

Electronic Supporting Information (ESI)

Catalytic Helix-Sense-Selective Polymerisation of Achiral Substituted Acetylenes Containing Bulky π -Conjugated Planar Substituents Yielding Soluble and Statically Stable One-Handed Helical Polymers

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1. Details for experimental procedure

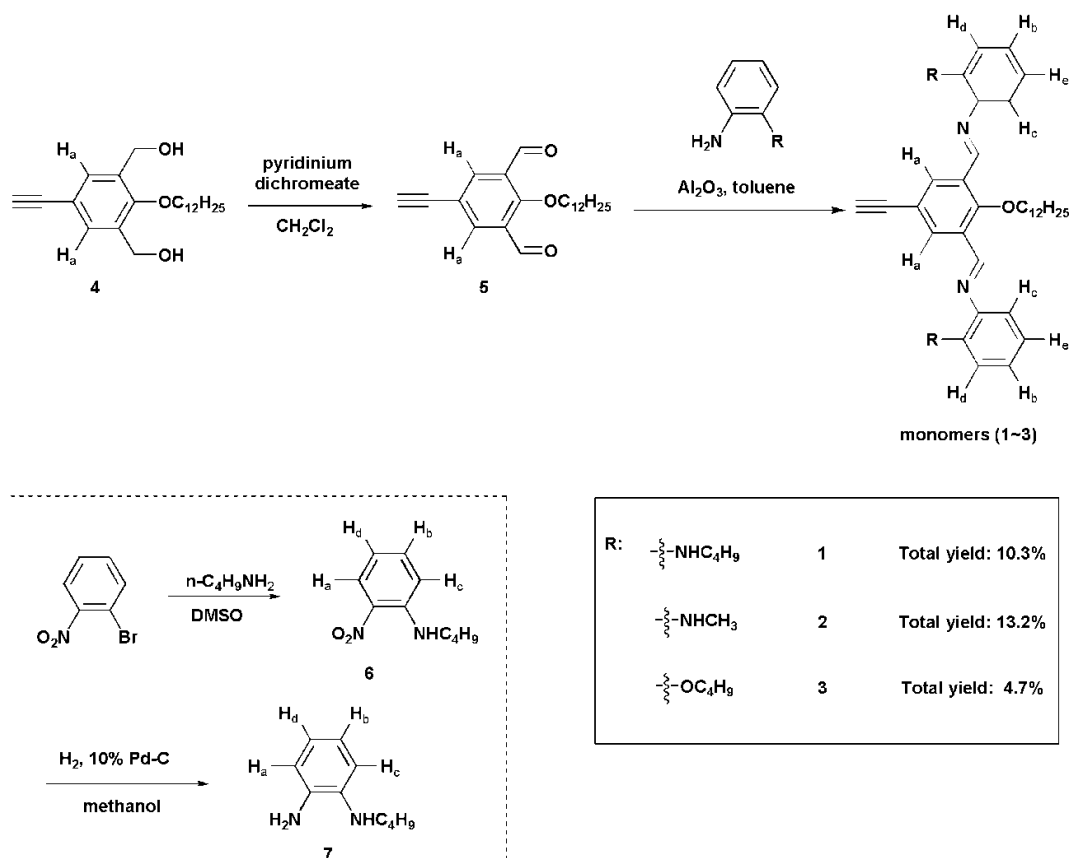
1.1. Materials

All the solvents used for synthesis and polymerisation of the monomers were distilled as usual. The polymerisation initiator, $[\text{Rh}(\text{nbd})\text{Cl}]_2$ (nbd = 2,5 norbornadiene), purchased from Aldrich Chemical was used as received. 4-Dodecyloxy-3,5-bis(hydroxymethyl)phenylacetylene (**4**) was synthesized from 4-bromophenol according to our previous report.^[2a]

1.2. Measurements

^1H NMR (400MHz) spectra were recorded on a JEOL LEOLEX-400 spectrometer. The average molecular weights (M_n and M_w) were evaluated by gel permeation chromatography (GPC) by using JASCO liquid chromatography instruments with PU-2080, DG-2080-53, CO-2060, UV-2070, CD-2095, and two polystyrene gel columns (Shodex KF-807 L, THF eluent, polystyrene calibration). We recorded CD spectra by using a JASCO J-720WI spectropolarimeter with a Peltier controller for temperatures at 20°C (a quartz cell of 1 mm path length; sample concentration: 0.100 to 2.00 mM based on the monomer unit). The infrared spectra were recorded on FT/IR-4200 (JASCO).

1.3. Synthesis of the monomers (1~3) (Scheme S1)



Scheme S1. Synthetic route to the monomers (1~3)

1) 4-Dodecyloxy-3,5-diformylphenylacetylene (5)

To a mixture of pyridinium dichromate (PDC) (63.0 g, 231 mmol) and dichloromethane (500 mL), a dichloromethane solution (200 mL) of **4** (8.00 g, 23.0 mmol) was added dropwise at 0°C. After the mixture was stirred for 48 h at room temperature, the mixture was filtered, and dichloromethane was removed by evaporation. The crude product was purified by silica-gel column chromatography to give **5** as a yellow solid. Yield: 95.3% (7.50 g). $R_f = 0.460$ (ethyl acetate / hexane = 1 / 2). $^1\text{H NMR}$ (400MHz, CDCl_3 , TMS, δ): 10.36 (s, 2H, CHO), 8.17 (s, 2H, Ar H_a), 4.12 (t, $J = 6.6$ Hz, 2H, OCH_2CH_2), 3.14 (s, 1H, $\text{HC}\equiv\text{C}$), 1.91 (m, 2H, $\text{OCH}_2\text{CH}_2\text{CH}_2$), 1.82~1.26 (m, 18H, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$), 0.86 (t, $J = 6.8$ Hz, 3H, CH_2CH_3). IR (KBr): 3270 (H-C \equiv), 2920 (CH), 2320 (C \equiv C), 1380 cm^{-1} ((H)C=O).

2) *N-n*-Butyl-2-nitroaniline (**6**)

To a mixture of 2-bromonitrobenzene (10.0 g, 50.0 mmol) and dimethyl sulfoxide (DMSO) (50.0 mL), *n*-butylamine (18.0 mL, 0.180 mol) was added. After the mixture was stirred for 18 h at 80°C, water (150 mL) was added. The mixture was extracted with dichloromethane, and the organic layer was dried over anhydrous MgSO₄. The crude product was purified by silica-gel column chromatography to give **6** as an orange liquid. Yield: 95.1% (9.10 g). $R_f = 0.360$ (ethyl acetate / hexane = 1 / 2). ¹H NMR (400MHz, CDCl₃, TMS, δ): 8.16 (dd, $J_1 = 1,6$ Hz, $J_2 = 8.7$ Hz, 1H, Ar H_a), 8.05 (br, 1H, Ar NH), 7.42 (m, 1H, Ar H_b), 6.83 (d, $J = 8.6$ Hz, 1H, Ar H_c), 6.61 (m, 1H, Ar H_d), 3.29 (m, 2H, NCH₂CH₂), 1.71 (m, 2H, CH₂CH₂CH₂), 1.47 (m, 2H, CH₂CH₂CH₃), 0.98 (t, $J = 7.4$ Hz, 3H, CH₂CH₃).

3) *N-n*-Butyl-1, 2-phenylenediamine (**7**)

A mixture of **6** (4.30 g, 22.0 mmol) and 10% Pd-C (0.470 g, 0.440 mol) in methanol (25.0 mL) was stirred at room temperature for 10 h under protection with H₂. The formed solid was filtered out, and methanol was removed from the resulting solution by evaporation. The crude product was purified by silica-gel column chromatography to give **7** as a purple solid. Yield: 78.0% (2.86 g). $R_f = 0.360$ (ethyl acetate / hexane = 1 / 3). ¹H NMR (400MHz, CDCl₃, TMS, δ): 6.83 (m, 1H, Ar H_b), 6.73~6.64 (m, 3H, Ar H_a , Ar H_c , Ar H_d), 3.29 (br, 3H, NH and NH₂), 3.10 (m, 2H, NCH₂CH₂), 1.63 (m, 2H, CH₂CH₂CH₂), 1.45 (m, 2H, CH₂CH₂CH₃), 0.97 (t, $J = 7.4$ Hz, 3H, CH₂CH₃).

