

# **Ligand Exchange Reaction for Controlling the Conformation of Platinum-Containing Polymers**

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**Figure S2.**  $^{31}\text{P}$  NMR (162 MHz) spectroscopic change of a mixture of compound **1** and dppe over a period of 0–24 hours measured in  $\text{CDCl}_2\text{CDCl}_2$  ( $c = 10$  mM) at 25 °C.

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**Figure S17.** Tilt view of a 12-mer model for polymer **2'**. The geometries were optimized by the DFT method [B3LYP/6-31G\* (C, H, N, O, P)-LANL2DZ (Pt)].

**Table S1:**  $\lambda_{\text{max}}$  and hydrodynamic diameters of polymer **4'**.

CIF files of **1**, **2**, **3<sub>dimer</sub>** and **3**  
mol2 files of **2'** and **3'**

## Experimental Procedures

**Measurements.**  $^1\text{H}$  (400 MHz),  $^{13}\text{C}$  (100 MHz) and  $^{31}\text{P}$  (162 and 240 MHz) NMR were recorded on a JEOL ECA-400, a JEOL ECS-400 and a JEOL ECS-600. IR spectra were measured on a JASCO FT/IR-4100 spectrophotometer. Melting points (mp) were measured on a Yanaco micro melting point apparatus. Number-average molecular weight ( $M_n$ ) and dispersity ( $D$ ) values of model compounds were determined by SEC (Shodex columns K803, K804, K805) eluted with  $\text{CHCl}_3$  as the eluent at 40 °C calibrated with polystyrene standards.  $M_n$  and  $D$  values of polymers were determined by SEC (TSK gel  $\alpha$ -3000) using a solution of LiBr (10 mM) in *N,N*-dimethylformamide (DMF) as the eluent at 40 °C calibrated with polystyrene standards. CD and UV-vis absorption spectra were recorded on a JASCO J-820 spectropolarimeter. DLS measurements were performed using a Malvern Instruments Zetasizer Nano ZSP at 20 °C. The measured autocorrelation function was analyzed using the cumulant method. The Z-average values of the polymers were calculated from the Stokes-Einstein equations. The X-ray experiments were carried out with a Rigaku RAXIS imaging plate area detector with graphite-monochromated  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71070 \text{ \AA}$ ). The crystal was mounted on a nylon loop at  $-150 \text{ }^\circ\text{C}$ . To determine the cell constant and orientation matrix, three oscillation photographs were taken for each frame with an oscillation angle of  $3^\circ$  and exposure time of 30 s. Intensity data were corrected from the oscillation photographs, and the reflection data were corrected for Lorentz and polarization effects. The structures were solved by the direct method.<sup>1</sup> Non-hydrogen atoms were refined anisotropically by a full-matrix least-squares calculation. Hydrogen atoms were found from the difference Fourier map and isotropically refined. All calculations were performed using the CrystalStructure<sup>2</sup> and Crystals<sup>3</sup> crystallographic software packages.

**Materials.** Reagents, including di-*tert*-butyl dicarbonate  $[(\text{Boc})_2\text{O}]$ , TOKUYAMA], 4-(4,6-dimethoxy-1,3,5-triazine-2-yl)-4-methylmorpholinium chloride (TRIAZIMOCH, TOKUYAMA), anhydrous THF (Wako, water max. 0.001%),  $\text{Pd}(\text{PPh}_3)_4$  (Aldrich, assay 99.9%) and  $\text{CuI}$  (Wako, 99.5%), were used as received. 3',5'-Diiodo-4'-hydroxy-*N*- $\alpha$ -*tert*-butoxycarbonyl-D-phenylglycine hexylamide<sup>4</sup> and dichlorobis(triphenylphosphine)platinum<sup>5</sup> were synthesized according to the literature. 1-Ethynyl-4-[2-(trimethylsilyl)ethynyl]benzene was synthesized from 1-bromo-4-iodobenzene in a manner similar to the synthesis of 1-ethynyl-3-[2-(trimethylsilyl)ethynyl]benzene.<sup>6</sup>

### Synthesis of Bis{4-ethynylphenylethynyl}bis(triphenylphosphine)platinum (1).

1-Ethynyl-4-[2-(trimethylsilyl)ethynyl]benzene (0.99 g, 5.0 mmol), dichlorobis(triphenylphosphine)platinum (1.973 g, 2.5 mmol) and CuI (0.095 g, 0.5 mmol) were dissolved in Et<sub>2</sub>NH (70 mL) under argon at 0 °C, and the resulting mixture was stirred with refluxing at 65 °C for 8 h. The mixture was filtered, and the filtrate was concentrated to obtain a yellow solid. The residual mass was purified by silica gel column chromatography eluted with hexane/CH<sub>2</sub>Cl<sub>2</sub> = 1/0–1/1 (v/v) to obtain bis{4-[2-(trimethylsilyl)ethynyl]phenylethynyl}bis(triphenylphosphine)platinum as a white solid. A KOH (1.224 g, 22 mmol) solution in water (11 mL) was added to a solution of bis{4-[2-(trimethylsilyl)ethynyl]phenylethynyl}bis(triphenylphosphine)platinum (2.430 g, 2.2 mmol) in THF/methanol (218 mL/174 mL) at 0 °C, and the resulting mixture was stirred at room temperature for 4 h. The mixture was filtered, and the filtrate was concentrated to obtain a yellow liquid. The residual mass was purified by silica gel column chromatography eluted with CHCl<sub>3</sub> to obtain **1** as a brown solid in 74% yield. No mp was observed up to 250 °C. IR (KBr): 3281, 3057, 2958, 2918, 2102, 1597, 1501, 1491, 1482, 1435, 1377, 1216, 1186, 1099, 1028, 999, 839, 741, 707, 693, 547, 524, 515 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 3.01 [s, 2H, –C≡C–H], 6.20–6.22 (d, *J* = 6.6 Hz, 4H, Ar), 7.02–7.05 (d, *J* = 6.6 Hz, 4H, Ar), 7.33–7.42 (m, 18H, P–Ar), 7.77–7.81 (m, 12H, P–Ar). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 77.2, 84.4, 113.3, 114.7 [–C≡C–H, –C≡C–], 117.8, 128.0, 130.4, 130.8, 131.0, 131.3, 131.6, 135.1 [Ar, P–Ar]. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>): δ 19.3 [*J*<sub>(Pt–P)</sub> = 2663 Hz, –PPh<sub>3</sub>]. Anal. Calcd for C<sub>56</sub>H<sub>40</sub>P<sub>2</sub>Pt: C, 69.34; H, 4.16. Found: C, 69.51; H, 4.52.

