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Anion variation on a cobalt(III) complex of salen-type ligand tethered by four quaternary ammonium salts for CO_2/epoxide copolymerization†

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Anion exchange of BF_4^- occurs by stirring a cobalt(III) complex of salen-type ligand tethered by four quaternary ammonium BF_4^- salts over a slurry of NaX in CH_2Cl_2, affording a complex containing four X's per cobalt (X = 2,4,5-trichlorophenolate, **6**; X = 4-nitrophenolate, **10**; X = 2,4-dichlorophenolate, **12**). The ^1H and ^{13}C NMR spectra are in agreement with an unusual imine uncoordinated structure. The two salen-phenoxys and the two X's persistently coordinate with cobalt(III) to form a square planar cobaltate complex while the other two X's scramble through coordination and decoordination to the axial sites of the square plane. Another form of the complex (X = 2,4,5-trichlorophenolate, **14**; X = 4-nitrophenolate, **15**; X = 2,4-dichlorophenolate, **16**) is also prepared, in which the scrambling two X's in **6**, **10**, or **12** are replaced with the corresponding $[X\cdots H\cdots X]^-$ homoconjugate. These complexes, which adopt an unusual imine uncoordinated structure, are excellent catalysts for CO_2/propylene oxide copolymerization (turnover frequency (TOF), 8300–16 000 h^{-1}). In all cases, the complex containing the homoconjugate $[X\cdots H\cdots X]^-$ shows higher activity than the corresponding phenol-free complex. Among the prepared complexes, 4-nitrophenol-4-nitrophenolate homoconjugate complex **15** showed the best performance (TOF, 16 000 h^{-1}; selectivity, 98%; M_n, 273 000), allowing for replacement of the explosive 2,4-dinitrophenolate complex.

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Introduction

Carbon dioxide/epoxide copolymerization was discovered four decades ago by Inoue *et al*.[1] The initial catalytic system, a Zn(II)-based heterogeneous catalyst generated by mixing diethylzinc and water in a 1 : 1 ratio, has been extensively improved through various modifications. The best catalytic activities for the Zn-based heterogeneous catalytic system are in the range of 350 g polymer per g of zinc.[2] Homogeneous catalysts of porphyrin-Al and salen-Al, Co, and Cr complexes as well as β-diketiminatoZn complexes have also been discovered.[3] Mechanistic studies have revealed or suggested that the two metal centers are involved in the propagation reaction, with the carbonate anion appended on a metal center attacking the epoxide that is activated by the coordination on the other metal center.[4] Based on these studies, bimetallic catalysts have been constructed to improve catalytic performance.[5] In the case of homogeneous (salen)Co (**1**) or (salen)Cr catalysts, the catalytic performance can be improved by the addition of a cocatalyst such as quaternary ammonium salt or amine base (Chart 1).[6,7] We further improved catalysis by binding the salen ligand and the quaternary ammonium unit in a molecule (**2** in Chart 1).[8] Binding enables the two components situated in proximity regardless of low catalyst concentration or high polymerization temperature, consequently resulting in a high turnover number (TON) and a high molecular weight (M_n). Using this concept, we recently discovered a highly active catalytic system (**3** and **4** in Chart 1).[9] It shows a TON of up to 16 000, which corresponds to 28 000 g polymer per g of cobalt, which is approximately 1000 times higher than that attained with the best heterogeneous Zn-based catalyst.

The polymerization rate is also very high; the high TON was achieved by running for 1.0 h (turnover frequency (TOF), 16 000 h^{-1}), producing a strictly alternating copolymer with a high molecular weight (M_n) of up to 300 000 and high selectivity (>99%). Another advantage of **3** or **4** is that the catalyst can be efficiently removed after polymerization from a polymer solution through filtration over a short pad of silica gel. The collected catalyst on the silica surface can then be recovered and reused. Removing the catalyst residue is crucial not only because catalyst residue colors the resin, but also because it causes toxicity as well as severe degradation during thermal processing.[10] All these merits allow for the design of a continuous commercial process to produce attractive CO_2/epoxide copolymers.

The structure of **3** or **4** had been initially identified as that of a conventional tetradentate salen-cobalt(III) complex, but we subsequently determined that it adopts an unusual structure as shown in Chart 1.[11] The imine-nitrogen's do not coordinate, but, instead, counter anions of the quaternary ammonium cations, 2,4-dinitrophenolates (DNPs), coordinate with cobalt. The extraordinarily high activity of **3** or **4** compared with **2** was attributed to the unusual binding mode of **3** or **4**. In this work, we report the derivatives of **3** or **4** by replacing DNPs with other anions. Polymer chains start to grow from DNPs in the catalysis of **3** or **4**, and, hence, all the polymer chains contain a DNP end group if the chain transfer reactions are excluded. Dry 2,4-dinitrophenol is explosive and so is sold as a hydrated product containing approximately 20% water. The dry sodium salt of 2,4-dinitrophenol, which is necessarily for the preparation of **3** or **4**, has also been reported to be highly explosive.[12] Complex **3** or **4** inherently has the potential

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† Electronic supplementary information (ESI) available: NMR spectra of **6**, **10**, **12**, **14**, **15**, and **16**. See DOI: 10.1039/b920992a

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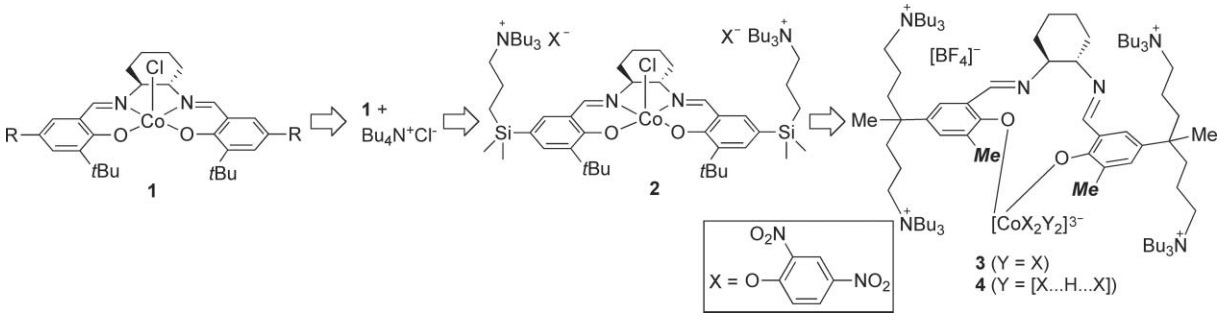

Chart 1 Salen-Co(III) catalysts for CO_2/epoxide copolymerizations.

