

Supporting Information

Sequential double click reactions: A highly efficient post-functionalization method for optoelectronic polymers

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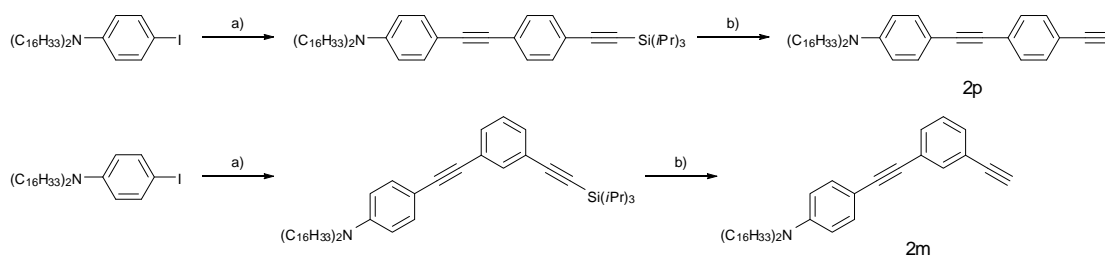
1. Materials and general methods.

Chemicals were purchased from Kanto, Tokyo Kasei, Wako, and Aldrich and used as received.

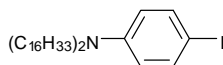
[[4-Ethynylphenyl]ethynyl](triisopropyl)silane¹, [(3-ethynylphenyl)ethynyl](triisopropyl)silane¹, and poly(4-azidomethylstyrene) **1**² were synthesized according to the reported methods. All reactions for the monomer preparation were carried out under an inert atmosphere. ¹H-NMR and ¹³C-NMR spectra were measured on a JEOL model AL300 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 s (singlet), br s (broad singlet), d (doublet), and m (multiplet). Infrared spectra (IR) were recorded on a JASCO FT/IR-4100 spectrometer. Elemental analysis was performed on a PerkinElmer 2400-SeriesII CHNS/O Analyzer. Gel permeation chromatography (GPC) was measured on a Shodex system equipped with polystyrene gel columns using THF as an eluent after calibration with standard polystyrene. UV/Vis spectra were recorded in a quartz cuvette of 1 cm on a JASCO V-550 spectrophotometer. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were carried out on a Seiko SII TG 6220 and a Seiko SII DSC 6220, respectively, under nitrogen flow, at a scanning rate of 10 °C min⁻¹. The electrochemical experiments were carried out at 20 °C in dehydrated CH₂Cl₂ containing 0.1 M (*n*C₄H₉)₄NClO₄ in a classical three-electrode cell. The working and auxiliary electrodes were a glassy carbon disk electrode (2 mm in diameter) and a platinum wire, respectively. The reference electrode was

Ag/AgCl/CH₃CN/(*n*C₄H₉)₄NPF₆. All potentials are referenced to the ferricinium/ferrocene (Fc⁺/Fc) couple used as an internal standard.

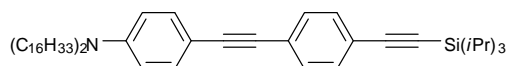
2. Synthesis of alkyne molecules.



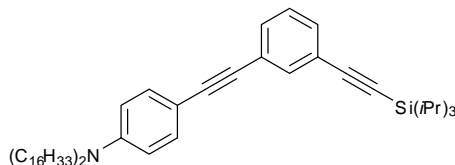
Scheme 1SI. Synthesis of **2p** and **2m**. (a) HC≡CPhC≡CSi(*i*Pr)₃, PdCl₂(PPh₃)₂, CuI, *i*Pr₂NH, N₂, 18 h; (b) TBAF, THF, 0 °C, 20 min.



