

Supporting Information

**Exact Helical Polymer Synthesis by Directionally Fixed Connection of
 C_2 -Chiral 9,9'-Spirobifluorene Unit with C_2 - or C_5 -Symmetric Unit**

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I. Experimental Section

1. Materials

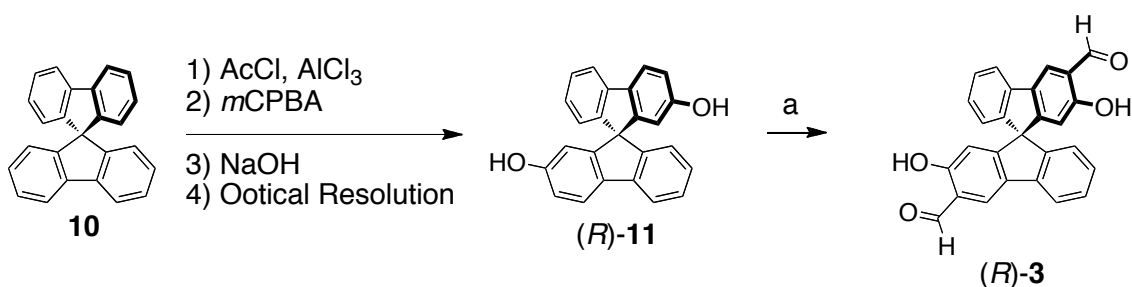
CH₂Cl₂ was purchased from Asahi Glass Co., Ltd. (Tokyo, Japan) and dried over freshly activated molecular sieves 4A (MS 4A). MeOH was purchased from Kanto Chemical Co. Inc. (Tokyo, Japan). Hexamethylenetetramine, NaBH₄, Zn(OAc)₂·2H₂O, and 1,6-diaminohexane (**4**) were purchased from Wako Pure Chemicals Industries, Ltd. (Osaka, Japan). Trifluoroacetic acid was purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). (*R*)-(+)-2,2'-Dihydroxy-9,9'-spirobifluorene (**11**) was prepared according to the literature¹ and the optical purity was checked by a chiral column (CHIRALPAC[®] AD-H, eluent : hexane/*i*-PrOH = 4/1, flow rate 1.0 mL/min). Compounds **12**² and **13**³ was prepared according to the literatures. Other commercially available materials were used without further purification.

2. Characterization

¹H- and ¹³C NMR spectra were recorded on a JEOL AL-400 spectrometer using CDCl₃ as the solvent and with tetramethylsilane as the internal standard. The glass transition temperatures (*T*_g) were taken with a Shimadzu DSC-60 instrument at a heating rate of 10 °C/min under a nitrogen flow (flow rate: 50 mL/min). The thermogravimetric analysis (TGA) was performed

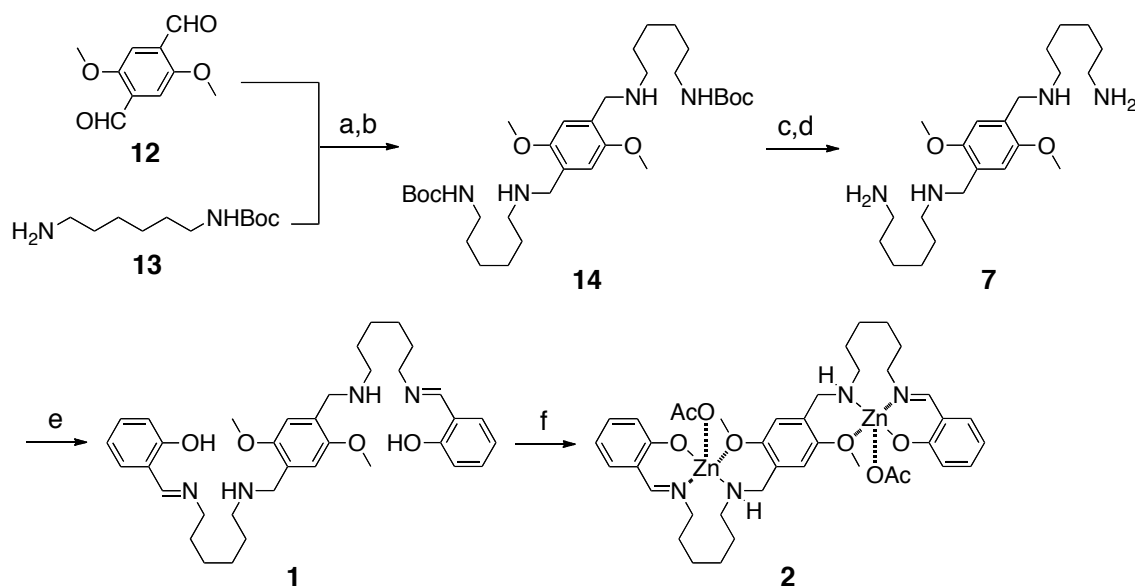
with a Shimadzu TGA-50 instrument at a heating rate of 10 °C/min under nitrogen atmosphere (flow rate 50 mL/min). FT-IR spectra were recorded on a JASCO FT/IR-460 Plus spectrophotometer. Melting points were measured with a Stuart Scientific SMP3. MALDI–TOF MS spectra were taken on a Shimadzu BIOTECH, AXIMA Performance mass spectrometer, where an aqueous solution of α -cyano-4-hydroxycinnamic acid (CHCA) in the presence of 1 vol% CF₃COOH was used as a matrix solution. FAB HR-MS spectra were obtained at National University Corporation Tokyo Institute of Technology Center for Advanced Materials Analysis on request. Ultraviolet-visible (UV-vis) spectra were recorded on a JASCO V-550 UV-vis spectrometer. Circular dichroism (CD) spectra were recorded on a JASCO J-820 CD spectrometer. Specific optical rotations were measured on a JASCO DIP-1000 digital polarimeter in a 10 cm cuvette. MM2 conformational analyses of polymers were carried out using CAChe version 6.1.12 for Windows.

3. Experimental Procedure



Scheme S1. Synthesis of C₂-chiral unit **(R)-3**. Reagents and conditions: a)

Hexamethylenetetramine (400 mol%), CF₃COOH, 80 °C, 1 d, 60% yield.

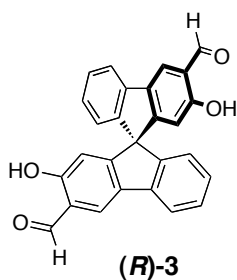


Scheme S2. Synthesis of model bis(Zn salalen complex) **2**. Reagents and conditions: a)

CH₂Cl₂, 25 °C, 12 h, quant. b) NaBH₄, MeOH, 0 °C, 1 h. c) 3 M aq HCl–Et₂O, 25 °C, 40 min.

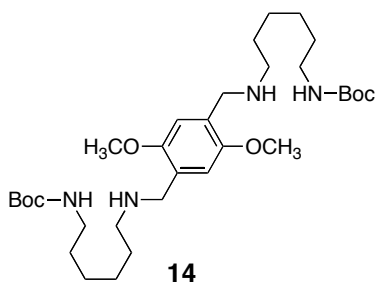
d) 4 M aq NaOH–Et₂O, 25 °C, 10 min, 32% yield for three steps. e) Salicylaldehyde (1.0 equiv.),

toluene, reflux, quant. f) Zn(OAc)₂ (200 mol%), THF, 25 °C, 10 min. quant.



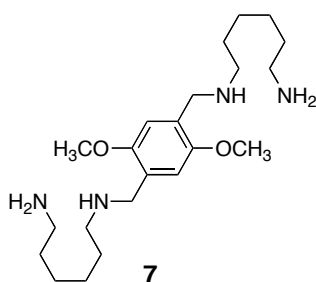
Synthesis of 2,2'-dihydroxy-3,3'-diformyl-9,9'-spirobifluorene ((**R**)-**3**). A solution of (**R**)-**11** (10.0 g, 28.7 mmol) and hexamethylenetetramine (16.1 g, 115 mmol) in trifluoroacetic acid (100 mL) was stirred for 24 h at 80 °C. To the mixture was quenched by the addition of water. The mixture was stirred for 12 h at 80 °C, cooled to room temperature, and extracted with CH₂Cl₂ (× 3). The combined organic layer was washed with brine, dried over MgSO₄, filtrated, and concentrated *in vacuo*. The crude mixture was purified by a silica gel column chromatography (eluent: hexane/CH₂Cl₂ = 1/1) to give (**R**)-**3** as yellow solids (6.97 g, 17.2 mmol, 60%): mp 255.0–257.0 °C; *R_f* value 0.2 (eluent: hexane/CH₂Cl₂ = 1/1); [α]_D²⁵ +50.7 (*c* = 0.10, CHCl₃); ¹H NMR (400 MHz, 293 K, CDCl₃, δ): 11.19 (s, 2H, Ph–OH), 10.02 (s, 2H, Ph–CHO), 8.00 (s, 2H, Ph–H), 7.83 (d, *J* = 7.6 Hz, 2H, Ph–H), 7.42 (ddd, *J* = 7.6, 7.6, 1.0 Hz, 2H, Ph–H), 7.13 (ddd, *J* = 7.6, 7.6, 1.0 Hz, 2H, Ph–H), 6.76 (d, *J* = 7.6 Hz, 2H, Ph–H), 6.36 (s, 2H, Ph–H) ppm; ¹³C NMR (100 MHz, 293 K, CDCl₃, δ): 196.1, 162.1, 158.1, 146.9, 140.0, 133.9, 128.5, 127.9, 124.5, 124.2, 120.2, 119.7, 113.4, 66.1 ppm; IR (KBr) ν 2841 (w, OC–H), 1648 (s, C=O), 1445 (m, C=C), 1333 (m, O–H), 1171 (m, Ph–O) cm⁻¹; FAB HR-MS (*m/z*):

$[M+Na]^+$ calc'd for $C_{27}H_{16}O_4Na^+$, 427.0946; found, 427.0951; UV (THF) λ_{max} , nm (ϵ): 258 (60200).

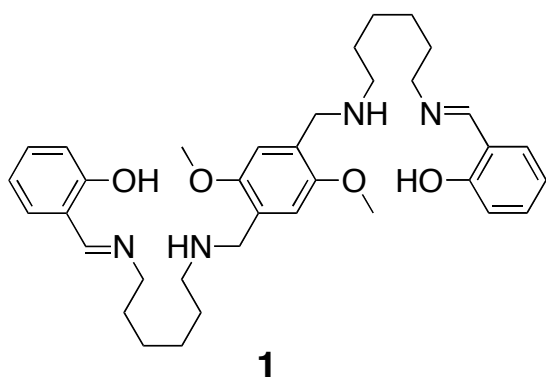


Synthesis of **14**. To a solution of **13** (2.65 g, 12.3 mmol) in CH_2Cl_2 (100 mL) was added a solution of **12** (880 mg, 4.53 mmol) in CH_2Cl_2 (50 mL) for 1 h and the mixture was stirred for 20 h at room temperature. The mixture was concentrated *in vacuo* to give the corresponding imine as a brown oil (2.97 g, 5.03 mmol, quant.). The crude material was used for next reaction without further purification: 1H NMR (400 MHz, 293 K, $CDCl_3$, δ): 8.67 (s, 2H, $-N=CH-$), 7.50 (s, 2H, Ph-*H*), 4.56 (s, 2H, N-*H*), 3.89 (s, 6H, $-OCH_3$), 3.84 (t, $J = 5.5$ Hz, 4H, $=N-CH_2-$), 3.62 (t, $J = 6.9$ Hz, 2H, $-NHCH_2-$), 1.44–1.27 (m, 34H, $-CH_2-$, $-C(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, 293 K, $CDCl_3$, δ): 156.5, 153.0, 127.3, 109.3, 108.6, 78.9, 61.9, 56.1, 42.0, 40.5, 33.5, 30.9, 30.0, 28.4, 27.0, 26.6 ppm; IR (KBr) ν 3361 (s, N-*H*), 2930 (m, C-*H*), 1697 (s, C=O, C=N), 1525 (m, C=C), 1410 (m, C=C), 1365 (m, C=C), 1172 (s, C-N), 1043 (Ph-O) cm^{-1} .