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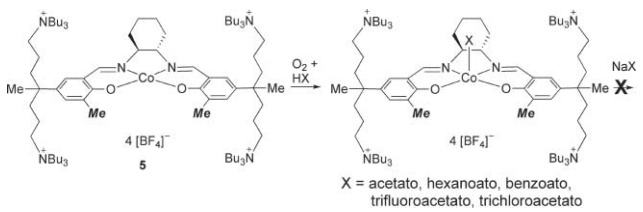
to be explosive because it contains many anhydrous DNP anions.[13] So, replacement of DNP in **3** or **4** with another and safe anion is required when considering a scalable synthesis of the catalyst for use in a pilot or commercial process. A scalable synthetic route for the ligand system of **3** or **4** has been already developed.[14]

Results

Trial for preparation of carboxylate complexes

The most attractive derivatization is a replacement of DNPs in **3** with carboxylates such as acetate. A similar type of active catalyst in the Nozaki system is an acetate complex.[15] A binary system of salen-Co(III) complex/quaternary ammonium salt has been reported to work well with an acetato complex as well as with quaternary ammonium acetate.[6] Presently, a cobalt(II) complex of salen-type ligand tethered by four quaternary ammonium BF_4^- salts (**5**) was oxidized under an oxygen (O_2) atmosphere in the presence of various carboxylic acids such as acetic acid, hexanoic acid, benzoic acid, trifluoroacetic acid, or trichloroacetic acid, generating the corresponding salen-Co(III) complexes (eqn (1)). In the case of acetic acid, trifluoroacetic acid, or trichloroacetic acid, the reaction rate was so fast that the oxidation could be completed in 3 h. For oxidation in the presence of hexanoic acid or benzoic acid, the rate was so slow that 4 days were required for complete oxidation. The ^{1}H NMR spectra clearly showed that all the paramagnetic cobalt(II) species were transformed to diamagnetic cobalt(III) complexes. Unsatisfactorily, the next BF_4^- replacement with acetate anion was not successful. In the preparation of **3**, anion exchange of BF_4^- was carried out by stirring a solution of the oxidized cobalt(III) complex containing four BF_4^- over a slurry of five equivalents of NaDNP in CH_2Cl_2. Under the same conditions using sodium carboxylate instead of NaDNP, BF_4^- was not replaced with carboxylate anion (eqn (1)).

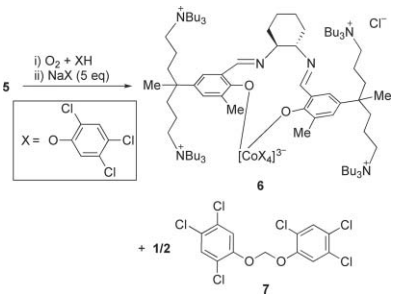


X = acetato, hexanoato, benzoato, trifluoroacetato, trichloroacetato

(1)

Preparation of trichlorophenolate complexes

The next targeted anion for replacement of explosive DNP anion in **3** was chlorinated phenolates, which are not explosive. Oxidation with O_2/4-chlorophenol or O_2/2,4-dichlorophenol was not successful, but cobalt(II) complex **5** was transformed to 2,4,5-trichlorophenolato cobalt(III) complex under an O_2 atmosphere in the presence of one equivalent of 2,4,5-trichlorophenol (eqn (2)). The reaction rate was so slow that 4 days were required for complete oxidation. The anion exchange reaction with five equivalents of 2,4,5-trichlorophenolate in CH_2Cl_2 produced the desired salen-Co(III) complex **6**.



(2)

In the ^{1}H NMR spectrum (dmso-d_6) of the crude product obtained after the anion exchange reaction, three sets of sharp 2,4,5-trichlorophenolate signals were clearly evident, along with a set of salen-signals (Fig. 1 and ESI†). A set of 2,4,5-trichlorophenolate signals comprised the coordinated one at 8.34 and 6.69 ppm with the integration value of two 2,4,5-trichlorophenolates per cobalt. Another set comprised the uncoordinated one at 7.10 and 6.36 ppm with the integration value of two 2,4,5-trichlorophenolates per cobalt. The chemical shifts of the uncoordinated one were observed to be close to that of sodium 2,4,5-trichlorophenolate (7.08, 6.35 ppm in dmso-d_6). The third set was observed at 7.79 and 7.76 ppm along with a signal at 6.15 ppm with an integration value of one 2,4,5-trichlorophenolate per cobalt (ESI†). The third set of signals could be removed by washing with diethyl ether, indicating that these signals are attributed to a neutral species, not an anion. We assigned the third set of signals to compound **7**, generated by the attack of 2,4,5-trichlorophenolate anion onto CH_2Cl_2 (eqn (2)). In the ^{19}F NMR spectrum, a negligible amount of BF_4 signal was evident, indicating that all the BF_4^- was replaced with 2,4,5-trichlorophenolate anion. Running the anion exchange reaction at low temperature (<15 °C) significantly suppressed the

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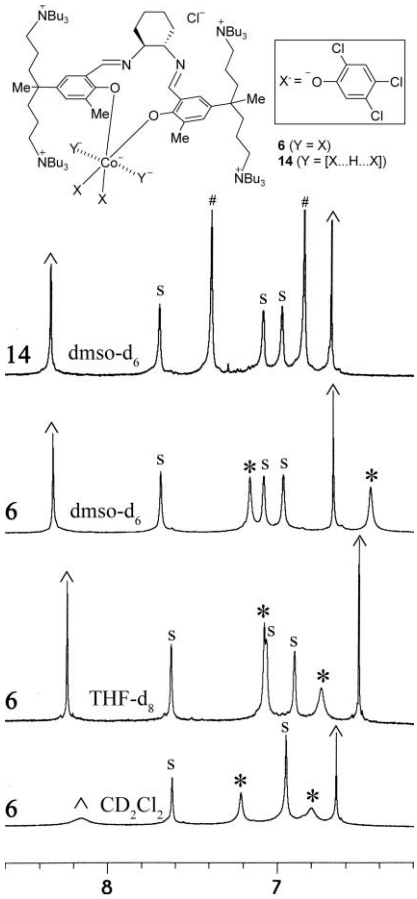

Fig. 1 ^{1}H NMR spectra of 2,4,5-trichlorophenolate (X) complex **6** and its homoconjugate (X···H···X) complex **14** ("s" signals for salen-unit; "^" signals for coordinated X; "*" signals for scrambling X; "#" signals for [X···H···X]).

formation of **7**; a trace amount of the third set of signals could be observed along with an increase of integration value of the uncoordinated 2,4,5-trichlorophenolate signals from two to three 2,4,5-trichlorophenolates/Co (ESI†).

Formation of **7** supported the suggestion that the product adopts an unusual imine uncoordinated octahedral structure previously proposed for DNP complex **3**.[11] Because 2,4,5-trichlorophenolate is more basic than DNP,[16] all four BF_4^- would be replaced with 2,4,5-trichlorophenolate in CH_2Cl_2. Only three among the four BF_4^- are replaced in the anion exchange reaction with NaDNP. After all four BF_4^- are replaced with 2,4,5-trichlorophenolate, we presume that an octahedral complex would be formed in CH_2Cl_2, where the four 2,4,5-trichlorophenolates and the two salen-phenoxys coordinate with cobalt (**6-A** in Chart 2). The remaining 2,4,5-trichlorophenolate exists as a free anion, which is sufficiently nucleophilic to attack CH_2Cl_2 above approximately 15 °C. The coordinated four 2,4,5-trichlorophenolates are not so nucleophilic that they are prevented from attacking CH_2Cl_2 to generate **6-B**. Even when three equivalents of sodium 2,4,5-trichlorophenolate was added in the final anion exchange reaction at 20 °C, the formation of a small amount of **7** (~10 mol%) was inevitable.

