Supplementary Information

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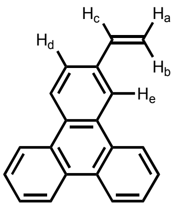
1. Synthesis and analytical data

General

^{1}H and ^{13}C NMR spectra were recorded on Bruker DRX-500 (500 MHz) or AV-500 (500 MHz) spectrometers at 300 K, and chemical shifts were reported as the delta scale in parts per million (ppm) relative to an internal standard tetramethylsilane (δ = 0.00 ppm for ^{1}H and ^{13}C NMR). IR measurements were recorded on Varian DIGILAB Scimitar instrument and DIGILAB FTS7000 instrument. Solvents and reagents were purchased from TCI Co., Ltd., WAKO Pure Chemical Industries Ltd. and Sigma-Aldrich Co. and were used without further purification. Separations were performed by silica gel chromatography with Wako gel C-300 for large scale column chromatography and with Merck TLC Silica gel 60 F_{254} for thin layer chromatography. MALDI-TOF mass data were recorded by an Applied Biosystem Voyager. The diffraction data were recorded on a Bruker APEX-II/CCD diffractometer equipped with a focusing mirror (MoKα radiation λ = 0.71073 Å) with a cryostat system equipped with a N_2 generator (Japan Thermal Eng. Co., Ltd.). The structures were solved by direct methods (SHELXS 97) and refined by full-matrix least-squares calculations on F^2 (SHELXL-97) using the SHELX-TL program package. Analytical HPLC–GPC chromatograms were recorded on a JASCO UV-970 spectrometer equipped with a JASCO PU-980 pump using a Shodex Asahipak GF-310 HQ column (eluent: tetrahydrofuran (HPLC grade, WAKO)). Averaged molecular weights of polymers were calculated from the calibration curve obtained with a series of TSK Standard Polystyrenes (TOSOH) using a Shodex Asahipak GF-310 HQ column (eluent: tetrahydrofuran (HPLC grade, WAKO)).



Synthesis of 2-vinyltriphenylene (1): A solution of methyltriphenylphosphonium iodide (4.60 g, 11.4 mmol) in dry THF (30 ml) was added dropwise to a solution of potassium *tert*-butoxide (1.27 g, 11.4 mmol) in dry THF (20 ml) under Ar atmosphere. After stirring at room temperature for 30 min, a solution of 2-formyltriphenylene (1.74 g, 6.8 mmol) (this was prepared according to the reported procedure: *Angew. Chem. Int. Ed.* **2010**, *49*, 5750.) in dry THF (20 ml) was added dropwise to this solution and stirred at room temperature for 2 h. The reaction was quenched with water (20 ml), and the organic layer was washed with brine, dried over magnesium sulfate, and concentrated with rotary evaporator. The yellow residue was purified by silica gel column chlomatography (eluent: CH$_2$Cl$_2$, R$_f$ = 0.93) to give 2-vinyltriphenylene (**1**) as a white powder (1.66 g, 96%). ^{1}H NMR (CDCl$_3$, 500 MHz) δ (ppm 8.65–8.54 (m, 6H, triphenylene-H), 7.73 (d, J = 8.5 Hz, 1H, H_d), 7.64–7.61 (m, 4H, triphenylene-H), 7.96 (dd, J = 10.5, 17.5 Hz, 1H, H_c), 5.95 (d, J = 17.5 Hz, 1H, H_b), 5.39 (d, J = 10.5 Hz, 1H, H_a); ^{13}C NMR (CDCl$_3$, 500 MHz) δ (ppm) 137.1, 136.4, 130.1 (2C), 129.9, 129.8 (2C), 129.5, 127.4 (2C), 127.3 (2C), 124.7, 123.7, 123.5 (2C), 123.4, 123.4, 121.9, and 114.6; MALDI TOM mass: m/z = 254.7 (calcd. for C$_{20}$H$_{14}$ = 254.1 [M]$^+$); IR (KBr) 1626 (m), 1606 (m), 1491 (m), 1437 (m), 1396 (m), 1245 (m), 993 (m), 904 (m), and 883 (m) cm^{-1}.

