

Cobalt(III) Complexes of Various Salen-Type Ligand Bearing Four Quaternary Ammonium Salts and Their Reactivity for CO₂/Epoxide Copolymerization

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Ligand variation was carried out on a cobalt(III) complex of Salen-type ligand comprised of 1,2-cyclohexanediamine and salicylaldehyde bearing a methyl substituent on 3-position and $-\text{[CMe(CH}_2\text{CH}_2\text{CH}_2\text{N}^+\text{Bu}_3\text{)]}_2$ on 5-position, which is a highly active catalyst for CO₂/propylene oxide copolymerization. Replacement of the methyl substituent with bulky isopropyl group resulted in alteration of the binding mode, consequently lowering turnover frequency significantly. Replacement with an ethyl group preserved binding mode and activity. Replacement of the tributylammonium unit with trihexylammonium or trioctylammonium, or replacement of 1,2-cyclohexanediamino unit with $-\text{NC(Me)}_2\text{CH}_2\text{N}-$ decreased activity, even though the binding mode was unaltered.

Key Words: Carbon dioxide, Epoxide, Salen-cobalt complexes, Quaternary ammonium salt, Polymerization

Introduction

Recently, we disclosed a highly active catalytic system (**1**) for CO₂/propylene oxide (PO) copolymerization, which showed a high turnover number (TON) up to 20000 and a high turnover frequency (TOF) of 20000 h⁻¹. It produced a strictly alternating copolymer with a high molecular weight (M_n) of up to 300000 and a high selectivity (> 99%). Another advantage of **1** was that the catalyst was efficiently removed after polymerization from a polymer solution through filtration over a short pad of silica gel. The collected catalyst on the silica surface could then be recovered and reused. Catalyst residue removal is crucial for the copolymerization not only because the catalyst residue colors the resin but also because the residue is toxic and causes a severe thermal degradation during processing.² These performances allow for the design of a continuous commercial process. The CO₂/PO copolymer is attractive due to its favorable properties.³ Catalyst **1** was discovered while trying to develop a catalyst based on the concept of binding two components or two metal centers.⁴ The binding situated both components in close proximity regardless of the low catalyst concentration or high polymerization temperature to achieve a TON as well as high molecular weight. Later, we elucidated that the cobalt(III) complex adopted an unusual binding mode, where imine-nitrogens on the Salen-type ligand did not coordinate but, instead, the counter anions of the tethered quaternary ammonium coordinated to cobalt.⁵

The structure of the catalyst is a kind of supramolecular assembly working properly on the ion-ion interaction and hydrogen bonding, and the performances were highly sensitive to the ligand structure. For example, substituting hydrogen in **1** with methyl at a remote site from the reaction site (**2**) reduced the TOF from 20000 h⁻¹ to 16000 h⁻¹.⁵ Catalyst **2** could be prepared on a large scale while preparation of **1** was not easy.⁶ Replacing the cyclohexanediamino group with ethylenediamino group (**3**) reduced the TOF further to 8300 h⁻¹. These observations prompted us to investigate thoroughly the influence of the ligand structure on the catalytic performances.

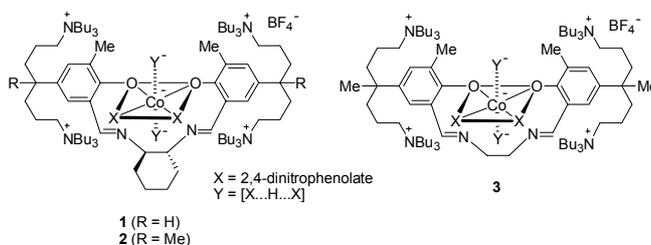
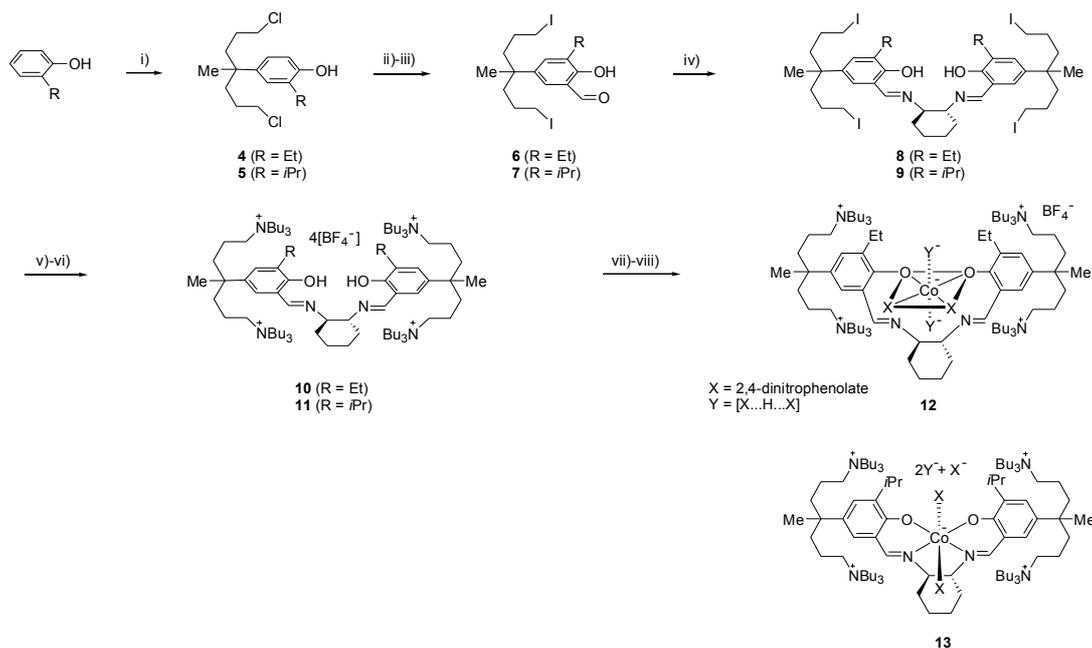