The ^{1}H NMR spectrum of **6** in CD_2Cl_2 (Fig. 1) revealed sharp salen-aromatic signals at 7.61 (1H) and 6.95 (2H) ppm while two sets of broad 2,4,5-trichlorophenolate signals were observed. The coordinated 2,4,5-trichlorophenolate signals are sharply evident at 6.66 ppm and very broadly evident at 8.15 ppm. The other set of 2,4,5-trichlorophenolate signals were very broad at 7.21 and 6.80 ppm. This signal pattern was consistent with structure **6-B** in Chart 2, where two 2,4,5-trichlorophenolate and two salen-phenoxy's persistently coordinate with cobalt to provide a square planar cobaltate complex. The other two 2,4,5-trichlorophenolates scramble through coordination and decoordination to the axial sites of the square plane. Due to the scrambling, the magnetic environment on the *ortho*-proton of the persistently coordinated 2,4,5-trichlorophenolate is severely perturbed and the signal at 8.15 ppm becomes very broad, while the perturbation on the *meta*-proton is negligible, producing the corresponding sharp signal. Signals of the scrambling 2,4,5-trichlorophenolates were very broad. Some tetradentate cobaltate(III) complexes bearing a –1 charge on cobalt have been previously reported.[17] They are also prone to interconversion between four-, five-, and six-coordinate states in the presence of additional neutral or anionic ligands.[18] Almost the same signal pattern was observed in THF-d_8 (Fig. 1). Signal broadness of the scrambling anion was less in THF-d_8 than in CD_2Cl_2, indicative of less staying in a coordination state in THF. In dmso-d_6, the signal of the scrambling anion became very narrow, indicative of staying mostly in a decoordination state in the highly coordinating dmso solvent (Chart 2). In variable temperature ^{1}H NMR studies over the range of –50 °C to 50 °C in THF-d_6, the salen-aromatic signals and the coordinated 2,4,5-trichlorophenolate signals were persistently sharp relative to the signals of scrambling 2,4,5-trichlorophenolate which became very broad by lowering the temperature (ESI†).

As a comparison, we prepared a *tert*-butyl analogue **8** (eqn (3)), which adopted the conventional imine coordinated structure. The *tert*-butyl substituents blocked formation of the unusual imine uncoordinated structure. Salen-cobalt complexes have been applied as versatile catalysts in various asymmetric syntheses such as hydrolytic kinetic resolution (HKR),[19] nitro-aldol reaction,[20] alkene hydrocyanation[21] and resolution of racemic *N*-benzyl α-amino acids.[22] In all these reactions, the utilized complexes are constructed from salicylaldehyde having a *tert*-butyl substituent on its 3-position. After metallation of the ligand bearing *tert*-butyl substituent with $Co(OAc)_2$, the cobalt(II) complex was completely oxidized to cobalt(III) species by the action of O_2 and 2,4,5-trichlorophenol, which was proved by the absence of any signal at the abnormal region below 0 ppm. After anion exchange with sodium 2,4,5-trichlorophenolate, the signal pattern observed in the ^{1}H NMR spectrum of **8** in dmso-d_6 was totally different from that observed for **6** (Fig. 2). A set of salen signals was evident at 7.59, 7.11, and 6.99 ppm, but a set of very broad 2,4,5-trichlorophenolate signals was observed at 7.18 and 6.31 ppm, in contrast with the observation of two sets of sharp 2,4,5-trichlorophenolate signals in the ^{1}H NMR spectrum of **6**. Paramagnetic signals were also evident at –2 to 0 ppm. This signal behavior can be explained by the conventional imine-coordinated structure as shown in eqn (3). In this structure, the coordinated 2,4,5-trichlorophenolates on the axial sites are exchangeable with the uncoordinated 2,4,5-trichlorophenolates in the NMR time scale. Consequently, the coordinated and the uncoordinated 2,4,5-trichlorophenolate signals collapsed to a set of broad signals. In this exchange reaction, the five coordinated, square pyramidal

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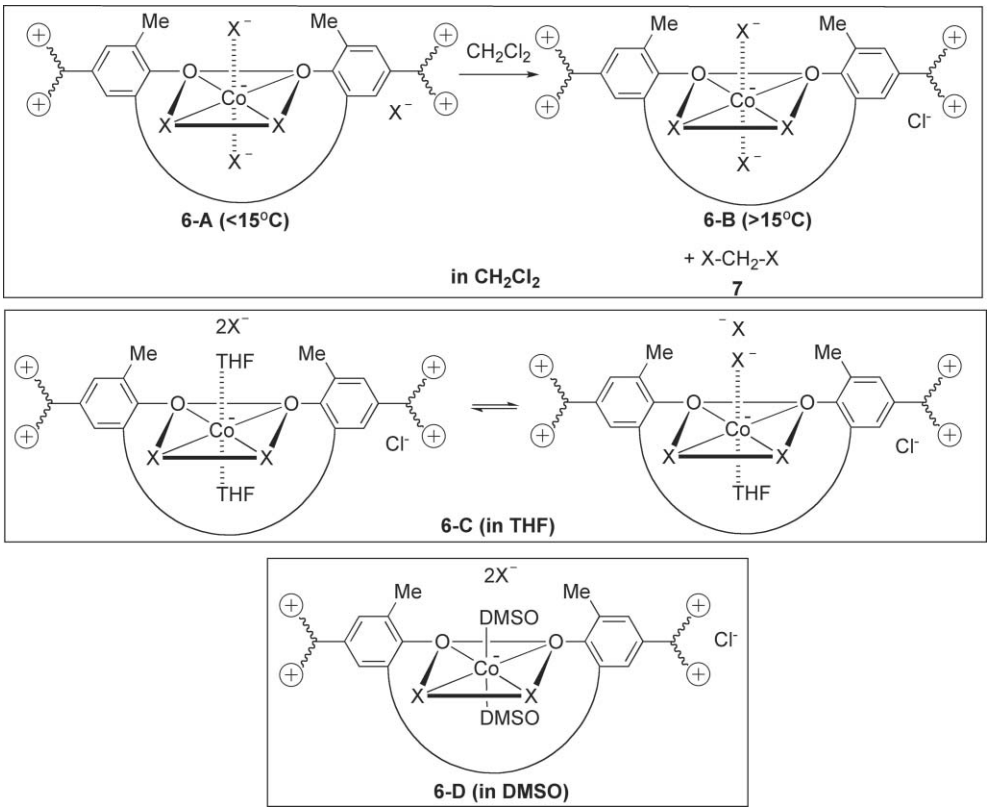
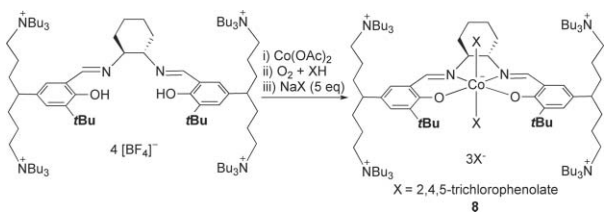


Chart 2 Structures of **6** in various solvents.

complex is a paramagnetic mediator, which produces signals at an abnormal region, –2 to 0 ppm. The pattern of the ^{1}H NMR spectrum in CD_2Cl_2 was similar to that observed in dmso-d_6 (Fig. 2).