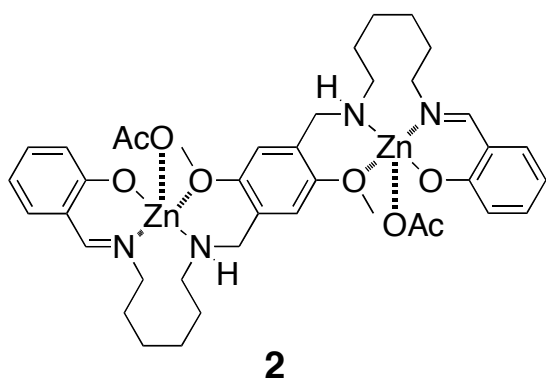
A solution of the imine (2.43 g, 8.24 mmol) in MeOH (200 mL) was stirred at 0 °C. To the solution was added portionwise NaBH₄ (623 mg, 153 mmol) at 0 °C and stirred for 1 h. The reaction was stopped by the addition of sat. aq. NaHCO₃ and the resulting mixture was concentrated *in vacuo*. The products were dissolved with CH₂Cl₂, washed with brine, dried over MgSO₄, filtrated, and concentrated *in vacuo*. The crude mixture was purified by a silica gel column chromatography (eluent: MeOH/CH₂Cl₂ = 1/9 with 1 vol% Et₃N) to give **14** as white solids (958 mg, 1.61 mmol, 39%): mp 196.5–197.3 °C; *R_f* value 0.1 (eluent: CH₂Cl₂:MeOH = 9:1); ¹H NMR (400 MHz, 293 K, CDCl₃, δ): 9.45 (s, 2H, Ph–CH₂NH–), 7.39 (s, 2H, Ph–H), 4.61 (s, 2H, –NH–CO–), 3.93 (s, 6H, Ph–OCH₃), 3.56 (s, 2H, Ph–CH₂–), 3.07 (t, *J* = 7.0 Hz, 4H, –CH₂NHCH₂–), 2.34 (t, *J* = 7.0 Hz, 4H, –CONHCH₂–), 1.86–1.83 (m, 4H, –CH₂NHCH₂CH₂–), 1.43 (s, 18H, –C(CH₃)₃), 1.36–1.30 (m, 12H, –CH₂–) ppm; ¹³C NMR (100 MHz, 293 K, CDCl₃, δ): 155.9, 151.6, 120.7, 114.5, 78.9, 56.6, 46.4, 44.2, 40.2, 29.6, 28.4, 26.2, 26.0, 25.6 ppm; IR (KBr) ν 3367 (br, N–H), 2931 (s, C–H), 1691 (s, C=O), 1507 (s, C=C), 1460 (s, C=C), 1406 (s, C=C), 1213 (s, C–N), 1044 (s, Ph–O) cm⁻¹.



Synthesis of **7**. A solution of **14** (185 mg, 0.312 mmol) in Et₂O (50 mL) and 3 M aq. HCl (50 mL) was stirred for 40 min at room temperature. To the solution was added portionwise NaOH (8.0 g) at 0 °C until the solution became basic. The resulting mixture was extracted with Et₂O (× 3). The combined organic layer was washed with water and brine, dried over MgSO₄, filtrated, and concentrated *in vacuo* (99.5 mg, 0.252 mmol, 81%) to give **7** as a yellow oil: ¹H NMR (400 MHz, 293 K, CDCl₃, δ): 6.80 (s, 2H, Ph-*H*), 3.79 (s, 6H, -OCH₃), 3.73 (s, 4H, Ph-CH₂-NH-), 2.66–2.64 (m, 4H, -NH-CH₂-CH₂-), 2.58–2.56 (m, 4H, -CH₂-NH₂), 1.58 (m, 22H, -CH₂-, -NH₂-, -NH-) ppm; ¹³C NMR (100 MHz, 293 K, CDCl₃, δ): 151.4, 127.8, 112.7, 56.0, 49.4, 42.2, 33.8, 30.1, 27.2, 26.8 ppm; IR (NaCl) ν 3421 (s, NH), 2930 (m, C-H), 1561 (m, C=C) cm⁻¹; FAB HR-MS (*m/z*): [M+Na]⁺ calc'd for C₂₂H₄₂N₄O₂Na⁺, 417.3200; found, 417.3218.



Synthesis of **1**. A solution of **7** (100 mg, 0.237 mmol) and salicylaldehyde (58.7 mg, 0.478 mmol) in toluene (20 mL) was poured into the round-bottle flask connected with Dean–Stark trap, and the mixture was refluxed for 12 h to remove water. After cooling to room temperature, the solvent was removed by evaporation. The resulting crude material was washed with hexane and dried *in vacuo* to give **1** (140 mg, 92%) as a yellow oil: ^1H NMR (400 MHz, 293 K, CDCl_3 , δ): 8.32 (s, 2H), 7.56–6.65 (m, 10H), 4.56 (s, 2H), 3.79–3.56 (m, 10H), 3.08 (brd, 4H), 2.61 (brd, 4H), 1.31–1.23 (m, 16H) ppm; ^{13}C NMR (100 MHz, 298 K, CDCl_3 , δ): 161.6, 151.6, 151.6, 137.0, 133.7, 129.1, 128.2, 119.8, 117.6, 59.4, 56.0, 40.3, 30.8, 30.0, 28.4, 26.6, 26.8 ppm; IR (KBr) ν 3384, 2927, 1700, 1635, 1559, 1457, 1043 cm^{-1} ; MALDI–TOF MS (m/z): $[\text{M}+\text{K}]^+$ calc'd for $\text{C}_{38}\text{H}_{50}\text{N}_4\text{NaO}_4^+$, 625.3724; found, 625.3703.

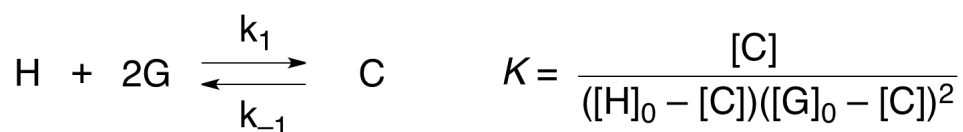


Synthesis of **2**.

To a solution of **1** (5.5 mg, 9.13 μmol) in THF (1.0 mL) was added $\text{Zn}(\text{OAc})_2 \cdot 6\text{H}_2\text{O}$ (4.0 mg, 18.3 μmol) and the mixture was stirred for 2 h and concentrated *in vacuo*. The resulting crude material was washed with hexane and dried *in vacuo* to give **2** as a yellow solid: ^1H NMR (400 MHz, 293 K, CDCl_3 , δ): 7.89 (s, 2H), 7.25–6.95 (m, 10H), 4.65 (s, 4H), 3.79–3.74 (m, 8H), 3.08–2.85 (m, 8H), 2.06 (s, 6H), 1.85 (m, 4H), 1.43–1.25 (m, 12H) ppm; IR (KBr) ν 3352, 2927, 1692, 1590, 1413, 1258 cm^{-1} ; MALDI-TOF MS (m/z): $[\text{M}+\text{TFA}+\text{H}]^+$ calc'd for $\text{C}_{42}\text{H}_{56}\text{F}_3\text{N}_4\text{O}_{10}\text{Zn}_2^+$, 961.25; found, 961.64.

Determination of association constants of **2**: The stoichiometry of the **1**-Zn complex is 1:2, which was evaluated by a Job's plot between **1** and $\text{Zn}(\text{OAc})_2$ (see, main text). In ^1H NMR spectrum of **2** in CDCl_3 , chemical exchange between free **1** and complexed species was fast on an NMR timescale. Thus, NMR titrations were performed by using solutions which had a

constant concentration of **1** (0.08 M) and varying concentrations of Zn(OAc)₂. For the evaluation of the association constant of **2**, the peak shift of the methoxy proton signal was utilized. By the following equations, the association constant for **2** in CDCl₃ was estimated to be 148.6 M⁻¹ for 1:2 stoichiometry:



, where [H]₀ and [G]₀ are the initial concentrations of host **1** and guest {Zn(OAc)₂}. The magnitude of this difference (Δδ = δ_h - δ_c) gives information about the structure of the complex.

Then, due to the relationship (equation 1),

$$n_c = \frac{\delta_h - \delta}{\delta_h - \delta_c} \quad \text{eq 1}$$

we can use the observed chemical shift δ to obtain the value of n_c and the following equation 2.

$$[\text{C}] = n_c[\text{H}_0] \quad \text{eq 2}$$

Therefore, K can be rewritten as

$$K = \frac{n_c[\text{H}_0]}{([\text{H}]_0 - n_c[\text{H}_0])([\text{G}]_0 - n_c[\text{H}_0])^2} \quad \text{eq 3}$$

ω B97X-D/6-31G(d) optimized geometry and energy of **2**.

Total Electronic energy = -5935.41124597 au

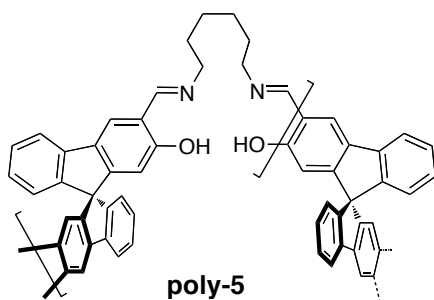
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C	0.95748200	-0.76814000	-0.82706300
C	0.00346200	-1.75762600	-0.61854200
C	-0.96023700	-1.63100400	0.37973100
O	1.87811000	1.30507900	-0.29167000
O	-1.89590500	-2.59315800	0.65287200
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H	5.58777800	-4.34634500	2.44741200
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H	-4.19065700	1.67172300	3.53657400
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H	2.74168600	3.07655500	0.04194300
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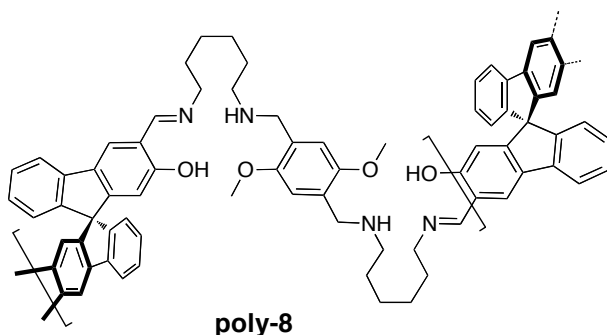
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H	6.01647300	5.15267200	-2.34899900
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H	-0.94175400	3.65943800	-1.38540300
H	3.17111800	1.19665300	4.08281100
H	3.08628300	-0.59057800	4.16291200
H	1.77570500	0.30644300	3.40091100

Typical procedure for the polycondensation of aldehyde and amine to give the poly(Schiff base): Synthesis of **poly-5**:



A mixture of **(R)-3** (53.2 mg, 0.132 mmol) and **4** (15.3 mg, 0.132 mmol) in CH₂Cl₂ (0.7 mL) was stirred for 30 min at room temperature. The reaction mixture was quenched by precipitation into hexane to give yellow solids. The solids were collected by filtration and dried *in vacuo* to give **poly-5** (64.0 mg, 0.132 mmol, 100%) as a yellow solid: M_w 5,100; M_n

3,600 (estimated by the peak distribution of MALDI-TOF MS); T_g 232 °C; T_{d5} 373 °C; $[\alpha]_D^{25}$ +68.4 ($c = 0.10$, CHCl_3); $^1\text{H NMR}$ (400 MHz, 293 K, CDCl_3 , δ): 13.84 (s, 2H, -OH), 8.39 (s, 2H, -N=C-H), 7.68 (dd, $J = 7.3$ Hz, 2H, Ph-H), 7.63 (s, 2H, Ph-H), 7.29 (dd, $J = 7.3$, 7.3 Hz, 2H, Ph-H), 7.02 (dd, $J = 7.3$, 7.3 Hz, 2H, Ph-H), 6.70 (d, $J = 7.3$ Hz, 2H, Ph-H), 6.30 (s, 2H, Ph-H), 3.62–3.45 (m, 4H, =NCH₂CH₂CH₂-), 1.73–1.51 (m, 4H, =NCH₂CH₂CH₂-), 1.43–1.30 (m, 4H, =NCH₂CH₂CH₂-) ppm; $^{13}\text{C NMR}$ (100 MHz, 293 K, CDCl_3 , δ): 164.5, 162.4, 153.9, 147.9, 141.2, 132.3, 127.9, 126.8, 124.1, 122.2, 119.0, 118.1, 113.0, 65.9, 59.0, 30.6, 26.7 ppm; IR (KBr) ν 3448 (br, OH), 2928 (m, C-H), 1631 (s, C=N), 1445 (m, C=C), 1405 (m, C=C) cm^{-1} ; UV (THF) λ_{max} , nm (ϵ): 261 (91100).