**Synthesis of Polymer 1'.** The polymerization was carried out in a glass tube equipped with a three-way stopcock under argon. A solution of Cl<sub>2</sub>Pd(PPh<sub>3</sub>)<sub>2</sub> (5.7 mg, 5 μmol) in THF (0.8 mL) and a solution of CuI (0.95 mg, 5 μmol) in Et<sub>3</sub>N (0.2 mL) were added to a mixture of monomers 3',5'-diiodo-4'-hydroxy-*N*-α-*tert*-butoxycarbonyl-D-phenylglycine hexylamide (30.1 mg, 0.05 mmol) and **1** (48.5 mg, 0.05 mmol) under argon, and the resulting solution was kept at 60 °C for 24 h. Then, the reaction mixture was poured into a large volume of hexane to precipitate a polymeric mass. It was separated by filtration using a membrane filter (ADVANTEC H100A047A), and dried under reduced pressure to obtain **1'**. Yield: quantitative. *M*<sub>n</sub> = 15,000, *D* = 1.9. The product was further purified by preparative high-performance liquid chromatography

in order to remove Pd and Cu residues. IR (KBr): 3413, 3053, 2955, 2926, 2673, 2199, 2102, 1711, 1672, 1593, 1560, 1482, 1435, 1391, 1366, 1228, 1161, 1120, 1098, 1071, 1028, 998, 912, 839, 796, 746, 723, 707, 692, 618, 542, 523, 514  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.63–0.94 (br, 3H,  $-\text{CH}_2(\text{CH}_2)_4\text{CH}_3$ ), 1.00–1.81 [br, 17H,  $-\text{CH}_2(\text{CH}_2)_4\text{CH}_3$ ,  $-\text{C}(\text{CH}_3)_3$ ], 3.00–3.40 [br, 2H,  $-\text{CH}_2(\text{CH}_2)_4\text{CH}_3$ ], 5.00–5.20 (br, 1H,  $\text{NHCO}$ ), 5.52–6.50 (br, 3H,  $\text{C}^*\text{H}$ ,  $\text{OCONH}$ ,  $\text{OH}$ ), 6.80–8.00 (br, 40H, Ar, PAr).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  19.3 [ $J_{(\text{Pt-P})} = 2684$  Hz,  $-\text{PPh}_3$ ].

**Ligand Exchange Reactions.** The ligand exchange reactions were carried out in a Schlenk flask under argon. In a typical experiment, a solution of a diphosphine (10  $\mu\text{mol}$ ) in  $\text{CHCl}_2\text{CHCl}_2$  (0.1 mL) was added to a solution of compound **1** or polymer **1'** (12.6 mg, 10  $\mu\text{mol}$ ) in  $\text{CHCl}_2\text{CHCl}_2$  (0.9 mL) under argon, and the resulting solution was kept at room temperature for 24 h. Then, the reaction mixture was poured into a large volume of hexane to precipitate a polymeric mass. It was separated by filtration using a membrane filter (ADVANTEC H100A047A), and dried under reduced pressure to obtain the polymers.

**Spectroscopic Data of the Products of Ligand Exchange Reactions of 1 with dppe, dppp and dppb.** **2:** IR (KBr): 3278, 3050, 2952, 2918, 2846, 2102, 1597, 1491, 1475, 1432, 1306, 1216, 1171, 1157, 1103, 1068, 1026, 998, 879, 838, 741, 693, 616, 547, 533, 511  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_2\text{CDCl}_2$ ):  $\delta$  2.35–2.53 [br, 4H,  $-\text{PPh}_2(\text{CH}_2)_2\text{Ph}_2\text{P}-$ ], 3.12 [s, 2H,  $-\text{C}\equiv\text{C}-\text{H}$ ], 6.96–6.98 (d,  $J = 8.0$  Hz, 4H, Ar), 7.24–7.26 (d,  $J = 8.0$  Hz, 4H, Ar), 7.28–7.52 (m, 16H, P–Ar), 7.79–7.92 (m, 4H, P–Ar).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_2\text{CDCl}_2$ ):  $\delta$  42.6 [ $J_{(\text{Pt-P})} = 2316$  Hz,  $-\text{PPh}_2(\text{CH}_2)_2\text{Ph}_2\text{P}-$ ]. **3:** IR (KBr): 3282, 3231, 3050, 2952, 2918, 2100, 1597, 1500, 1491, 1434, 1308, 1217, 1158, 1101, 1069, 1026, 998, 970, 837, 791, 742, 693, 664, 546, 515  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_2\text{CDCl}_2$ ):  $\delta$  2.42–2.58 [br, 6H,  $-\text{PPh}_2(\text{CH}_2)_3\text{Ph}_2\text{P}-$ ], 3.11 [s, 2H,  $-\text{C}\equiv\text{C}-\text{H}$ ], 6.99–7.01 (d,  $J = 8.0$  Hz, 4H, Ar), 7.12–7.23 (m, 12H, P–Ar, Ar), 7.25–7.38 (m, 8H, P–Ar), 7.66–7.75 (m, 4H, P–Ar).  $^{31}\text{P}$  NMR (240 MHz,  $\text{CDCl}_2\text{CDCl}_2$ ):  $\delta$  -6.04 [ $J_{(\text{Pt-P})} = 2212$  Hz,  $-\text{PPh}_2(\text{CH}_2)_3\text{Ph}_2\text{P}-$ ]. **3<sub>dimer</sub>:** IR (KBr): 3284, 3050, 2959, 2920, 2099, 1597, 1500, 1491, 1435, 1308, 1215, 1170, 1100, 1070, 1026, 998, 955, 838, 741, 692, 618, 546, 512  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_2\text{CDCl}_2$ ):  $\delta$  2.80–3.02 [br, 12H,  $-\text{PPh}_2(\text{CH}_2)_3\text{Ph}_2\text{P}-$ ], 3.08 [s, 4H,  $-\text{C}\equiv\text{C}-\text{H}$ ], 6.39–6.46 (d,  $J = 8.4$  Hz, 8H, Ar), 6.97–7.04 (d,  $J = 8.4$  Hz, 8H, Ar), 7.16–7.22 (m, 16H, P–Ar), 7.27–7.42 (m, 16H, P–Ar), 7.60–7.68 (br, 8H, P–Ar).  $^{31}\text{P}$  NMR (240 MHz,  $\text{CDCl}_2\text{CDCl}_2$ ):  $\delta$  11.8 [ $J_{(\text{Pt-P})} = 2594$  Hz,  $-\text{PPh}_2(\text{CH}_2)_3\text{Ph}_2\text{P}-$ ]. **4<sub>dimer</sub>:** IR (KBr): 3283, 3049, 2923, 2098, 1597, 1500,

1476, 1434, 1308, 1214, 1179, 1100, 1069, 1025, 998, 836, 741, 693, 546, 513  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_2\text{CDCl}_2$ ):  $\delta$  2.18, 2.89 [br, 16H,  $-\text{PPh}_2(\text{CH}_2)_4\text{Ph}_2\text{P}-$ ], 3.11 [s, 4H,  $-\text{C}\equiv\text{C}-\text{H}$ ], 6.52–6.54 (d,  $J = 6.6$  Hz, 8H, Ar), 7.11–7.13 (d,  $J = 6.6$  Hz, 8H, Ar), 7.14–7.42 (m, 32H, P–Ar), 7.67–7.80 (m, 8H, P–Ar).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_2\text{CDCl}_2$ ):  $\delta$  9.79 [ $J_{(\text{Pt-P})} = 2555$  Hz,  $-\text{PPh}_2(\text{CH}_2)_4\text{Ph}_2\text{P}-$ ]. **4''**: IR (KBr): 3282, 3050, 2923, 2098, 1596, 1477, 1434, 1308, 1261, 1199, 1119, 1100, 1026, 997, 836, 742, 721, 692, 540  $\text{cm}^{-1}$ .