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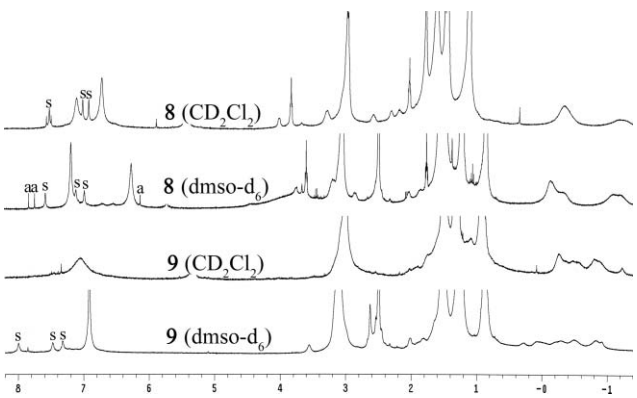
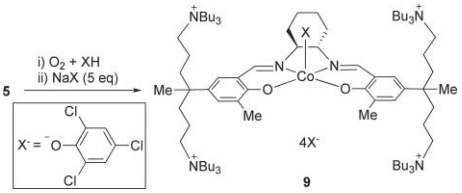


Fig. 2 The ^{1}H NMR spectra of **8** and **9** of the conventional imine-coordinated structure ("s" signals for salen-unit; "a" signals for CH_2Cl_2-attack product, **7**).

Cobalt(II) complex **5** could be transformed to a diamagnetic cobalt(III) complex by the action of O_2/2,4,6-trichlorophenol, even though the reaction rate was slow, requiring 4 days for complete oxidation (eqn (4)). The anion exchange reaction with five equivalents of sodium 2,4,6-trichlorophenolate occurred, yielding product **9**, whose behavior in the ^{1}H NMR spectra was totally different from that observed for 2,4,5-trichlorophenolate complex **6** (Fig. 2). In dmso-d_6, a set of broad 2,4,6-trichlorophenolate signals and salen-signals were observed with an integration value of [2,4,6-trichlorophenolate]/[Co] = 5. The chemical shift of the 2,4,6-trichlorophenolate signal (6.91 ppm) was almost identical with that of sodium 2,4,6-trichlorophenolate (6.93 ppm), indicating uncoordinated behavior of 2,4,6-trichlorophenolate in dmso-d_6. In CD_2Cl_2 and THF-d_8, paramagnetic signals at –2 to 0 ppm were observed, while the aromatic salen-signals disappeared. A very broad 2,4,6-trichlorophenolate signal was observed at 6.8–7.3 ppm. Cobalt(III) complexes of five coordinated, square-pyramidal structure were reported to be high spin paramagnetic, causing abnormal signals in NMR spectra.[23] We presume that the conventional imine-coordinated square-pyramidal salen-Co(III) complex is formed in CH_2Cl_2 (eqn (4)). Since the coordinating power of 2,4,6-trichlorophenolate is weaker than that of 2,4,5-trichlorophenolate or DNP, 2,4,6-trichlorophenolate anions around the cobalt center cannot substitute the imine-coordination.



(4)

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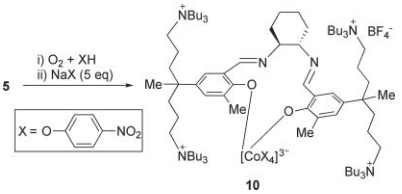
Preparation of 4-nitrophenolate complex

Cobalt(II) complex **5** was also oxidized with O_2/4-nitrophenol with a slow rate (4 days for complete oxidation). Anion exchange reaction with sodium 4-nitrophenolate occurred in CH_2Cl_2 yielding the desired complex **10** (eqn (5)). Integration value in the ^{1}H NMR spectrum indicated that three among the four BF_4^- were replaced with 4-nitrophenolate and that the side reaction of the attack onto CH_2Cl_2 was absence. The ^{1}H NMR patterns in dmso-d_6 and THF-d_8 were similar to that observed for 2,4,5-trichlorophenolate complex **6** (ESI†). In the ^{1}H NMR spectrum in dmso-d_6, two sets of broad 4-nitrophenolate signals – a coordinated one (7.31 and 6.91 ppm) and a scrambling one (7.75 and 6.21 ppm) – were observed along with broad salen-signals at 7.66, 7.97, and 6.90 ppm. In THF-d_8, the signal pattern was the same as that obtained in dmso-d_6 except for sharpened signals. In CD_2Cl_2, the salen-signals were sharp while both sets of 4-nitrophenolate signals were very broad.

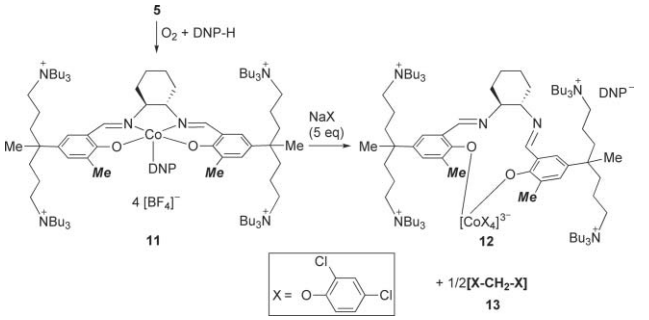


(5)

Preparation of 2,4-dichlorophenolate complex

Cobalt(II) complex **5** cannot be oxidized under O_2 atmosphere in the presence of phenol, 4-chlorophenol, or 2,4-dichlorophenol. Accordingly, anion exchange of BF_4^- was tried with cobalt(III) complex **11** that was obtained through oxidation of **5** with O_2/2,4-dinitrophenol (eqn (6)). Anion exchange reaction of BF_4^- occurs with sodium phenolate or sodium 4-chlorophenolate, but concomitant reduction of Co(III) complex to Co(II) species is accompanied, which is inferred from the observation of paramagnetic signals at –2 to 0 ppm in the ^{1}H NMR spectra in dmso-d_6. Furthermore, diamagnetic ^{1}H NMR signals indicate that two anions among the exchanged four attack CH_2Cl_2 to generate PhO-CH_2-OPh or ClC_6H_4O-CH_2-OC_6H_4Cl.