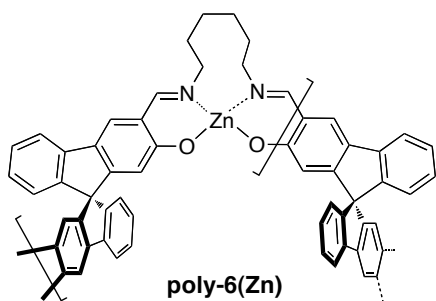


poly-8: An yellow solid (246 mg, 0.322 mmol, 100%); M_w 6,000; M_n 3,900 (estimated by the peak distribution of MALDI-TOF MS); T_g 187 °C; T_{d5} 290 °C; $[\alpha]_D^{25}$ +26.7 ($c = 0.10$, CHCl_3); $^1\text{H NMR}$ (400 MHz, 293 K, CDCl_3 , δ): 8.40 (s, 2H, Ph-CH=N), 7.71 (d, $J = 7.2$ Hz, 2H, Ph-H),

7.32 (dd, $J = 7.2, 7.2$ Hz, 2H, Ph- H), 7.03 (dd, $J = 7.2, 7.2$ Hz, 2H, Ph- H), 6.78 (s, 2H, Ph- H),
6.71 (d, $J = 7.2$ Hz, 2H, Ph- H), 6.31 (s, 2H, Ph- H), 3.76 (s, 6H, $-OCH_3$), 3.72 (s, 4H,
 $-POCH_2NH-$), 3.56 (t, $J = 6.3$ Hz, 4H, $=NCH_2CH_2-$), 2.57 (t, $J = 6.5$ Hz, 4H, $-NHCH_2CH_2-$),
1.71–1.62 (m, 4H, $=NCH_2CH_2-$), 1.54–1.45 (m, 4H, $-NHCH_2CH_2-$), 1.40–1.29 (m, 8H,
 $-CH_2CH_2CH_2-$) ppm; ^{13}C NMR (100 MHz, 293 K, $CDCl_3$, δ): 164.4, 162.5, 153.8, 151.2, 147.8,
141.1, 132.2, 128.2, 127.8, 127.5, 126.8, 124.2, 124.0, 122.1, 119.0, 118.0, 112.9, 112.7, 112.6,
65.7, 59.0, 56.2, 55.8, 49.2, 32.3, 30.7, 29.8, 27.0 ppm; IR (KBr) ν 3435 (br, O-H), 2927 (m,
C-H), 1631 (s, C=N), 1445 (m, C=C), 1406 (m, C=C) cm^{-1} ; UV (THF) λ_{max} , nm (ϵ): 262
(82700).

Typical procedure for the coordination reaction of zinc ions to poly(Schiff base): Synthesis of

poly-6(Zn):



To a solution of **poly-5** (500 mg, 0.655 mmol) in THF (60 mL) was added a solution of $Zn(OAc)_2 \cdot 2H_2O$ (316 mg, 1.44 mmol) in MeOH (2.0 mL) at room temperature and stirred for

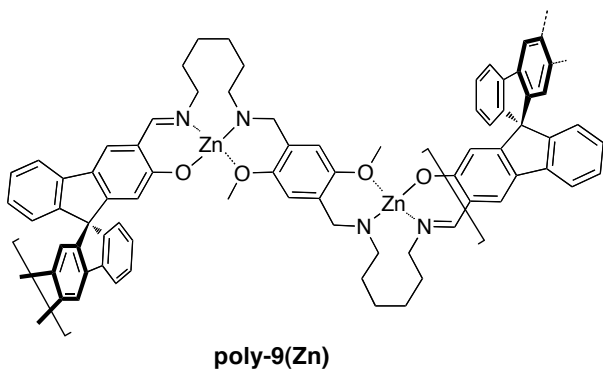
30 min. The reaction was quenched by precipitation into MeOH to give yellow precipitates.

The solids were collected by filtration, washed with MeOH, and dried *in vacuo* to give

poly-6(Zn) (870 mg, 0.976 mmol, quant.) as an yellow solid: no T_g was observed; T_{d5} 83 °C; IR

(KBr) ν 3406 (br, O–H), 2930 (m, C–H), 1618 (s, C=N), 1442 (m, C=C), 1398 (m, C=C) cm^{-1} ;

UV (THF) λ_{max} , nm (ϵ): 274 (72600).



poly-9(Zn): An yellow solid: no T_g was observed; T_{d5} 93 °C; IR (KBr) ν 3391 (br, O–H), 2972

(m, C–H), 1626 (s, C=N), 1398 (m, C=C), 1219 (m, C=C) cm^{-1} ; UV (THF) λ_{max} , nm (ϵ): 272

(59600).

References

- (a) Hass, G.; Prelog, V. *Helv. Chim. Acta*, **1969**, 52, 1202–1218. (b) Prelog, V.; Bedekovic, D. *Helv. Chim. Acta*, **1979**, 62, 2285–2302. (c) Toda, F.; Tanaka, K.; *J. Org. Chem.* **1988**, 53,

3607–3609. (d) Thiemann, F.; Piehler, T.; Haase, D.; Saak, W.; Lützen, A. *Eur. J. Org. Chem.*

2005, *2005*, 1991–2001.

2. Leighton, P.; Sunders, J. K. M. *J. Chem. Soc. Perkin Trans I*, **1987**, *11*, 2385–2393.

3. Yu, X.-M. Ramiandrasoa, F.; Guetzoyan, L.; Pradines, B.; Quintino, E.; Gadelle, D.; Forterre,

P.; Cresteil, T.; Mahy, J.-P.; Pethe, S. *ChemMedChem*, **2012**, *7*, 587–605.

II. Original spectra (^1H NMR, ^{13}C NMR, and IR spectra) of all new monomers and polymers.

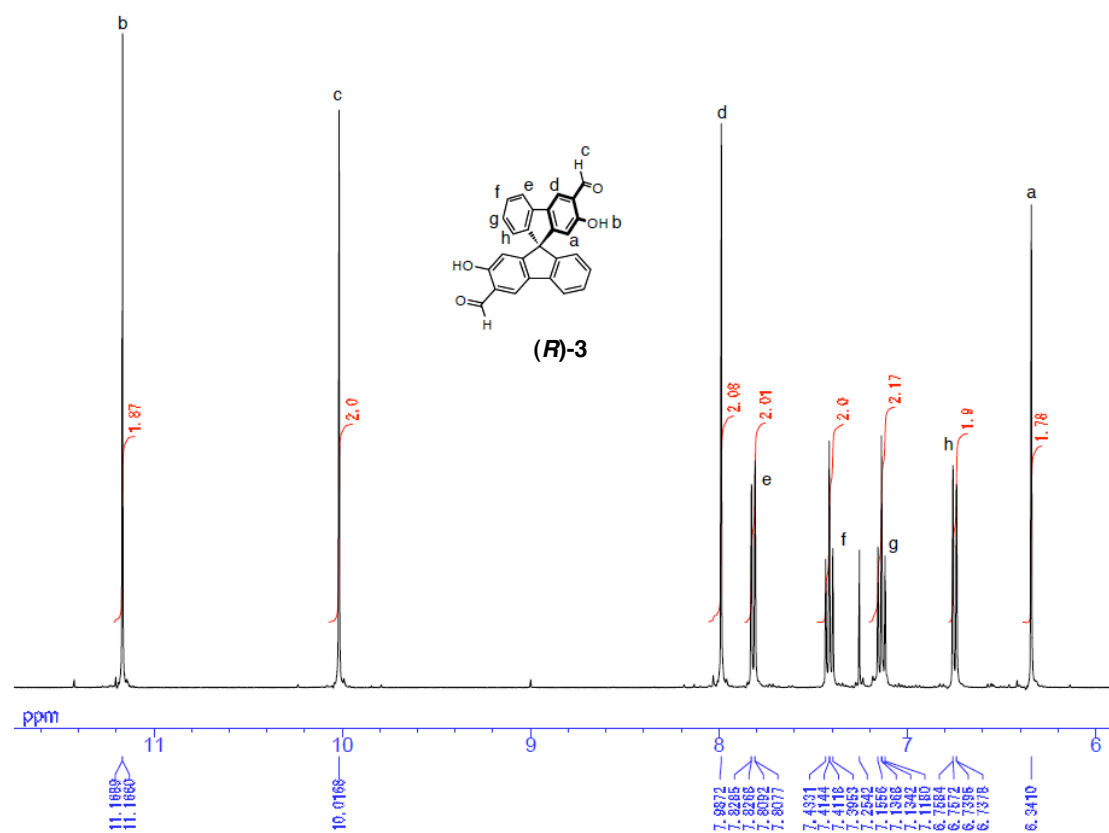


Figure S1. ^1H NMR spectrum of **(R)-3** (CDCl_3 , 400 MHz, 293 K).

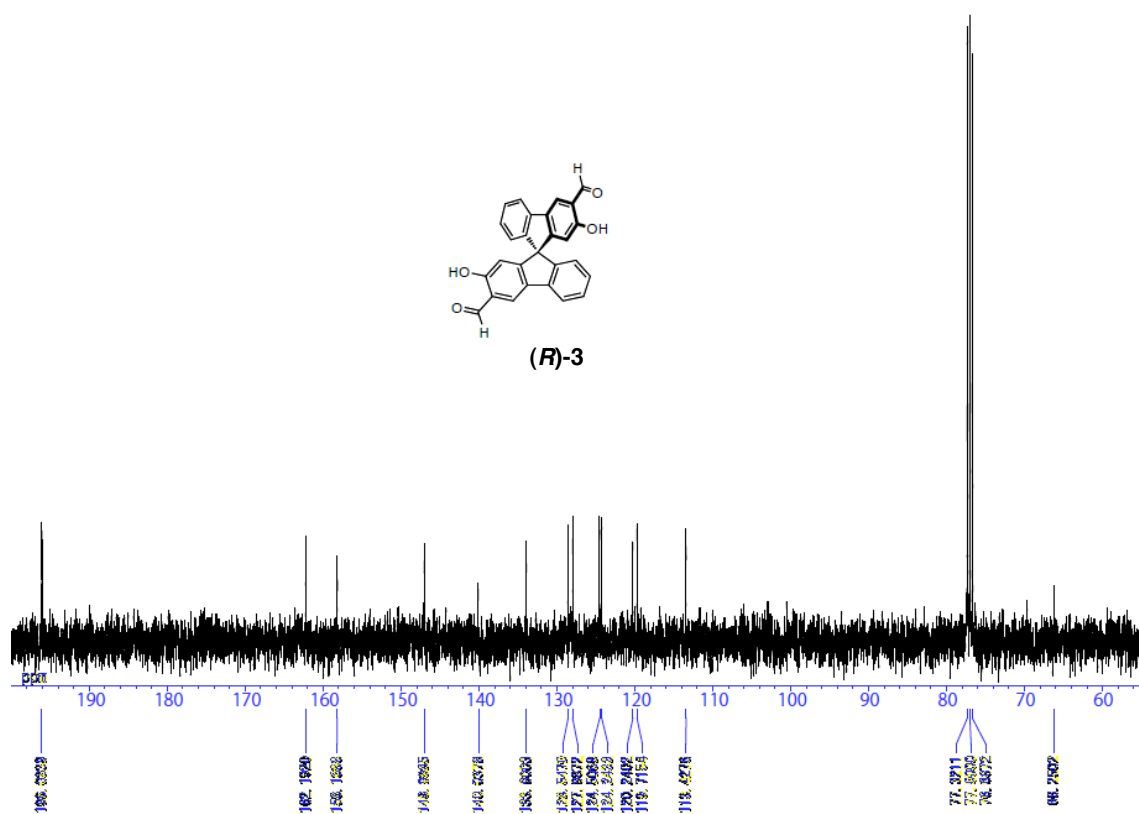


Figure S2. ¹³C NMR spectrum of **(R)-3** (CDCl₃, 100 MHz, 293 K).

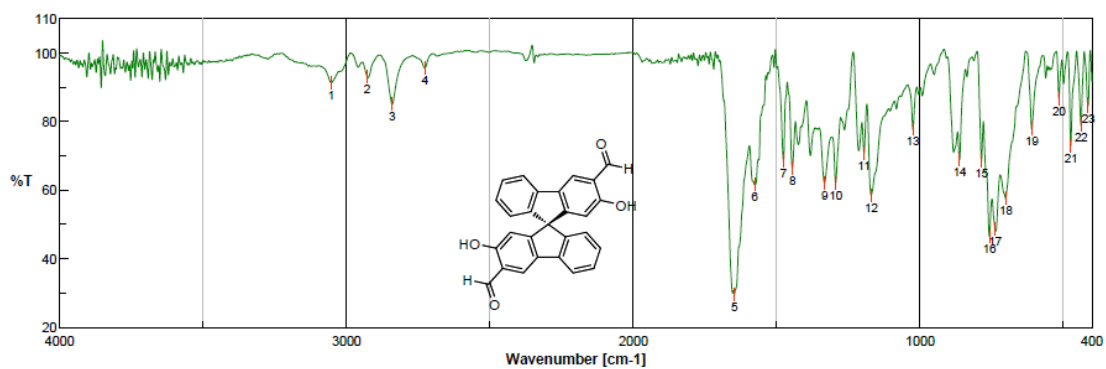


Figure S3. IR spectrum of **(R)-3** (KBr).