4) 4-Dodecyloxy-3,5-bis(2'-*n*-butylaminophenyliminomethyl)phenylacetylene (**1**)

A mixture of **5** (0.200 g, 0.580 mmol), **7** (0.220 g, 1.33 mmol) and Al₂O₃ (0.300 g, 2.90 mmol) in dry toluene (20.0 mL) was stirred for 18h at room temperature. After the mixture was filtered, the solvent was removed to yield a yellow solid. The crude product was purified by recrystallization in dry hexane to give **1** as a yellow solid. Yield: 64.9% (0.240 g). ¹H NMR (400MHz, CDCl₃, TMS, δ): 8.86 (s, 2H, HC=N), 8.37 (s, 2H, Ar H_a), 7.19 (t, $J = 7.4$ Hz, 2H, Ar H_b), 7.06 (d, $J = 7.6$ Hz, 2H, Ar H_c), 6.71(d, $J = 7.9$ Hz, 2H, Ar H_d), 6.67 (t, $J = 7.5$ Hz, 2H,

Ar H_e), 5.06 (s, 2H, NH), 3.95 (t, $J = 6.6$ Hz, 2H, OCH_2CH_2), 3.23 (m, 4H, $NHCH_2CH_2$), 3.14 (s, 1H, $HC\equiv C$), 1.84 (m, 2H, $OCH_2CH_2CH_2$), 1.71 (m, 4H, $NHCH_2CH_2CH_2$), 1.50~1.47 (m, 4H, $NH(CH_2)_2CH_2CH_3$), 1.33~1.25 (m, 18H, $CH_2(CH_2)_9CH_3$), 0.99 (t, $J = 7.4$ Hz, 6H, $NH(CH_2)_3CH_3$), 0.88 (t, $J = 6.8$ Hz, 3H, $O(CH_2)_{11}CH_3$); IR (KBr): 3317 (H-C \equiv), 2926 (CH), 2359 (C \equiv C), 1597 (C=N), 1446 cm^{-1} (N-C); UV-vis ($CHCl_3$): $\lambda_{max}(\epsilon) = 262$ (3300), 313 (1300), 436 nm (1150); Anal. calcd for $C_{42}H_{58}N_4O$: C 79.4, H 9.21, N 8.82, O 2.52; found: C 79.0, H 9.48, N 8.93, O 2.58.

5) 4-Dodecyloxy-3,5-bis(2'-methylaminophenyliminomethyl)phenylacetylene (**2**)

A mixture of **5** (0.200 g, 0.580 mmol), *N*-methyl-phenylenediamine (0.140 mL, 1.20 mmol) and Al_2O_3 (0.530 g, 5.20 mmol) in dry toluene (20.0mL) was stirred for 18h at room temperature. After the mixture was filtered, the solvent was removed to yield a yellow solid. The crude product was purified by recrystallization in dry hexane to give **2** as a yellow solid. Yield: 83.8% (0.270 g). 1H NMR (400MHz, $CDCl_3$, TMS, δ): 8.87 (s, 2H, $HC=N$), 8.39 (s, 2H, Ar H_a), 7.20 (t, $J = 7.5$ Hz, 2H, Ar H_b), 7.07 (d, $J = 6.7$ Hz, 2H, Ar H_c), 6.72(d, $J = 5.1$ Hz, 2H, Ar H_d), 6.67 (t, $J = 8.0$ Hz, 2H, Ar H_e), 5.08 (br, 2H, NH), 3.93 (t, $J = 6.6$ Hz, 2H, OCH_2CH_2), 3.13 (s, 1H, $HC\equiv C$), 2.95 (s, 6H, NCH_3), 1.81 (m, 2H, $OCH_2CH_2CH_2$), 1.40~1.15 (m, 18H, $CH_2(CH_2)_9CH_3$), 0.85 (t, $J = 6.8$ Hz, 3H, CH_2CH_3); IR (KBr): 3313 (H-C \equiv), 2924 (CH), 2345 (C \equiv C), 1597 (C=N), 1446 cm^{-1} (N-C); UV-vis ($CHCl_3$): $\lambda_{max}(\epsilon) = 267$ (3400), 320 (1460), 440 nm (1900). Anal. calcd for $C_{36}H_{46}N_4O$: C 78.5, H 8.42, N 10.2, O 2.90; found: C 78.3, H 8.43, N 10.2, O 2.79.

6) 4-Dodecyloxy-3,5-bis(2'-*n*-butylaminophenyliminomethyl)phenylacetylene (**3**)

A mixture of **5** (0.200 g, 0.580 mmol), 2-butoxyaniline (0.210 g, 1.30 mmol) and Al_2O_3 (0.300 g, 2.90 mmol) in dry toluene (20.0mL) was stirred for 18h at room temperature. After the mixture was filtered, the solvent was removed to yield a yellow solid. The crude product was purified by recrystallization in dry hexane to give **3** as a yellow solid. Yield: 84.1% (0.310 g). 1H NMR (400MHz, $CDCl_3$, TMS, δ): 8.82 (s, 2H, $HC=N$), 8.45 (s, 2H, Ar H_a), 7.16 (m,

2H, Ar H_b), 7.06 (m, 2H, Ar H_c), 6.98 (m, 4H, Ar H_d and H_e), 4.04 (t, $J = 6.6$ Hz, 4H, $OCH_2CH_2CH_2CH_3$), 3.97 (t, $J = 6.6$ Hz, 2H, $OCH_2CH_2CH_2CH_2$), 3.07 (s, 1H, $HC\equiv C$), 1.78 (m, 6H, $OCH_2CH_2CH_2CH_3$ and $OCH_2CH_2CH_2CH_2$), 1.49~1.47 (m, 6H, $O(CH_2)_2CH_2CH_3$ and $O(CH_2)_2CH_2CH_2$), 1.30~1.22 (m, 16H, $OCH_2CH_2CH_2(CH_2)_8CH_3$), 0.93 (t, $J = 7.4$ Hz, 6H, $OCH_2CH_2CH_2CH_3$), 0.86 (t, $J = 6.8$ Hz, 3H, $OCH_2CH_2CH_2(CH_2)_8CH_3$); UV-vis ($CHCl_3$): $\lambda_{max}(\epsilon) = 252$ (3500), 279 (2200), 360 nm (1200); Anal. calcd for $C_{42}H_{56}N_2O_3$: C 79.2, H 8.86, N 4.40, O 7.54; found: C 79.0, H 9.03, N 4.38, O 7.56.

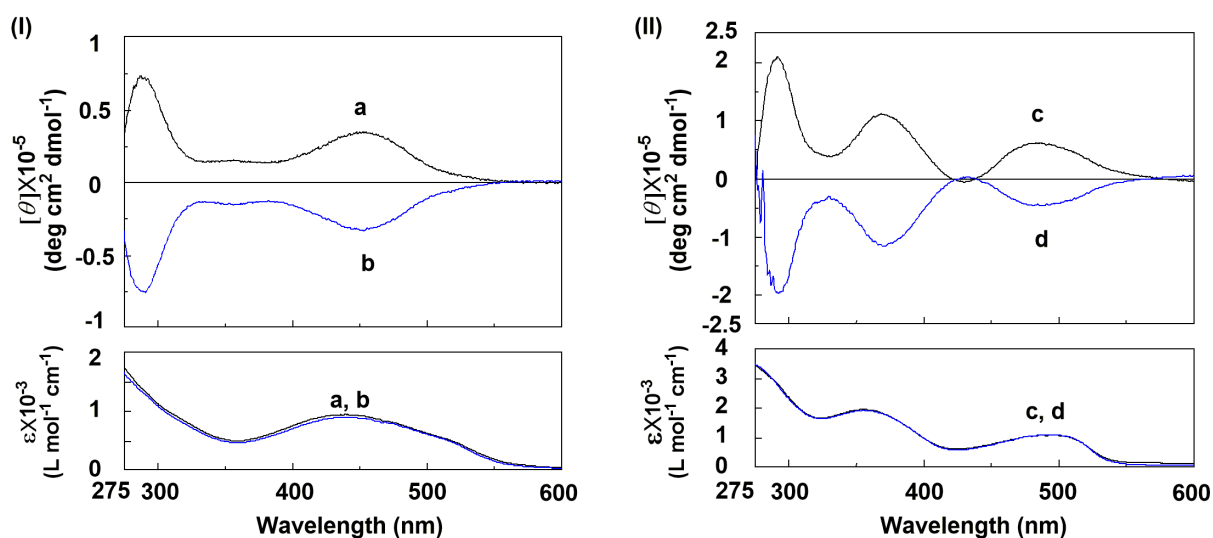


Fig. S1. CD and UV-vis spectra of (I) poly(2) by using (R)-PEA (a) and (S)-PEA (b) as a cocatalyst; (II) poly(3) by using (R)-PEA (c) and (S)-PEA (d) as a cocatalyst in THF.