***N,N*-Dihexadecyl-4-iodoaniline:** To a solution of 4-iodoaniline (5.30 g, 24.2 mmol) in dehydrated DMF (50 ml), 1-iodohexadecane (28.0 g, 79.5 mmol) and sodium carbonate (4.50 g, 42.5 mmol) were added. The mixture was stirred at 95 °C for 20 h. After cooling to room temperature, the mixture was washed with water (200 ml) and extracted by dichloromethane (200 ml). The organic phase was collected and dried over sodium sulfate. Evaporation and column chromatography (SiO₂, hexane) afforded the desired product (13.0 g, 78%), δ_{H} (300 MHz; CDCl₃) 0.88 (6 H, m), 1.26 (52 H, s), 1.52 (4 H, m), 3.18 (4 H, m), 6.38 (2 H, d, *J* 9.0), 7.39 (2 H, d, *J* 9.0); δ_{C} (75 MHz; CDCl₃) 14.13, 22.70, 27.02, 27.11, 28.56, 29.37, 29.43, 29.51, 29.56, 29.61, 29.67, 29.70, 30.52, 31.94, 33.58, 50.99, 75.29, 113.95, 137.60, 147.56.

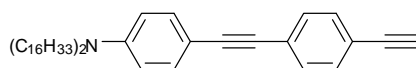


***N,N*-Dihexadecyl-4-((4-((triisopropylsilyl)ethynyl)phenyl)ethynyl)aniline:** To a degassed solution of [(4-ethynylphenyl)ethynyl](triisopropyl)silane (1.00 g, 3.54 mmol) and *N,N*-dihexadecyl-4-iodoaniline (2.36 g, 3.53 mmol) in diisopropylamine (40 ml), bis(triphenylphosphine)palladium(II) dichloride (50 mg, 0.070 mmol) and cuprous iodide (25 mg, 0.13 mmol) were added. The mixture was stirred at room temperature under nitrogen for 18 h. After removal of the precipitated salt by filtration, evaporation and column chromatography (SiO₂, hexane) afforded the desired product (2.16 g, 74%) as a viscous liquid, $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2923, 2853, 2208, 2152, 1610, 1596, 1521, 1465, 1401, 1368, 1195, 1134, 882, 835, 812; $\delta_{\text{H}}(300 \text{ MHz}; \text{CDCl}_3)$ 0.89 (6 H, m), 1.14 (18 H, s), 1.27 (52 H, m), 1.58 (7 H, m), 3.27 (4 H, m), 6.57 (2 H, d, *J* 8.7), 7.36 (2 H, d, *J* 8.7), 7.41 (4 H, s); $\delta_{\text{C}}(75 \text{ MHz}; \text{CDCl}_3)$ 11.33, 14.12, 18.67, 22.68, 27.17, 29.54, 31.95, 50.95, 87.00, 91.98, 92.99, 107.01, 108.35, 111.17, 122.16, 124.33, 130.89, 131.85, 132.93, 148.07; MALDI-TOF MS calcd for C₅₇H₉₅NSi⁺ (*M*⁺): 821.72; found 823.5 (*[M+H]*⁺).



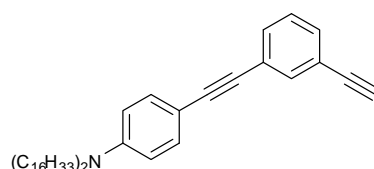
***N,N*-Dihexadecyl-4-((3-((triisopropylsilyl)ethynyl)phenyl)ethynyl)aniline:** To a degassed solution of [(3-ethynylphenyl)ethynyl](triisopropyl)silane (1.00 g, 3.54 mmol) and *N,N*-dihexadecyl-4-iodoaniline (2.36 g, 3.53 mmol) in diisopropylamine (40 ml), bis(triphenylphosphine)palladium(II) dichloride (50 mg, 0.070 mmol) and

cuprous iodide (25 mg, 0.13 mmol) were added. The mixture was stirred at room temperature under nitrogen for 18 h. After the removal of the precipitated salt by filtration, evaporation and column chromatography (SiO₂, hexane) afforded the desired product (1.98 g, 68%) as a viscous liquid, $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2924, 2853, 2203, 2150, 1608, 1590, 1519, 1465, 1399, 1368, 1221, 1189, 1125, 1074, 883, 811, 790; $\delta_{\text{H}}(300 \text{ MHz}; \text{CDCl}_3)$ 0.81 (6 H, m), 1.07 (18 H, s), 1.22 (52 H, m), 1.51 (7 H, m), 3.19 (4 H, m), 6.49 (2 H, d, J 7.2), 7.17 (1 H, m), 7.28 (3 H, m), 7.34 (1 H, m), 7.53 (1 H, s); $\delta_{\text{C}}(75\text{Hz}; \text{CDCl}_3)$ 11.31, 14.13, 18.67, 22.70, 22.17, 29.54, 31.94, 50.96, 86.30, 90.86, 91.56, 106.49, 108.38, 111.15, 123.65, 124.55, 128.13, 130.74, 131.00, 132.92, 134.62, 148.03; MALDI-TOF MS calcd for C₅₇H₉₅NSi⁺ (M^+): 821.72; found 823.5 ($[M+H]^+$).