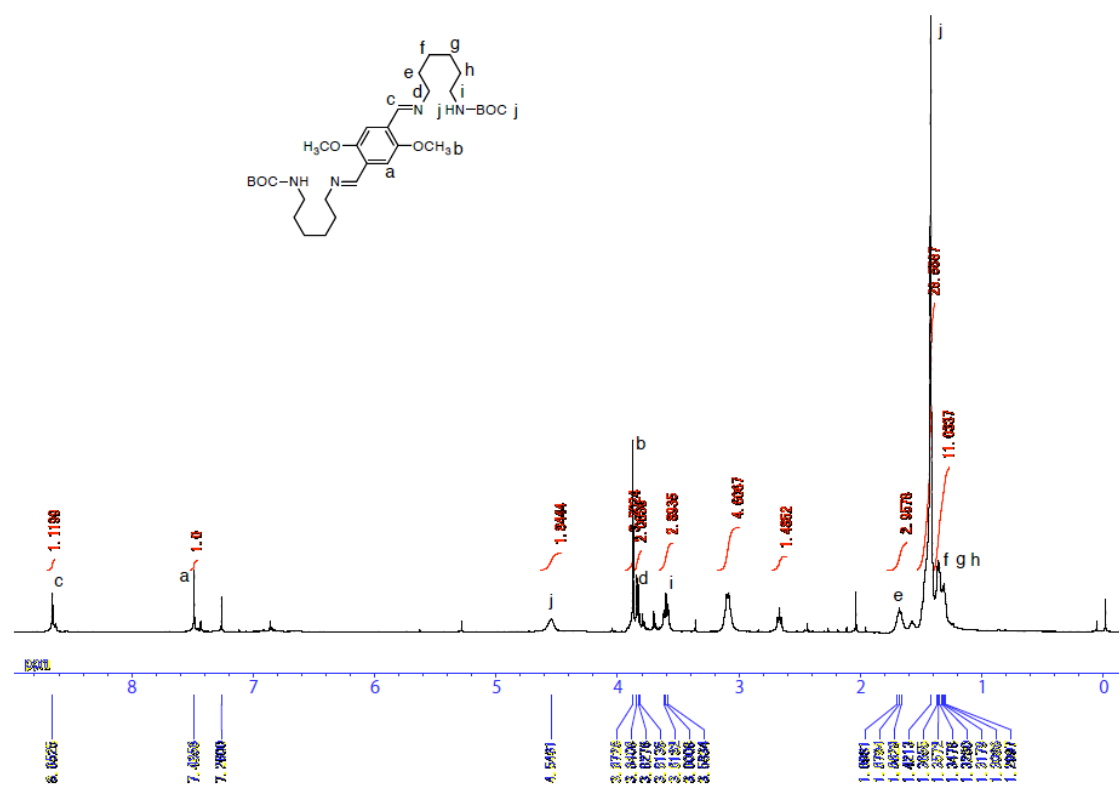


Figure S4. ¹H NMR spectrum of imine (CDCl₃, 400 MHz, 293 K).

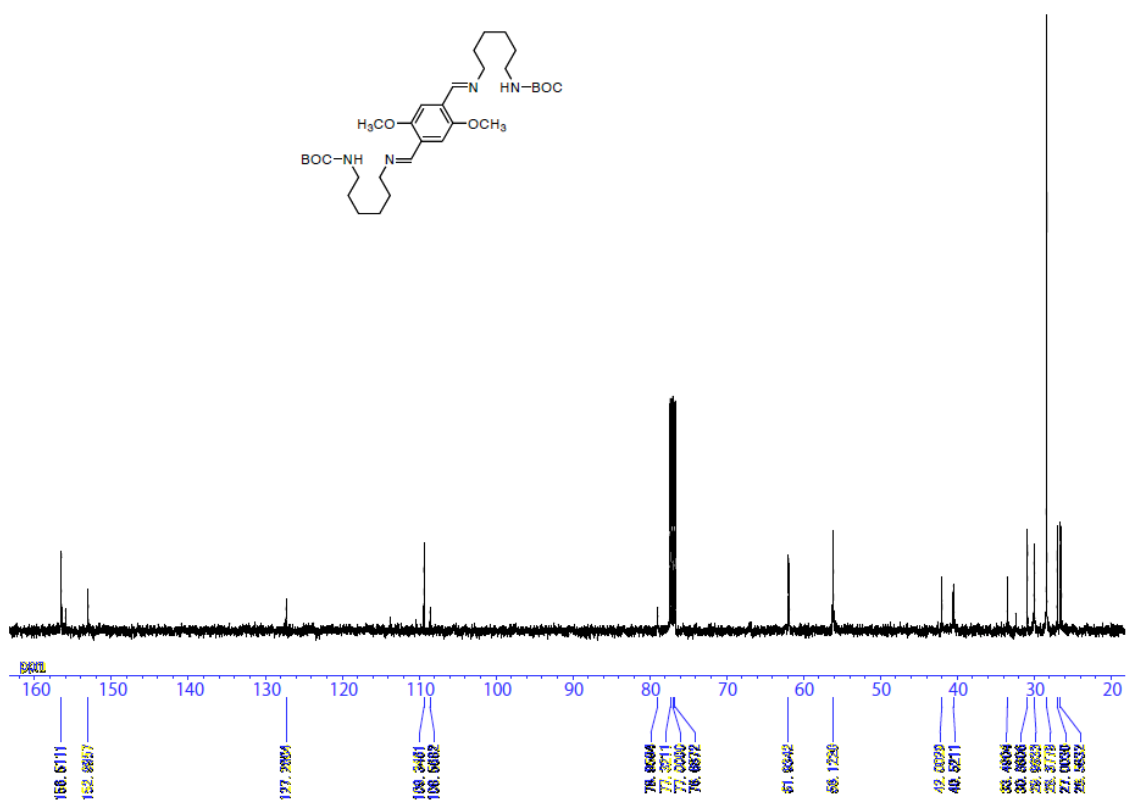


Figure S5. ^{13}C NMR spectrum of imine (CDCl₃, 100 MHz, 293 K).

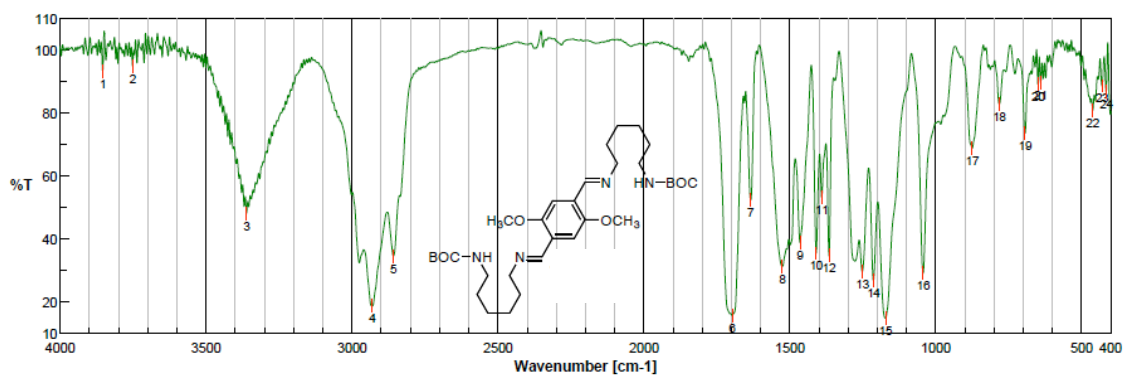


Figure S6. IR spectrum of imine (KBr).

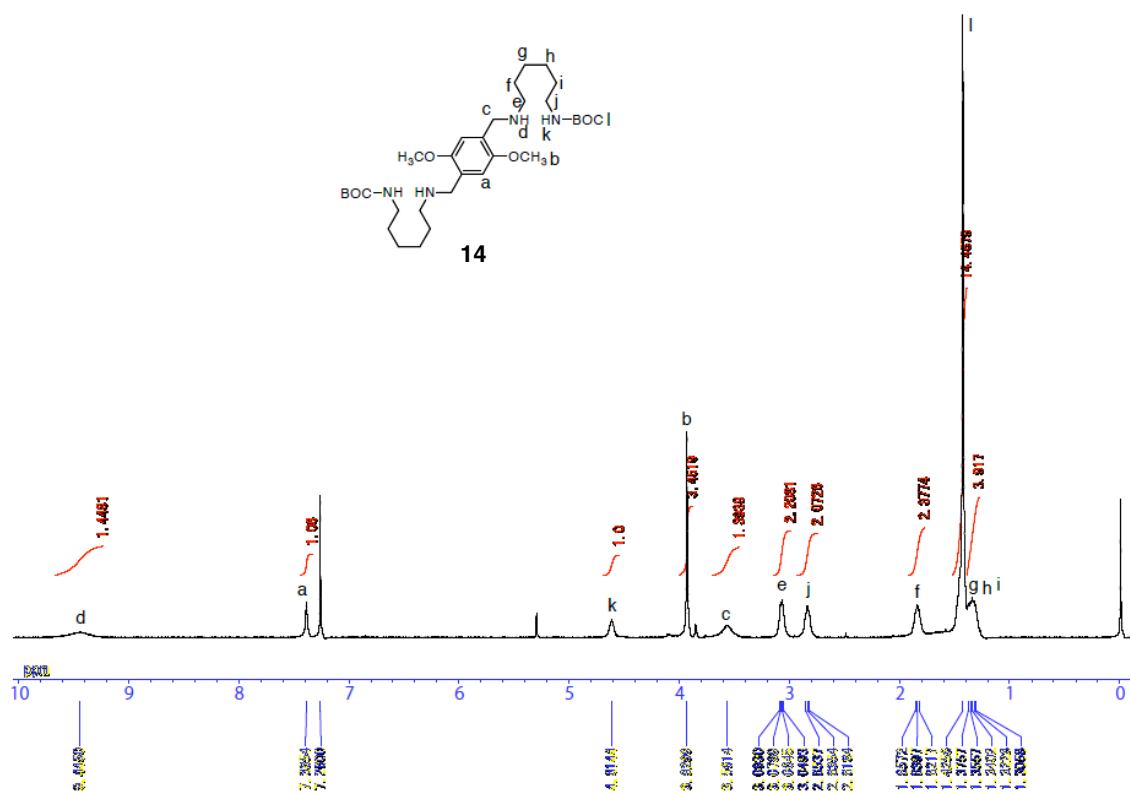


Figure S7. ¹H NMR spectrum of **14** (CDCl₃, 400 MHz, 293 K).