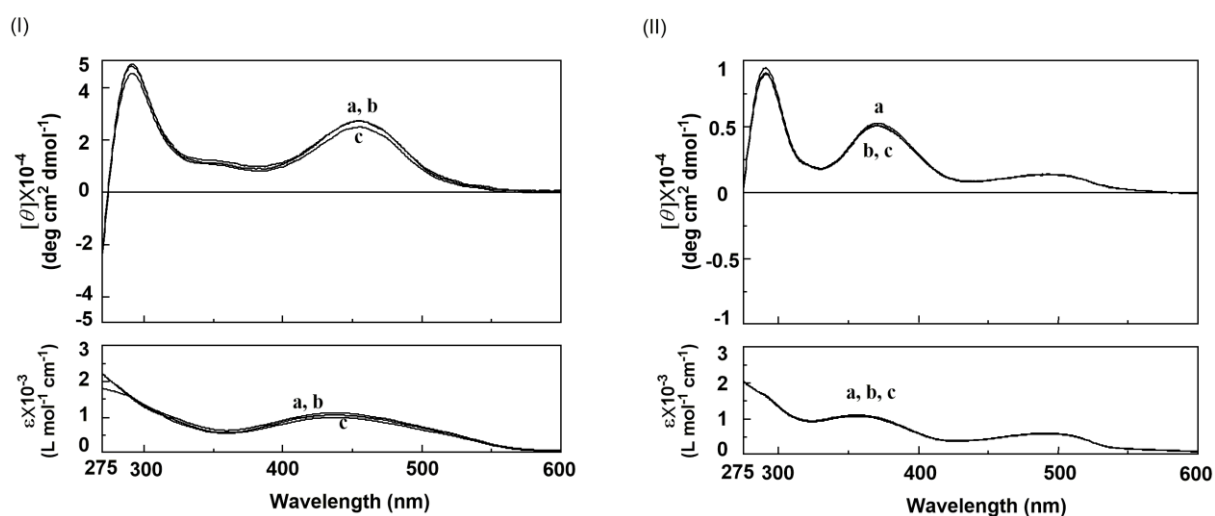


Fig. S2. CD and UV-vis spectra of poly(2) (I) and poly(3) (II) in (a) THF; (b) THF / DMSO = 95 / 5 (v / v); (c) THF / DMSO = 90 / 10 (v / v).

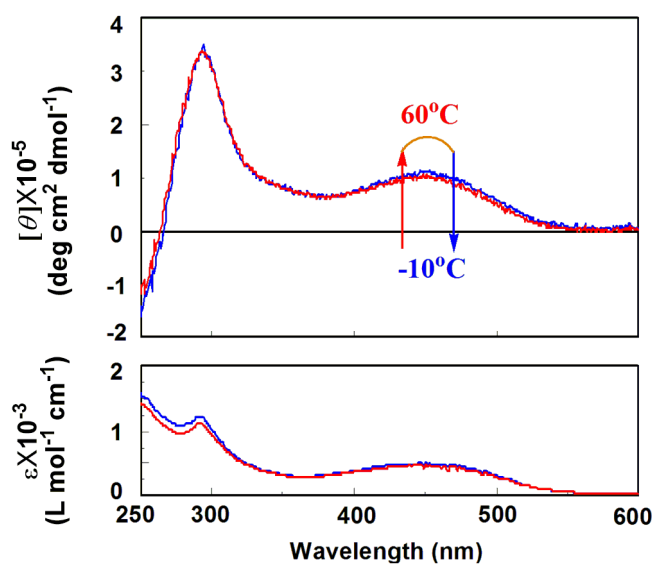


Fig. S3. Dependence of temperature on $[\theta]$ of poly(2) in THF.

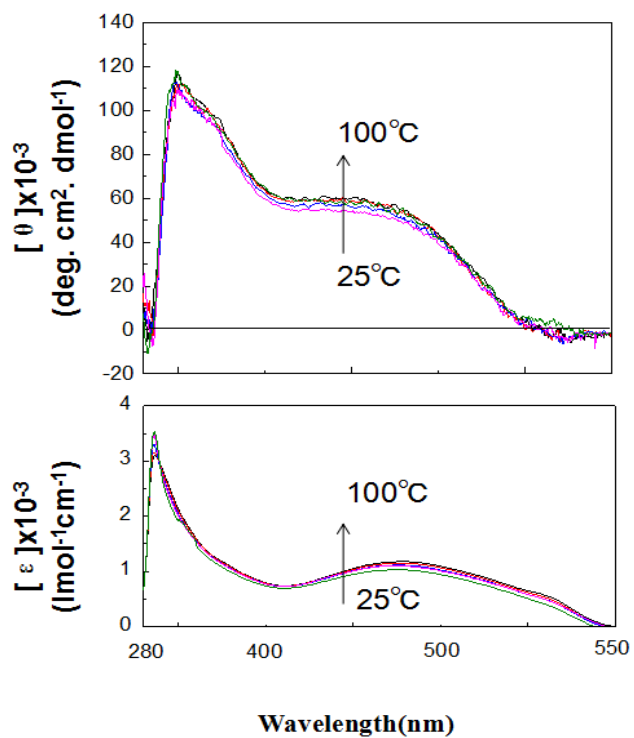


Fig.S4. CD and UV-vis spectra of poly(1) in toluene.(a) 25°C; (b) 40°C; (c) 60°C; (d) 80°C; (e)100°C.

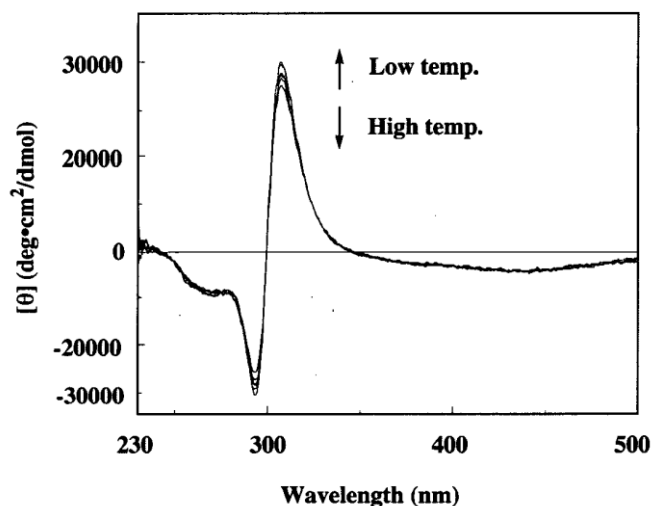


Fig. S5. Dependence of temperature on $[\theta]$ of poly(DoDHPA) in CHCl_3 .