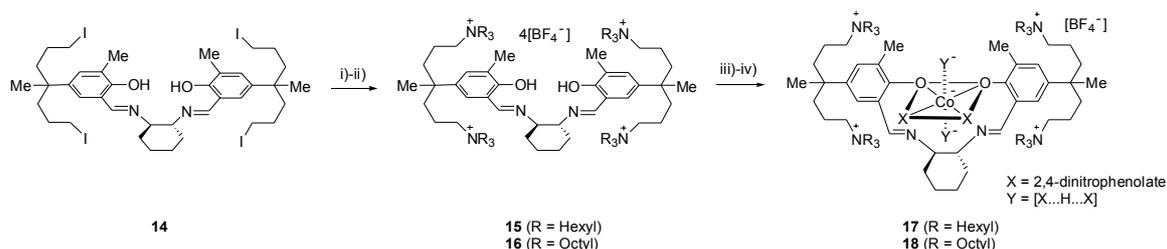
Chart 1. Salen-Co(III) catalysts for CO₂/epoxide copolymerization.

Results and Discussion

Synthesis and characterization. Variation was made on the *ortho*-substituent of the Salen-phenoxy ligand. It was already revealed that bulky *tert*-butyl substituent on the *ortho*-position blocks formation of the imine uncoordinated binding mode of complexes **1** and **2**. The complex bearing *tert*-butyl substituent was not highly active. Complexes bearing ethyl and isopropyl substituent were prepared according to the same synthetic route employed for the synthesis of **2** (Scheme 1).⁶ Thus, Friedel-Craft alkylation of 2-ethylphenol using 1,7-dichloro-4-methylheptan-4-ol in the presence of AlCl₃ produced compound **4** in 95% yield. In this reaction, 2-ethylphenol was used as both a reactant and a solvent, and no additional solvent was required. The excess 2-ethylphenol was recovered by vacuum distillation (60 °C/2 mmHg) and the remaining residue was pure **4** as determined by ¹H and ¹³C NMR, and was amenable for the next reaction without further purification. Formylation of **4** using paraformaldehyde, triethylamine, and magnesium chloride was successful with good efficiency (92% yield).⁷ Because tributylamine could not attack chloroalkane, the chloro-compound was transformed into a more reactive iodo-compound **6** in 81% yield. After Salen-type ligand was generated from **6**, tributylamine could attack the iodo-group yielding a Salen-type ligand containing four quaternary ammonium salts (**8**) in 86% yield. Because iodide anion intervenes in the metallation reaction, it was replaced with an inert BF₄⁻ through treatment of AgBF₄.



Scheme 1. i) 1,7-Dichloro-4-methylheptan-4-ol/ AlCl_3 ; ii) Paraformaldehyde/ $\text{NEt}_3/\text{MgCl}_2$; iii) NaI in CH_3CN ; iv) 1,2-*Trans*-diaminocyclohexane in CH_2Cl_2 ; v) Bu_3N in CH_3CN ; vi) AgBF_4 ; vii) $\text{Co}(\text{OAc})_2$ in ethanol; viii) O_2 and 2,4-dinitrophenol in CH_2Cl_2 , then $3[2,4-(\text{NO}_2)_2\text{C}_6\text{H}_3\text{O}]\text{Na} + 2[2,4-(\text{NO}_2)_2\text{C}_6\text{H}_3\text{OH}]$



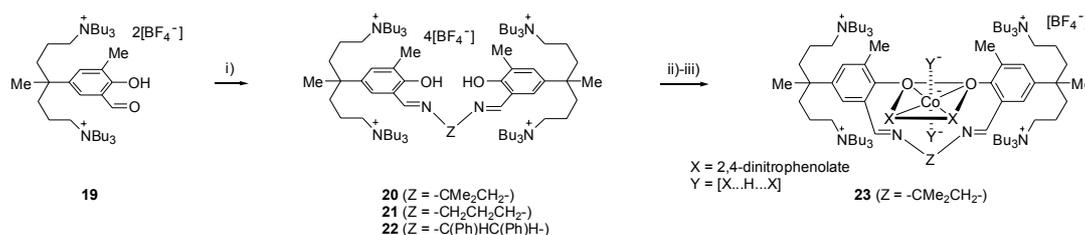
Scheme 2. i) Trihexylamine or trioctylamine in CH_3CN ; ii) AgBF_4 ; iii) $\text{Co}(\text{OAc})_2$ in ethanol; iv) O_2 and 2,4-dinitrophenol in CH_2Cl_2 , then $3[2,4-(\text{NO}_2)_2\text{C}_6\text{H}_3\text{O}]\text{Na} + 2[2,4-(\text{NO}_2)_2\text{C}_6\text{H}_3\text{OH}]$

Metallation was carried out by a routine method involving the treatment of $\text{Co}(\text{OAc})_2$ in ethanol and oxidation using O_2 in the presence of an equivalent amount of 2,4-dinitrophenol. Finally, anion exchange reaction was carried out by stirring the BF_4^- complex over a slurry of three equivalents of sodium 2,4-dinitrophenolate and two equivalents of 2,4-dinitrophenol in CH_2Cl_2 . The Salen-aromatic signals were very broad at 7.87, 7.36 and 7.24 ppm in the ^1H NMR spectrum of the final complex **12** in $\text{DMSO}-d_6$. Observation of broad Salen-aromatic signals in $\text{DMSO}-d_6$ was indicative of formation of the unusual imine uncoordinated binding mode. For the complex of the conventional imine coordinated Salen-complexes, the Salen-aromatic signals were sharp in $\text{DMSO}-d_6$. In $\text{THF}-d_8$, only two 2,4-dinitrophenolate signals per cobalt were observed at the region of 8.8 ~ 9.0 ppm, of which chemical shifts are significantly different from those of free 2,4-dinitrophenolate anion allowing assignment of the observed signals to the persistently coordinated two 2,4-dinitrophenolate. The remaining 2,4-dinitrophenol-2,4-dinitrophenolate homoconjugate was fluxional and the signals were missing due to severe broadening. Observation of the two 2,4-dinitrophenolate signals at the region of 8.8 ~ 9.0 ppm was also an

evidence for formation of the unusual imine uncoordinated binding mode.