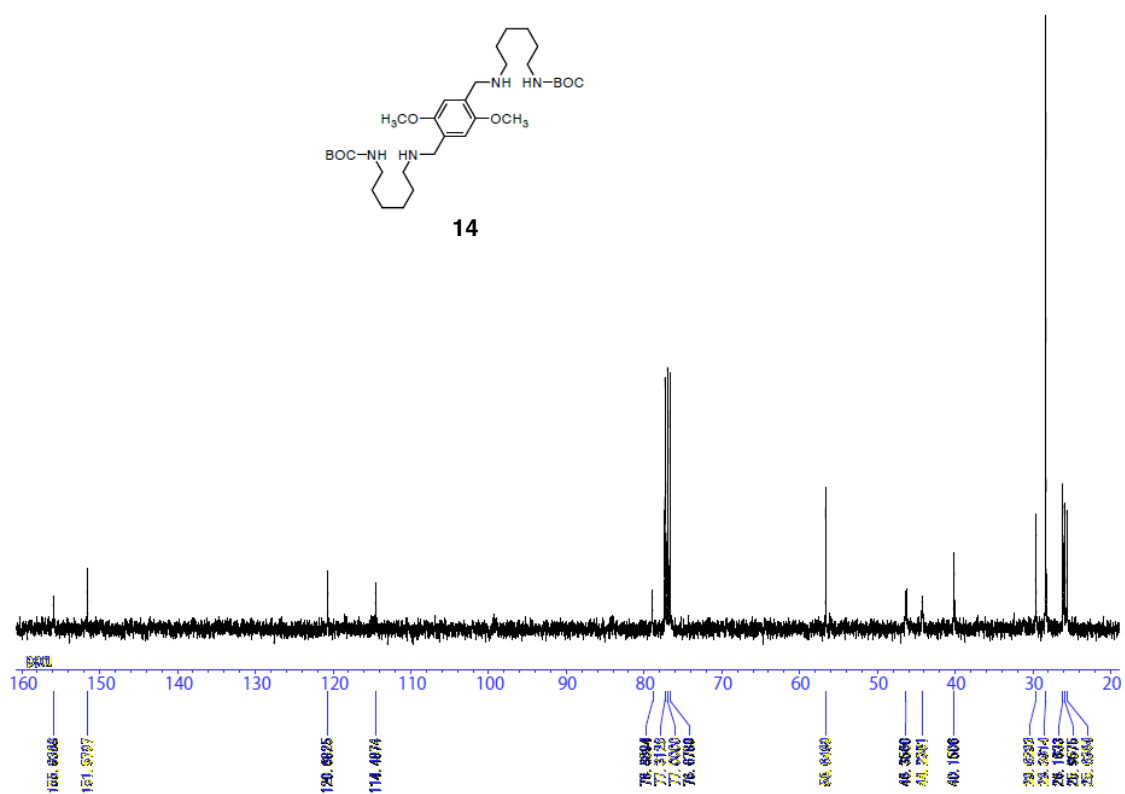


Figure S8. ^{13}C NMR spectrum of **14** (CDCl_3 , 100 MHz, 293 K).

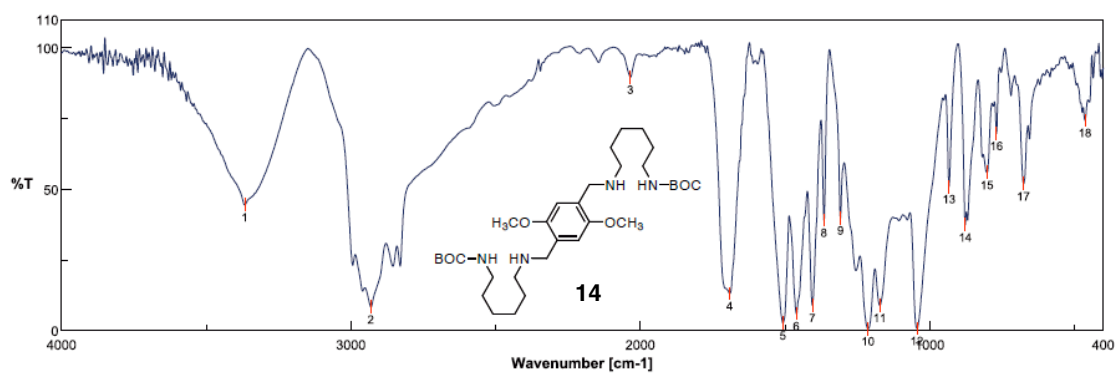


Figure S9. IR spectrum of **14** (KBr).

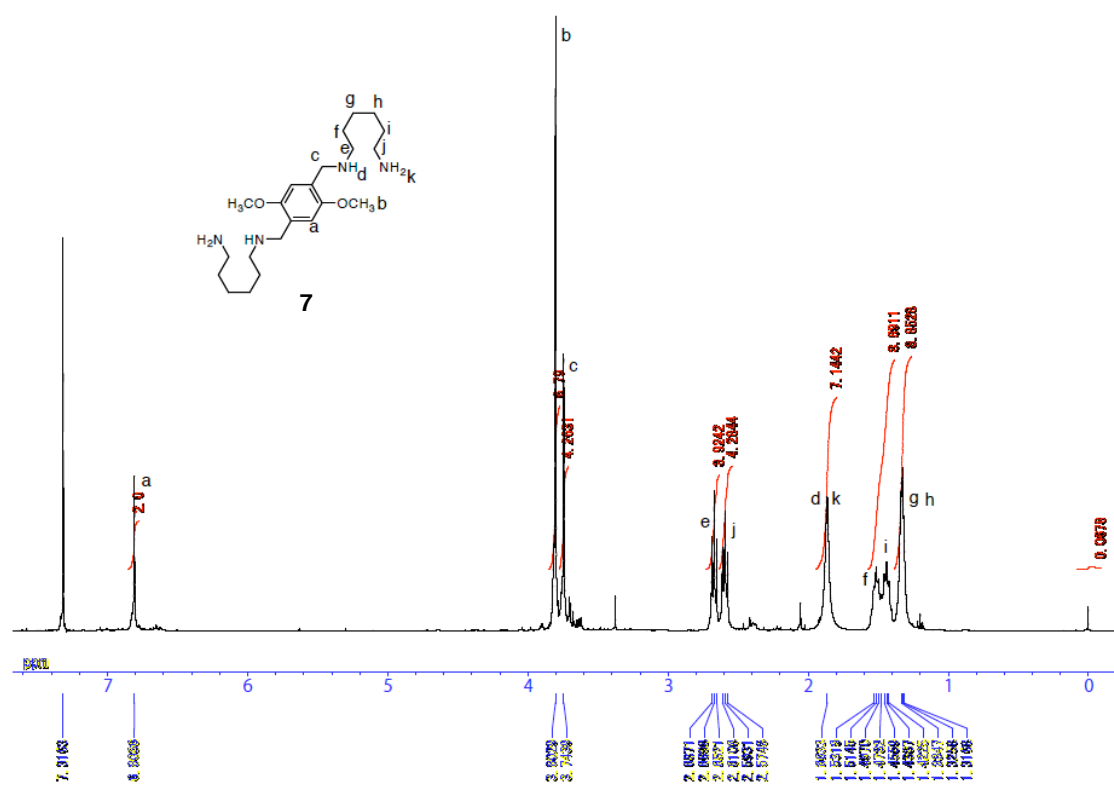


Figure S10. ¹H NMR spectrum of 7 (CDCl₃, 400 MHz, 293 K).

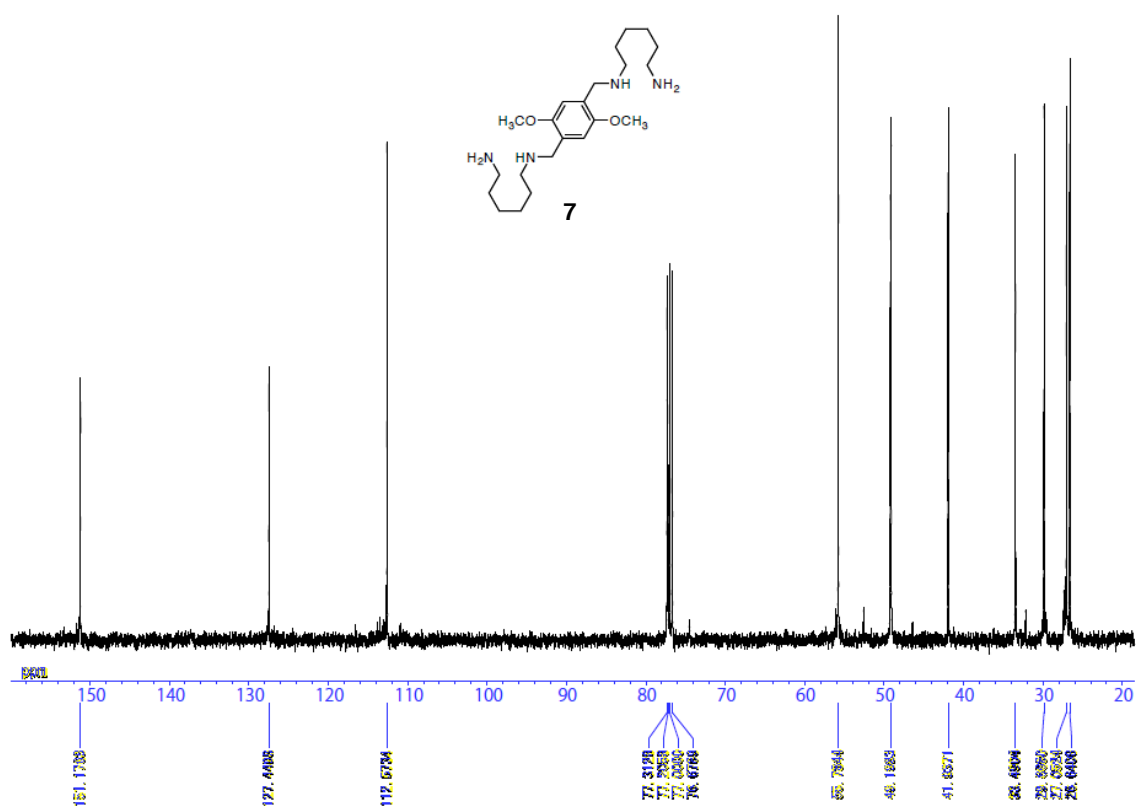


Figure S11. ^{13}C NMR spectrum of **7** (CDCl_3 , 100 MHz, 293 K).

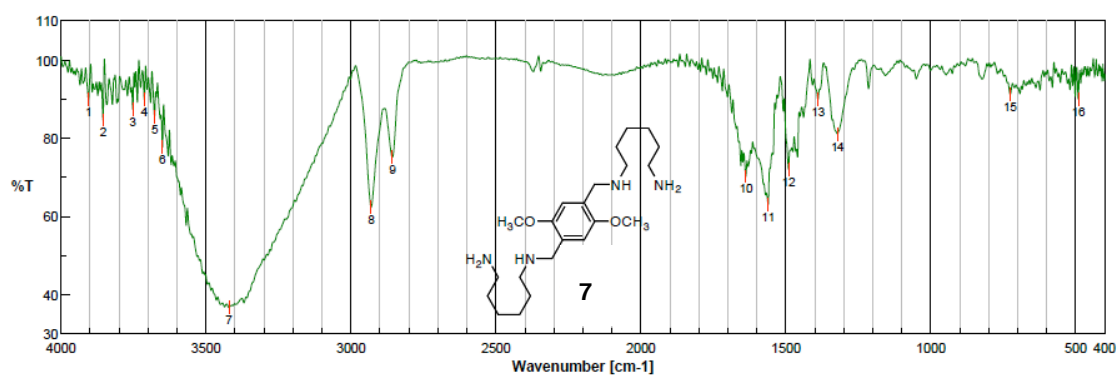


Figure S12. IR spectrum of **7** (KBr).

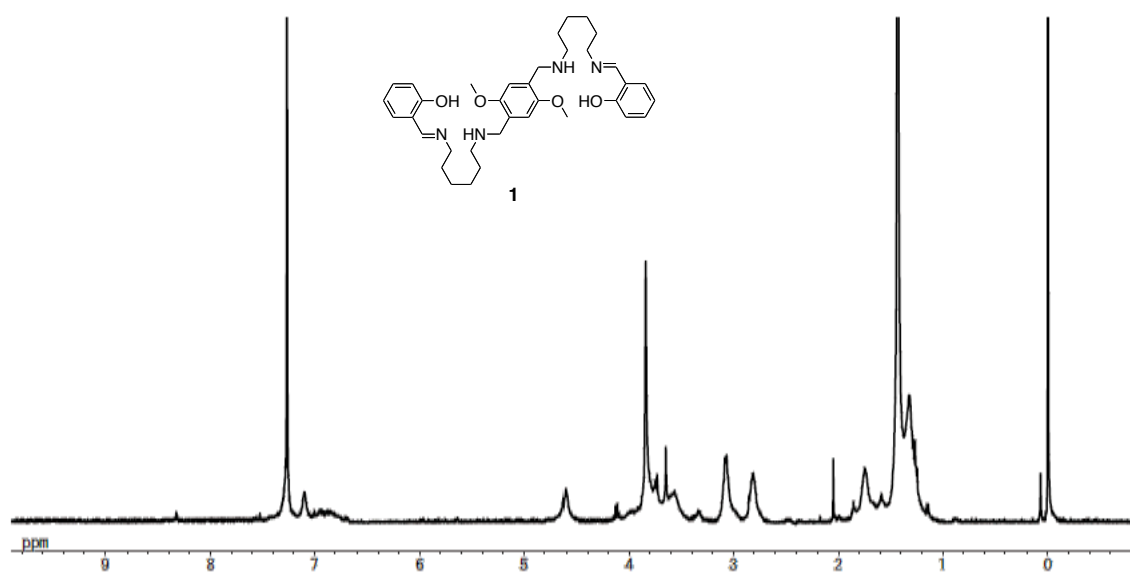


Figure S13. ¹H NMR spectrum of **1** (CDCl₃, 400 MHz, 293 K).