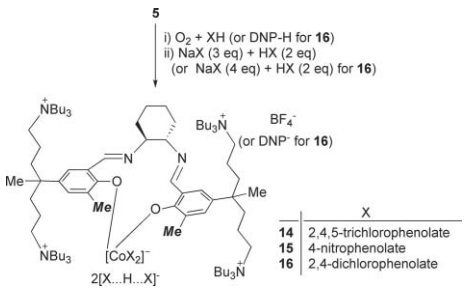
With less basic sodium 2,4-dichlorophenolate, the exchange reaction occurred without the reductive side reaction (eqn (6)). In the ^{1}H NMR spectrum in dmso-d_6, three sets of 2,4-dichlorophenolate signals and a set of DNP signals were observed along with a set of salen-signals at the aromatic region (ESI†). A set of sharp signals at 7.59 (1H), 7.42 (2H), and 6.02 (1H), which could be removed by washing with diethyl ether and assigned to $Cl_2C_6H_3O$-CH_2-$OC_6H_3Cl_2$ (**13**), is indicative of the generation of the compound by the attack of 2,4-dichlorophenolate anion onto CH_2Cl_2. The ether-extracted compound was isolated and purified by silica gel column chromatography. The ^{1}H and ^{13}C NMR data and high resolution mass data agreed with the proposed structure. The signals of the second set were sharp at 7.88 (d, J = 9.2 ppm), 6.57 (dd, J = 9.2, 2.0 Hz), and 6.50 (d, J = 2.0 Hz) with an integration value of two 2,4-dichlorophenolates per cobalt, which were assignable to the coordinated ones. The signals of the third set were observed to be very broad at 7.10, 6.79, and 6.27 ppm, with an integration value of two 2,4-dichlorophenolates per cobalt, characteristic of scrambling 2,4-dichlorophenolates. DNP signals were observed as sharp signals at 8.58 (d, J = 3.6 Hz), 7.76 (dd, J = 10, 3.6 Hz), and 6.28 (d, J = 10 Hz), of which the chemical shift indicated that DNPs exist as an uncoordinated free anion. Because 2,4-dichlorophenolate is more basic than 2,4,5-trichlorophenolate, scrambling of the two 2,4-dichlorophenolate is more severe, consistent with the very broad corresponding signals even in dmso-d_6 (ESI†).



(6)

Preparation of homoconjugate complexes

In previous studies with DNP complexes, we fortuitously found that the activity, selectivity, and induction time were improved by employing five equivalents of 60 mol% NaDNP (that is, three equivalents of NaDNP + two equivalents of DNP-H) in the anion exchange reaction. We presumed that a complex involving two 2,4-dinitrophenolate-2,4-dinitrophenol homoconjugates ($[DNP\cdots H\cdots DNP]^-$) loosely bound on cobalt was created. It is well-established that a hydrogen bond between a proton donor and an acceptor whose ΔpK_a is 0 is extraordinarily strong, especially in an aprotic solvent.[24] The formation constant of homoconjugate for $[DNP\cdots H\cdots DNP]^-$ was previously determined electrochemically in acetonitrile to be approximately 100.[16] Presently, the same type of complexes (**14–16**), 2,4,5-trichlorophenolate, 4-nitrophenolate, and 2,4-dichlorophenolate were prepared by carrying out the anion exchange reaction using a mixture of three equivalents of sodium salt and two equivalents of the corresponding phenol (eqn (7)). The side reaction of CH_2Cl_2-attack of the anion did not take place in these cases.



(7)

In the ^{1}H and ^{13}C NMR spectra (THF-d_8) of 2,4,5-trichlorophenol-2,4,5-trichlorophenolate homoconjugate complex (**14**), we observed the signals of the salen-unit and the two coordinated 2,4,5-trichlorophenolates at the same chemical shifts observed in the ^{1}H and ^{13}C NMR spectra of phenol-free 2,4,5-trichlorophenolate complex **6**. The only observable difference between the ^{1}H and ^{13}C NMR spectra of **14** and those of **6** was the replacement of the broad scrambling 2,4,5-trichlorophenolate signals in the spectra of **6** with a set of sharp 2,4,5-trichlorophenol-2,4,5-trichlorophenolate homoconjugate signals in the spectra of

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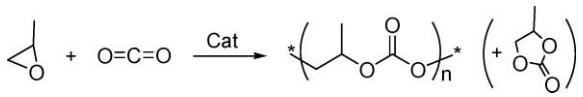
Table 1 CO_2/(propylene oxide) copolymerization results[a]



Entry	Cat	TOF[b]	Selectivity[c]	M_n[d] ($\times 10^{-3}$)	M_w/M_n
1[e]	**3** (DNP)	11 000	96	140	1.17
2[e]	**4** (DNP···H···DNP)	15 000	>99	270	1.26
3[f]	**6** (2,4,5-$Cl_3C_6H_2O$)	10 000	94	176	1.21
4	**8** (*t*Bu, 2,4,5-$Cl_3C_6H_2O$)	0			
5	**9** (2,4,6-$Cl_3C_6H_2O$)	0			
6	**10** (4-$NO_2C_6H_4O$)	8800	96	374	1.27
7	**12** (2,4-$Cl_2C_6H_3O$)	8300	94	253	1.17
8	**14** (2,4,5-$Cl_3C_6H_2O$···H···X)	11 000	96	310	1.16
9	**15** (4-$NO_2C_6H_4O$···H···X)	16 000	98	273	1.26
10	**16** (2,4-$Cl_2C_6H_3O$···H···X)	13 000	97	182	1.15

[a] Polymerization condition: PO (10 g, 170 mmol), [PO]/[Cat] = 100 000, CO_2 (2.0–1.7 MPa), 70–75 °C, 60 min. [b] Calculated based on the weight of the isolated polymer including the cyclic carbonate. [c] Selectivity of polycarbonate over cyclic carbonate in units of % as determined by ^{1}H NMR spectroscopy of the crude product. [d] Determined on GPC using a polystyrene standard. [e] Data from reference 11. [f] Induction time of 140 min was observed.

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14. The same trend was evident in the ^{1}H and ^{13}C NMR spectra of **15** and **16**.

CO_2/propylene oxide (PO) copolymerization studies

Complexes **8** and **9**, which adopt the conventional imine coordinated structure, did not show any activity for CO_2/PO copolymerization at conditions of [PO]/[Cat] = 100 000, 70–75 °C, and P_{CO_2} = 17–20 bar (entries 4 and 5 in Table 1), whereas the other complexes adopted an unusual imine uncoordinated structure exhibit excellent activities (TOF, 8300–16 000 h^{-1}). Complexes bearing homoconjugate anions **14**, **15**, or **16** were found to be more active than the corresponding phenol-free complexes **6**, **10**, or **12**. In the case of the 4-nitrophenolate and 2,4-dichlorophenolate complexes, the activity difference between the homoconjugate complex (**15** or **16**) and its corresponding phenol-free complex (**10**, or **12**) was pronounced with activities 1.6–1.8 times higher being observed for the homoconjugate complexes. In case of phenol-free complex **6**, an induction time was observed (entry 3). Among the complexes, the 4-nitrophenol-4-nitrophenolate homoconjugate complex (**15**) displayed the highest activity (TOF, 16 000 h^{-1}, entry 9), which was slightly higher than that attained with 2,4-dinitrophenol-2,4-dinitrophenolate homoconjugate complex **4** (entry 2). A viscous polymerization solution that was incapable of being stirred was obtained by running the polymerization for 1.0 h with **15** (ESI†). All the complexes screened in this study displayed selectivity for formation of polycarbonate over cyclic carbonate above 90%. Complex **15**, which displayed the highest activity, also showed the highest selectivity (98%). High M_n's (>180 000) were attained due to the high activities. The molecular weight of the polymer obtained with the most highly active catalyst **15** was satisfactorily high (M_n, 273 000, entry 9).