Synthesis of network complex 3: 2-Vinyltriphenylene (**1**) (12.6 mg, 0.05 mmol) and 2,4,6-tris(4-pyridyl)-1,3,5-triazine (**2**) (6.3 mg, 0.02 mmol) were dissolved in a mixture of nitrobenzene/methanol (4.0 ml/1.0 ml), and the resulting solution was placed in a 20 ml test tube. After addition of methanol (0.50 ml) to the top of the solution as a buffer, 0.50 ml ZnI$_2$ solution in methanol (60 mM) was carefully layered onto the top. Total 10 test tubes that were prepared in the same manner were allowed to stand in the dark at room temperature for a week during which yellow needle-like crystals formed on glass wall. The yellow crystals were filtered and washed with nitrobenzene to give network complex (**3**) (118.3 mg from 10 test tubes) in 50% yield. Elemental analysis (%); calcd for $\{[(\mathrm{ZnI_2})_3(\mathbf{2})_2(\mathbf{1})]\bullet(\mathrm{C_6H_5NO_2})_{4.6}\}_n$: C 41.79, H 2.56, N 9.68; found: C 42.01 , H 2.62, N 9.46; IR (single crystal, FLUOROLUBE) 3738 (m), 3055 (m), 2360 (m), 2335 (m), 1955 (m), 1848 (m), 1620 (s), 1576 (m), 1508 (m), 1421 (m), and 1373 (m).

2. NMR and HPLC analyses

Reaction of 2-vinyltriphenylene (1) with AIBN

• Reactions in network crystals 3

As-synthesized network crystals **3** (50.1 mg, 20.0 μmol) were immersed in 5 ml of cyclohexane for 3 d to replace the pore guests. Then the crystals were filtered and soaked into a 12 mM cyclohexane solution of AIBN (5 ml).

(I) The resulting suspension was heated to 80 ºC for 24 h under Ar atmosphere.

(II) The resulting suspension was heated to 80 ºC for 24 h under air.

Then, crystals were filtered, and the intercalated guests were extracted with CH_2Cl_2 after the decomposition of crystals with THF/water, and the extracted reaction mixture was analyzed by TLC, HPLC and ^{1}H NMR methods. (TCL analysis: compound **1** $R_f = 0.85$, aldehyde **4** $R_f = 0.42$, and epoxide **5** $R_f = 0.57$ (eluent: CH_2Cl_2/hexane = 2:1).) Since any other byproducts were not detected by TLC and NMR analyses, the yields of **4** and **5** were determined by integral ratio of proton signals.

• Control experiment in solution

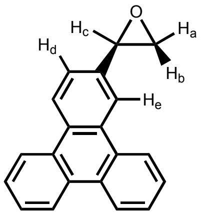
2-Vinyltriphenylene (**1**) (50.8 mg, 0.200 mmol) was dissolved in 0.5 ml of hexafluorobenzene* at 80 ºC, and AIBN (1.0 mg, 6.0 μmol) was added to the solution. The resulting mixture was stirred at 80 ºC under air for 24 h. The solvent was evaporated and the residue was analyzed by ^{1}H NMR spectroscopy. The conversion yield was determined by using an internal standard (1,2-dimethoxyethane).

* Note that: in order to increase the concentration of **1**, hexafluorobenzene was selected as a solvent.

• Characterization of oxygenated products

Spectroscopic data for 2-formyltriphenylene (**4**) were reported in the literature.

(F. J. Frank *et al. J. Am. Chem. Soc.* **1995,** *117,* 9408-9414.)



2-(1,2-epoxiethyl)triphenylene (5): ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm) 8.69–8.63 (m, 5H, triphenylene-*H*), 8.58 (d, J = 1.5 Hz, 1H, H_e), 7.69–7.66 (m, 4H, triphenylene-*H*), 7.55 (dd, J = 1.5, 8.5 Hz, 1H, H_d), 4.14 (dd, J = 2.5, 4.0 Hz, 1H, H_c), 3.29 (dd, J = 4.0, 5.5 Hz, 1H, H_b), 2.98 (dd, J = 2.5, 5.5 Hz, 1H, H_c); ^{13}C NMR ($CDCl_3$, 500 MHz), δ (ppm) 136.6, 130.1, 130.0, 129.9 (2C), 129.7, 129.6, 127.6, 127.5, 127.4 (2C), 124.3, 123.9, 123.5, 123.5 (3C), 120.6, 52.9, and 51.7; MALDI-TOF-MS (9-nitroanthracene): m/z = 269.9 (calcd. for $C_{20}H_{14}O$ = 270.1, $[M]^+$); IR (KBr) 1720 (m), 1695 (m), 1607 (m), 1494 (m), 1438 (m), 1171 (m), 1100 (m), 900 (m), and 824 (m) cm^{-1}.