**Spectroscopic Data of the Polymers Obtained by the Ligand Exchange Reactions of 1' with dppe, dppp and dppb.**

**2'**: IR (KBr): 3422, 3289, 3053, 2958, 2927, 2851, 2205, 2107, 1735, 1701, 1685, 1671, 1648, 1596, 1570, 1560, 1540, 1522, 1484, 1466, 1436, 1406, 1365, 1228, 1162, 1105, 1028, 999, 913, 839, 750, 705, 692, 533  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_2\text{CDCl}_2$ ):  $\delta$  0.60–0.90 (br, 3H,  $-\text{CH}_2(\text{CH}_2)_4\text{CH}_3$ ), 1.00–1.60 [br, 17H,  $-\text{CH}_2(\text{CH}_2)_4\text{CH}_3$ ,  $-\text{C}(\text{CH}_3)_3$ ], 2.90–3.30 [br, 6H,  $-\text{CH}_2(\text{CH}_2)_4\text{CH}_3$ ,  $-\text{PPh}_2(\text{CH}_2)_2\text{Ph}_2\text{P}-$ ], 5.00–5.90 (br, 3H,  $\text{C}^*\text{H}$ ,  $\text{OCONH}$ ,  $\text{OH}$ ), 6.60–8.20 (br, 30H, Ar,  $-\text{PPh}_2(\text{CH}_2)_2\text{Ph}_2\text{P}-$ ).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_2\text{CDCl}_2$ ):  $\delta$  42.6 [ $J_{(\text{Pt-P})} = 2316$  Hz,  $-\text{PPh}_2(\text{CH}_2)_2\text{Ph}_2\text{P}-$ ]. **3'**: IR (KBr): 3414, 3295, 3053, 2952, 2927, 2857, 2205, 2100, 1707, 1671, 1595, 1560, 1484, 1435, 1406, 1391, 1366, 1231, 1161, 1100, 1028, 999, 972, 913, 838, 792, 743, 693, 513  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_2\text{CDCl}_2$ ):  $\delta$  0.70–0.90 (br, 3H,  $-\text{CH}_2(\text{CH}_2)_4\text{CH}_3$ ), 1.00–1.80 [br, 17H,  $-\text{CH}_2(\text{CH}_2)_4\text{CH}_3$ ,  $-\text{C}(\text{CH}_3)_3$ ], 2.80–3.70 [br, 8H,  $-\text{CH}_2(\text{CH}_2)_4\text{CH}_3$ ,  $-\text{PPh}_2(\text{CH}_2)_3\text{Ph}_2\text{P}-$ ], 5.00–5.95 (br, 3H,  $\text{C}^*\text{H}$ ,  $\text{OCONH}$ ,  $\text{OH}$ ), 6.80–8.00 (br, 30H, Ar,  $-\text{PPh}_2(\text{CH}_2)_3\text{Ph}_2\text{P}-$ ).  $^{31}\text{P}$  NMR (240 MHz,  $\text{CDCl}_2\text{CDCl}_2$ ):  $\delta$  12.2 [ $J_{(\text{Pt-P})} = 2547$  Hz,  $-\text{PPh}_2(\text{CH}_2)_3\text{Ph}_2\text{P}-$ ]. **4'**: IR (KBr): 3422, 3300, 3053, 2928, 2857, 2205, 2100, 1701, 1676, 1595, 1570, 1560, 1540, 1522, 1484, 1435, 1406, 1366, 1229, 1167, 1101, 1028, 838, 741, 693, 520  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_2\text{CDCl}_2$ ):  $\delta$  0.70–0.85 (br, 3H,  $-\text{CH}_2(\text{CH}_2)_4\text{CH}_3$ ), 0.90–1.80 [br, 17H,  $-\text{CH}_2(\text{CH}_2)_4\text{CH}_3$ ,  $-\text{C}(\text{CH}_3)_3$ ], 2.40–3.35 [br, 10H,  $-\text{CH}_2(\text{CH}_2)_4\text{CH}_3$ ,  $-\text{PPh}_2(\text{CH}_2)_4\text{Ph}_2\text{P}-$ ], 5.00–5.95 (br, 3H,  $\text{C}^*\text{H}$ ,  $\text{OCONH}$ ,  $\text{OH}$ ), 6.30–8.10 (br, 30H, Ar,  $-\text{PPh}_2(\text{CH}_2)_4\text{Ph}_2\text{P}-$ ).

**Computation.** All calculations were performed with the GAUSSIAN 09 program,<sup>7</sup> EM64L-G09 Rev E.01, running on the supercomputer system, Academic Center for Computing and Media Studies, Kyoto University. The HOMO-LUMO energy levels were calculated by the DFT method with the B3LYP functional<sup>8</sup> in conjunction with the LANL2DZ<sup>9–12</sup> basis set for Pt and the 6-31G\* basis set for the other elements.