Summary and discussion

Attempts for BF_4^--exchange reaction of a cobalt(III) complex of salen-type ligand tethered by four quaternary ammonium BF_4^- salts with caboxylate anion such as acetate, hexanoate, benzoate, or trifluoroacetate anion were not presently successful, but the anion exchange reaction with an excess (five equivalents) of sodium 2,4,5-trichlorophenolate, 4-nitrophenolate, or 2,4-dichlorophenolate occurred in CH_2Cl_2 to give the desired complexes (**6**, **10**, and **12**, respectively). In each complex, the number of 2,4,5-trichlorophenolate, 2,4-dichlorophenolate, or 4-nitrophenolate per cobalt is four. In case of 4-nitrophenolate, substitution reaction stops at the stage of four 4-nitrophenolate/Co. In case of 2,4,5-trichlorophenolate or 2,4-dichlorophenolate, the excessively substituted anions over four anions/Co react with CH_2Cl_2. This observation is consistent with the formation of an imine uncoordinated octahedral complex, which is coordinated by four anions and two salen-phenoxys, in the anion exchange reactions in CH_2Cl_2 (Chart 1).

The ^{1}H and ^{13}C NMR spectra of the obtained cobalt(III) complexes of 2,4,5-trichlorophenolate, 2,4-dichlorophenolate, and 4-nitrophenolate are in agreement with an unusual imine uncoordinated structure. The two salen-phenoxys and two BF_4^--replacing anions persistently coordinate to cobalt(III) to form a square planar cobaltate structure. The other two BF_4^--replacing anions scramble through coordination and decoordination to the axial sites of the square plane. The signals of the scrambling anion are broad in the ^{1}H and ^{13}C NMR spectra while those of persistently coordinated ones are sharp. Another form of 2,4,5-trichlorophenolate, 4-nitrophenolate, and 2,4-dichlorophenolate complexes (**14**, **15**, and **16**, respectively) could also be prepared, in which the scrambling anions in **6**, **10**, and **12** are replaced with the corresponding phenol-phenolate homoconjugates, respectively.

Substitution of methyls with bulky *tert*-butyl on the *ortho*-position of the salen-phenoxys blocks formation of the unusual imine uncoordinated structure, affording a conventional imine coordinated complex (**8** in eqn (3)). The anion exchange reaction occurs with sodium 2,4,6-trichlorophenolate, but its coordinated power is not enough to replace the imine-coordination, consequently affording the conventional imine-coordinated structure **9**. The signal pattern in the ^{1}H NMR spectrum of complexes **8** and **9** adopting the conventional imine coordinated structure is totally different from that observed for the complexes of an unusual imine uncoordinated structure (Fig. 1 *versus* 2).

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Complexes **8** and **9** of the conventional imine-coordinated structure do not show any activity in CO_2/PO copolymerization at the condition of [PO]/[Cat] = 100 000, 70–75 °C, and P_{CO_2} = 17–20 bar. However, 2,4,5-trichlorophenolate, 4-nitrophenolate, and 2,4-dichlorophenolate complexes (**6**, **10**, and **12**, respectively), which adopt an unusual imine uncoordinated structure, and their homoconjugate analogues (**14**, **15**, and **16**, respectively), show excellent activities for CO_2/PO copolymerization (TOF, 8300–16 000 h^{-1}). In all cases, the complex containing the homoconjugate $[X\cdots H\cdots X]^-$ shows higher activities than the corresponding phenol-free complex. Among the prepared complexes, 4-nitrophenol-4-nitrophenolate homoconjugate complex **15** shows the best performance (TOF, 16 000 h^{-1}; selectivity, 98%; M_n, 273 000).

2,4,5-Trichlorophenol is expensive. 2,4-Dichlorophenol is inexpensive but is classified as a highly toxic and possible carcinogenic chemical. Furthermore, chlorinated aromatic compounds are typically resistant in environmental degradation. 4-Nitrophenol or its anion is neither explosive nor expensive. Furthermore, bioaccumulation of this compound rarely occurs. So, the attachment of 4-nitrophenol unit in each polymer chain end by employing 4-nitrophenolate complex as a catalyst is not a problem. Consequently, 4-nitrophenol-4-nitrophenolate homoconjugate complex **15** is the best choice for replacement of explosive 2,4-dinitrophenolate complex **4** in the view of activity, cost, and environmental impact.

Experimental

General remarks

All manipulations were performed under an inert atmosphere using standard glove box and Schlenk techniques. THF and diethyl ether were distilled from benzophenone ketyl. Ethanol was dried as previously described using sodium and diethyl phthalate.[25] CH_2Cl_2, and $CDCl_3$ were dried by stirring over CaH_2, and were subsequently vacuum-transferred to reservoirs. CO_2 gas (99.999% purity) was dried by storing in a column of molecular sieves 3 Å at a pressure of 30 bar. Propylene oxide was dried by stirring over CaH_2 for several days and was vacuum-transferred to a reservoir. ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz), and ^{19}F (376 MHz) NMR spectra were recorded on a Varian Mercury Plus 400 apparatus. The ^{19}F NMR spectra were calibrated and reported downfield from external α,α,α-trifluorotoluene. Gel permeation chromatograms (GPC) were obtained at room temperature in $CHCl_3$ using a Waters Millennium apparatus with polystyrene standards.