As an alternative method, the title compound can be prepared from 2-vinyltriphenylene (**1**): To a solution of 2-vinyltriphenylene (**1**) (254 mg, 1.00 mmol) in CH_2Cl_2 (20 ml), *m*-chloroperoxybenzoic acid (223 mg, 1.00 mmol) was added, and the resulting solution was stirred for 3 h at room temperature. The solvent was evaporated and the residue was purified by preparative thin-layer chromatography (eluent: CH_2Cl_2/hexane = 2 : 1) to give 2-(1,2-epoxiethyl)triphenylene (**5**) (200.0 mg, 0.74 mmol) as a white powders in 74 % yield.

• NMR spectroscopy

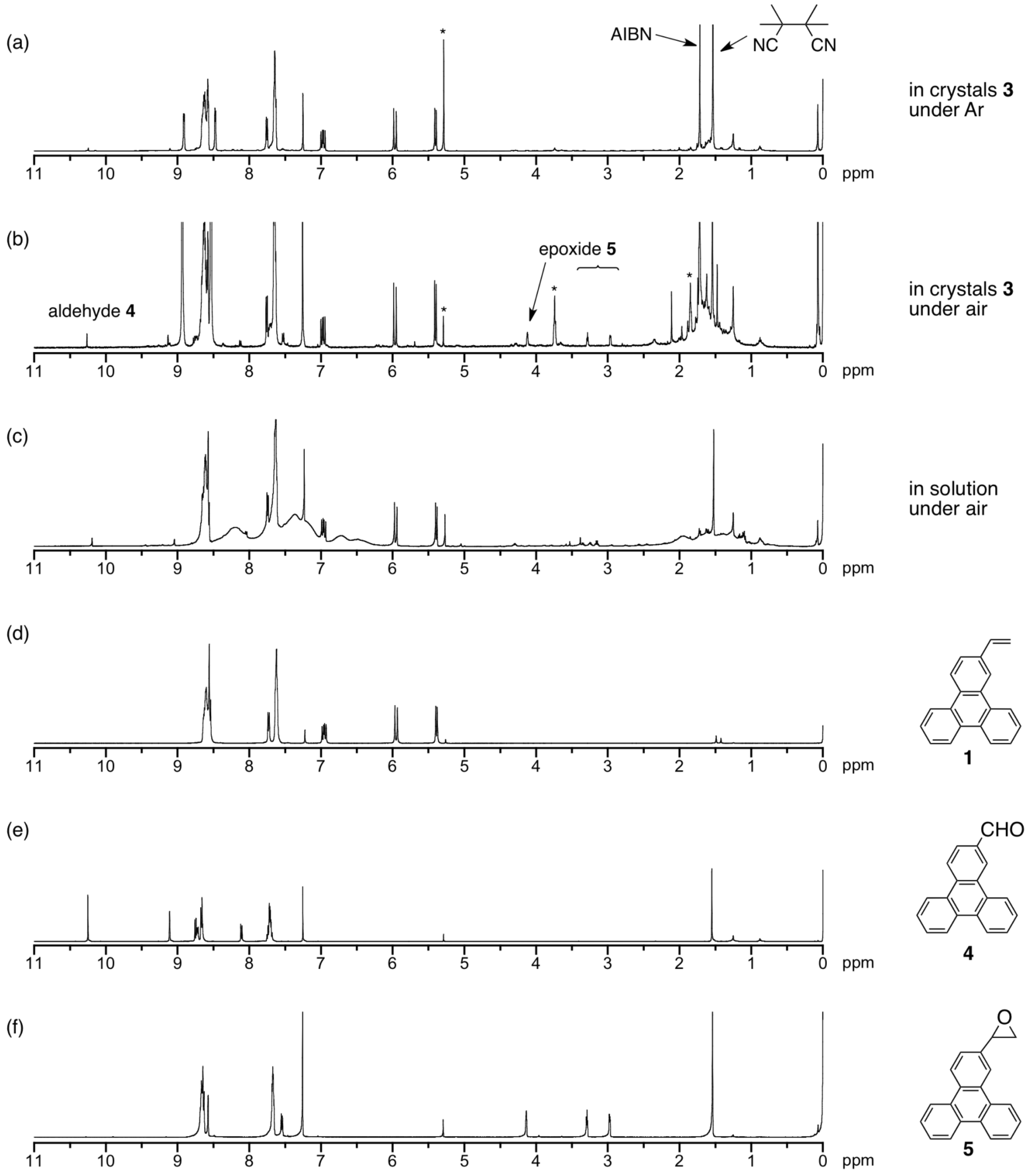