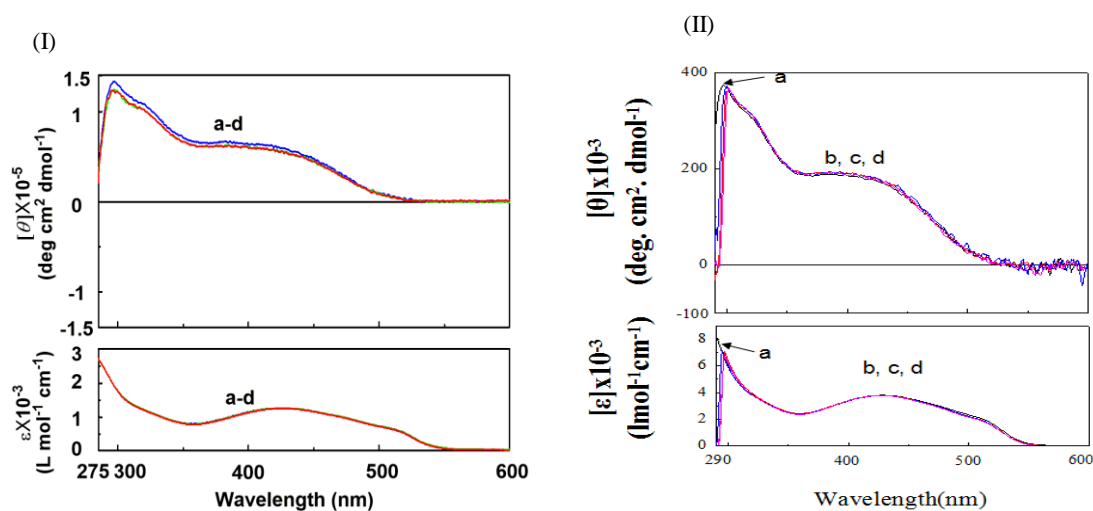


Fig.S6. CD and UV-vis spectra of poly(1) in (I) (a) CHCl_3 /hexamethylphosphoramide (HMPA) = 95 / 5 (v / v); (b) CHCl_3 / HMPA = 90 / 10 (v / v); (c) CHCl_3 / HMPA =80 / 20 (v / v); (d) CHCl_3 / HMPA =70 / 30 (v / v). (II) (a) CHCl_3 ; (b) CHCl_3 / Pyrimidine = 90 / 10 (v / v); (c) CHCl_3 / Pyrimidine =80 / 20 (v / v); (d) CHCl_3 / Pyrimidine =75 / 35 (v / v).

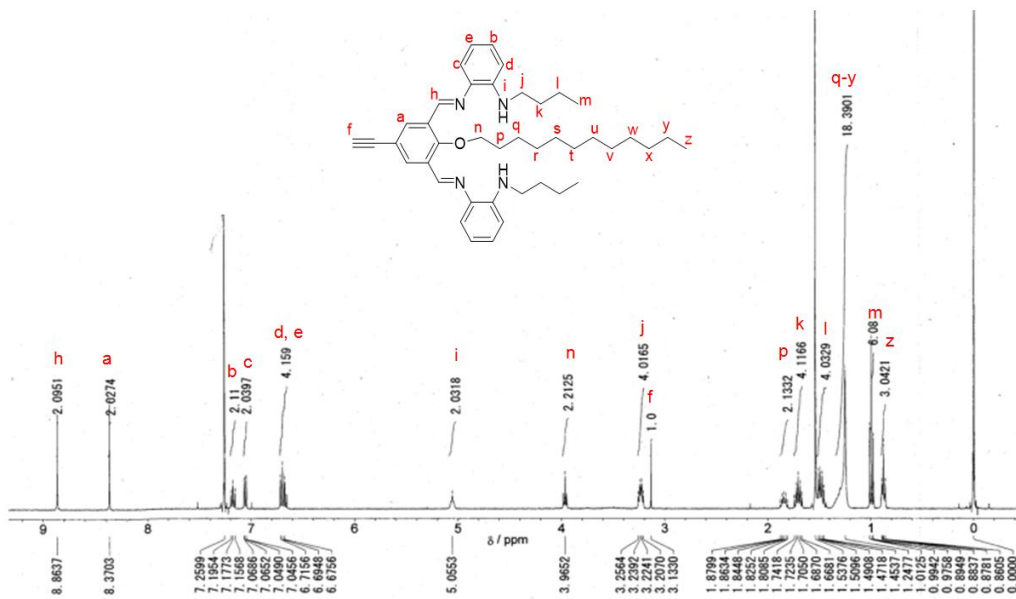


Fig.S7. $^1\text{H-NMR}$ spectra of monomer **1** in CDCl_3 .

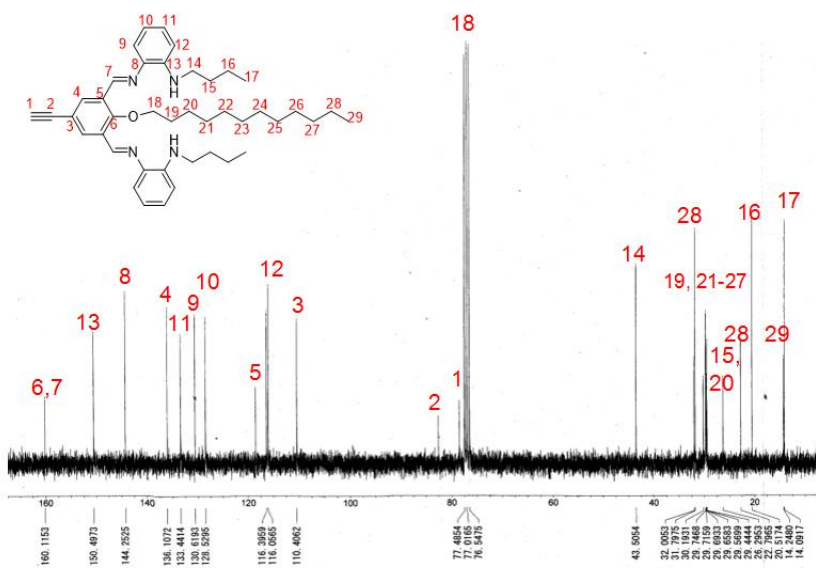


Fig8.S. $^{13}\text{C-NMR}$ spectra of monomer **1** in CDCl_3 .

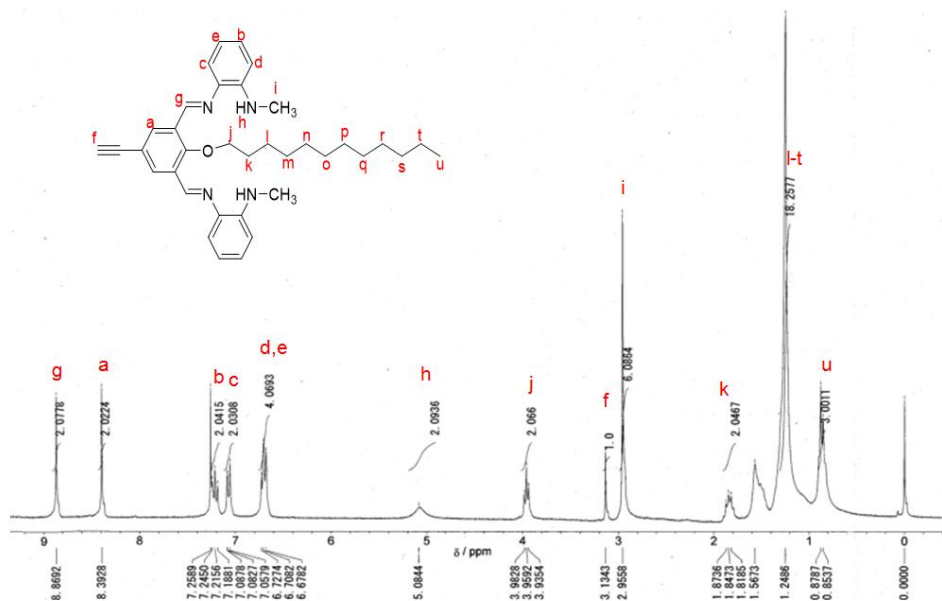


Fig.S9. ¹H-NMR spectra of monomer **2** in CDCl₃.

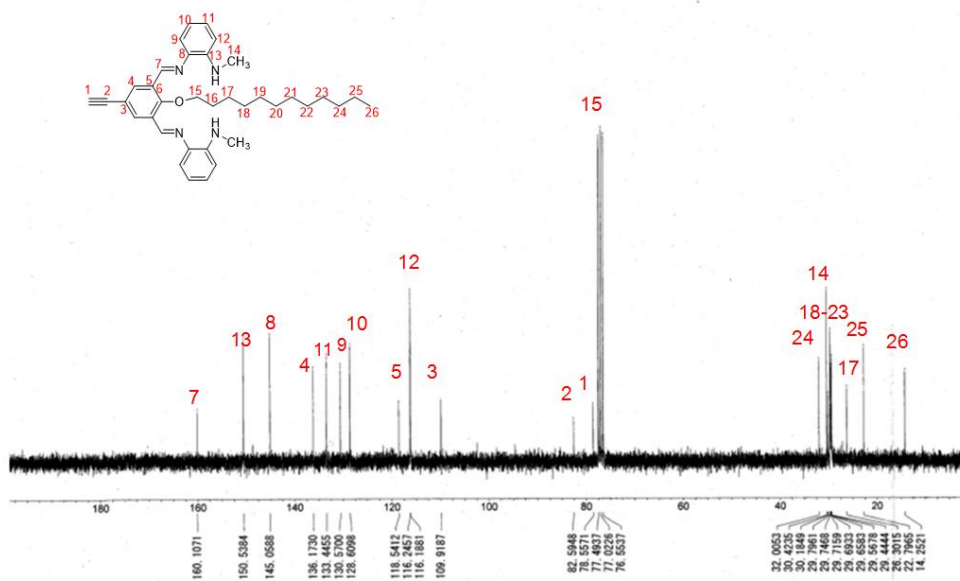


Fig.S10. ¹³C-NMR spectra of monomer **2** in CDCl₃.

