

Supplementary Material (ESI) for *PCCP*

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**Cross-linking and postfunctionalization of polymer films by utilizing the
orthogonal reactivity of 7,7,8,8-tetracyanoquinodimethane**

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1. Materials

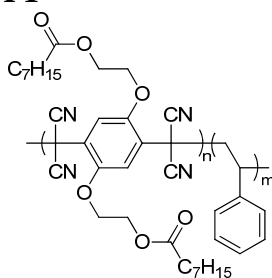
[3,6-Bis(dicyanomethylidene)cyclohexa-1,4-diene-1,4-diyl]bis(oxyethane-2,1-diyl)dioctanoate **1**, bis[2-(3,6-bis(dicyanomethylidene)-4-[2-(octanoyloxy)ethoxy]cyclohexa-1,4-dien-1-yloxy)ethyl]decanedioate **2**, and TCNQ polyester **P4** were prepared according to the literature.^{S1,S2} Styrene and α -chloromethylstyrene were purchased from Tokyo Kasei (TCI) and purified by distillation under reduced pressure. Other reagents were purchased from Kanto, Tokyo Kasei (TCI), and Wako and used as received.

2. Measurements

¹H-NMR spectra were measured on a JEOL model AL300 or AL400 spectrometer at 20 °C. Chemical shifts are reported in ppm downfield from SiMe₄, using the solvent's residual signal as an internal reference. The resonance multiplicity is described as br s (broad singlet) and m (multiplet). Attenuated total reflectance Fourier transform infrared (ATR-FT-IR) spectra were recorded on a JASCO FT/IR-4100 spectrometer. Gel permeation chromatography (GPC) was measured on a JASCO system equipped with polystyrene gel columns using THF as an eluent at the flow rate of 1.0 mL min⁻¹ after calibration with standard polystyrenes. Thermogravimetric analysis (TGA) was carried out on a Rigaku Thermoplus TG8120 under flowing nitrogen at the heating rate of 10 °C min⁻¹. UV-Vis-near IR spectra were recorded on a JASCO V-670 spectrophotometer. Electrochemical measurements were carried out at 20 °C in dehydrated CH₂Cl₂ containing 0.1 M (nC₄H₉)₄NClO₄ in a classical three-electrode cell. The working, reference, and auxiliary electrodes were a glassy carbon disk electrode (2 mm in diameter), Ag/AgCl/CH₃CN/(nC₄H₉)₄NPF₆, and a platinum wire, respectively. All potentials are referenced to the ferrocene/ferricinium (Fc/Fc⁺) couple used as an internal standard. Film thicknesses were measured on an AlphaStep D100.

3. Synthesis

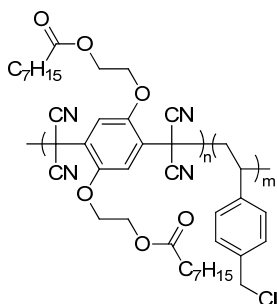
P1



To an ampoule tube, **1** (57.95 mg, 0.10 mmol), freshly distilled styrene (90 μ L, 0.095 mmol), and freshly distilled benzene (0.600 μ L) were added. AIBN (1.12 mg, 6.8 μ mol) was also added if necessary. The tube was attached to a vacuum line, sealed off, and then heated to 60 °C for 1 d. After cooling to 20 °C, the mixture was poured into MeOH, and the precipitate was collected (53.5 mg, 92%). GPC (THF): M_w 230000, M_n 130000. ¹H NMR (300 MHz, CDCl₃,) δ 0.88-2.44 (m, 30n+2m H), 3.20-4.70 (m, 8n+m H), 6.30-7.76 (m, 2n+5m H) ppm; IR (neat): ν 2929.34, 2856.06, 2250.52, 1737.55, 1506.13, 1455.99, 1405.85, 1220.72, 1160.94, 1108.87, 1054.87, 95.73, 863.95, 781.03, 732.82, 701.96 cm⁻¹; elemental analysis calcd. (%) for the

perfect alternating polymer ($C_{32n+8m}H_{40n+8m}N_{4n}O_{6n}$): C 70.56, H 7.21, N 8.23, found: C 68.31, H 6.43, N 9.02.