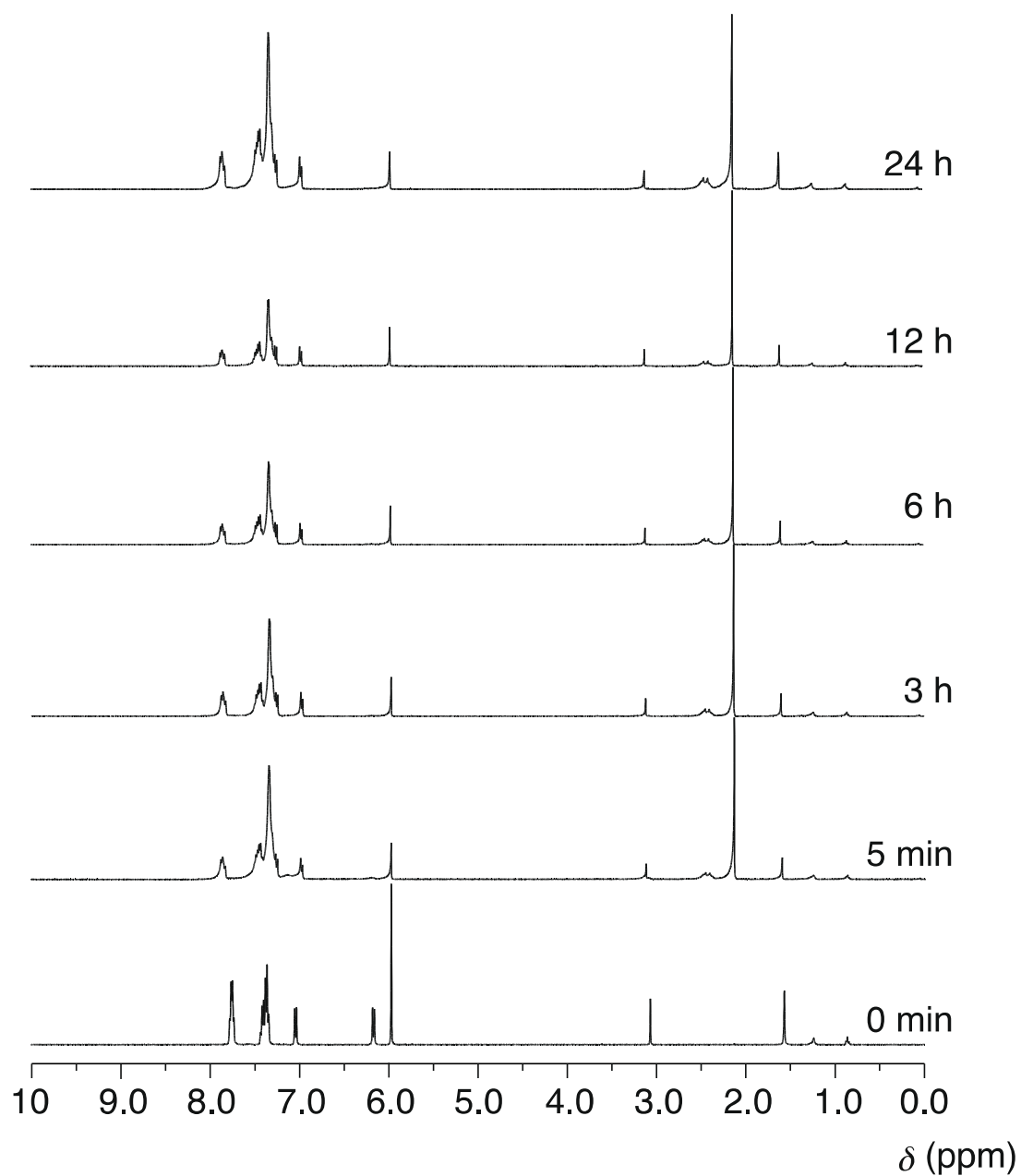


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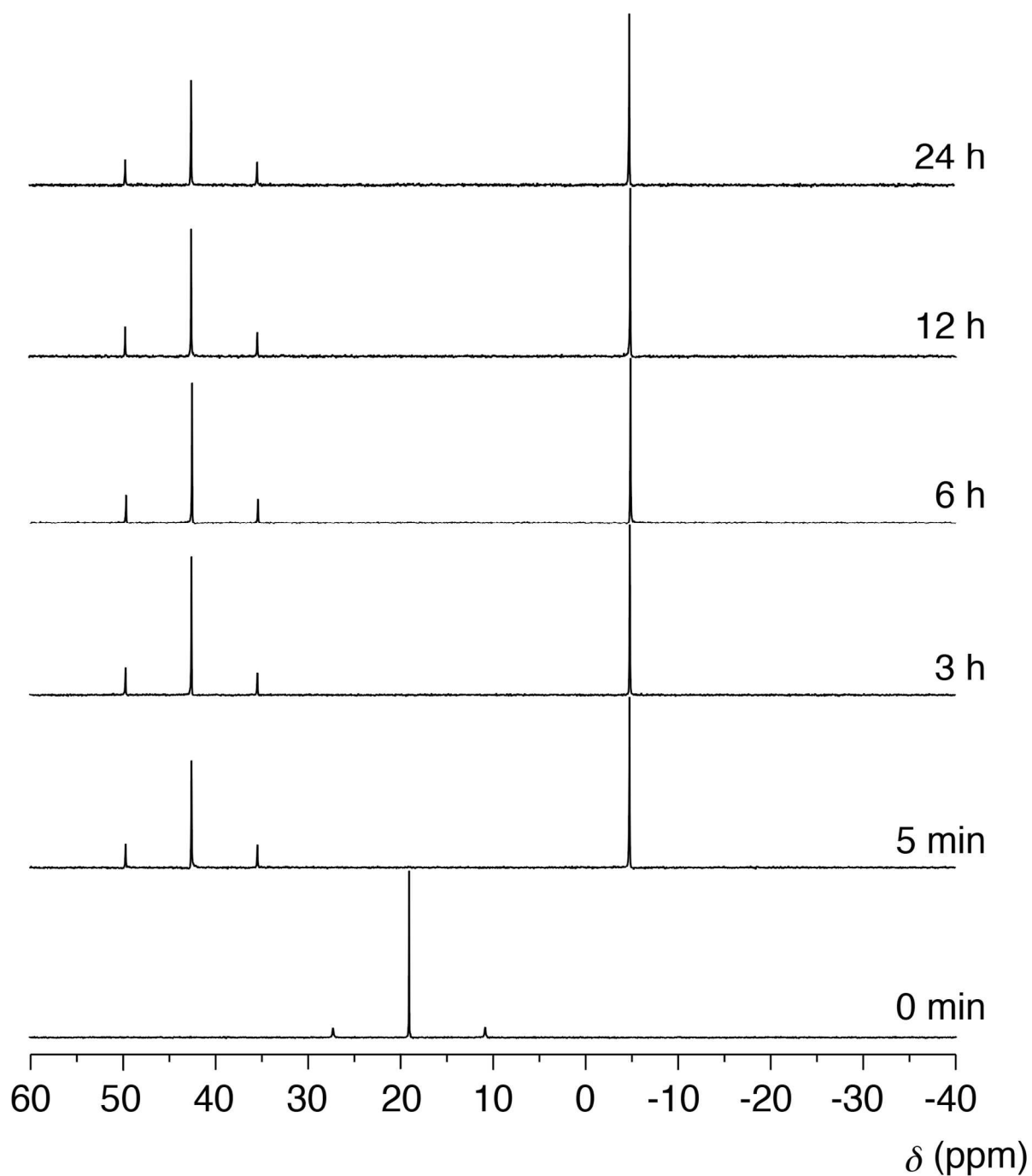
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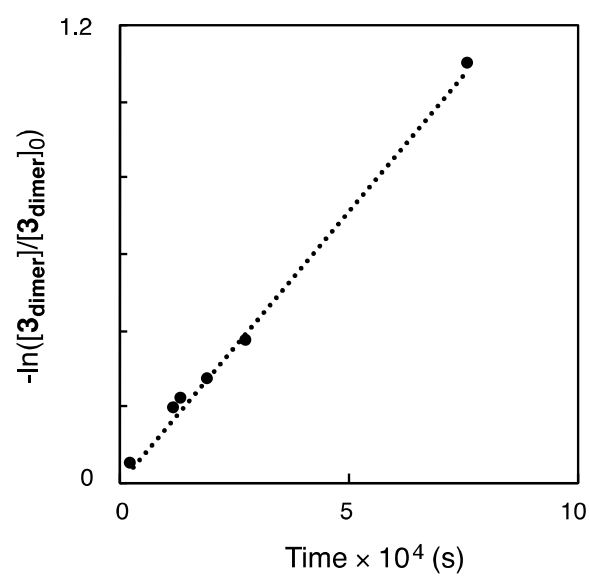
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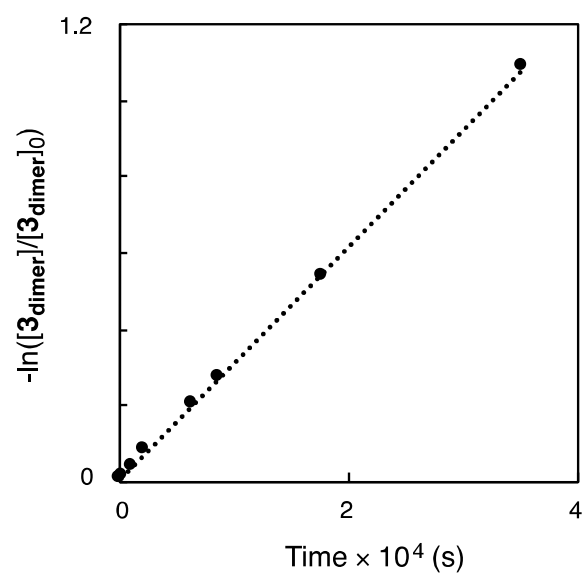
**Figure S1.**  $^1\text{H}$  NMR (400 MHz) spectroscopic change of a mixture of compound **1** and dppe over a period of 0–24 hours measured in  $\text{CDCl}_2\text{CDCl}_2$  ( $c = 10 \text{ mM}$ ) at 25 °C.



