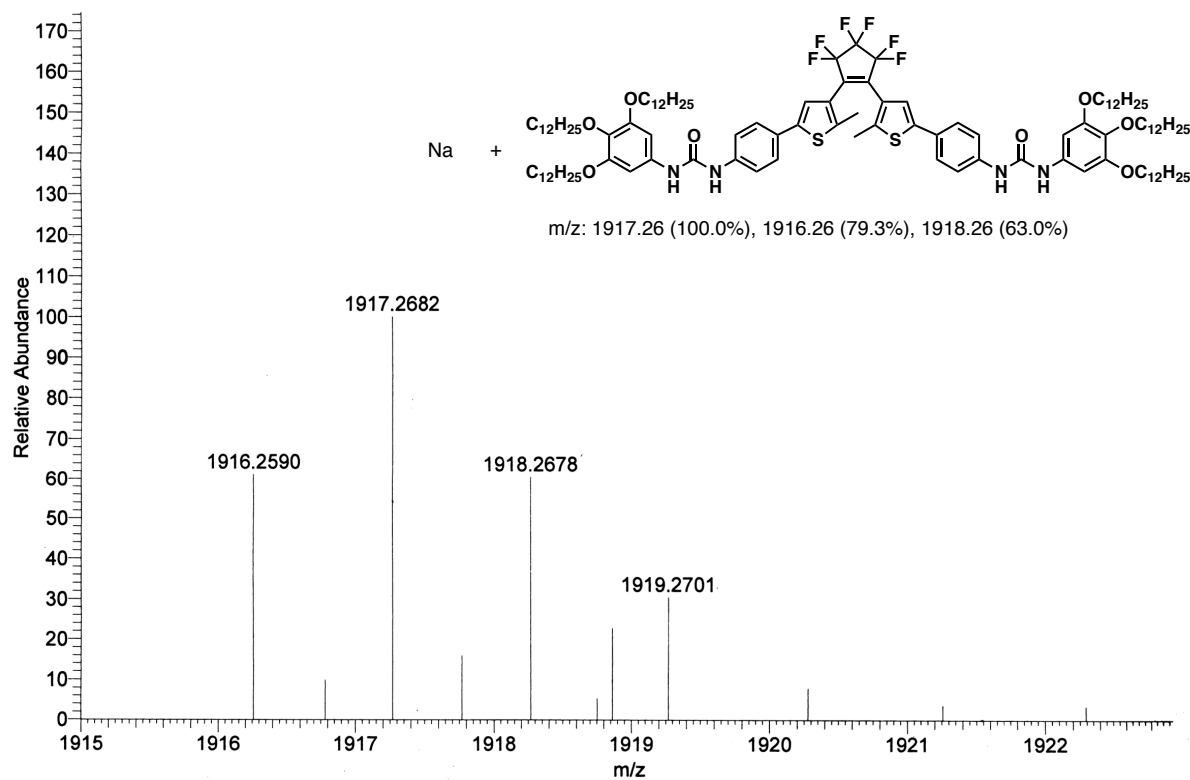
¹H



¹³C



20141016_141016110057 #155 RT: 1.76 AV: 1 NL: 1.50E4
T: FTMS + c NSI Full ms [150.00-2000.00]



13. References

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