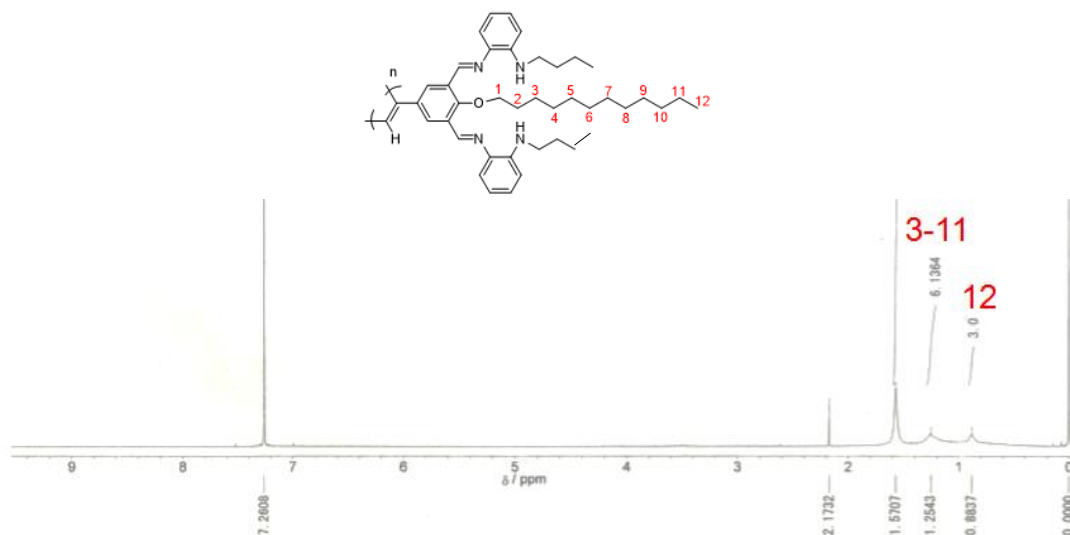


Fig.S13. $^1\text{H-NMR}$ spectra of poly(1) in CDCl_3 .

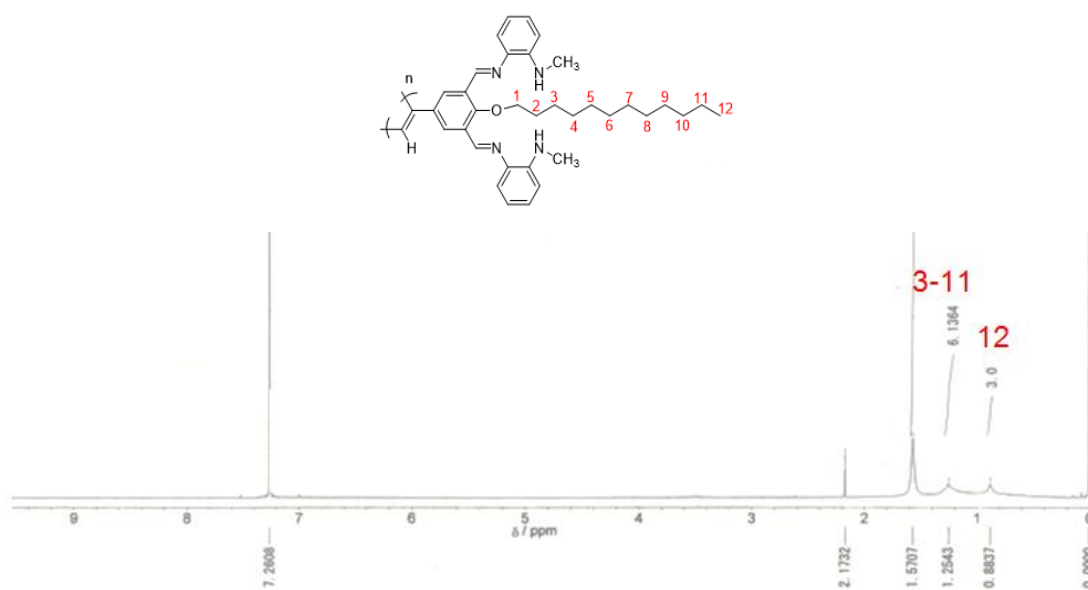


Fig.S14. $^1\text{H-NMR}$ spectra of poly(2) in CDCl_3 .

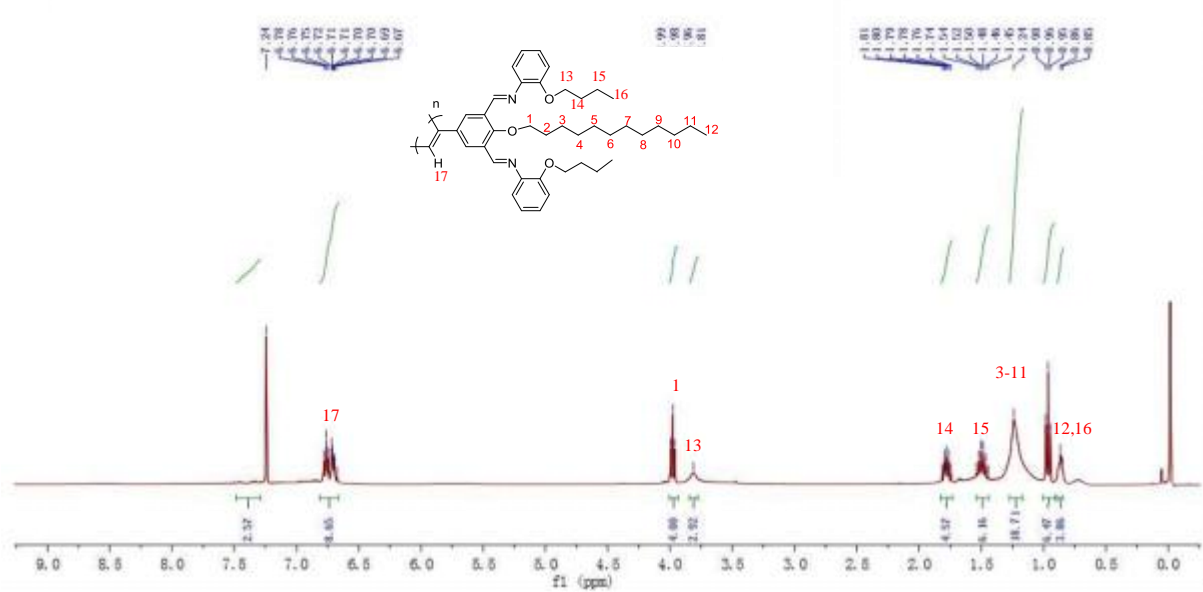


Fig.S15. $^1\text{H-NMR}$ spectra of poly(3) in CDCl_3 .