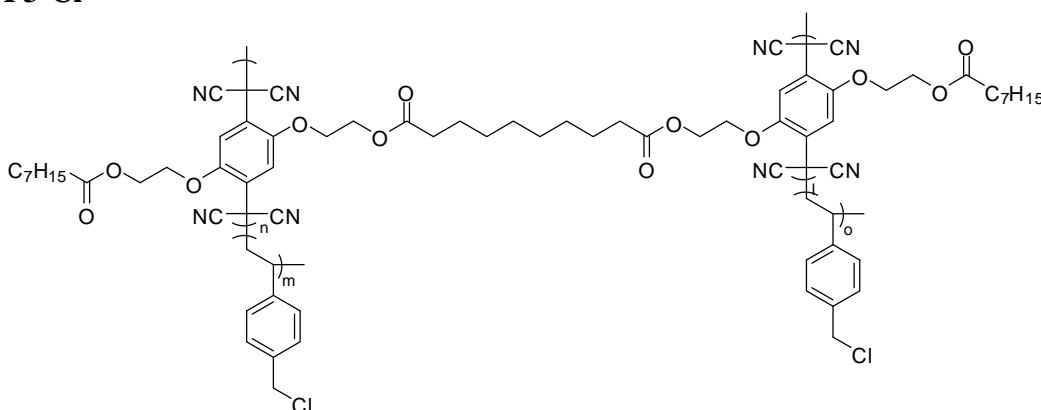
P2



To an ampoule tube, **1** (2.87 g, 4.98 mmol), freshly distilled α -chloromethylstyrene (700 μ L, 4.97 mmol), and freshly distilled benzene (30 μ L) were added. The tube was attached to a vacuum line, sealed off, and then heated to 60 $^{\circ}$ C for 1 d. After cooling to 20 $^{\circ}$ C, the mixture was poured into MeOH, and the precipitate was collected (2.57 g, 71%).

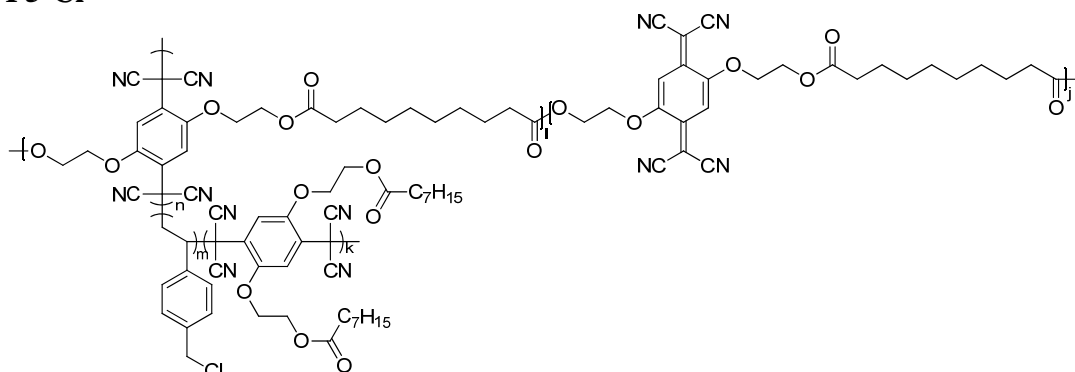
GPC (THF): M_w 160000, M_n 68000; 1 H NMR (400 MHz, $CDCl_3$) δ 0.39-2.59 (m, $30n+2m$ H), 3.22-4.89 (m, $8n+m$ H), 6.30-7.52 (m, $2n+4m$ H) ppm; IR (neat): ν 2953.45, 2929.34, 2856.06, 2249.56, 1734.66, 1506.13, 1455.99, 1409.71, 1352.82, 1297.86, 1268.93, 1222.65, 1160.94, 1106.94, 1058.73, 1035.59, 951.70, 862.025, 774.28, 741.50, 721.25, 698.11, 675.93, 649.89, 633.50, 618.07, 605.54 cm^{-1} ; elemental analysis calcd. (%) for the perfect alternating polymer ($C_{32n+9m}H_{40n+9m}N_{4n}O_{6n}$): C: 67.52, H: 6.77, N: 7.68, found: C 67.53, H 6.82, N 7.59.