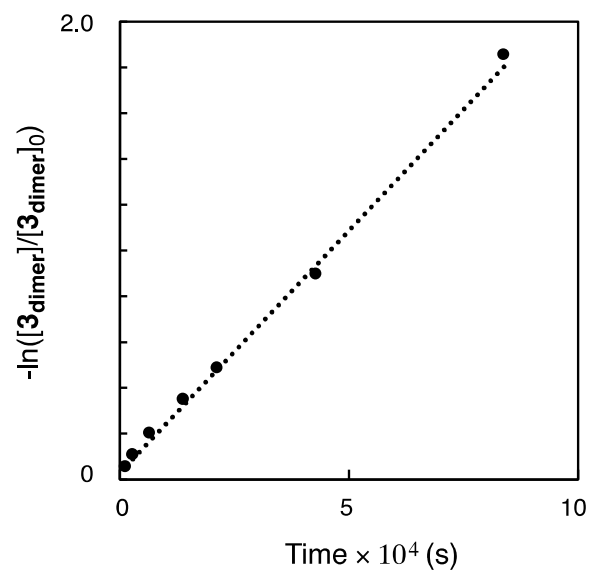
**Figure S2.**  $^{31}\text{P}$  NMR (162 MHz) spectroscopic change of a mixture of compound **1** and dppe over a period of 0–24 hours measured in  $\text{CDCl}_2\text{CDCl}_2$  ( $c = 10 \text{ mM}$ ) at 25 °C.



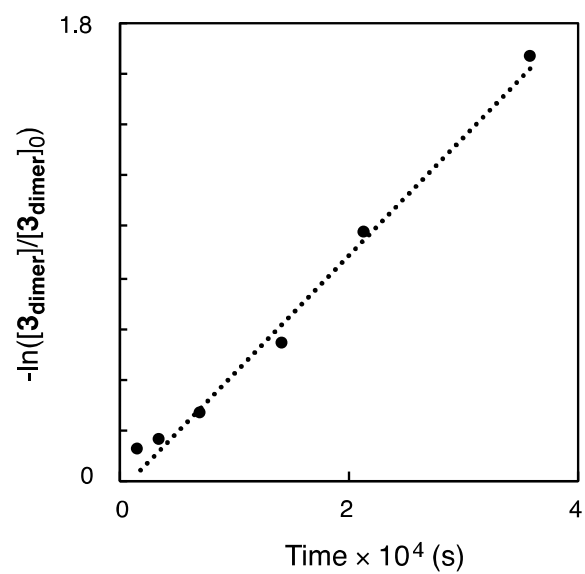
**Figure S3.** First-order plot of the transformation from  $\mathbf{3}_{\text{dimer}}$  into  $\mathbf{3}$  in  $\text{CDCl}_2\text{CDCl}_2$  ( $c = 10 \text{ mM}$ ) at 45°C.



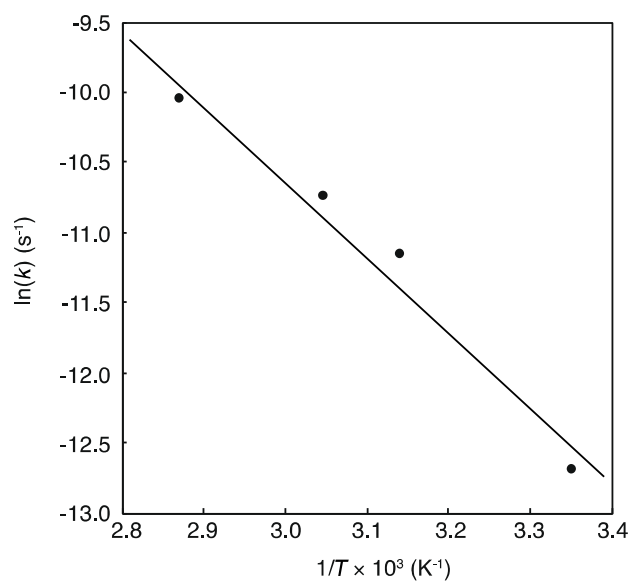
**Figure S4.** First-order plot of the transformation of  $\mathbf{3}_{\text{dimer}}$  into  $\mathbf{3}$  in  $\text{CDCl}_2\text{CDCl}_2$  ( $c = 10 \text{ mM}$ ) at 25 °C.



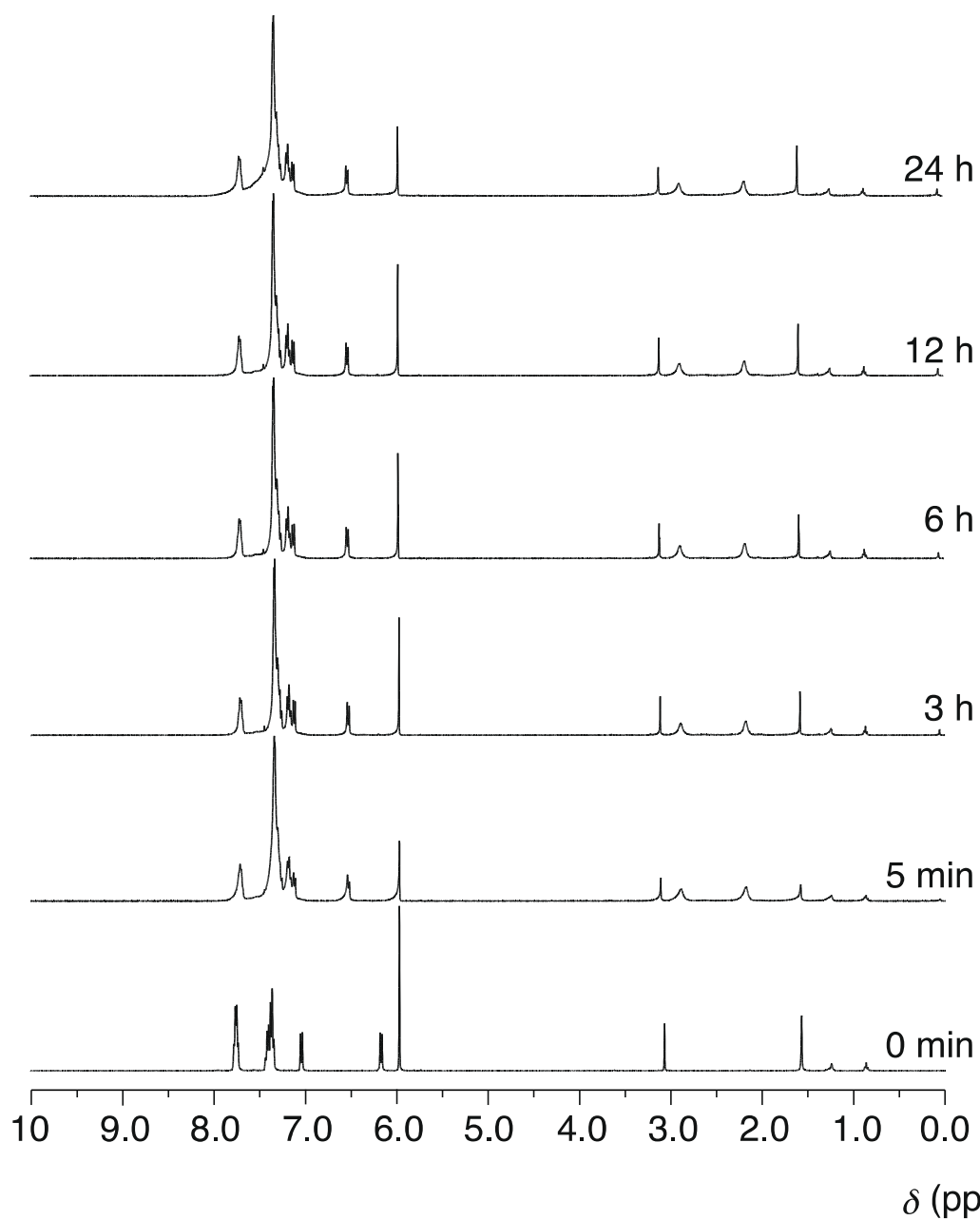
**Figure S5.** First-order plot of the transformation of  $\mathbf{3}_{\text{dimer}}$  into  $\mathbf{3}$  in  $\text{CDCl}_2\text{CDCl}_2$  ( $c = 10 \text{ mM}$ ) at  $55^\circ\text{C}$ .