Isopropyl complex **13** was also prepared by the same method and conditions employed for preparation of **12** (Scheme 1). In the ^1H NMR spectrum of **13** in $\text{DMSO}-d_6$, the Salen-aromatic signals were sharp at 7.83, 7.32, and 7.21 ppm as was observed for the *tert*-butyl complex, which was indicative of formation of the conventional imine coordinated binding mode. In $\text{THF}-d_8$, the characteristic coordinated 2,4-dinitrophenolate signals at 7.8 ~ 9.0 ppm were not observed. Instead, very broad signals were observed in the aromatic region, which was also indicative of formation of the conventional imine coordinated binding mode.

In the binary catalytic system of [(Salen)Co-complexes]/(quaternary ammonium salt), it was reported that the activity was improved by replacing the tetrabutylammonium salt with a more bulky tetraheptylammonium salt.⁸ So, we prepared the derivatives by variation of the ammonium salt unit (Scheme 2). Trioctylamine, trihexylamine, and tripropylamine attacked the iodo-group to generate the corresponding quaternary ammonium salts. After treatment of AgBF_4 to replace the iodide anion



Scheme 3. i) $\text{H}_2\text{N-Z-NH}_2$; ii) $\text{Co}(\text{OAc})_2$ in ethanol; iii) O_2 and 2,4-dinitrophenol in CH_2Cl_2 , then $3[2,4-(\text{NO}_2)_2\text{C}_6\text{H}_3\text{O}]\text{Na} + 2[2,4-(\text{NO}_2)_2\text{C}_6\text{H}_3\text{OH}]$

with BF_4^- , the product was purified by passing through a short pad of silica gel with a mixture of CH_2Cl_2 and ethanol (v/v, 5:1) to afford clean trihexylammonium salt (**15**) and trioctylammonium salt (**16**). In the case of tripropylammonium salt, the salt was destroyed during the chromatography. Metallations were carried out by the same method and condition applied for the preparation of **2** or **12**. Observation of broad Salen-aromatic signals in the ^1H NMR spectra of **17** and **18** in $\text{DMSO}-d_6$ were indicative of formation of the unusual imine uncoordinated binding mode.

We attempted the variation of the cyclohexanediamino unit (Scheme 3). Compound **19** was prepared by the hydrolysis of the corresponding Salen-type ligand by the action of HBF_4 .^{5(a)} Schiff bases **20-22** were generated quantitatively just by mixing the corresponding diamine and equivalent amount of **19**. From ligand **20** containing $-\text{NC}(\text{Me})_2\text{CH}_2\text{N}-$ unit, the desired complex **23** was obtained. In the ^1H NMR spectrum in $\text{DMSO}-d_6$, the Salen-phenoxy signals were broad indicating the unusual imine uncoordinated binding mode. In $\text{THF}-d_8$, two sets of sharp Salen-phenoxy signals were observed at 7.67, 7.56, 6.60, 6.60, 6.49, and 6.39 ppm along with the characteristic signals of the coordinated two 2,4-dinitrophenolate. From the ligands **21** and **22** containing $-\text{CH}_2\text{CH}_2\text{CH}_2-$ and $-\text{C}(\text{Ph})\text{HC}(\text{Ph})\text{H}-$ units, respectively, we failed in preparation of a clean complex. The signals in the ^1H NMR spectrum were very complicated and broad.

Polymerization studies. Complex **12** bearing ethyl substituent, which adopted the unusual imine uncoordinated binding mode, was highly active (TOF, 11000 h^{-1}) for the CO_2/PO copolymerization at conditions of $[\text{PO}]/[\text{Cat}] = 50000$, $70 \sim 75^\circ\text{C}$, and $P_{\text{CO}_2} = 17 \sim 20$ bar (entry 1 in Table 1), while isopropyl **13** adopting the conventional imine coordinated structure exhibited significantly lower activity (TOF, 3200 h^{-1}). This trend of an extraordinary high activity for the unusual binding mode is in agreement with the previous reports.⁵ The selectivity for the formation of polymer over cyclic carbonate was also excellent for the high active **12** ($> 99\%$), but it was lowered (94%) for the less active **13**. However, the activity of the ethyl complex **12** was not better than that of the methyl complex **2**. The activity was also sensitive to the bulkiness of the ammonium salt. Replacing tributylammonium units with trihexylammonium ones resulted in lowering activity (TOF) from 15000 h^{-1} to 10000 h^{-1} , and replacing with more bulky trioctylammonium units lowered the activity significantly to 6100 h^{-1} (entries 3-4 vs. entry 6). Reaction site of the cobalt center might be blocked by the bulky ammonium units to lower the activity. Replacing the cyclohexanediamino group with $-\text{NC}(\text{Me})_2\text{CH}_2\text{N}-$ group also drama-

Table 1. $\text{CO}_2/(\text{propylene oxide})$ copolymerization results^a

Entry	Catalyst	TOF ^b (h^{-1})	Selectivity ^c	$M_n^d \times 10^{-3}$	M_w/M_n
1	12	11000	> 99	142	1.02
2	13	3200	94	75	1.29
3	17	10000	> 99	126	1.07
4	18	6100	92	84	1.09
5	23	3300	94	60	1.04
6 ^e	2	15000	> 99	270	1.26

^aPolymerization condition: PO (10 g, 170 mmol), $[\text{PO}]/[\text{Cat}] = 50000$, CO_2 ($2.0 \sim 1.7$ MPa), $70 \sim 75^\circ\text{C}$, 60 minutes. ^bCalculated based on the weight of the isolated polymer including the cyclic carbonate. ^cSelectivity of polycarbonate over cyclic carbonate in units of % as determined by ^1H NMR spectroscopy of the crude product. ^dDetermined on GPC using a polystyrene standard. ^eData from reference 5.

tically decreased the activity from 15000 h^{-1} to 3300 h^{-1} , even though the binding mode of **23** was identical with the cyclohexanediamino complex **2** (entry 5 vs. entry 6). Molecular weight distributions (M_w/M_n) were narrow ($1.02 \sim 1.29$) indicating an immortal polymerization.