Complex 6

Cobalt(II) complex **5** (200 mg, 0.120 mmol) and 2,4,5-trichlorophenol (24 mg, 0.12 mmol) were dissolved in CH_2Cl_2 inside a glove box. The resulting solution was stirred for 4 days under an O_2 atmosphere. After sodium 2,4,5-trichlorophenolate (182 mg, 0.600 mmol) was added, the reaction mixture was stirred overnight at room temperature. The solution was filtered over Celite, and the solvent was removed under vacuum to give a brown powder, which was washed with diethyl ether several times. M.p. 85 °C. ^{1}H NMR (THF-d_8): δ 8.41 (s, 2H, coordinated X), 7.75 (s, 2H, N=CH), 7.16 (s, 2H, salen), 7.14 (s, 2H, scrambling X), 6.96 (s, 2H, salen), 6.79 (br, 2H, scrambling X), 6.56 (s, 2H, coordinated X), 4.27 (s, 2H, cyclohexyl-CH), 3.31–2.83 (br, 32H, NCH_2), 2.72 (s, 6H, CH_3), 2.14 (s, 2H, cyclohexyl), 1.97 (s, 2H, cyclohexyl), 1.87–1.14 (m, 74H, CH_2), 0.89 (t, J = 7.2 Hz, 36H, CH_3) ppm. ^{13}C{^{1}H} NMR (THF-d_8): δ 164.93, 164.18 (scrambling X), 163.39, 160.54, 132.28, 131.45, 130.67, 130.49, 129.80, 129.52, 128.34 (scrambling X), 127.53 (scrambling X), 125.81, 124.61, 123.27 (scrambling X), 120.61 (scrambling X), 118.43, 112.76, 111.98 (scrambling X), 70.19, 59.89, 59.06, 40.42, 39.65, 30.94, 30.81, 26.50, 24.63, 20.70, 19.05, 18.12, 14.31 ppm. Anal. Calcd. ($C_{110}H_{168}C_{113}CoN_6O_6$): C, 60.32; H, 7.73; N, 3.84%. Found: C, 60.71; H, 8.22; N, 4.12%.

Complex 8

Cobalt(II) acetate (39.4 mg, 0.223 mmol) and *tert*-butyl salen ligand (401 mg, 0.223 mmol) were dissolved in ethanol inside a glove box. The resulting red solution was stirred for 3.5 h at room temperature. The solvent was removed under vacuum to give a red solid that was subsequently triturated twice in diethyl ether to remove the acetic acid that had been generated. The solid (50 mg, 0.028 mmol) was dissolved in CH_2Cl_2 containing 2,4,5-trichlorophenol (5.6 mg, 0.028 mmol), and the solution was stirred under an O_2 atmosphere for 4 days. Sodium 2,4,5-trichlorophenolate (42.6 mg, 0.141 mmol) 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 brown powder.

Complex 9

This compound was synthesized using the same conditions and procedure as those for **6** with 2,4,6-trichlorophenol and its sodium salt instead of 2,4,5-trichlorophenol and its sodium salt. M.p. 82 °C. ^{1}H NMR (dmso-d_6): δ 7.99 (s, 2H, N=CH), 7.47 (s, 2H, salen), 7.32 (s, 2H, salen), 6.92 (s, 10H, uncoordinated X), 3.56 (s, 2H, cyclohexyl-CH), 3.26–2.91(br, 32H, NCH_2), 2.63 (s, 6H, CH_3), 2.01 (s, 2H, cyclohexyl), 1.81 (s, 2H, cyclohexyl), 1.72–1.16 (m, 74H, CH_2), 0.88 (t, J = 7.2 Hz, 36H, CH_3) ppm. ^{13}C{^{1}H} NMR (dmso-d_6): δ 163.92, 160.85, 159.18, 132.37, 131.76, 130.11, 129.18, 126.14, 123.38, 117.22, 108.01, 69.41, 58.02, 57.43, 55.89, 55.79, 29.42, 24.37, 23.95, 23.02, 21.54, 21.38, 19.16, 17.37, 16.77, 13.44, 11.02, 10.68 ppm. Anal. Calcd. ($C_{116}H_{170}C_{115}CoN_6O_7$): C, 59.25; H, 7.29; N, 3.57%. Found: C, 59.59; H, 7.68; N, 3.95%.

Complex 10

This compound was synthesized using the same conditions and procedure as those for **6** with 4-nitrophenol and its sodium salt instead of 2,4,5-trichlorophenol and its sodium salt. M.p. 75 °C. ^{1}H NMR (dmso-d_6): δ 7.86 (s, 4H, scrambling X), 7.77 (s, 2H, N=CH), 7.48 (s, 4H, coordinated X), 7.10 (s, 2H, salen), 7.02 (s, 6H, coordinated X, salen), 6.32 (s, 4H, scrambling X), 3.97 (s, 2H, cyclohexyl-CH), 3.15–2.85 (br, 32H, NCH_2), 2.61 (s, 2H, cyclohexyl), 2.09 (s, 2H, cyclohexyl), 1.89 (s, 6H, CH_3), 1.60–0.92 (br, 74H, CH_2), 0.83 (t, J = 7.2 Hz, 36H, CH_3) ppm. ^{13}C{^{1}H} NMR (dmso-d_6): δ 177.08, 173.56 (scrambling X), 162.61, 160.35, 133.19 (scrambling X), 132.17, 130.90, 129.96, 129.62, 127.95, 126.59 (scrambling X), 123.68, 119.88, 117.47 (scrambling X),

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116.34, 68.82, 57.99, 57.39, 29.46, 24.62, 23.77, 22.93, 19.11, 17.72, 16.71, 13.35 ppm. ^{19}F NMR (dmso-d_6): δ −50.56, −50.62 ppm. Anal. Calcd. ($C_{110}H_{176}BCoF_4N_{10}O_{14}$): C, 65.78; H, 8.83; N, 6.97%. Found: C, 65.29; H, 8.54; N, 6.41%.

Complex 12

Cobalt(III) complex **11** and sodium 2,4-dichlorophenolate were dissolved in CH_2Cl_2 inside a glove box. After the resulting solution was stirred overnight at room temperature, it was filtered over Celite. The solvent was removed under vacuum to give a brown powder which was washed several times with diethyl ether. M.p. 78 °C. ^{1}H NMR (dmso-d_6): δ 8.60 (d, J = 3.6 Hz, 1H, DNP), 7.89 (d, J = 8.8 Hz, 2H, coordinated X), 7.77 (dd, J = 9.6, 3.2 Hz, 1H, DNP), 7.64 (s, 2H, N=CH), 7.10 (s, 2H, scrambling X), 7.05 (s, 2H, salen), 6.94 (s, 2H, salen), 6.78 (s, 2H, scrambling X), 6.58 (dd, J = 8.8, 2.8 Hz, 2H, coordinated X), 6.51 (d, J = 2.4 Hz, 2H, coordinated X), 6.31 (d, J = 10 Hz, 1H, DNP), 6.25 (s, 2H, scrambling X), 4.16 (s, 2H, cyclohexyl-CH), 3.24–2.79 (br, 32H, NCH_2), 2.53 (s, 6H, CH_3), 2.09 (s, 2H, cyclohexyl), 1.83 (s, 2H, cyclohexyl), 1.68–1.06 (m, 74H, CH_2), 0.86 (t, J = 7.2 Hz, 36H, CH_3) ppm. ^{13}C{^{1}H} NMR (dmso-d_6): δ 169.99 (DNP), 163.24, 162.23 (scrambling X), 160.91, 158.93, 135.76 (DNP), 129.91, 129.66, 129.11, 127.38 (DNP), 127.26 (DNP), 126.98, 126.79, 126.63, 126.25, 125.43 (DNP), 125.25, 124.78 (DNP), 124.67, 123.52, 119.39 (scrambling X), 116.84, 113.22, 111.49 (scrambling X) ppm. Anal. Calcd. ($C_{116}H_{175}Cl_8CoN_8O_{11}$): C, 63.32; H, 8.02; N, 5.09%. Found: C, 62.86; H, 7.72; N, 4.92%.