**Figure S6.** First-order plot of the transformation of  $\mathbf{3}_{\text{dimer}}$  into  $\mathbf{3}$  in  $\text{CDCl}_2\text{CDCl}_2$  ( $c = 10 \text{ mM}$ ) at  $75^\circ\text{C}$ .

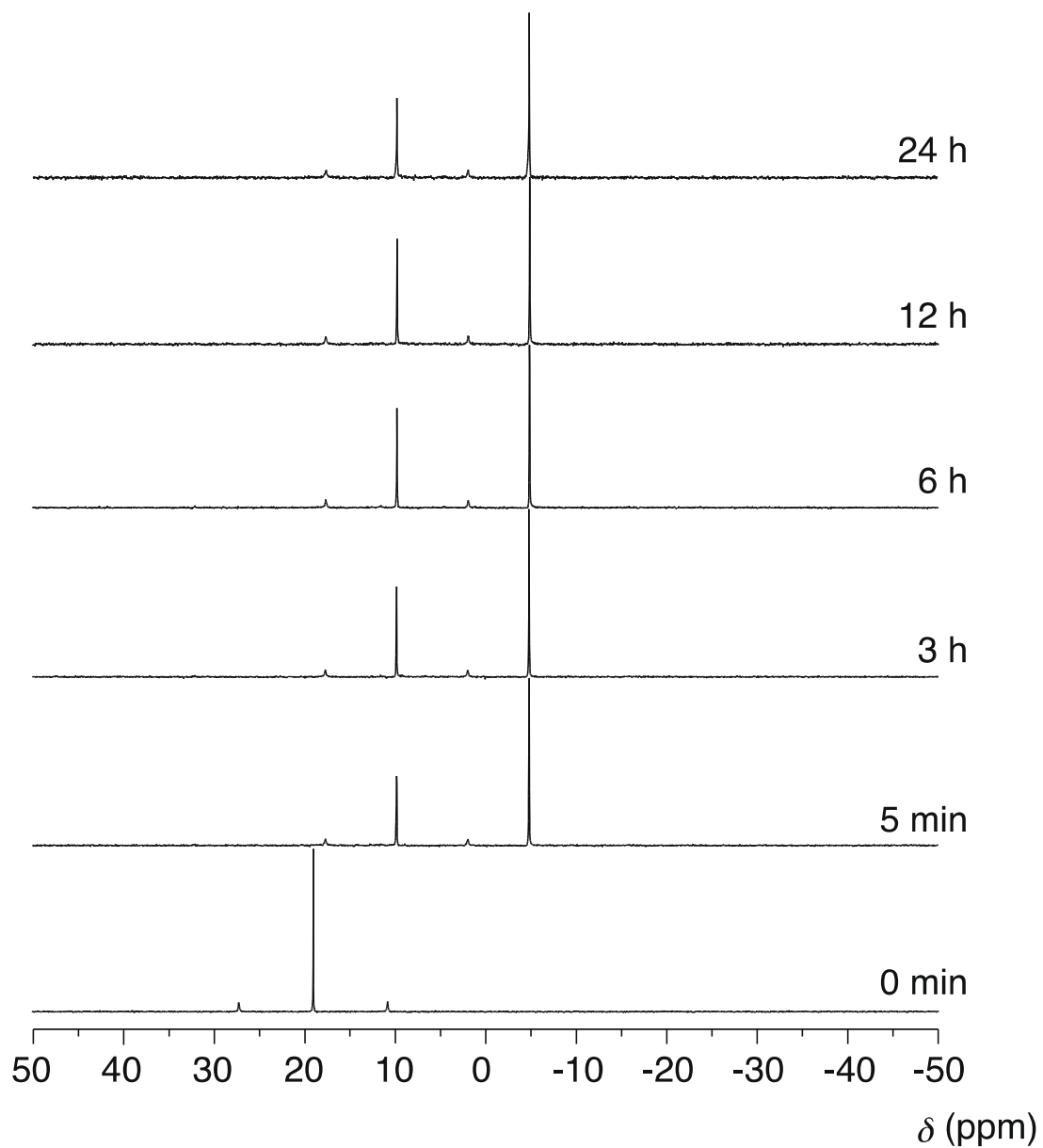


**Figure S7.** Arrhenius plot of the transformation from **3**<sub>dimer</sub> into **3** in CDCl<sub>2</sub>CDCl<sub>2</sub> ( $c = 10$  mM). Rate constants  $k$  were evaluated from the slopes of the first-order plots.

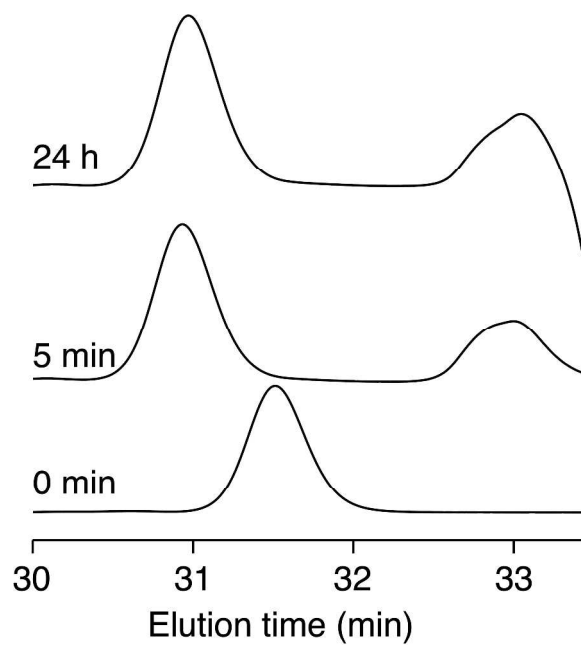


**Figure S8.**  $^1\text{H}$  NMR (400 MHz) spectroscopic change of a mixture of compound **1** and dppb over a period of 0–24 hours measured in  $\text{CDCl}_2\text{CDCl}_2$  ( $c = 10 \text{ mM}$ ) at 25 °C.