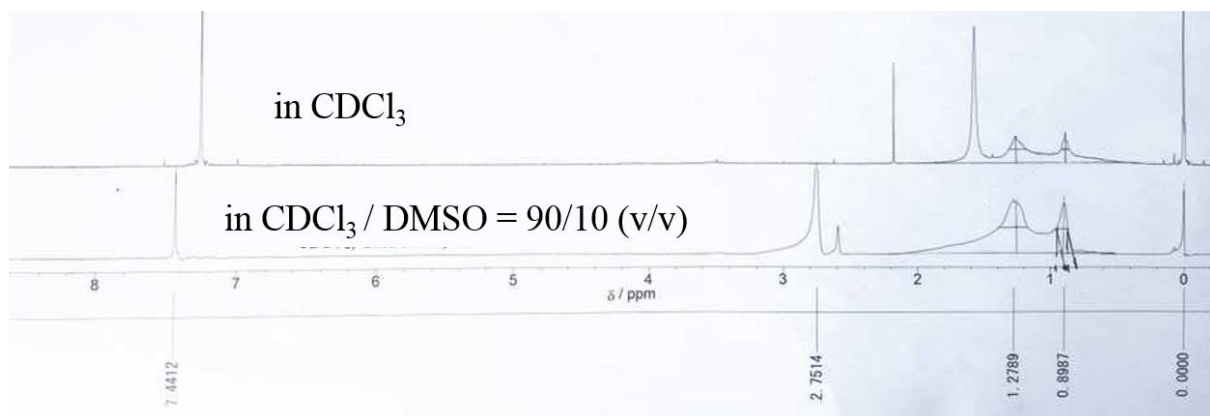


Fig.S16. $^1\text{H-NMR}$ spectra of poly(1) in CDCl_3 and $\text{CDCl}_3/\text{DMSO}=90/10(\text{v/v})$.

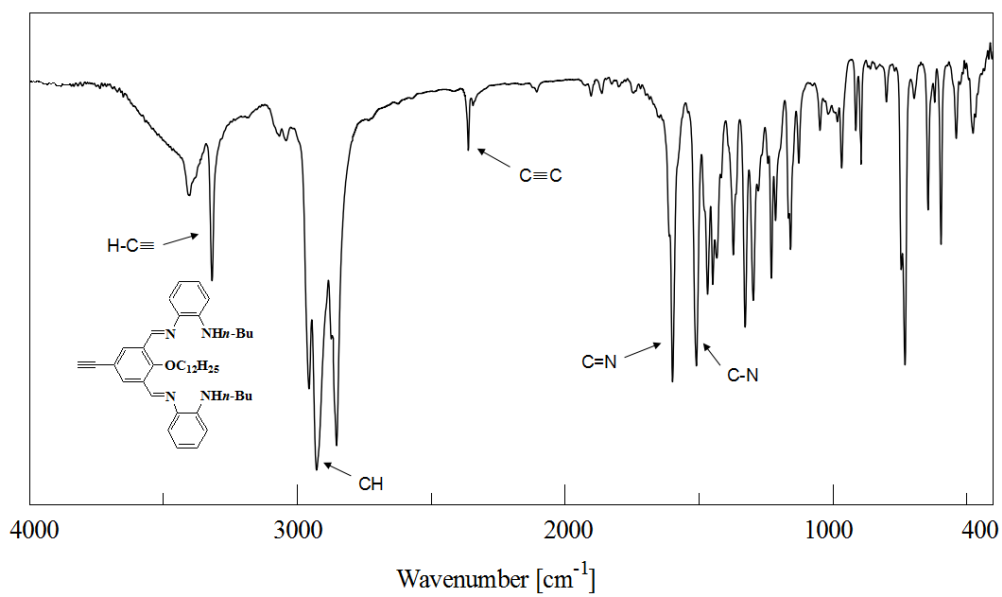


Fig.S17. FT-IR spectra of monomer **1**.

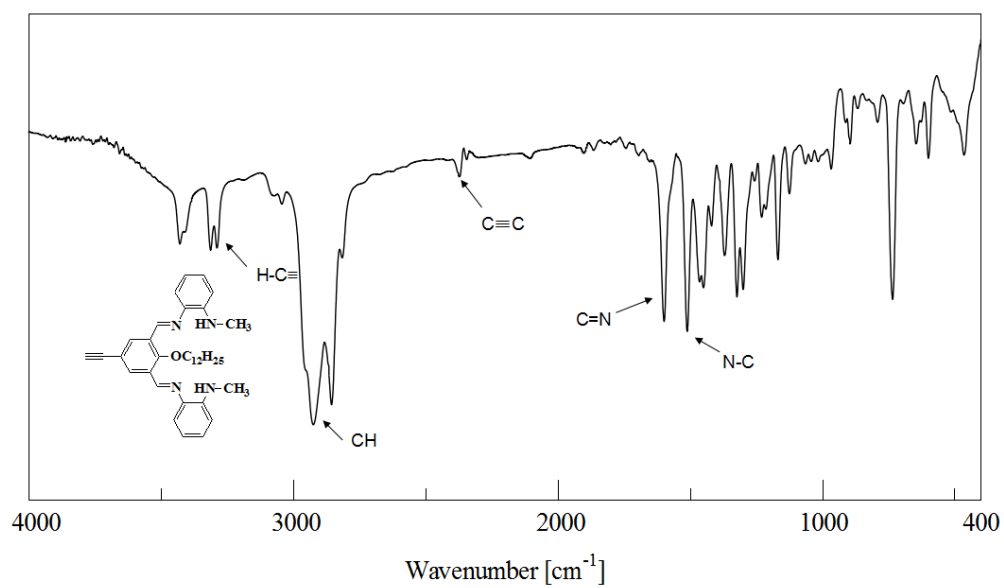


Fig.S18. FT-IR spectra of monomer **2**.

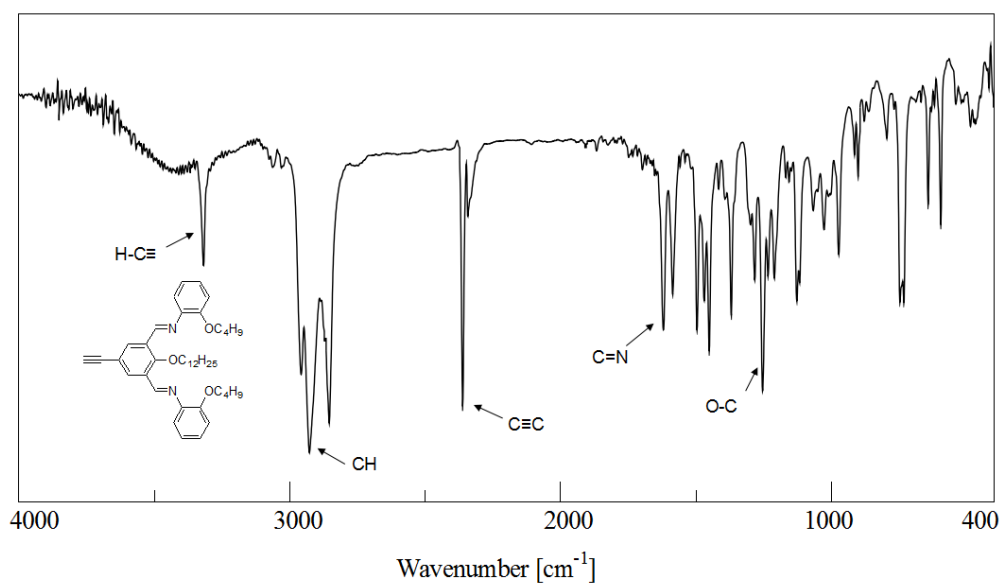


Fig.S19. FT-IR spectra of monomer **3**.

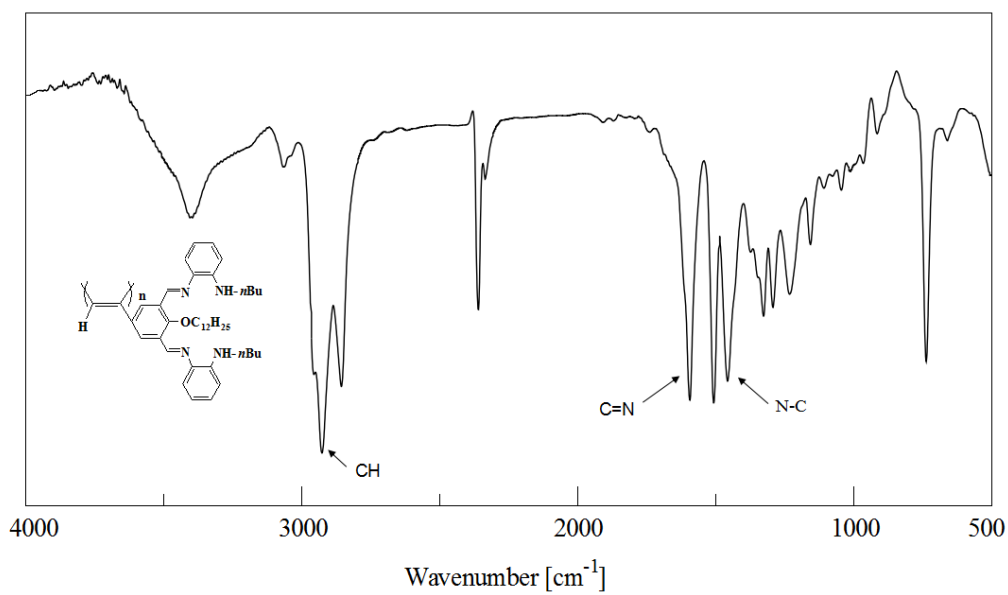


Fig.S20. FT-IR spectra of poly(**1**).