P3-Cl



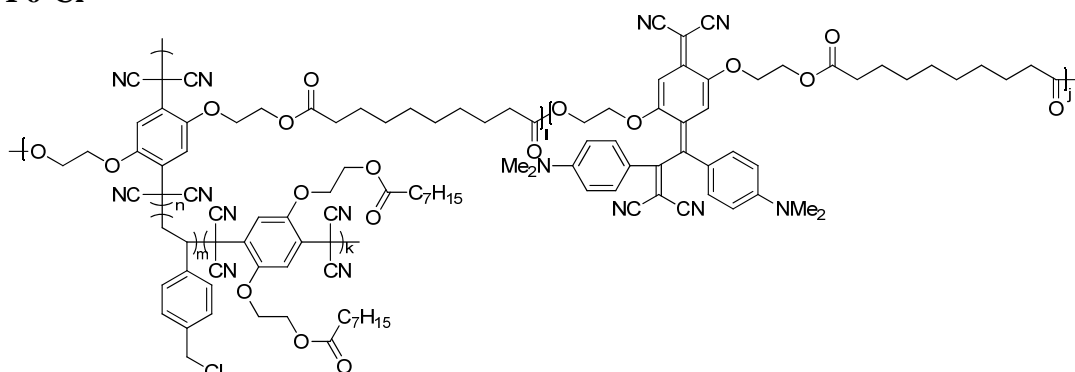
To an ITO plate, a mixture of **2** (62.47 mg, 58.53 μ mol) and freshly distilled α -chloromethylstyrene (800 μ L, 5.66 mmol) was cast. The plate was heated to 60 $^{\circ}$ C for 1 d under moderately reduced pressure. After cooling to 20 $^{\circ}$ C, the formed thin film was washed with dichloromethane.

IR (neat): ν 2928.38, 2856.06, 2100.10, 1734.66, 1507.10, 1455.99, 1407.78, 1352.82, 1267.97, 1221.68, 1160.94, 1106.94, 1056.80, 917.95, 846.60, 825.38, 766.57, 749.21, 722.21, 699.07, 679.79, 647.97, 639.29, 626.75, 618.07 cm^{-1} .

P5-Cl

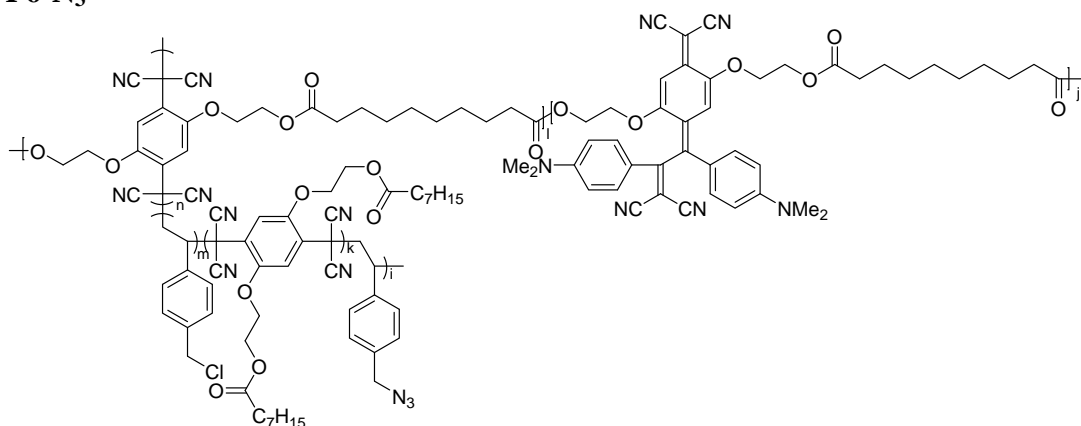
To an ITO plate, a mixture of **1** (20.10 mg, 34.85 μmol), TCNQ polyester **P4** (11.86 mg, 24.18 μmol repeat unit⁻¹), and flexibly distilled α -chloromethylstyrene (1.5 mL, 11 mmol) was cast. The plate was heated to 60 °C for 1 d under moderately reduced pressure. After cooling to 20 °C, the formed thin film was washed with dichloromethane.