Summary

Ligand variation was carried out on a cobalt(III) complex of Salen-type ligand comprised of 1,2-cyclohexanediamine and salicylaldehyde bearing a methyl substituent on 3-position and $-\text{CMe}(\text{CH}_2\text{CH}_2\text{CH}_2\text{N}^+\text{Bu}_3)_2$ on 5-position, which is a highly active catalyst for $\text{CO}_2/\text{propylene oxide}$ copolymerization. Replacement of the methyl substituent with bulky isopropyl group resulted in alteration of the binding mode from unusual imine uncoordinated structure to the conventional imine coordinated one, consequently lowering TOF significantly from 15000 h^{-1} to 3200 h^{-1} . Replacement with ethyl group preserved binding mode and activity. Replacement of tributylammonium unit with trihexylammonium and trioctylammonium or replacement of 1,2-cyclohexanediamino unit with $-\text{NC}(\text{Me})_2\text{CH}_2\text{N}-$ also reduced the activity to 10000 h^{-1} , 6100 h^{-1} , and 3300 h^{-1} , respectively, even though the binding mode was unaltered.

Experimental Section

General remarks. All manipulations were performed under an inert atmosphere using standard glove box and Schlenk techniques. THF and C_6D_6 were distilled from benzophenone ketyl.

Ethanol was dried as previously described using sodium and diethyl phthalate.⁹ CH₃CN, CH₂Cl₂, and CDCl₃ were dried by stirring over CaH₂, and were subsequently vacuum-transferred to reservoirs. The CO₂ gas (99.999%) was dried by storing in a column of molecular sieves 3A at 30 bar. Propylene oxide (PO) was dried by stirring over CaH₂ for several days, and it was vacuum-transferred to a reservoir. The ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were recorded on a Varian Mercury Plus 400. Gel permeation chromatograms (GPC) were obtained at room temperature in chloroform using Waters Millennium with polystyrene standards. Compounds **14** and **19** were prepared by the method reported previously in the literature.^{6,5(a)}

Compound 4. 2-Ethylphenol (4.91 g, 40.2 mmol), 1,7-dichloro-4-methylheptan-4-ol (1.00 g, 5.02 mmol), and AlCl₃ (0.736 g, 5.52 mmol) were mixed and the mixture was stirred overnight under an atmosphere of N₂. The reaction was quenched by the addition of diethyl ether (25 mL) and water (15 mL). The organic phase was collected and the water phase was further extracted with additional diethyl ether (3 × 25 mL). After the combined diethyl ether was dried over anhydrous MgSO₄, the solvent was removed with a rotary evaporator. The excess 2-ethylphenol was recovered by vacuum distillation (60 °C/2 mmHg). Yellowish oily product was obtained (1.49 g, 95%). IR (KBr) 3289 (OH) cm⁻¹. ¹H NMR (CDCl₃) δ 7.03 (d, *J* = 2.0 Hz, 1H, *m*-H), 6.96 (dd, *J* = 8.0 Hz, 2.0 Hz, 1H, *m*-H), 6.71 (d, *J* = 8.0 Hz, 1H, *o*-H), 4.71 (s, 1H, OH), 3.45 (t, *J* = 6.4 Hz, 4H, CH₂Cl), 2.75 (q, *J* = 7.6 Hz, 2H, CH₂), 1.80-1.42 (m, 8H, CH₂), 1.33 (s, 3H, CH₃), 1.28 (t, *J* = 7.6 Hz, 3H, CH₃). HRMS (EI) *m/z* calcd (M⁺ C₁₆H₂₄Cl₂O) 302.1246, found 302.1248.

Compound 5. This compound was synthesized using the same conditions and procedure as compound **4** starting with 2-*iso*-propylphenol. Yellowish oily product was obtained in 92% yield. IR (KBr) 3294 (OH) cm⁻¹. ¹H NMR (CDCl₃) δ 7.09 (d, *J* = 2.0 Hz, 1H, *m*-H), 6.95 (dd, *J* = 8.0 Hz, 2.0 Hz, 1H, *m*-H), 6.68 (d, *J* = 8.0 Hz, 1H, *o*-H), 4.68 (s, 1H, OH), 3.45 (t, *J* = 6.4 Hz, 4H, CH₂Cl), 3.21 (septet, 1H, CH), 1.90-1.45 (m, 8H, CH₂), 1.29 (s, 3H, CH₃), 1.27 (d, *J* = 6.0 Hz, 6H, CH₃). ¹³C {¹H} NMR (CDCl₃) δ 151.34, 139.43, 134.76, 125.23, 125.09, 115.79, 46.89, 41.77, 40.91, 28.77, 28.37, 25.03, 23.79. HRMS (EI) *m/z* calcd (M⁺ C₁₇H₂₆Cl₂O) 316.1426, found 316.1427.

Compound 6. Compound **4** (1.30 g, 4.30 mmol) was dissolved in anhydrous THF (30 mL). Paraformaldehyde (0.517 g, 17.2 mmol), triethylamine (1.83 g, 18.1 mmol) and magnesium chloride (1.64 g, 17.2 mmol) were added under a N₂ atmosphere. The reaction mixture was heated to reflux for 5 hours and cooled to room temperature. The solvent was removed with a rotary evaporator. Water (15 mL) and CH₂Cl₂ (25 mL) were added to the residue, and the mixture was filtered over Celite. The organic phase was collected, and the aqueous phase was further extracted using CH₂Cl₂ (2 × 15 mL). The combined organic phase was dried over anhydrous MgSO₄. The solvent was removed with a rotary evaporator to give an oily residue that was evacuated further to remove some residual triethylamine. The residue was dissolved in CH₃CN (6 mL) and NaI (6.49 g, 43.3 mmol) was added. After the resulting mixture was refluxed for 20 hours, it was cooled to room temperature. After water (15 mL) was added, the product was extracted using