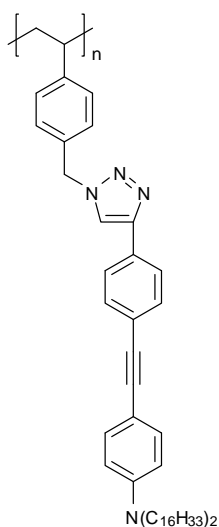
4-[(4-Ethynylphenyl)ethynyl]-*N,N*-dihexadecylaniline (2p): To a solution of *N,N*-dihexadecyl-4-({4-[(triisopropylsilyl)ethynyl]phenyl}ethynyl)aniline (1.00 g, 1.21 mmol) in tetrahydrofuran (12 ml), tetrabutylammonium fluoride (1M in tetrahydrofuran) (2.4 ml) was added. The mixture was stirred at 0 °C under air for 20 min. Column chromatography (SiO₂, CH₂Cl₂) afforded the desired product (786 mg, 95%) as a yellow solid, $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3308, 2919, 2850, 2206, 2098, 1611, 1595, 1524, 1467, 1398, 1352, 1132, 842, 820; $\delta_{\text{H}}(300 \text{ MHz}; \text{CDCl}_3)$ 0.90 (6 H, m), 1.31 (52 H, m), 1.55 (4 H, m), 3.15 (1 H, s), 3.34 (4 H, m), 6.58 (2 H, d, J 9), 7.37 (2 H, d, J 9), 7.44 (4 H, s); $\delta_{\text{C}}(75\text{Hz}; \text{CDCl}_3)$ 14.11, 22.69, 27.17, 29.61, 31.93, 50.94,

78.32, 83.57, 86.76, 93.24, 108.26, 111.17, 120.67, 124.97, 120.67, 124.97, 130.99, 131.92, 132.94, 148.11; MALDI-TOF MS calcd for $C_{48}H_{75}N^+$ (M^+): 665.59; found 667.1 ($[M+H]^+$).

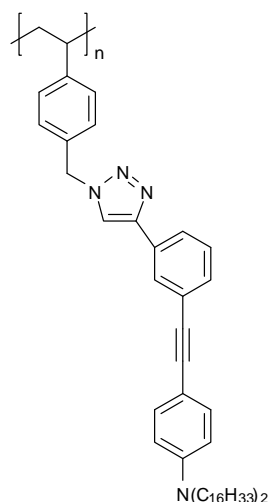


4-[(3-Ethynylphenyl)ethynyl]-*N,N*-dihexadecylaniline (2m): To a solution of *N,N*-dihexadecyl-4-({3-[(triisopropylsilyl)ethynyl]phenyl}ethynyl)aniline (650 mg, 0.790 mmol) in tetrahydrofuran (8 ml), tetrabutylammonium fluoride (1M in tetrahydrofuran) (2.4 ml) was added. The mixture was stirred at 0 °C under air for 20 min. Column chromatography (SiO_2 , CH_2Cl_2) afforded the desired product (520 mg, 99%) as a yellow solid, $\nu_{max}(KBr)/cm^{-1}$ 3309, 2923, 2852, 2200, 1611, 1591, 1419, 1466, 1398, 1369, 1122, 811, 791; $\delta_H(300\text{ MHz}; CDCl_3)$ 0.88 (6 H, m), 1.29 (52 H, m), 1.56 (4 H, s), 3.07 (1 H, s), 3.27 (4 H, m), 6.56 (2 H, d, J 9), 7.29 (1 H, m), 7.36 (3 H, m), 7.46 (1 H, d, J 7.5), 7.52 (1 H, s); $\delta_C(75\text{ Hz}; CDCl_3)$ 14.13, 22.70, 27.15, 29.62, 31.94, 50.93, 83.04, 86.10, 91.75, 108.19, 111.10, 122.21, 124.70, 128.24, 130.76, 131.45, 132.92, 134.68, 148.01; MALDI-TOF MS calcd for $C_{48}H_{75}N^+$ (M^+): 665.59; found 667.1 ($[M+H]^+$).