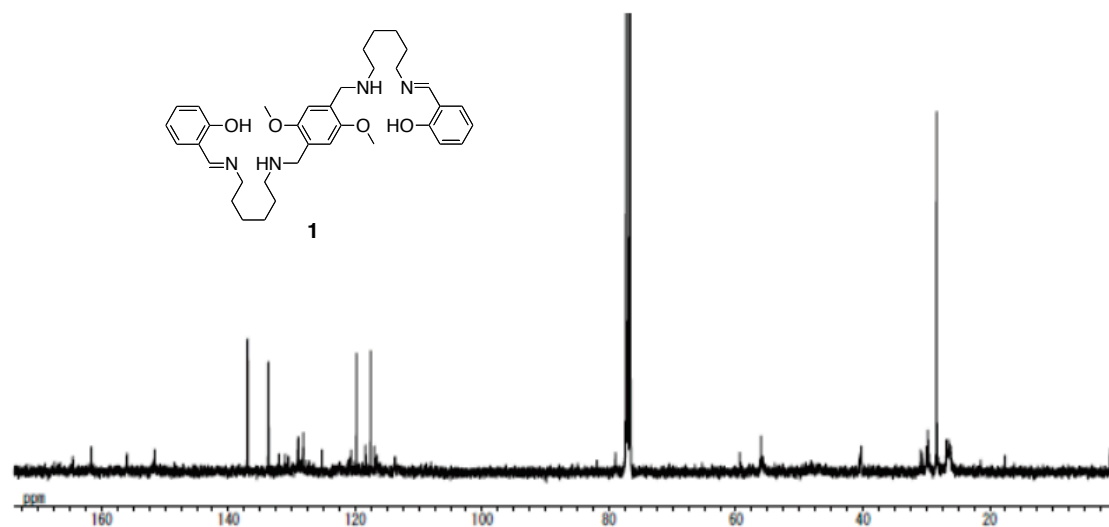


Figure S14. ¹³C NMR spectrum of **1** (CDCl₃, 100 MHz, 293 K).

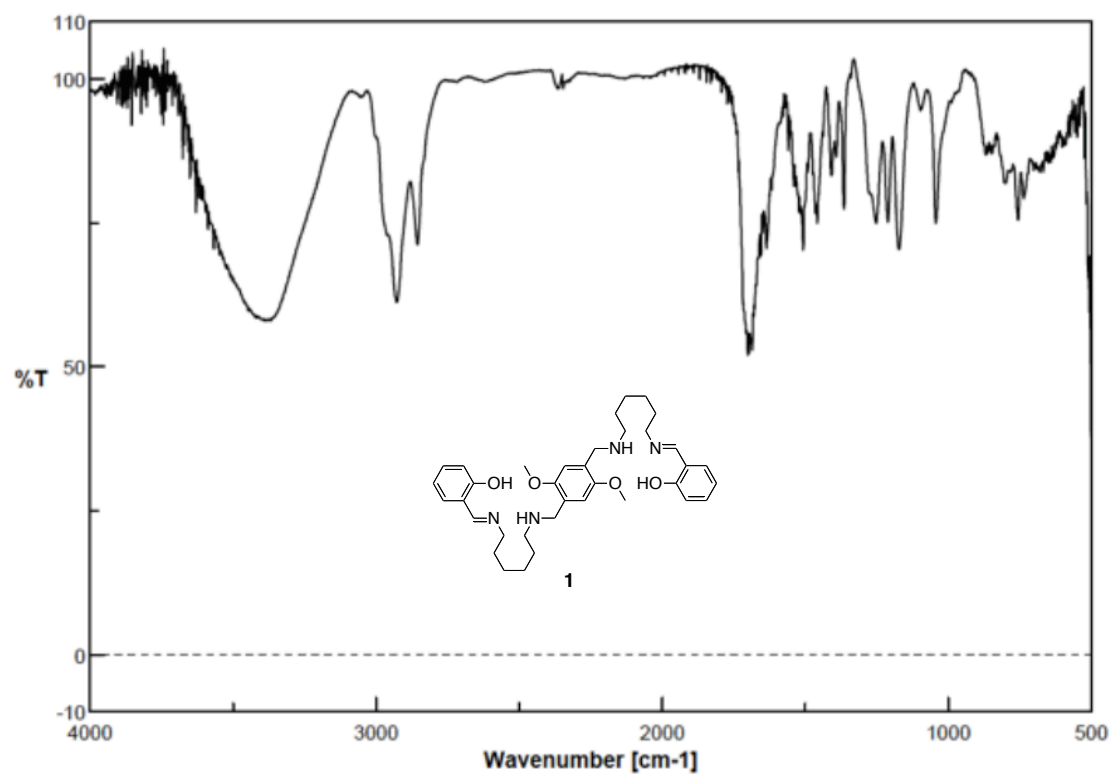


Figure S15. IR spectrum of **1** (NaCl).

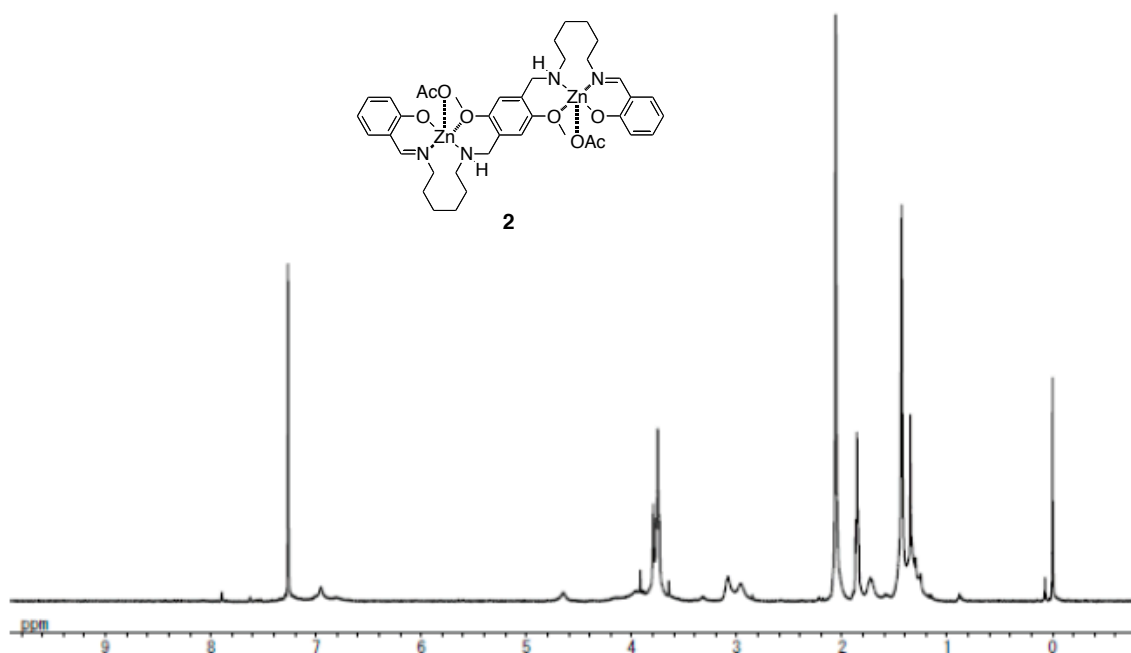


Figure S16. ^1H NMR spectrum of **2** (CDCl_3 , 400 MHz, 293 K).

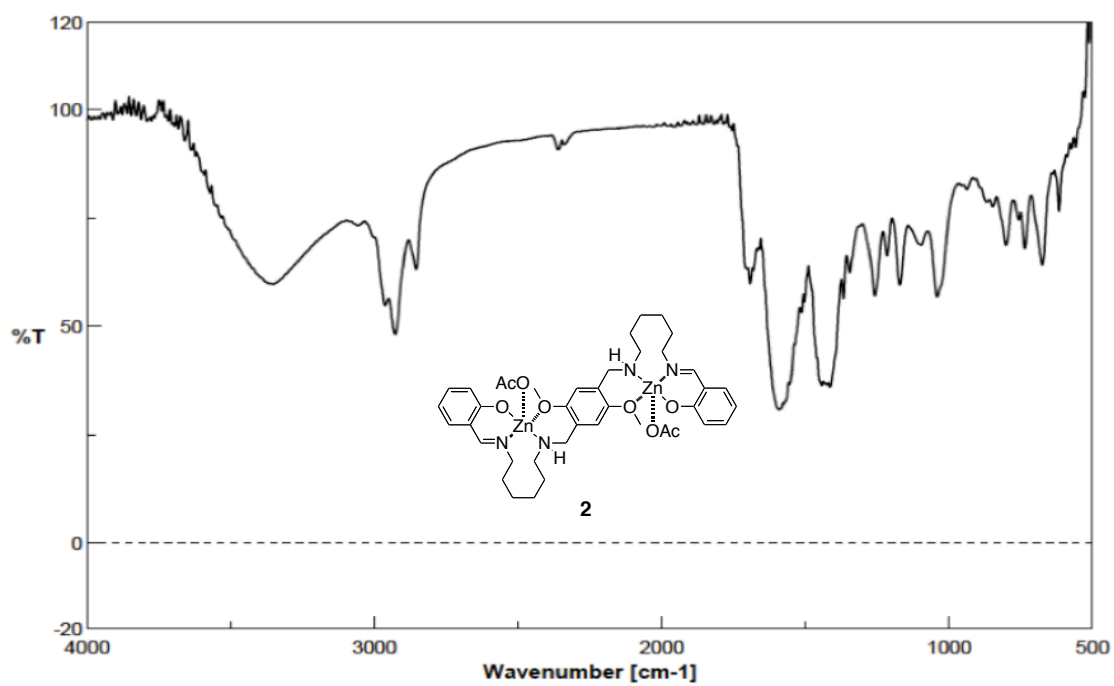


Figure S17. IR spectrum of **2** (KBr).

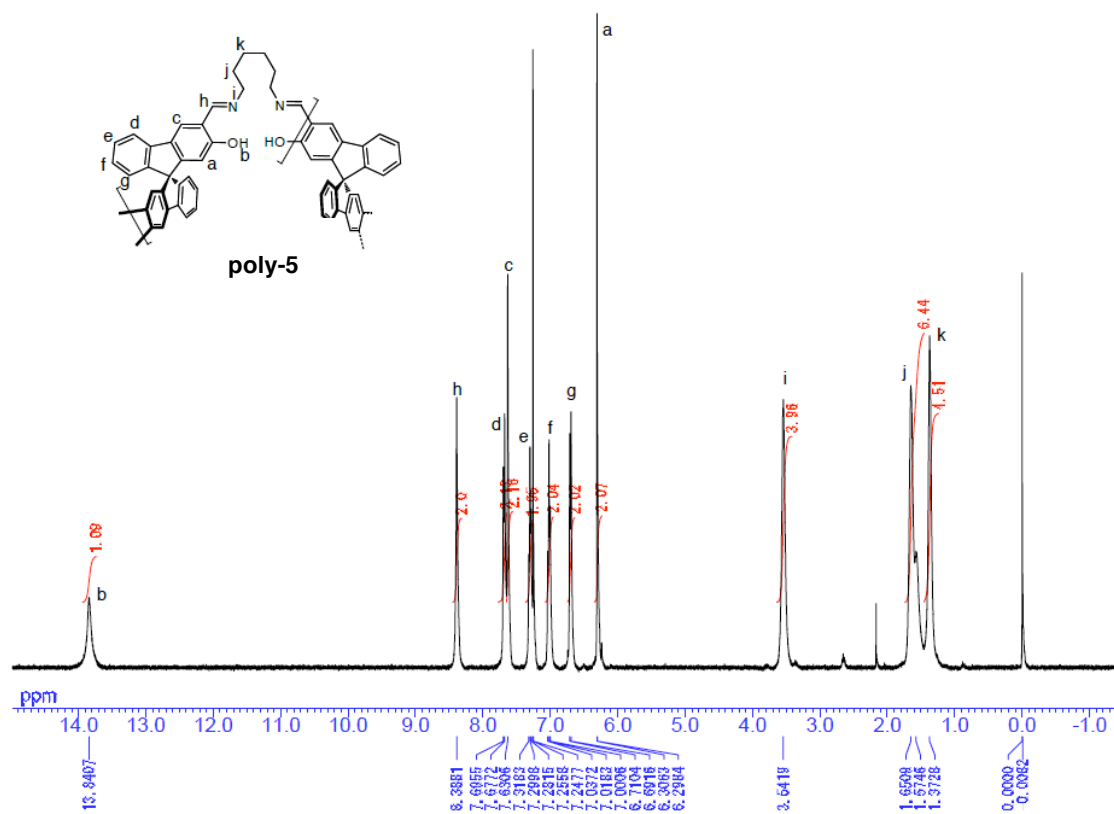


Figure S18. ¹H NMR spectrum of poly-5 (CDCl₃, 400 MHz, 293 K).