diethyl ether (3 × 15 mL). After the collected organic phase was dried over anhydrous MgSO₄, all volatiles were removed with a rotary evaporator to give yellow oil. The product was purified by column chromatography on silica gel, eluting with hexane and ethyl acetate (v/v, 20:1). The yield was 81% (1.8 g). IR (KBr) 3258 (OH), 1649 (C=O) cm⁻¹. ¹H NMR (CDCl₃) δ 11.15 (s, 1H, OH), 9.87 (s, 1H, CHO) 7.35 (s, 1H, *m*-H), 7.24 (s, 1H, *m*-H), 3.12 (m, 4H, CH₂I), 2.71 (q, *J* = 7.6 Hz, 2H, CH₂), 1.90-1.40 (m, 8H, CH₂), 1.34 (s, 3H, CH₃), 1.26 (t, *J* = 7.6 Hz, 3H, CH₃). ¹³C {¹H} NMR (CDCl₃) δ 196.92, 157.97, 137.60, 134.59, 132.93, 128.85, 119.75, 44.27, 40.05, 28.64, 24.26, 23.05, 14.41, 8.06. HRMS (EI) *m/z* calcd (M⁺ C₁₇H₂₄I₂O₂) 513.9931, found 513.9931.

Compound 7. This compound was synthesized using the same conditions and procedure as compound **6** starting with **5**. Yield was 86%. IR (KBr) 3289 (OH), 1651 (C=O) cm⁻¹. ¹H NMR (CDCl₃) δ 11.25 (s, 1H, OH), 9.86 (s, 1H, CHO) 7.41 (s, 1H, *m*-H), 7.23 (s, 1H, *m*-H), 3.38 (septet, 1H, CH), 3.13 (m, 4H, CH₂I), 1.94-1.42 (m, 8H, CH₂), 1.35 (s, 3H, CH₃), 1.28 (d, *J* = 6.0 Hz, 6H, CH₃). ¹³C {¹H} NMR (CDCl₃) δ 197.01, 157.58, 137.54, 137.24, 131.87, 128.76, 119.77, 44.28, 40.18, 28.60, 27.01, 24.34, 22.81, 8.12. HRMS (EI) *m/z* calcd (M⁺ C₁₈H₂₆I₂O₂) 528.0032, found 528.0030.

Compound 8. Compound **6** (1.73 g, 3.37 mmol) and (±)-*trans*-1,2-diaminocyclohexane (0.192 g, 1.69 mmol) were weighed into a one-neck flask, and then CH₂Cl₂ (20 mL) and small amount of molecular sieves were added. The solution was stirred overnight under a N₂ atmosphere. The solvent was removed under vacuum to give a pure yellow compound (1.82 g, 98%). IR (KBr) 3447 (OH), 1628 (C=N) cm⁻¹. ¹H NMR (CDCl₃) δ 13.44 (s, 2H, OH), 8.33 (s, 2H, CH=N), 7.07 (s, 2H, *m*-H), 6.92 (s, 2H, *m*-H), 3.38-3.36 (m, 2H, cyclohexyl-CH), 3.16-3.04 (m, 8H, CH₂I), 2.70-2.64 (m, 4H, CH₂), 1.98-1.84 (m, 4H, cyclohexyl-CH₂), 1.84-1.40 (m, 20H, cyclohexyl-CH₂ and CH₂), 1.30 (m, 12H, Et-CH₃ and CH₃). ¹³C {¹H} NMR (CDCl₃) δ 165.07, 156.97, 136.16, 131.54, 129.70, 126.87, 117.74, 72.81, 44.36, 39.83, 33.72, 28.60, 24.40, 24.41, 14.59, 8.52. Anal. Calcd. (C₄₀H₅₈I₄N₂O₂): C, 43.42; H, 5.28; N, 2.53%. Found: C, 42.43; H, 5.25; N, 2.51%.

Compound 9. This compound was synthesized using the same conditions and procedure as compound **8** starting with **7**. Yield was 97%. IR (KBr) 3437 (OH), 1628 (C=N) cm⁻¹. ¹H NMR (CDCl₃) δ 13.53 (s, 2H, OH), 8.35 (s, 2H, CH=N), 7.14 (s, 2H, *m*-H), 6.92 (s, 2H, *m*-H), 3.44-3.31 (m, 4H, *i*Pr-CH and cyclohexyl-CH), 3.14-3.04 (m, 8H, CH₂I), 1.98-1.84 (m, 4H, cyclohexyl-CH₂), 1.84-1.40 (m, 20H, cyclohexyl-CH₂ and CH₂), 1.28 (d, *J* = 6.0 Hz, 12H, *i*Pr-CH₃), 1.26 (s, 6H, CH₃). ¹³C {¹H} NMR (CDCl₃) δ 165.16, 156.54, 136.08, 135.91, 126.81, 126.75, 117.73, 72.72, 44.24, 39.95, 33.76, 28.63, 27.08, 24.51, 22.97, 8.42. Anal. Calcd. (C₄₂H₆₂I₄N₂O₂): C, 44.46; H, 5.51; N, 2.47%. Found: C, 44.53; H, 5.11; N, 2.42%.