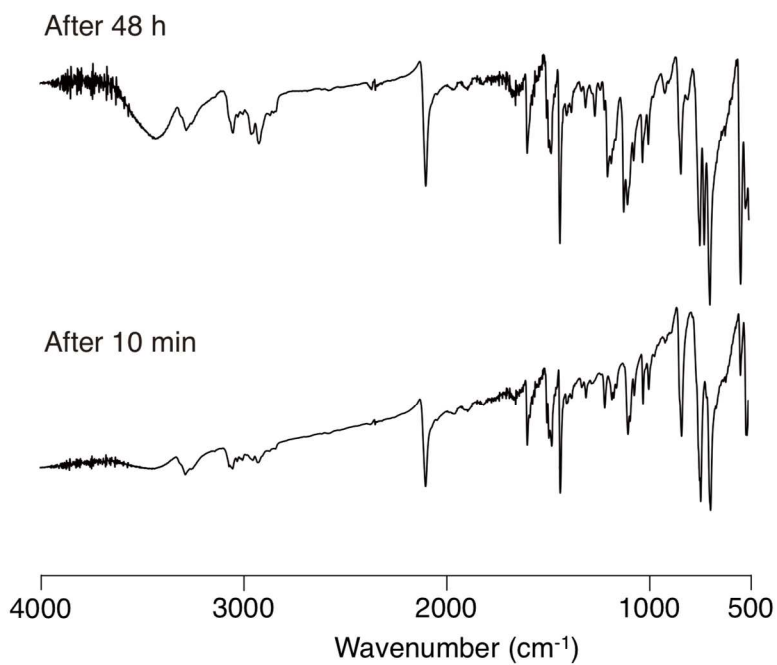




**Figure S9.**  $^{31}\text{P}$  NMR (162 MHz) spectroscopic change of a mixture of compound **1** and dppb over a period of 0–24 hours measured in  $\text{CDCl}_2\text{CDCl}_2$  ( $c = 10 \text{ mM}$ ) at  $25^\circ\text{C}$ .

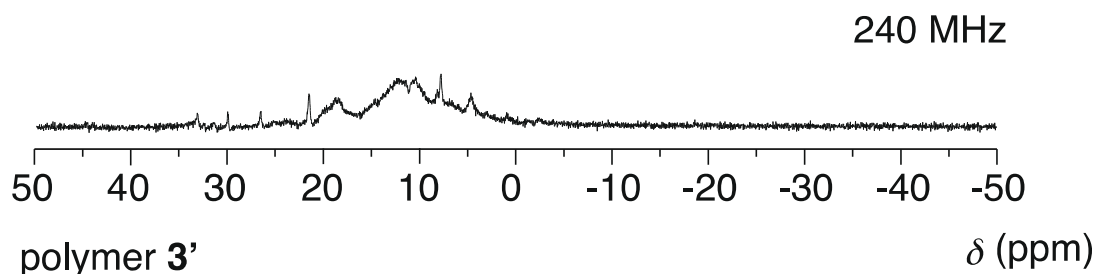


**Figure S10.** SEC charts (eluent:  $\text{CHCl}_3$ , detector: RI) of a mixture of compound **1** and dppb in  $\text{CHCl}_3$  ( $c = 10 \text{ mM}$ ) over a period of 0–24 hours at  $25^\circ\text{C}$ .

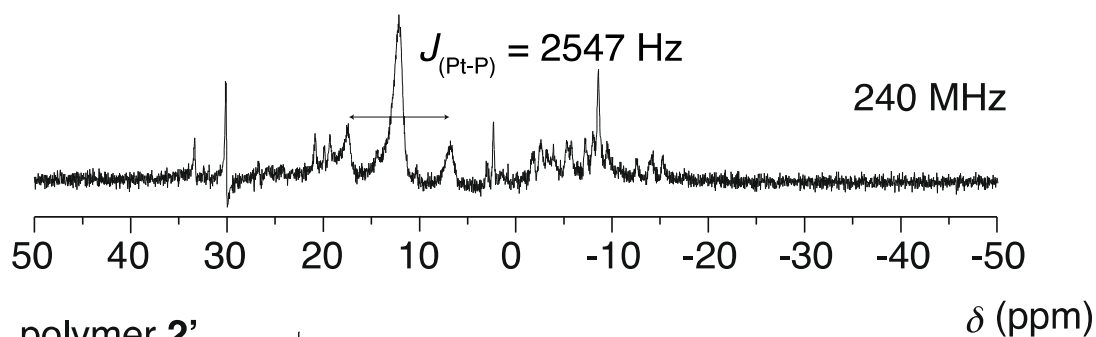


**Figure S11.** IR spectra of a mixture of compound **1** and dppb in  $\text{CHCl}_3$  ( $c = 10 \text{ mM}$ ) over a period of 10 min and 48 hours at  $25^\circ\text{C}$ .

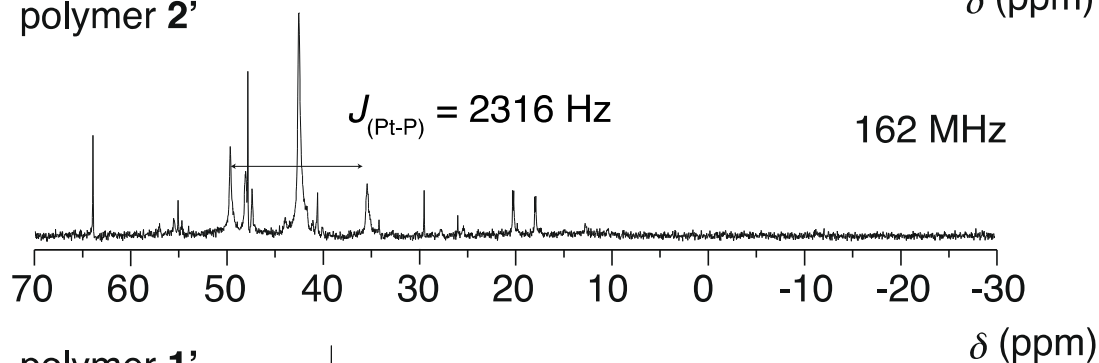
polymer 4'



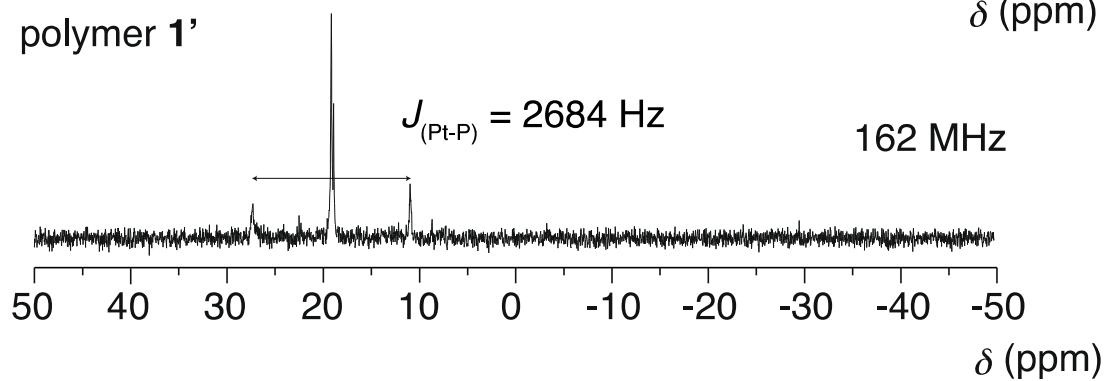
polymer 3'



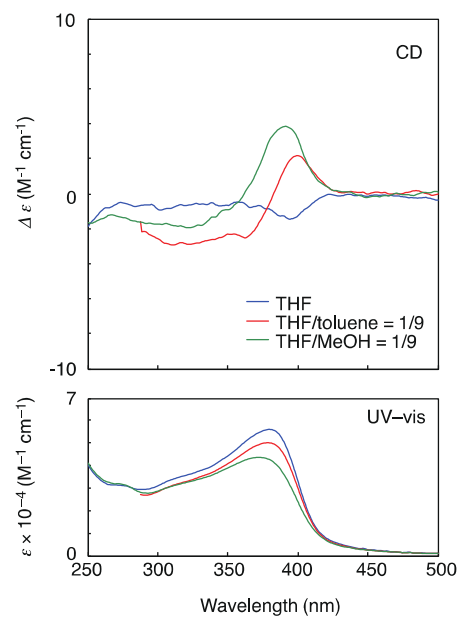
polymer 2'