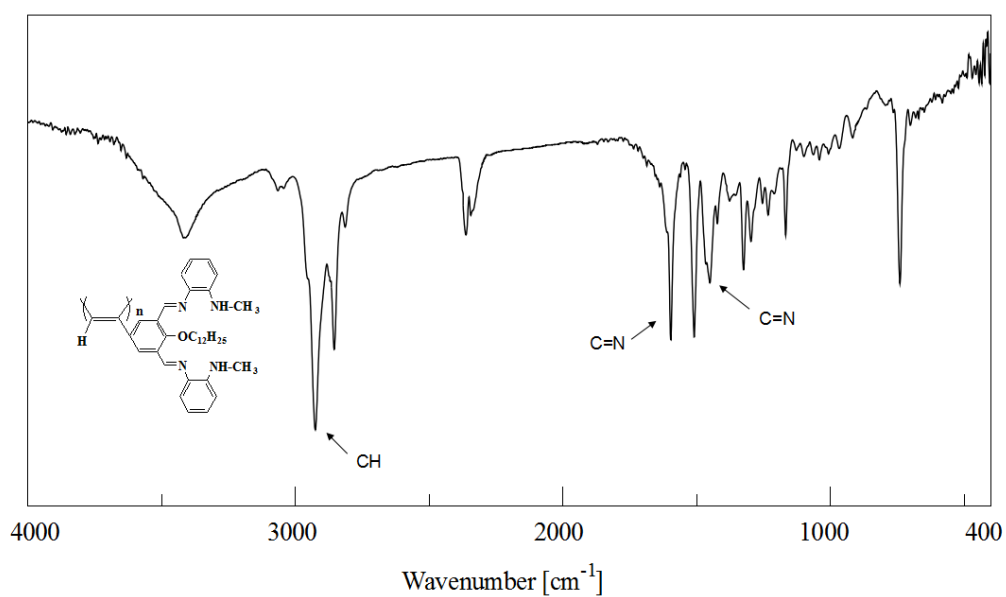


Fig.S21. FT-IR spectra of poly(2).

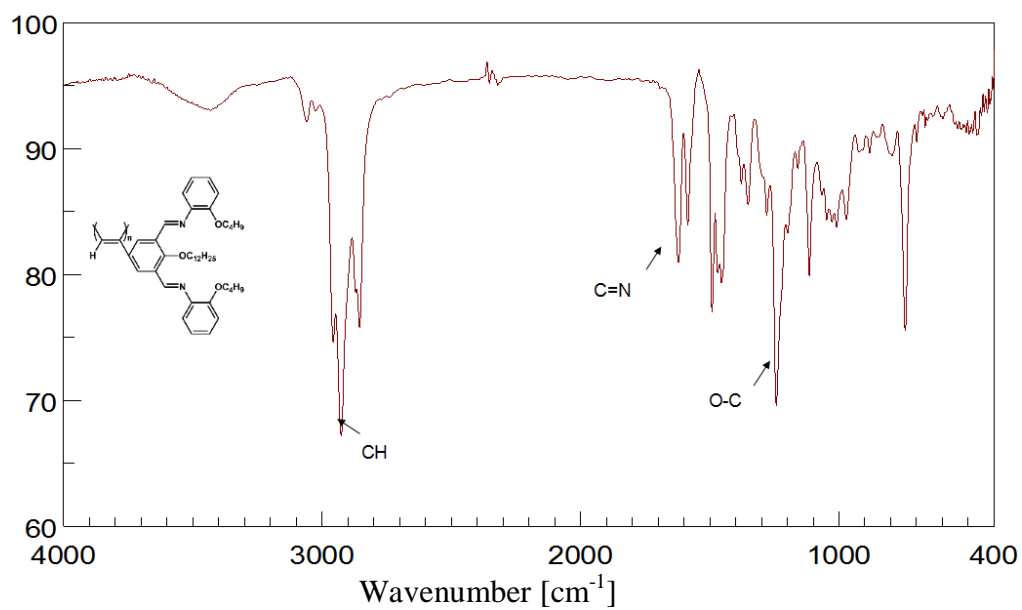


Fig.S22. FT-IR spectra of poly(3).

2. Estimation of the backbone rigidity by the peak width in NMR

2.1 Experimental results

Poly(**2**): ^1H NMR (400MHz, CDCl_3 , TMS, δ): 1.25 (br, $\Delta W_{1/2} = 0.15$ ppm, 18H, $\text{CH}_2(\text{CH}_2)_9\text{CH}_3$), 0.88 (br, $\Delta W_{1/2} = 0.083$ ppm, 3H, $\text{O}(\text{CH}_2)_{11}\text{CH}_3$), the other peaks were not detectable; IR (KBr): 2923 (CH), 1594 (C=N), 1448 cm^{-1} (N-C).

Poly(**3**): ^1H NMR (400MHz, CDCl_3 , TMS, δ): ^1H NMR (400MHz, CDCl_3 , δ): 1.25 (br, $\Delta W_{1/2} = 0.11$ ppm, 18H, $\text{CH}_2(\text{CH}_2)_9\text{CH}_3$), 0.88 (br, $\Delta W_{1/2} = 0.040$ ppm, 6H, $\text{O}(\text{CH}_2)_3\text{CH}_3$), 0.70 (br, $\Delta W_{1/2} = 0.080$ ppm, 3H, $\text{O}(\text{CH}_2)_{11}\text{CH}_3$), the other peaks were not detectable; IR (KBr): 2920 (CH), $1621(\text{C}=\text{N})$, 1455 cm^{-1} (C-O).

2.2 Discussion

The backbone of poly(DoDIPA) was thought to be very rigid because the peaks in NMR spectrum were very broad and the peaks about the main chain such as vinylene on the main chain and aromatic protons close to the main chain could not be detected (For the detail, see the experimental parts). The similar phenomena were observed for poly(DoDHPA) in non-polar solvent. Therefore, the stable one-handed helical polymer should have a rigid main chain. In addition, when DMSO was added to the CD solution of poly(DoDHPA) and the CD disappeared, undetectable peaks appeared and the width of broad peaks became sharper. On the other hand, in the case of poly(DoDIPA), no change happened in CD and NMR when adding DMSO. It also supports the stable main chain was kept by not hydrogen bonds.

3. Discussion of the reason for the stable chiral conformation of poly(DoDIPA) by semiempirical calculations

3.1 Calculation procedure

Semiempirical calculations were carried out on a PC equipped with an Inter (R) Core (TM) 2 processor (1.87 GHz) using Spartan Student v 5.0.0.0. All the conformations of monomers were calculated by MMFF.

The initial condition for the calculation of monomer energies and structures was as follows: the dihedral angles of C=N-Ar of monomers were constrained at 180°, 0° and -180° in advance, then the MMFF was used for optimization of monomer energies and structures. The results are shown in Table S1.

The initial condition for calculation of polymer energies and structures was as follows: the dihedral angles of polymer main chain were constrained at a different degree in advance, the MMFF level was used for optimization of polymers structures. Then, the dihedral angles of the polymer main chain were unconstrained, the MMFF calculation was carried out once again. The results are shown in Table S2.

3.2 Discussion

As mentioned above, RDIPAs were much better monomers than RDHPAs and **1** was the best in the three RDIPAs. Since RDIPAs had a bulky π -conjugated planar substituent, the one-handed helical main chains were thought to be stabilized by the steric hindrance. Therefore, the main chains were thought to be intrinsically stable.