Compound 10. Compound **8** (1.45 g, 1.32 mmol) and tri-butylamine (1.01 g, 5.43 mmol) were weighed into a one-neck flask, and CH₃CN (15 mL) was added. The solution was refluxed for 2 days under a N₂ atmosphere. After the solution was cooled to room temperature, the solvent was removed under vacuum to give a residue that was subsequently triturated three times in diethyl ether (3 mL) to give a light yellow powder in

99% yield. To a flask containing this yellow powder (2.42 g, 1.31 mmol), AgBF_4 (1.02 g, 5.24 mmol) and CH_2Cl_2 (25 mL) was added. The solution was stirred for a day in the dark. AgI generated as a grey precipitate was filtered off over Celite inside a glove box. The solvent was removed under vacuum to yield a yellow residue that was subsequently purified by column chromatography on a short pad of silica gel, eluting with ethanol and CH_2Cl_2 (v/v, 1:5). The yield was 1.78 g (82%). IR (KBr) 3440 (OH), 1627 (C=N) cm^{-1} . ^1H NMR (CDCl_3) δ 13.57 (s, 2H, OH), 8.44 (s, 2H, CH=N), 7.10 (s, 4H, *m*-H), 3.40 (br, 2H, cyclohexyl-CH), 3.09 (br, 32H, NCH_2), 2.64 (br, 4H, Et- CH_2), 1.94-1.84 (br, 4H, cyclohexyl- CH_2), 1.84-1.22 (br, 74H, cyclohexyl- CH_2 and CH_2), 1.19 (t, $J = 7.6$ Hz, 6H, Et- CH_3), 0.99-0.82 (t, $J = 6.8$ Hz, 36H, CH_3). ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3) δ 165.32, 157.45, 135.58, 131.83, 129.69, 127.16, 118.11, 72.19, 59.34, 58.66, 40.17, 37.66, 25.04, 23.96, 23.55, 19.86, 17.36, 14.73, 13.85. Anal. Calcd. ($\text{C}_{88}\text{H}_{166}\text{B}_4\text{F}_{16}\text{N}_6\text{O}_2$): C, 62.63; H, 9.92; N, 4.98%. Found: C, 62.42; H, 9.61; N, 4.54%.

Compound 11. This compound was synthesized using the same conditions and procedure as compound **10** starting with **9**. Yield was 80%. IR (KBr) 3437 (OH), 1628 (C=N) cm^{-1} . ^1H NMR (CDCl_3) δ 13.66 (s, 2H, OH), 8.46 (s, 2H, CH=N), 7.11 (s, 2H, *m*-H), 7.10 (s, 2H, *m*-H), 3.39 (br, 2H, cyclohexyl-CH), 3.28 (sept, $J = 6.8$ Hz, 2H, CH-*i*Pr), 3.04 (br, 32H, NCH_2), 1.96-1.21 (br, 84H), 0.85 (t, $J = 6.8$ Hz, 36H, CH_3). ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3) δ 165.47, 157.02, 136.08, 135.48, 127.04, 126.65, 118.11, 71.98, 59.35, 58.67, 40.37, 37.91, 27.27, 24.84, 24.00, 22.88, 19.89, 17.38, 13.88. Anal. Calcd. ($\text{C}_{90}\text{H}_{170}\text{B}_4\text{F}_{16}\text{N}_6\text{O}_2$): C, 63.01; H, 9.99; N, 4.90%. Found: C, 63.24; H, 9.72; N, 4.72%.

Complex 12. Complex **9** (83 mg, 0.050 mmol) and $\text{Co}(\text{OAc})_2$ (8.9 mg, 0.050 mmol) were added into a vial and anhydrous ethanol (2.0 mL) was added. After the solution was stirred for 3 hours at room temperature, the solvent was removed under a vacuum to give a residue, which was washed with diethyl ether (2 mL \times 2). The solid was dissolved in CH_2Cl_2 (2 mL) containing 2,4-dinitrophenol (9 mg, 0.05 mmol), and the solution was stirred under an O_2 atmosphere for 3 hours. A mixture of three equivalents of sodium-2,4-dinitrophenolate and two equivalents of 2,4-dinitrophenol was added. After the solution was stirred overnight at room temperature, it was filtered over Celite. The solvent was removed under vacuum to give a dark brown powder that was pure enough to be used for polymerization. Yield was quantitative. ^1H NMR ($\text{DMSO}-d_6$, 40 $^\circ\text{C}$) δ 8.62 (br, 5H, $(\text{NO}_2)_2\text{C}_6\text{H}_3\text{O}$), 7.98 (br, 5H, $(\text{NO}_2)_2\text{C}_6\text{H}_3\text{O}$), 7.87 (s, 2H, CH=N), 7.36 (s, 2H, *m*-H), 7.24 (s, 2H, *m*-H), 6.69 (br, 5H, $(\text{NO}_2)_2\text{C}_6\text{H}_3\text{O}$), 3.75 (br s, 2H, NCH_2 bridged), 3.30-2.88 (br, 32H, NCH_2), 2.51 (br, 4H, Et- CH_2), 2.05-1.85 (br, 4H, cyclohexyl- CH_2), 1.70-1.40 (br, 80H), 0.86 (t, $J = 6.4$ Hz, 36H, CH_3). ^{13}C $\{^1\text{H}\}$ NMR ($\text{DMSO}-d_6$) δ 162.12, 159.88, 135.40, 135.71, 129.77, 128.56, 127.69, 122.32, 116.55, 68.30, 57.12, 56.55, 38.11, 37.47, 28.47, 23.30, 22.46, 21.96, 18.07, 15.74, 13.78, 12.20.

Complex 13. This compound was synthesized using the same conditions and procedure as complex **12** starting with **10**. Dark brown powder was obtained in quantitative yield. ^1H NMR ($\text{DMSO}-d_6$, 40 $^\circ\text{C}$) δ 8.87 (br, 5H, $(\text{NO}_2)_2\text{C}_6\text{H}_3\text{O}$), 8.30 (br, 5H, $(\text{NO}_2)_2\text{C}_6\text{H}_3\text{O}$), 7.83 (s, 2H, CH=N), 7.32 (s, 2H, *m*-H), 7.21 (s, 2H, *m*-H), 7.05 (br, 5H, $(\text{NO}_2)_2\text{C}_6\text{H}_3\text{O}$), 4.08 (br, 2H,

*i*Pr-CH), 3.64 (br, 2H, NCH_2 bridged), 3.30-2.80 (br, 32H, NCH_2), 2.09-1.75 (br, 4H, cyclohexyl- CH_2), 1.70-1.12 (br, 86H), 0.86 (t, $J = 6.4$ Hz, 36H, CH_3). ^{13}C $\{^1\text{H}\}$ NMR ($\text{DMSO}-d_6$) δ 159.27, 147.23, 146.16, 139.79, 131.67, 130.49, 128.29, 122.67, 118.61, 116.77, 68.21, 57.07, 56.52, 38.20, 37.49, 28.45, 23.32, 22.41, 21.94, 21.63, 21.03, 18.06, 15.74, 12.24.