IR (neat): ν 2920.66, 2855.10, 2250.52, 1746.23, 1729.83, 1616.06, 1505.17, 1455.99, 1415.49, 1377.89, 1352.82, 1296.89, 1202.40, 1149.37, 1106.94, 1052.94, 957.48, 864.92 cm^{-1} .

P6-Cl

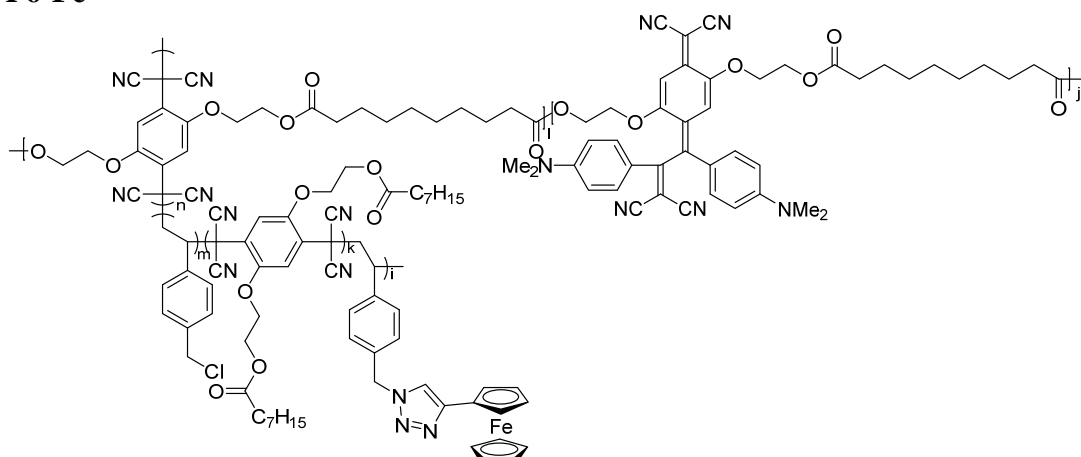
To the film surface of **P5-Cl**, 4,4'-ethyne-1,2-diylbis(*N,N*-dimethylaniline) in 1,2-dichlorobenzene (1 g L⁻¹, 3 mL) was cast. The plate was heated to 160 °C for 3 h. After cooling to 20 °C, the film was washed with dichloromethane.

IR (neat): ν 2920.66, 2855.10, 2515.69, 2360.44, 2341.16, 2250.52, 1915.93, 1724.05, 1651.73, 1610.27, 1505.17, 1455.99, 1414.53, 1353.78, 1277.61, 1246.75, 1187.94, 1061.62, 957.84, 894.81, 864.92, 818.63, 799.35, 769.46, 747.28, 725.10, 714.50, 700.03, 685.57, 661.46 cm^{-1} .

P6-N₃

To the film surface of **P6-Cl**, a DMF solution of NaN₃ (1 g L⁻¹, 3 mL) was cast and kept at 20 °C for 1 d. The film was washed with dichloromethane.