Compound 13

The extracted ether solution in the preparation of **12** was collected, and the solvent was removed under vacuum. It was purified by column chromatography on silica gel eluting with hexene and ethyl acetate (v/v, 10 : 1). ^{1}H NMR ($CDCl_3$): δ 7.40 (d, ^4J = 2.4 Hz, 2H, *m*-H), 7.26 (d, J = 8.8 Hz, 2H, *o*-H), 7.22 (dd, J = 8.8, 2.4 Hz, 2H, *m*-H), 5.78 (s, 2H, O-CH_2-O) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 151.08, 130.33, 130.24, 128.00, 124.81, 117.79, 92.26 ppm. HRMS (EI): m/z calcd for ([M]$^+$ $C_{13}H_8Cl_4O_2$) 335.9278, found 335.9277.

Complex 14

This compound was synthesized using the same conditions and procedure as those for **6** with a mixture of 3 equivalents of sodium 2,4,5-trichlorophenolate and 2 equivalents of 2,4,5-trichlorophenol instead of 5 equivalents of pure sodium 2,4,6-trichlorophenolate. M.p. 85 °C. ^{1}H NMR (THF-d_8): δ 8.38 (s, 2H, coordinated X), 7.71 (s, 2H, N=CH), 7.28 (s, 4H, homocoujugate), 7.06 (s, 2H, salen), 7.03 (s, 2H, coordinated X), 6.94 (s, 2H, salen), 6.56 (s, 4H, homoconjugate), 4.24 (s, 2H, cyclohexyl-CH), 3.38–2.83 (br, 32H, NCH_2), 2.72 (s, 6H, CH_3), 2.13 (s, 2H, cyclohexyl), 1.96 (s, 2H, cyclohexyl), 1.69–1.07 (m, 74H, CH_2), 0.90 (t, J = 7.6 Hz, 18H, CH_3), 0.89 (t, J = 7.2 Hz, 18H, CH_3) ppm. ^{13}C{^{1}H} NMR (THF-d_8): δ 164.99, 163.26, 160.36 (homoconjugate), 132.41, 131.28, 130.93 (homoconjugate), 130.46, 129.52, 127.98 (homoconjugate), 127.53, 125.83, 124.56, 122.37 (homoconjugate), 119.64 (homoconjugate), 118.37, 116.54 (homoconjugate), 112.87, 100.14, 59.71, 59.01, 40.41, 40.22, 39.95, 30.89, 26.44, 24.81, 24.59, 20.67, 19.06, 18.02, 14.28 ppm. ^{19}F NMR (dmso-d_6): δ −50.64, −50.70 ppm. Anal. Calcd. ($C_{122}H_{174}BCl_{18}CoF_4N_6O_8$): C, 55.58; H, 6.65; N, 3.19%. Found: C, 55.12; H, 6.33; N, 3.03%.

Complex 15

This compound was synthesized using the same conditions and procedure as those for **10** with a mixture of 3 equivalents of sodium 4-nitrophenolate and 2 equivalents of 4-nitrorophenol instead of 5 equivalents of pure sodium 4-nitrorophenolate. M.p. 75 °C. ^{1}H NMR (dmso-d_6): δ 7.96 (s, 8H, homoconjugate), 7.77 (s, 2H, N=CH), 7.49 (s, 4H, coordinated X), 7.28–6.84 (br, 8H, coordinated X, salen), 6.56 (s, 8H, homocomjugate), 3.97 (s, 2H, cyclohexyl-CH), 3.25–2.74 (br, 32H, NCH_2), 2.61 (s, 6H, CH_3), 2.09 (s, 2H, cyclohexyl), 1.89 (s, 2H, cyclohexyl), 1.68–1.02 (m, 74H, CH_2), 0.83 (t, J = 7.2 Hz, 36H, CH_3) ppm. ^{13}C{^{1}H} NMR (dmso-d_6): δ 177.06, 176.08, 170.63 (homoconjugate), 162.63, 161.84, 160.30, 135.33 (homoconjugate), 132.19, 130.87, 130.02, 129.62, 127.88, 126.38 (homoconjugate), 123.70, 119.87, 116.74 (homoconjugate), 116.31, 68.79, 57.95, 57.37, 29.48, 24.59, 23.56, 22.95, 19.12, 17.77, 16.70, 13.38 ppm. ^{19}F NMR (dmso-d_6): δ −50.63, −50.69 ppm. Anal. Calcd. ($C_{122}H_{186}BCoF_4N_{12}O_{20}$): C, 64.08; H, 8.20; N, 7.35%. Found: C, 64.20; H, 8.22; N, 7.72%.

Complex 16

This compound was synthesized using the same conditions and procedure as those for **12** with a mixture of 4 equivalents of sodium 2,4-dichlorophenolate and 2 equivalents of 2,4-dichlorophenol instead of 5 equivalents of pure sodium 2,4-dichlorophenolate. M.p. 83 °C. ^{1}H NMR (dmso-d_6): δ 8.59 (d, J = 3.2 Hz, 1H, DNP), 7.89 (d, J = 8.4 Hz, 2H, coordinated X), 7.77 (dd, J = 9.6, 3.2 Hz, 1H, DNP), 7.64 (s, 2H, N=CH), 7.19 (s, 4H, homoconjugate), 7.70 (s, 2H, salen), 6.60–6.94 (m, 6H, homoconjugate, salen), 6.71 (d, J = 8.4 Hz, 4H, homoconjugate), 6.58 (d, J = 8.4 Hz, 2H, coordinated X), 6.51 (d, J = 1.6 Hz, 2H, coordinated X), 6.31 (d, J = 9.6 Hz, 1H, DNP), 4.16 (s, 2H, cyclohexyl-CH), 3.19-2.83 (br, 32H, NCH_2), 2.53 (s, 6H, CH_3), 2.09 (s, 2H, cyclohexyl), 1.84 (s, 2H, cyclohexyl), 1.68–1.06 (m, 74H, CH_2), 0.86 (t, J = 7.2 Hz, 36H, CH_3) ppm. ^{13}C{^{1}H} NMR (dmso-d_6): δ 170.00, 163.25, 160.91, 158.69, 158.54 (homoconjugate), 129.87, 129.69, 129.14, 127.90 (homoconjugate), 127.20, 126.97,126.88 (homoconjugate), 126.21, 125.44, 124.65, 122.58, 122.10 (homoconjugate), 118.56 (homoconjugate), 116.84, 116.46 (homoconjugate), 113.24, 68.49, 66.81, 57.98, 57.37, 54.67, 29.42, 25.02, 23.52, 22.90, 19.02, 17.65, 16.66, 13.26 ppm. Anal. Calcd. ($C_{128}H_{183}Cl_{12}CoN_8O_{13}$): C, 60.86; H, 7.30; N, 4.44%. Found: C, 61.20; H, 7.22; N, 4.82%.

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