Compound 15. Compound **14** (0.270 g, 0.250 mmol) and trihexylamine (0.276 g, 1.03 mmol) were weighed into a one-neck flask, and CH_3CN (5 mL) was added. The solution was refluxed for 2 days under a N_2 atmosphere. After the solution was cooled to room temperature, the solvent was removed under vacuum to give a residue that was subsequently triturated three times in pentane (2 mL) then dried to give light yellow powder over 99% yield. To a flask containing this yellow powder (0.320 g, 0.150 mmol) and AgBF_4 (0.116 mg, 0.600 mmol), CH_2Cl_2 (3 mL) was added. The solution was stirred for a day in the dark. AgI generated as a grey precipitate was filtered off over Celite inside a glove box, the solvent was removed under vacuum to yield a yellow residue that was subsequently purified by column chromatography on a short pad of silica gel, eluting with ethanol and CH_2Cl_2 (v/v, 1:5). Yield was 95% (0.284 g). IR (KBr) 3445 (OH), 1629 (C=N) cm^{-1} . ^1H NMR (CDCl_3) δ 13.57 (s, 2H, OH), 8.44 (s, 2H, CH=N), 7.26 (s, 2H, *m*-H), 7.17 (s, 2H, *m*-H), 3.53 (br, 2H, cyclohexyl-CH), 3.40-3.15 (br, 32H, NCH_2), 2.27 (s, 6H, CH_3), 2.04-1.20 (br, 126H), 0.88 (t, $J = 6.4$ Hz, 36H, CH_3). ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3) δ 164.91, 157.57, 135.19, 130.86, 126.97, 125.50, 117.79, 72.36, 68.07, 59.09, 58.63, 39.87, 37.21, 31.22, 25.98, 25.80, 24.97, 22.57, 21.86, 17.17, 15.91, 14.12. Anal. Calcd. ($\text{C}_{108}\text{H}_{206}\text{B}_4\text{F}_{16}\text{N}_6\text{O}_2$): C, 65.91; H, 10.55; N, 4.27%. Found: C, 65.62; H, 10.75; N, 4.24%.

Compound 16. This compound was synthesized using the same conditions and procedure as compound **15** using trioctylamine. Yield was 97%. IR (KBr) 3447 (OH), 1635 (C=N) cm^{-1} . ^1H NMR (CDCl_3) δ 13.62 (s, 2H, OH), 8.65 (s, 2H, CH=N), 7.25 (s, 2H, *m*-H), 7.22 (s, 2H, *m*-H), 3.50 (br, 2H, cyclohexyl-CH), 3.40-3.12 (br, 32H, NCH_2), 2.26 (s, 6H, CH_3), 2.02-1.18 (br, 158H), 0.89 (t, $J = 6.4$ Hz, 36H, CH_3). ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3) δ 165.11, 157.73, 135.30, 131.13, 127.09, 125.68, 117.87, 72.13, 59.21, 58.57, 40.11, 38.04, 37.57, 31.94, 29.30, 26.95, 25.08, 23.94, 22.88, 19.82, 17.31, 16.04, 14.40, 13.83. Anal. Calcd. ($\text{C}_{132}\text{H}_{254}\text{B}_4\text{F}_{16}\text{N}_6\text{O}_2$): C, 68.79; H, 11.11; N, 3.65%. Found: C, 68.65; H, 11.15; N, 3.42%.

Complex 17. This compound was synthesized using the same conditions and procedure as complex **12** starting with compound **15**. Dark brown sticky solid was obtained in quantitative yield. ^1H NMR ($\text{DMSO}-d_6$, 40 $^\circ\text{C}$) δ 8.66 (br, 5H, $(\text{NO}_2)_2\text{C}_6\text{H}_3\text{O}$), 8.03 (br, 5H, $(\text{NO}_2)_2\text{C}_6\text{H}_3\text{O}$), 7.86 (s, 2H, CH=N), 7.36 (s, 2H, *m*-H), 7.27 (s, 2H, *m*-H), 6.73 (br, 5H, $(\text{NO}_2)_2\text{C}_6\text{H}_3\text{O}$), 3.67 (br, 2H, cyclohexyl-CH), 3.30-2.88 (br, 32H, NCH_2), 2.64 (s, 6H, CH_3), 2.06 (br, 2H, cyclohexyl- CH_2), 1.86 (br, 2H, cyclohexyl- CH_2), 1.72-1.02 (br, 122H), 0.86 (t, $J = 6.4$ Hz, 36H, CH_3). ^{13}C $\{^1\text{H}\}$ NMR ($\text{DMSO}-d_6$) δ 162.10, 138.22, 129.81, 129.66, 127.27, 127.05, 124.59, 123.58, 120.01, 116.42, 65.88, 57.93, 57.57, 30.27, 28.66, 25.17, 24.26, 13.85, 13.40, 21.61, 20.75, 19.38, 16.56, 13.46, 11.78.

Complex 18. This compound was synthesized using the same conditions and procedure as complex **12** starting with compound **16**. Dark brown sticky solid was obtained in quantitative yield.

^1H NMR (DMSO- d_6 , 40 °C) δ 8.66 (br, 5H, (NO₂)₂C₆H₃O), 8.09 (br, 5H, (NO₂)₂C₆H₃O), 7.86 (s, 2H, CH=N), 7.40-7.32 (br, 4H, *m*-H), 6.76 (br, 5H, (NO₂)₂C₆H₃O), 3.47 (br s, 2H, cyclohexyl-CH), 3.29-2.90 (br, 32H, NCH₂), 2.56 (s, 6H, CH₃), 2.28-1.10 (br, 174H), 0.86 (t, J = 6.4 Hz, 36H, CH₃). ^{13}C { ^1H } NMR (DMSO- d_6) δ 162.10, 138.22, 129.81, 129.66, 127.27, 127.05, 124.59, 123.58, 120.01, 116.42, 65.88, 57.24, 55.88, 30.66, 28.22, 27.92, 27.81, 25.83, 25.24, 23.86, 22.98, 21.57, 20.51, 13.34, 12.24.