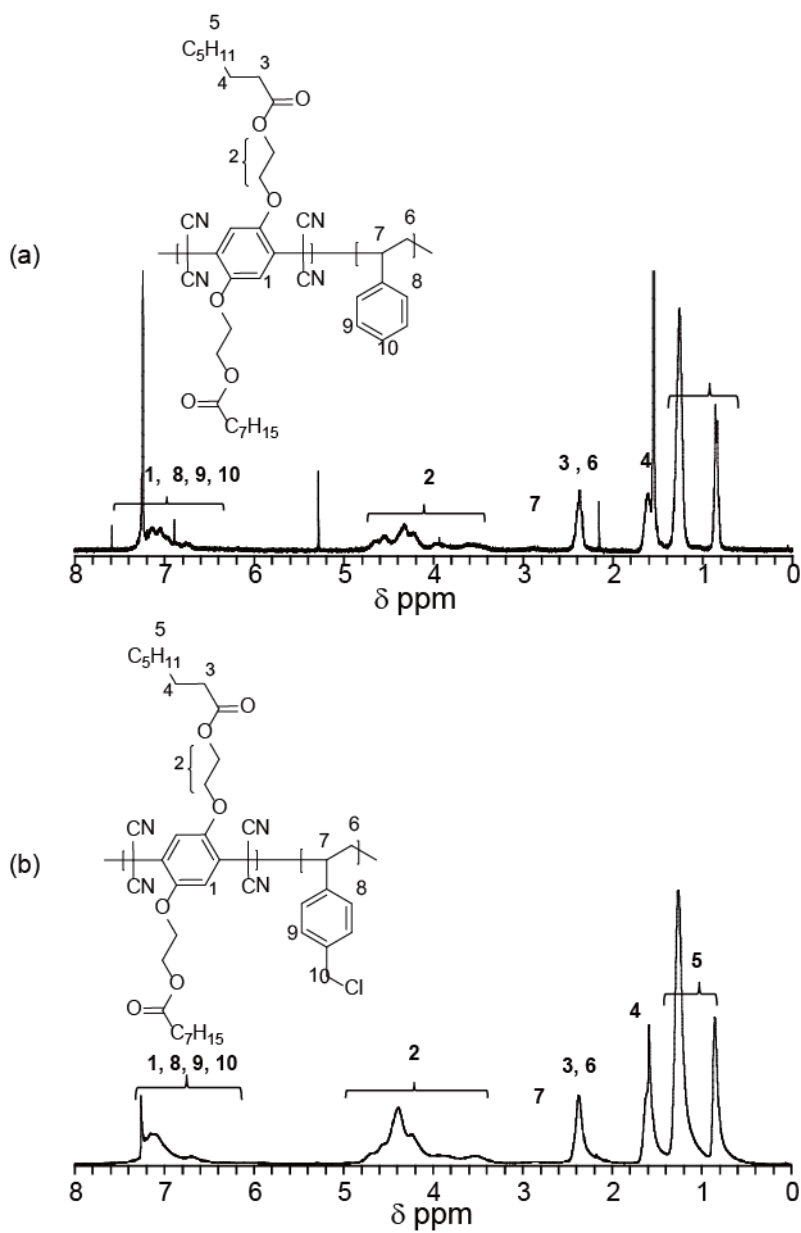
IR (neat): ν 2921.63, 2855.10, 2674.78, 2568.72, 2250.52, 2109.74, 1748.16, 1614.13, 1503.24, 1454.06, 1402.96, 1280.50, 1230.36, 1168.65, 1069.69, 963.27, 864.92, 725.10 cm⁻¹.

P6-Fc

To the film surface of **P6-N₃**, a solution of ethynylferrocene (5.06 mg, 24.1 μ mol), CuSO₄·5H₂O (2.79 mg, 11.2 μ mol), and sodium ascorbate (3.89 mg, 19.6 μ mol) in DMF (2 mL) was cast and it was left at 20 °C for 1 d. The film was washed with dichloromethane.

IR (neat): ν 2921.63, 2855.10, 2250.52, 2109.74, 1748.16, 1614.13, 1556.27, 1503.24, 1454.06, 1402.96, 1352.82, 1280.50, 1230.36, 963.27, 864.92 cm⁻¹.

4. ^1H NMR spectra



5. UV-Vis spectra

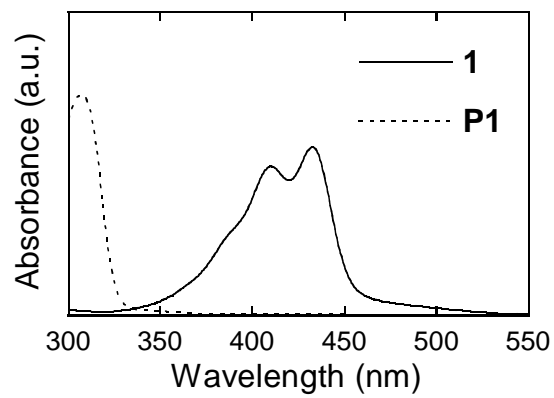


Fig. S2 UV-Vis absorption spectra of **1** and **P1** in CH_2Cl_2 .