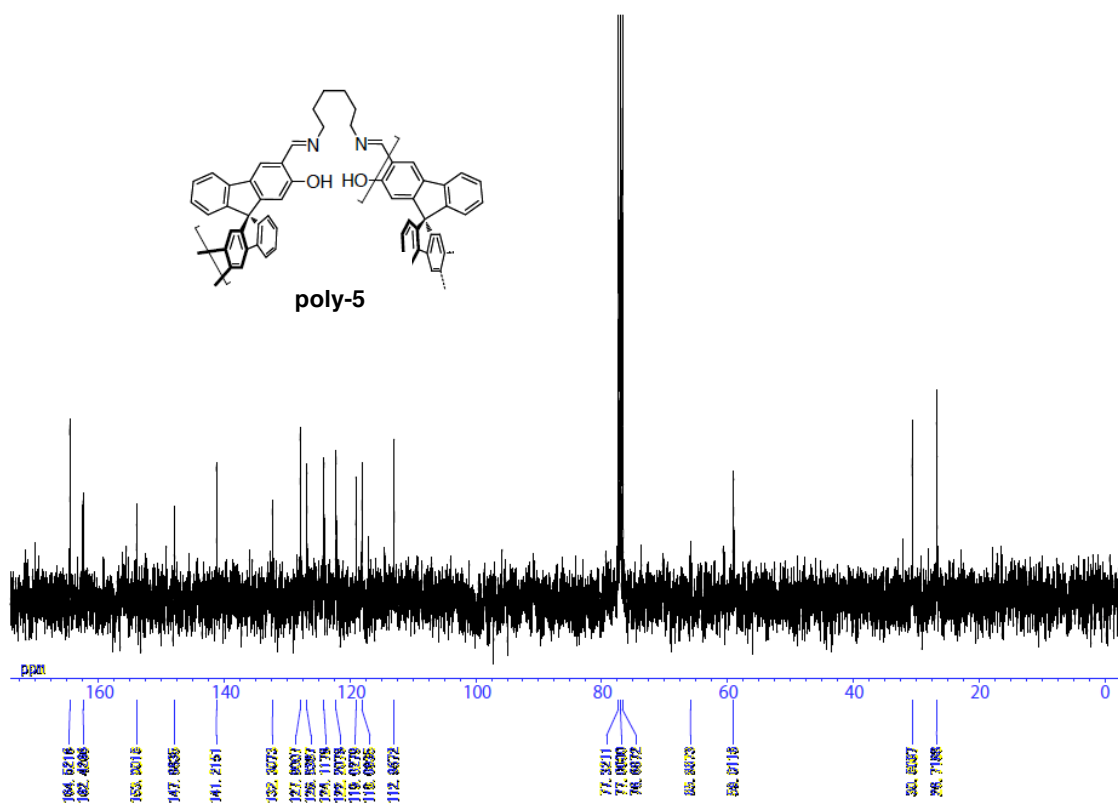


Figure S19. ¹³C NMR spectrum of poly-5 (CDCl₃, 100 MHz, 293 K).

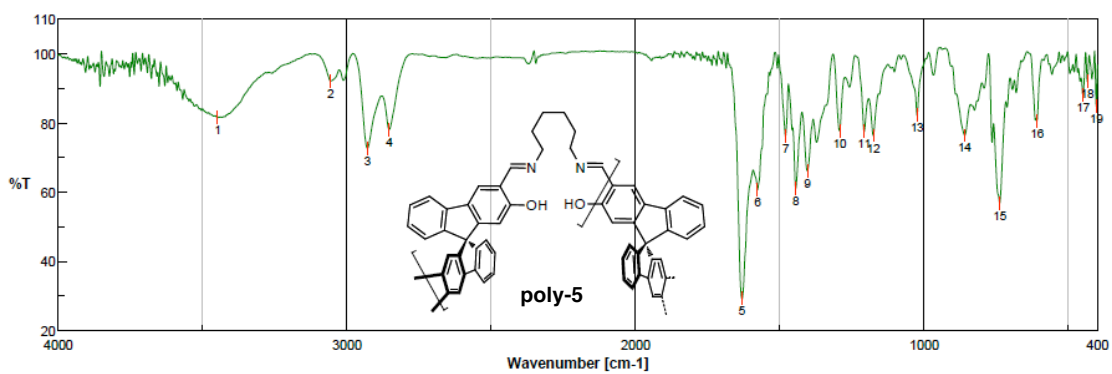


Figure S20. IR spectrum of poly-5 (KBr).

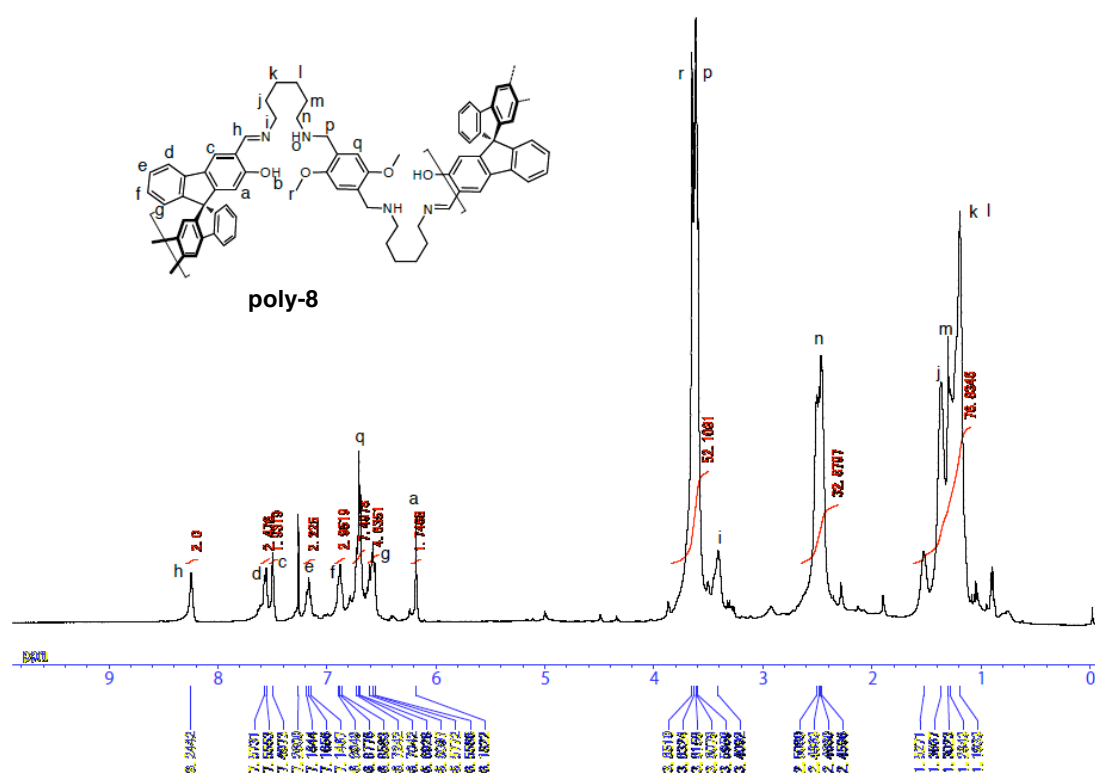


Figure S21. ¹H NMR spectrum of poly-8 (CDCl₃, 400 MHz, 293 K).

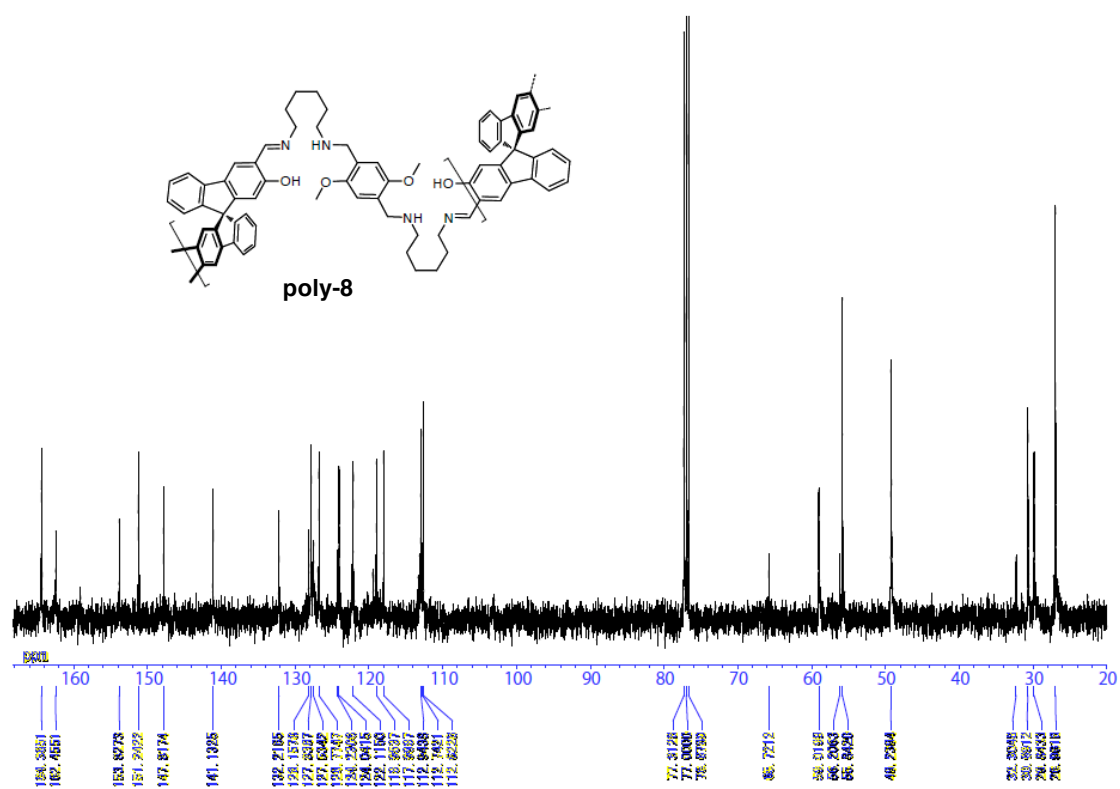


Figure S22. ¹³C NMR spectrum of poly-8 (CDCl₃, 100 MHz, 293 K).

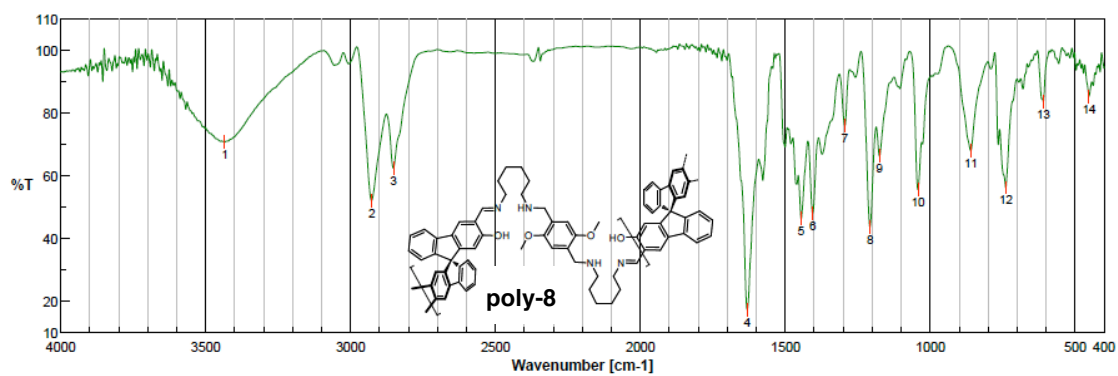


Figure S23. IR spectrum of poly-8 (KBr).