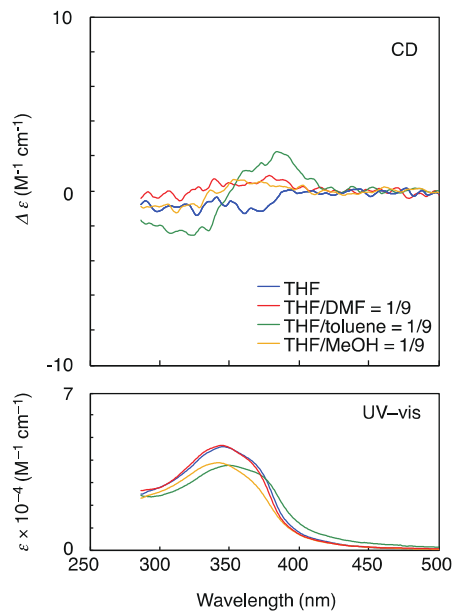
polymer 1'



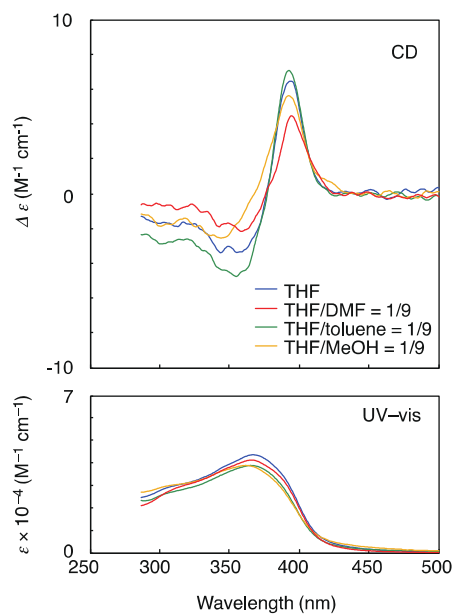
**Figure S12.**  $^{31}\text{P}$  NMR (162 and 240 MHz) spectra of polymers 1' , 2' , 3' and 4' measured in  $\text{CDCl}_2\text{CDCl}_2$  (20 °C).



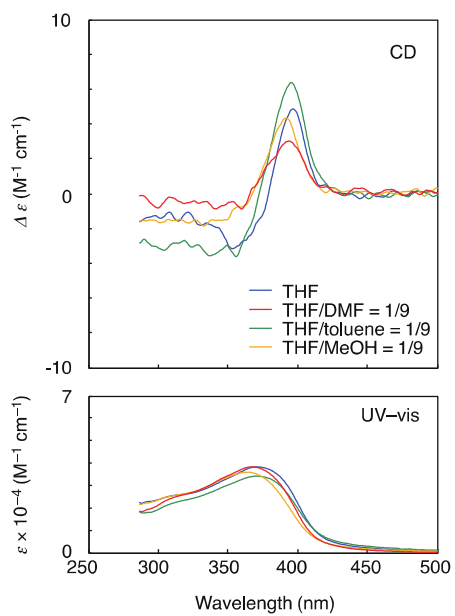
**Figure S13.** CD and UV-vis spectra of polymer **1'** measured in various solvents ( $c = 0.02$  mM, 20 °C).



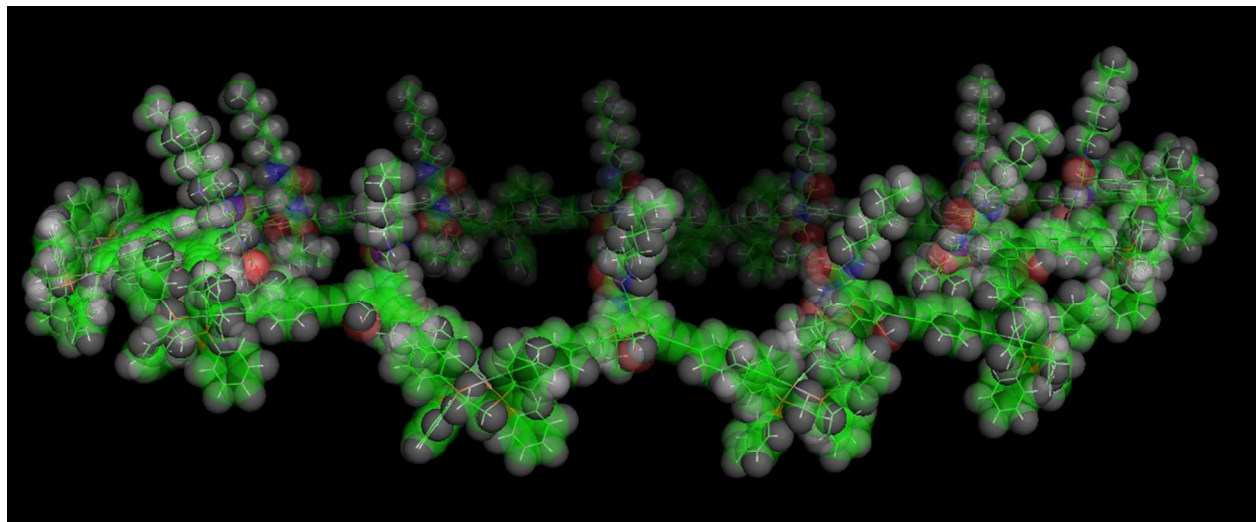
**Figure S14.** CD and UV-vis spectra of polymer **2'** measured in various solvents ( $c = 0.02$  mM, 20 °C).



**Figure S15.** CD and UV-vis spectra of polymer **3'** measured in various solvents ( $c = 0.02 \text{ mM}$ ,  $20 \text{ }^{\circ}\text{C}$ ).



**Figure S16.** CD and UV-vis spectra of polymer **4'** measured in various solvents ( $c = 0.02 \text{ mM}$ ,  $20 \text{ }^{\circ}\text{C}$ ).



**Figure S17.** Tilt view of a 12-mer model for polymer **2'**. The geometries were optimized by the DFT method [B3LYP/6-31G\* (C, H, N, O, P)-LANL2DZ (Pt)].

**Table S1.  $\lambda_{\text{max}}$  and Hydrodynamic Diameters of Polymer 4'**

polymer	$\lambda_{\text{max}}^a$ (nm)	hydrodynamic diameter $^b$ (nm)				
		CHCl <sub>2</sub> CHCl <sub>2</sub>	CHCl <sub>2</sub> CHCl <sub>2</sub> / MeOH = 1/9	CHCl <sub>2</sub> CHCl <sub>2</sub> / hexane = 1/9	CHCl <sub>2</sub> CHCl <sub>2</sub> / toluene = 1/9	CHCl <sub>2</sub> CHCl <sub>2</sub> / DMF = 1/9
<b>4'</b>	370	28	— <sup>c</sup>	1200	3000	20

<sup>a</sup> Measured in CHCl<sub>2</sub>CHCl<sub>2</sub> ( $c = 0.02$  mM) at 20 °C. <sup>b</sup> Measured by DLS ( $c = 0.02$  mM) at 25 °C. <sup>c</sup> Could not be determined.