6. Thermogravimetric analysis

Thermal stability of some selected cross-linked polymer films was investigated. Both **P3-Cl** and its azidated derivative **P3-N₃** showed no decomposition up to 220 °C, and the 5% weight loss temperatures ($T_{d5\%}$) were 270 and 255 °C, respectively. This result suggested the sufficient stability of the cross-linked polymer films, prepared by spontaneous radical copolymerization, for the subsequent functionalization experiments. The azide units would be decomposed by releasing nitrogen gas, and the formed reactive nitrenes undergo further intramolecular cross-linking reactions. Thus, the char amount of **P3-N₃** at 500 °C was greater than that of **P3-Cl** (47% for **P3-Cl** vs. 58% for **P3-N₃**).

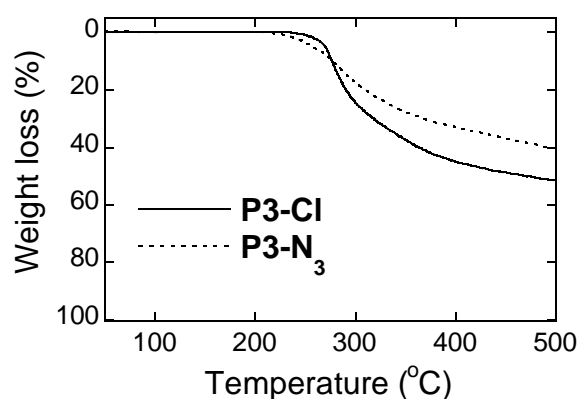


Fig. S3 Thermogravimetric analysis of **P3-Cl** and **P3-N₃** at the heating rate of 10 °C min⁻¹ under nitrogen flow.

7. Click functionalization

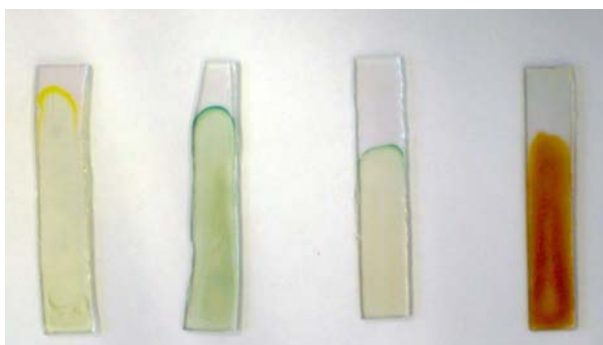


Fig. S4 Visual images of polymer films: (a) **P5-Cl**, (b) **P6-Cl**, (c) **P6-N₃**, and (d) **P6-Fc**.

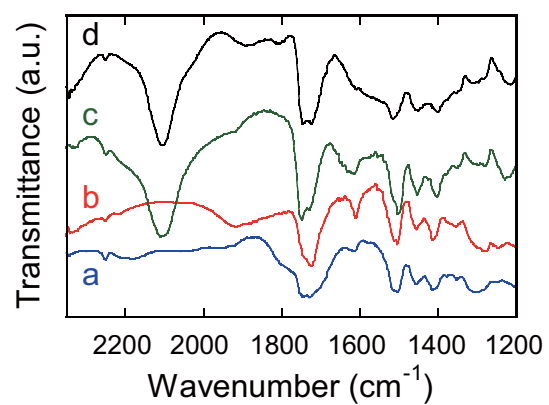


Fig. S5 FT-IR spectra of polymer films: (a) **P5-Cl**, (b) **P6-Cl**, (c) **P6-N₃**, and (d) **P6-Fc**.

8. References

- S1 Y. Washino, K. Murata, M. Ashizawa, S. Kawauchi and T. Michinobu, *Polym. J.*, 2011, **43**, 364.
- S2 Y. Washino and T. Michinobu, *Macromol. Rapid Commun.*, 2011, **32**, 644.