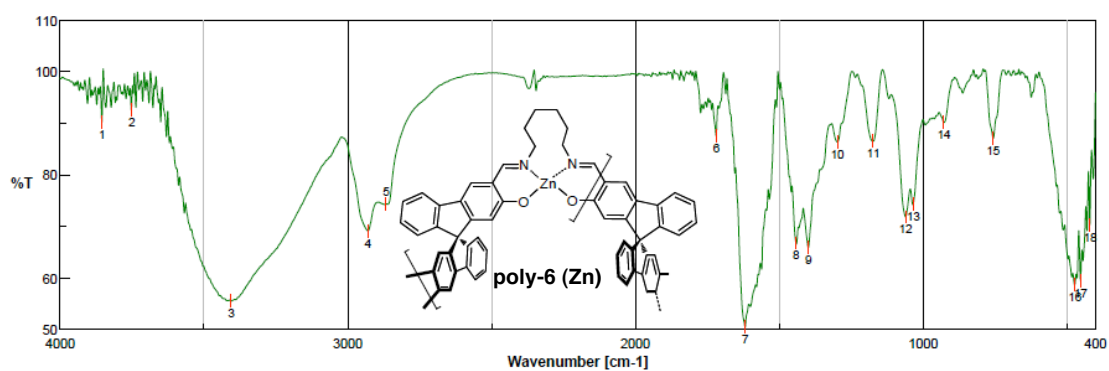


Figure S24. IR spectrum of **poly-6(Zn)** (KBr).

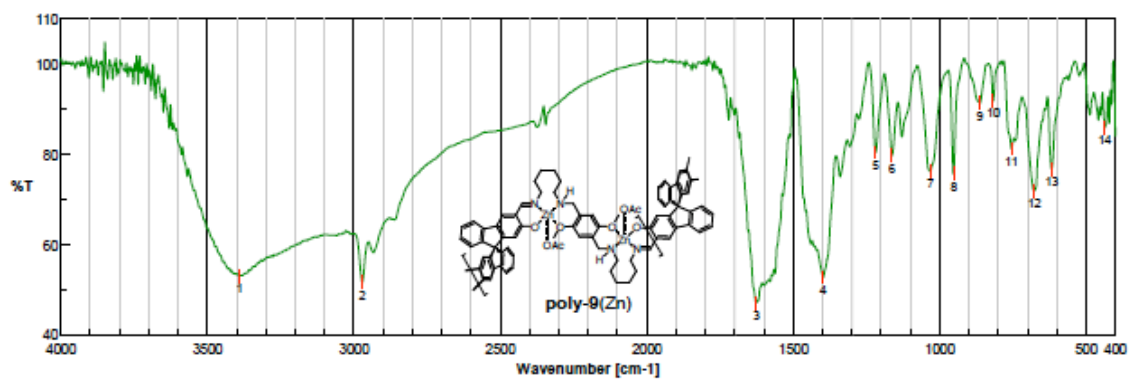


Figure S25. IR spectrum of **poly-9(Zn)** (KBr).

III. MALDI-TOF MS spectra of polymers.

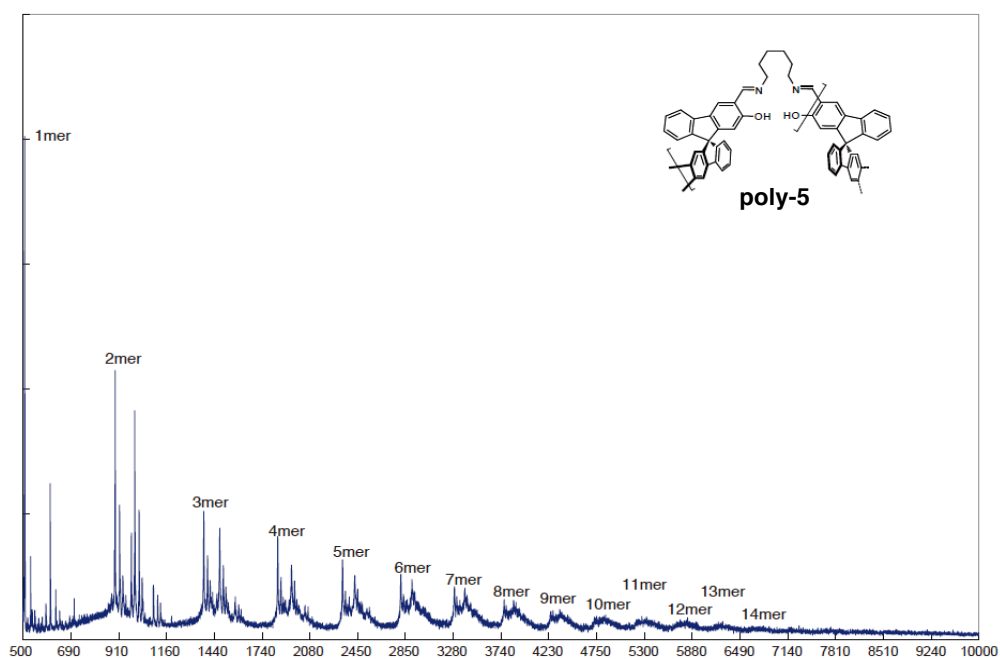


Figure S26. MALDI-TOF MS spectrum of **poly-5**.

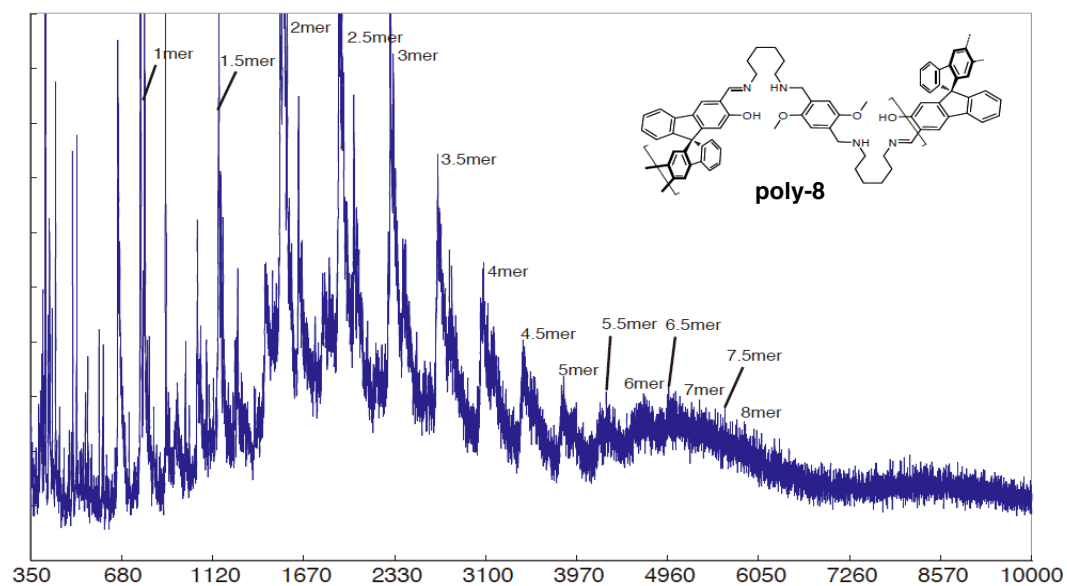


Figure S27. MALDI-TOF MS spectrum of **poly-8**.

IV. CD spectra of polymers.

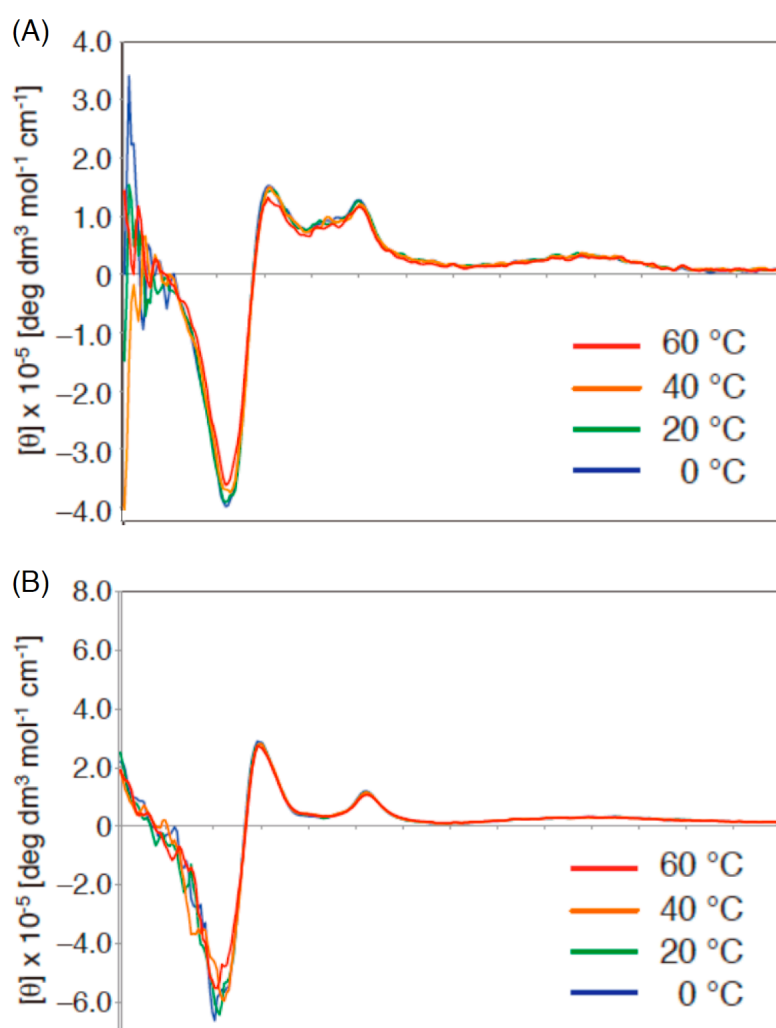


Figure S28. CD spectra of (A) **poly-6(Zn)** and (B) **poly-9(Zn)** at various temperatures (THF, 20 μM).

V. Energy-Minimized Structure of 16-mer models.

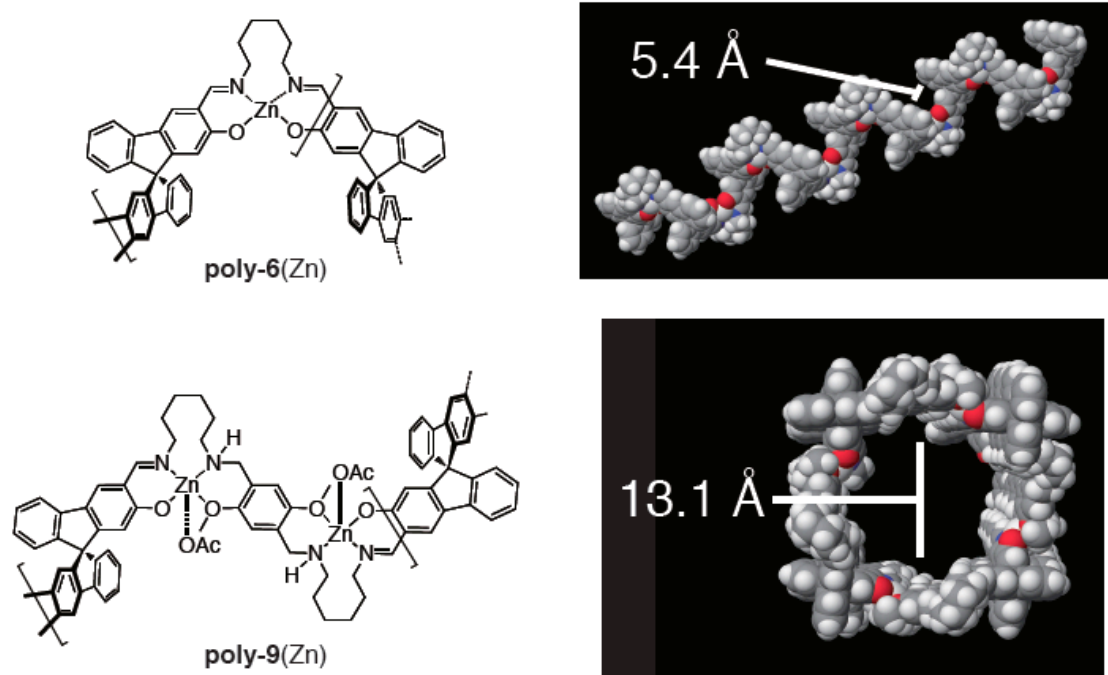


Figure S29. Energy-Minimized Structure of 16-mer models of **poly-6(Zn)** and **poly-9(Zn)**.