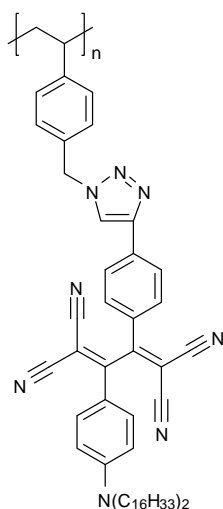
3. Click reactions.



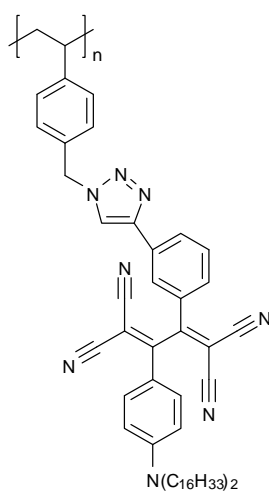
3p: To a solution of **1** (31 mg, 0.20 mmol repeat unit⁻¹) in DMF (8 ml), **2m** (130 mg, 0.20 mmol), sodium ascorbate (3.9 mg, 0.012 mmol), and copper(II) sulfate pentahydrate (2.3 mg, 0.0098 mmol) were added. The mixture was stirred at room temperature under argon for 24 h, yielding a yellow precipitate as shown in the above picture. The precipitate was filtered and washed with DMF, followed by methanol and water to afford the yellow solid (135 mg, 87%). The filtrate was poured into methanol to yield the residual desired polymer (total: 152 mg, 98%), $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2923, 2852, 2207, 1603, 1524, 1458, 1368, 1190, 1136, 842, 812; $\delta_{\text{H}}(300\text{MHz};\text{CDCl}_3)$ 0.86 (6n H, m), 1.25 (52n H, s), 1.57 (7n H, m), 3.19 (4n H, br s), 5.47 (2n H, s), 6.48 (2n H, br s), 6.75 (2n H, br s), 7.30 (4n H, d, J 12.6), 7.74 (5n H, br s).



3m: To a solution of **1** (47.7 mg, 0.300 mmol repeat unit⁻¹) in DMF (12 ml), **2m** (200 mg, 0.300 mmol), sodium ascorbate (6.0 mg, 0.030 mmol), and copper(II) sulfate pentahydrate (3.7 mg, 0.0015 mmol) were added. The mixture was stirred at room temperature under argon for 24 h, yielding a yellow precipitate. The precipitate was filtered and washed with DMF, followed by methanol and water to afford the yellow solid (209 mg, 87%). The filtrate was poured into methanol to yield the residual desired polymer (total: 235 mg, 98%), $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2923, 2852, 2210, 1603, 1579, 1519, 1458, 1368, 1198, 1130, 1045, 812, 791; $\delta_{\text{H}}(300 \text{ MHz}; \text{CDCl}_3)$ 0.86 (6n H, m), 1.24 (52n H, s), 1.50 (7n H, m), 3.18 (4n H, br s), 5.30 (2n H, s), 6.19 (2n H, br s), 6.49 (4n H, br s), 6.72 (3n H, br s), 7.68 (2n H, br s), 7.96 (2n H, br s).

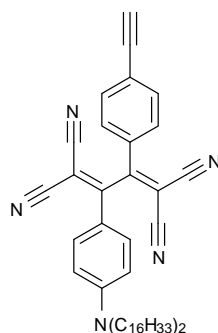


4p: To a solution of **3p** (24.5 mg, 0.0295 mmol repeat unit⁻¹) in chloroform (0.3 ml), a TCNE solution in 1,2-dichloroethane (0.163 M, 0.18 ml) was added. The mixture was stirred at room temperature under air for 1 h. The solution was evaporated to afford **4p** (28.2 mg, 100%), $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2923, 2852, 2214, 1604, 1489, 1418, 1346, 1212, 1182, 971, 820; $\delta_{\text{H}}(300 \text{ MHz}; \text{CDCl}_3)$ 0.86 (6n H, m), 1.24 (52n H, s), 1.59 (7n H, s), 3.34 (4n H, m), 5.48 (2n H, s), 6.68 (4n H, br s), 7.69 (8n H, br s), 7.98 (n H, s); EA calcd for $(\text{C}_{63}\text{H}_{84}\text{N}_8)_n$: C 79.37, H 8.88, N 11.75; found: C 79.56, H 9.27, N 11.17%.