Figure S1. ^{1}H NMR spectra of the reaction mixture obtained from (a) crystalline state reaction (I), and (b) reaction (II), and (c) control experiment (in solution under aerobic conditions). (d), (e) and (f) show the reference spectra of 2-vinyltriphenylene (**1**), 2-formyltriphenylene (**4**) and epoxide **5**, respectively. (* denotes residual solvent peaks.)

• HPLC analysis

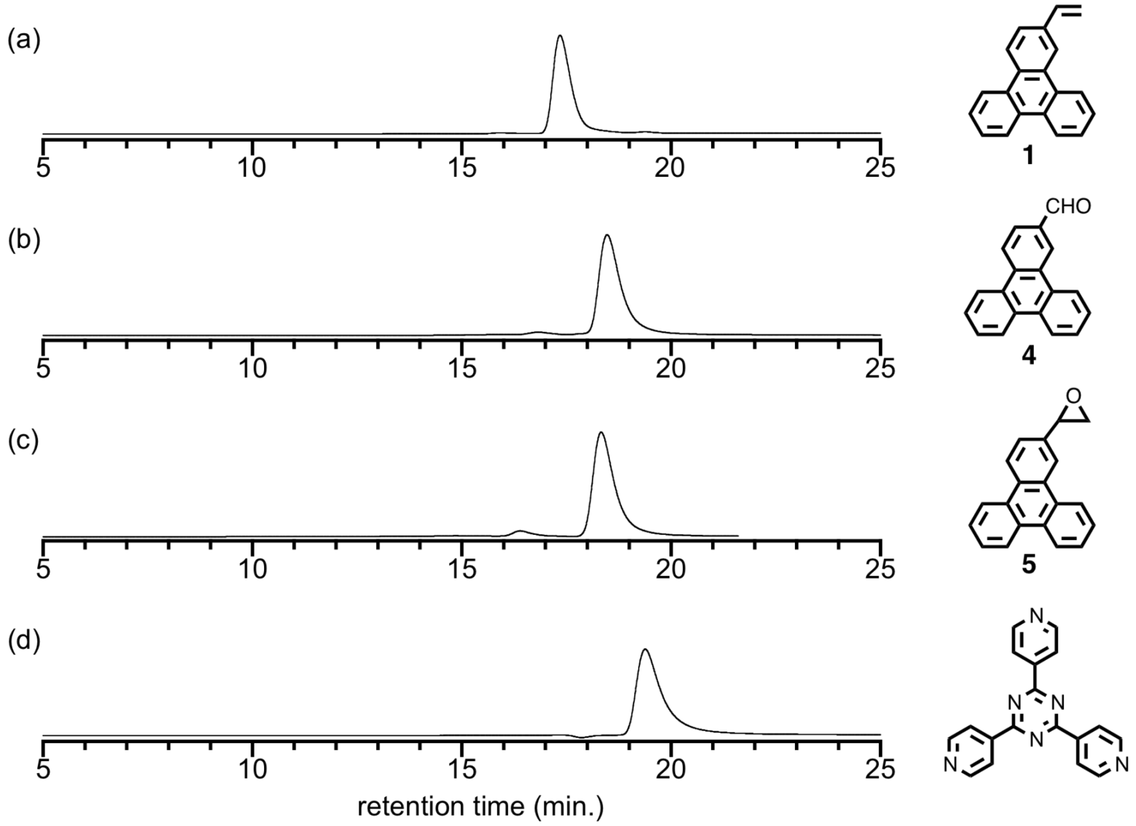


Figure S2. HPLC chromatograms of the reference compounds: (a) 2-vinyltriphenylene (**1**), (b) 2-formyltriphenylene (**4**), (c) epoxide **5**, and (d) ligand **2**.