Compound 20. 1,1-Dimethylethylenediamine (15 mg, 0.17 mmol) and [3-Methyl-5- $\{[\text{Bu}_3\text{N}^+(\text{CH}_2)_3\}_2\text{CH}\}$]-salicylaldehyde][BF₄⁻] (264 mg, 0.340 mmol) were added into a vial and anhydrous CH₂Cl₂ (3 mL) was added. This solution was stirred overnight over molecular sieves. After filtration over Celite, CH₂Cl₂ was removed under vacuum to give a yellow pure solid (236 mg, 96%). IR (KBr) 3414 (OH), 1628 (C=N) cm⁻¹. ^1H NMR (CDCl₃) δ 14.22 (s, 1H, OH), 13.53 (s, 1H, OH), 8.53 (s, 1H, CH=N), 8.49 (s, 1H, CH=H), 7.24 (s, 1H, *m*-H), 7.21 (s, 1H, *m*-H), 7.19 (s, 1H, *m*-H), 7.17 (s, 1H, *m*-H), 3.75 (s, 2H, NCH₂-bridged), 3.11 (br, 32H, NCH₂), 2.26 (s, 6H, CH₃), 1.72-1.20 (br, 76H), 1.04-0.77 (m, 36H, CH₃). ^{13}C { ^1H } NMR (CDCl₃) δ 167.41, 165.38, 157.78, 135.53, 131.30, 127.32, 125.84, 117.83, 66.00, 66.78, 59.51, 58.74, 54.22, 40.09, 37.32, 37.30, 29.59, 25.72, 24.02, 21.16, 20.09, 19.90, 17.35, 16.07, 16.11, 14.49, 13.87. Anal. Calcd. (C₈₄H₁₆₀B₄F₁₆N₆O₂): C, 61.77; H, 9.87; N, 5.15%. Found: C, 61.72; H, 9.67; N, 5.14%.

Compound 21. This compound was synthesized using the same conditions and procedure as complex **20** starting using 1,3-diaminopropane. Yield was quantitative. IR (KBr) 3437 (OH), 1630 (C=N) cm⁻¹. ^1H NMR (CDCl₃) δ 13.76 (s, 2H, OH), 8.44 (s, 2H, CH=N), 7.20 (s, 4H, *m*-H), 3.68 (br, 4H, NCH₂-bridged), 3.11 (br, 32H, NCH₂), 2.29 (s, 6H, CH₃), 2.12 (m, 2H, CH₂-bridged), 1.82-1.20 (br, 70H), 0.93 (t, J = 7.2 Hz, 36H, CH₃). ^{13}C { ^1H } NMR (CDCl₃) δ 166.03, 158.02, 135.16, 131.05, 127.38, 125.93, 117.65, 77.43, 59.41, 58.63, 53.73, 40.20, 37.41, 23.98, 19.88, 17.26, 16.08, 13.88. Anal. Calcd. (C₈₃H₁₅₈B₄F₁₆N₆O₂): C, 61.56; H, 9.83; N, 5.19%. Found: C, 61.52; H, 9.85; N, 5.20%.

Compound 22. This compound was synthesized using the same conditions and procedure as complex **20** starting using *meso*-1,2-diphenylethylenediamine. Yield was 92%. IR (KBr) 3444 (OH), 1626 (C=N) cm⁻¹. ^1H NMR (CDCl₃) δ 13.30 (s, 2H, OH), 8.47 (s, 2H, CH=N), 7.29-6.94 (m, 10H), 4.85 (s, 2H, NCH₂), 3.09 (br, 32H, NCH₂), 2.63 (s, 6H, CH₃), 1.88 (br, 2H, CH), 1.82-1.16 (br, 70H), 0.93 (m, 36H, CH₃). ^{13}C { ^1H } NMR (CDCl₃) δ 157.52, 139.12, 135.64, 131.51, 128.31, 128.21, 127.52, 125.81, 117.84, 79.83, 77.43, 59.45, 58.69, 57.79, 53.73, 40.06, 23.96, 19.85, 17.26, 16.13, 13.86. Anal.

Calcd. (C₉₄H₁₆₄B₄F₁₆N₆O₂): C, 64.24; H, 9.41; N, 4.78%. Found: C, 64.47; H, 9.68; N, 4.98%.

Complex 23. This compound was synthesized using the same conditions and procedure as complex **12** starting with compound **20**. Yield was quantitative. ^1H NMR (DMSO- d_6 , 40 °C) δ 8.64 (br, 5H, (NO₂)₂C₆H₃O), 8.03 (d, J = 10.4 Hz, 5H, (NO₂)₂C₆H₃O), 7.35 (s, 2H, CH=N), 7.27 (s, 2H, *m*-H), 7.23 (s, 2H, *m*-H), 6.69 (br, 5H, (NO₂)₂C₆H₃O), 4.06 (br s, 2H, NCH₂), 3.30-2.88 (br, 32H, NCH₂), 2.67 (s, 3H, CH₃), 2.64 (s, 3H, CH₃), 2.52 (s, 6H, CH₃), 1.80-1.40 (br, 36H, CH₂), 1.40-1.02 (br, 34H), 0.86 (t, J = 6.4 Hz, 36H, CH₃). ^{13}C NMR (DMSO- d_6) δ 164.52, 161.17, 159.88, 131.19, 130.16, 129.31, 129.37, 128.13, 127.99, 123.199, 70.75, 66.21, 57.66, 57.12, 38.65, 38.12, 28.54, 23.09, 22.95, 22.57, 18.68, 17.47, 16.93, 16.36, 12.86, 10.44.

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