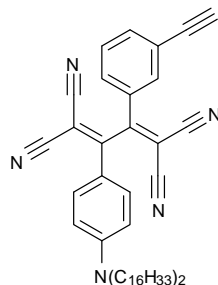
4m: To a solution of **3m** (22.7 mg, 0.0275 mmol repeat unit⁻¹) in chloroform (4 ml), a

TCNE solution in 1,2-dichloroethane (8.6 mM, 3.2 ml) was added. The mixture was stirred at room temperature under air for 1 h. The solution was evaporated to afford **4m** (26.2 mg, 100%), $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 2923, 2852, 2214, 1603, 1490, 1417, 1342, 1211, 1183, 819, 701; $\delta_{\text{H}}(300 \text{ MHz}; \text{CDCl}_3)$ 0.86 (6n H, m), 1.24 (52n H, s), 1.59 (7n H, s), 3.34 (4n H, br s), 5.36 (2n H, br s), 6.63 (7n H, s), 7.46 (2n H, br s), 7.76 (2n H, br s), 8.00 (n H, br s), 8.44 (n H, br s); EA calcd for $(\text{C}_{63}\text{H}_{84}\text{N}_8)_n$: C 79.37, H 8.88, N 11.75; found: C 79.44, H 8.99, N 11.57%.

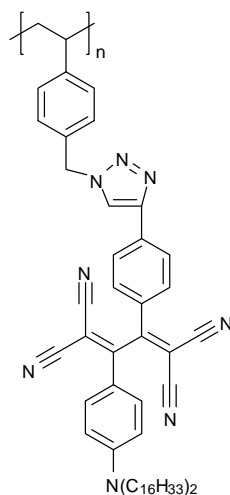


2-[4-(Dihexadecylamino)phenyl]-3-(4-ethynylphenyl)buta-1,3-diene-1,1,4,4-tetracarbonitrile (5p): TCNE (19 mg, 0.15 mmol) was added to a solution of **2p** (99 mg, 0.15 mmol) in 1,2-dichloroethane (7 ml). The mixture was stirred at room temperature under air for 1 h. Evaporation and column chromatography (SiO_2 , CH_2Cl_2) afforded the desired product (117 mg, 100%), $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3300, 2923, 2853, 2217, 1604, 1490, 1420, 1365, 1344, 1211, 1185, 846, 823; $\delta_{\text{H}}(300 \text{ MHz}; \text{CDCl}_3)$ 0.88 (6 H, m), 1.30 (52 H, m), 1.64 (4 H, s), 3.34 (1 H, s), 3.38 (4 H, m), 6.67 (2 H, d, J 9.3), 7.63 (2 H, d, J 8.7), 7.64 (2 H, d, J 8.7), 7.68 (2 H, d, J 9.3); $\delta_{\text{C}}(75 \text{ Hz}; \text{CDCl}_3)$ 14.11, 22.68, 26.99, 29.55, 31.90, 51.48, 82.04, 82.40, 87.39, 111.19, 111.90, 112.23, 113.60, 114.49, 117.23, 128.32, 129.39, 131.76, 132.74, 133.16, 153.08,

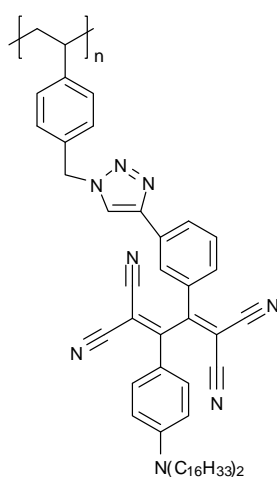
161.95, 168.33; MALDI-TOF MS calcd for $C_{54}H_{75}N_5^+$ (M^+): 793.60; found 795.1
($[M+H]^+$).