In order to know more information of the reason for the best suitability of **1** for the HSSP, we calculated the energy of the four possible π -conjugated planar conformations, trans-transoid, trans-cisoid, cis-cisoid, and cis-transoid as shown in **Chart S1** of the three DoDIPA monomers (**1~3**) using MMFF (**Table S1**). There seems to be mainly two factors determinate the energy: steric repulsion between the dodecyl group and the N- or O-alkyl groups for the three monomers (**1~3**) and hydrogen bonds between the amino groups and imino group for the monomers **1** and **2**. Since the ether-containing monomer **3** can not make hydrogen bonds, the stability must be determined only by the steric repulsion. The increasing order of the energy of the conformation of monomer **3** was trans-cisoid < trans-transoid < cis-cisoid < cis-transoid as shown in **Table S1**. On the other hand, in the case of the amine-containing monomers **1** and **2** which can make intramolecular hydrogen bonds at trans-transoid and cis-

transoid conformations as shown in **Chart S1**, the orders were trans-transoid < trans-cisoid and cis-transoid < cis-cisoid which were different from those of **3**. The energy may be lowered by the hydrogen bonds in trans-transoid and cis-transoid as shown in **Fig. 3**. Therefore, the orders between trans-transoid and trans-cisoid, and cis-transoid and cis-cisoid were different between monomers **1**, **2** and **3**. As a result, trans-transoid had the lowest energy in the amine-containing monomers, **1** and **2**.

To stabilize one handed helical conformation of the resulting polymers of the HSSP of RDIPA, the conformer trans-transoid of a monomer unit is thought to be the best, because the trans-transoid conformer (**Fig. 3a**) can keep sterically the helicity more easily than the other conformers like cis-transoid (**Fig. 3b**). Therefore, the amine-containing monomers **1** and **2** having trans-transoid conformation as the most stable conformer were better monomers than **3**. When we compared **1** with **2**, the energy difference (ΔE) of **1** between the lowest and the second lowest was higher than **2** (**Table S1**). Therefore, monomer **1** may be the best.

To confirm this speculation, that is, the conformer trans-transoid was the best, the energies of the polymers of trans-transoid and trans-cisoid of **1** were calculated (**Table S2**). As a result, the former one was more stable. Therefore, monomer **1** was the best. It was supported by the experimental facts that **1** showed the best results in the HSSP.

In summary, chiral induction efficiency during the HSSP of monomer **1** having two longer alkyl groups via imino and amino groups was the highest because the monomer can take a conformation (trans-transoid) which are favorable to stabilize sterically the one-handed helical conformation of the resulting polymers.

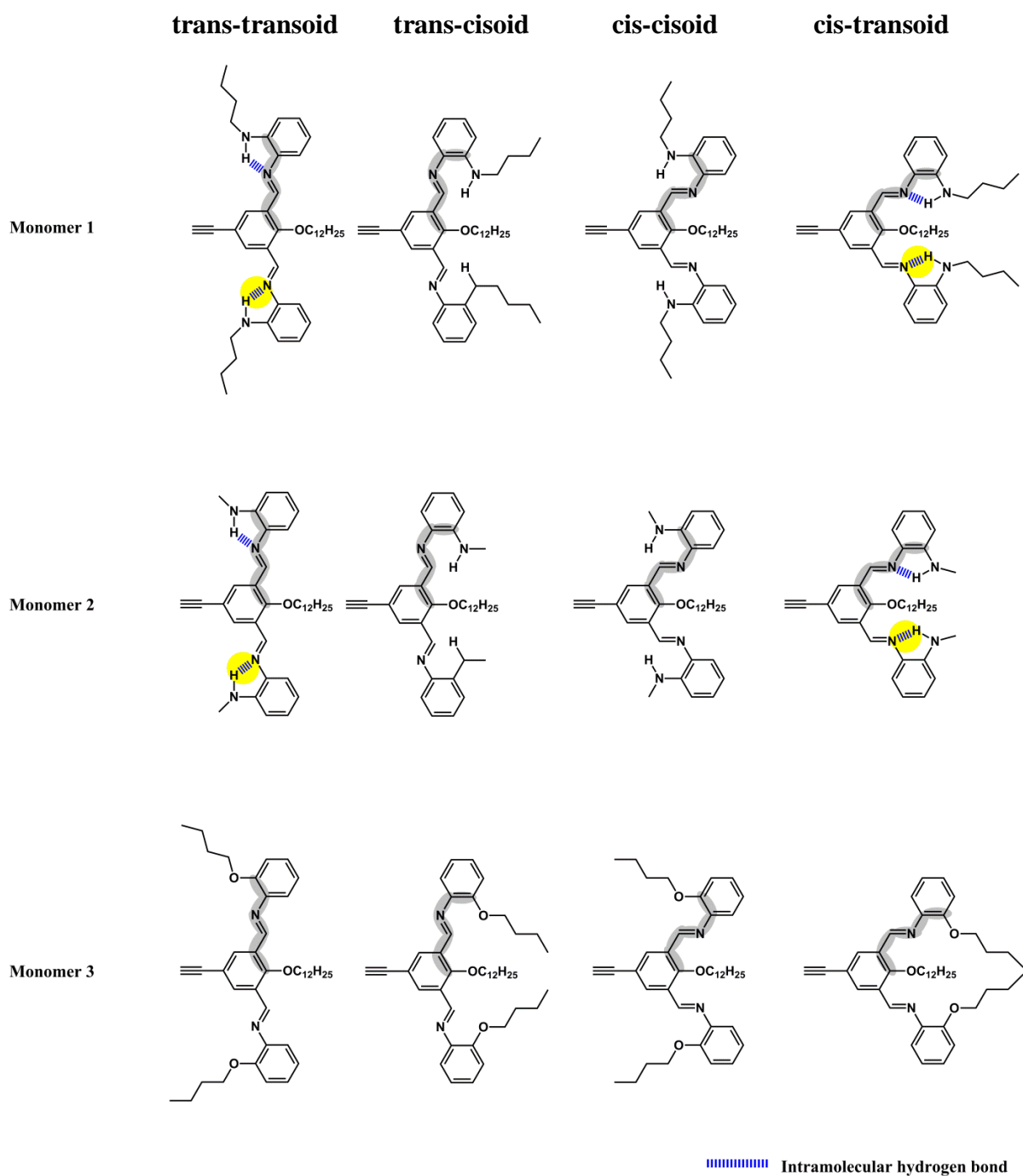


Chart S1. Possible π -conjugated planar conformations of DoDIPA monomers (1~3).

Table S1. Calculation data of π -conjugated planar structures of DoDIPA monomers (1~3) by MMFF.

Monomer	Energy [kJ/mol]				ΔE^b [kJ/mol]
	trans-transoid ^{a)}	trans-cisoid ^{a)}	cis-cisoid ^{a)}	cis-transoid ^{a)}	
1	331.42	410.04	591.64	480.29	79
2	352.35	437.45	495.32	405.43	53
3	412.55	393.45	452.29	475.51	19

^{a)}For the conformation, see Chart S1; ^{b)}The energy difference between conformation having the lowest energy and the second lowest energy.

Table S2. Calculation data of 3D structures of poly(1) by MMFF.

Conformation ^{a)}	Dihedral angle [$^\circ$] ^{b)}		Energy [kJ/mol]	Dihedral angle [$^\circ$] ^{b)}		Energy [kJ/mol]
	A (constrained)	B		A (unconstrained)	B	
trans-transoid	110	-58.16	2350	123.27	-70.10	2310
trans-cisoid	120	-65.54	6540	111.67	-54.46	2679

^{a)}See Chart S1; ^{b)}See Chart S2

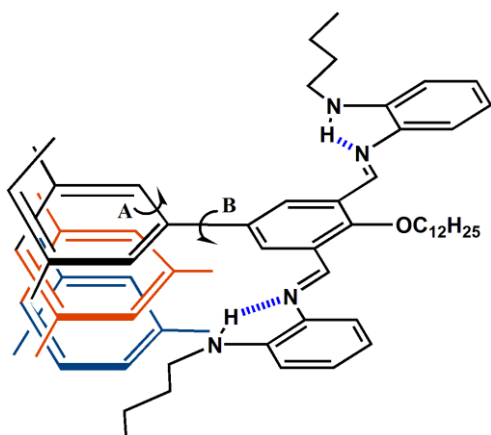


Chart S2. Dihedral angles of A (main chain) and B (side chain) of poly(1).