2-[4-(Dihexadecylamino)phenyl]-3-(3-ethynylphenyl)buta-1,3-diene-1,1,4,4-tetracarbonitrile (5m): TCNE (53.5 mg, 0.417 mmol) was added to a solution of **2m** (278 mg, 0.417 mmol) in 1,2-dichloroethane (8 ml). The mixture was stirred at room temperature under air for 1 h. Evaporation and column chromatography (SiO₂, CH₂Cl₂) afforded the desired product (331 mg, 100%), $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3299, 2920, 2851, 2220, 1604, 1541, 1496, 1419, 1342, 1212, 1183, 824; $\delta_{\text{H}}(300 \text{ MHz}; \text{CDCl}_3)$ 0.88 (6 H, m), 1.29 (52 H, m), 1.63 (4 H, s), 3.19 (1 H, s), 3.39 (4 H, m), 6.68 (2 H, d, J 9.6), 7.52 (1 H, m), 7.72 (3 H, m), 7.79 (2 H, m); $\delta_{\text{C}}(75 \text{ Hz}; \text{CDCl}_3)$ 14.12, 22.67, 27.14, 29.54, 31.89, 51.48, 80.02, 81.41, 87.97, 111.04, 111.67, 112.27, 113.63, 114.50, 117.45, 124.18, 129.46, 129.78, 132.22, 132.43, 132.74, 133.80, 137.26, 152.05, 165.03, 176.89; MALDI-TOF MS calcd for $C_{54}H_{75}N_5^+$ (M^+): 793.60; found 795.1 ($[M+H]^+$).



6p: To a solution of **1** (20 mg, 0.13 mmol repeat unit⁻¹) in DMF (6 ml), **5p** (100 mg, 0.0126 mmol), sodium ascorbate (2.5 mg, 0.013 mmol) and copper(II) sulfate pentahydrate (1.6 mg, 0.0063 mmol) were added. The mixture was stirred at room temperature under argon for 24 h. The solution was reduced in vacuo and the polymer was precipitated to methanol/dichloromethane (3:1) to afford **6p** (113 mg, 96%), EA calcd for $(C_{63}H_{84}N_8)_n$: C 79.37, H 8.88, N 11.75; found: C 79.79, H 9.07, N 11.14%.



6m: To a solution of **1** (33.7 mg, 0.212 mmol repeat unit⁻¹) in DMF (8 ml), **5m** (168 mg, 0.212 mmol), sodium ascorbate (4.2 mg, 0.021 mmol) and copper(II) sulfate

pentahydrate (2.6 mg, 0.011 mmol) were added. The mixture was stirred at room temperature under argon for 24 h. The solution was reduced in vacuo and the polymer was precipitated to methanol/dichloromethane (3:1) to afford **6m** (152 mg, 78%), EA calcd for $(C_{63}H_{84}N_8)_n$: C 79.37, H 8.88, N 11.75; found: C 78.86, H 8.85, N 12.29%.

Table 1SI. Summary of molecular weights and thermal properties of the polymers.

polymer	M_w^a	M_n^a	M_w/M_n^a	$T_g / ^\circ C^b$	$T_d / ^\circ C^c$
1	20100	11500	1.75	–	–
3p	81100	52300	1.55	-34	381
3m	90500	49000	1.85	-42	393
4p	105600	58500	1.80	-48	345
4m	101600	51000	1.99	-48	342
6p	165100	42800	3.85	-52	348
6m	122200	44800	2.73	-67	369

^a Determined by GPC (eluent: THF, calibrated by polystyrene standards)

^b Determined by DSC at the scanning rate of 10 °C min⁻¹.

^c Onset decomposition temperatures determined by TGA.

4. UV/Vis spectra

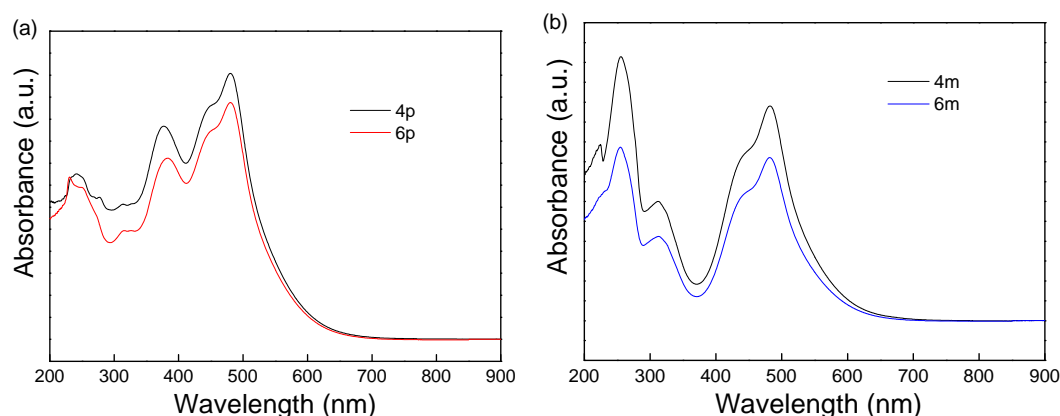


Fig 1SI. Comparison of the UV-Vis spectra (a) between **4p** and **6p** and (b) between **4m** and **6m** at the same concentration ($0.50 \text{ mM repeat unit}^{-1}$) in chloroform at $20 \text{ }^\circ\text{C}$.

5. Electrochemistry

Table 2SI. Electrochemistry data of the polymers employed in this work in CH_2Cl_2 (+ $0.1 \text{ M } (n\text{C}_4\text{H}_9)_4\text{NClO}_4$).^a

polymer	E° [V] ^b	E_{pa} [V]	E_{pc} [V]
3p	0.28	0.38	0.17
3m	0.17	0.20	0.14
4p	0.84	0.89	0.78
	-0.91	-0.85	-0.97
4m	0.73	0.79	0.68
	-0.98	-0.93	-1.02

^a Potentials vs. Fc^+/Fc . Working electrode: glassy carbon electrode; counter electrode: Pt; reference electrode: Ag/AgCl.

^b $E^\circ = (E_{\text{pc}} + E_{\text{pa}})/2$, where E_{pc} and E_{pa} correspond to the cathodic and anodic peak potentials, respectively.

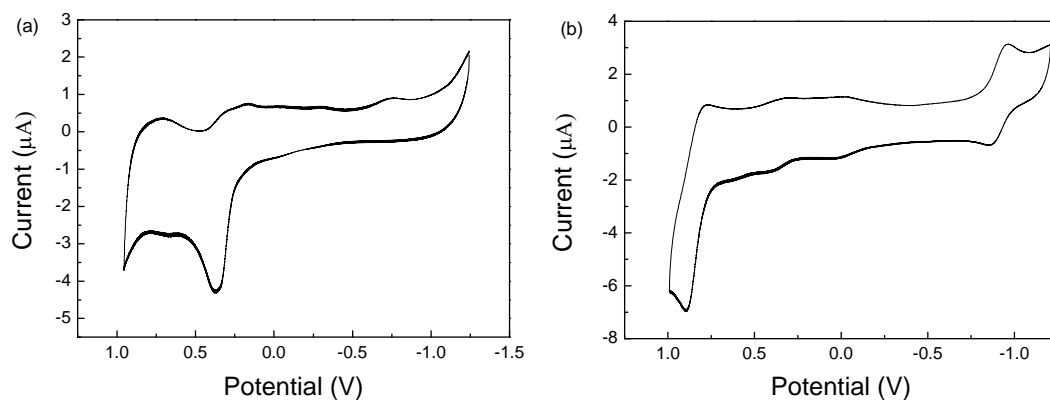


Fig 2SI. Cyclic voltammograms of (a) **3p** and (b) **4p** in CH_2Cl_2 (+0.1 M $(n\text{C}_4\text{H}_9)_4\text{NClO}_4$) at 20 °C.

References

1. (a) F. Wang, B. R. Kaafarani and D. C. Neckers, *Macromolecules*, 2003, **36**, 8225.
(b) A. Godt, *J. Org. Chem.*, 1997, **62**, 7471.
2. C. Ornelas, D. Mry, E. Cloutet, J. R. Aranzaes and D. Astruc, *J. Am. Chem. Soc.*, 2008, **130**, 1495.