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Synthesis, Structure and Application of Chiral Copper(II) Coordination Polymers for Asymmetric Acylation

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Chiral copper(II) coordination polymers **1a**−**c** have been prepared by one-pot synthesis in high yield. Their single-crystal X-ray analysis showed that repeating units are connected to each other by carboxylate linker and copper(II) atoms are pentacoordinated with distorted square-pyramidal geometry for **1a**−**b** and square-planar geometry for **1c**. These polymers have catalyzed the kinetic resolution of secondary alcohols by acylation with up to 90% ee (*s* = 50).

Introduction

The study of stereoregular chiral coordination polymers is a very active interdisciplinary research topic with potential applications in asymmetric catalysis, chiral sensor, nonlinear optical, and chiral magnetic materials.[1,2] The building blocks approach includes the possibility of introducing chiral centers in either metal complexes or ligands to obtain a chiral network.[3] Transition-metal complexes of chiral Schiff base ligands having multifunctional coordination groups (carbonyl and carboxylate oxygen) could be good candidates to be used as metalloligands for constructing extended multidimensional chiral supramolecular coordination polymers. In continuation of our study on chiral macromolecules,[4] we herein report the synthesis, structure, and application of chiral copper(II) polymers **1a**−**c** for the kinetic resolution of secondary alcohols by acylation with up to 90% ee. The repeating units of the polymers **1a**−**c** having OH interaction are connected to each other by perpendicular fashion through carboxylate linker. They are stereoregular and copper(II) atoms are pentacoordinated with distorted square pyramidal and square-planar geometries.[5]

Experimental Section

Materials and Methods. All experiments were carried out under nitrogen atmosphere. L-*tert*-Leucine (99%) and $Cu(OAc)_2 \cdot 1H_2O$ (99.99%) were obtained from Aldrich and used without further purification. 3,5-di*tert*-butyl salicylaldehyde,[6a] 3-*tert*-butyl-5-bromosalicylaldehyde,[6b] and 3-*tert*-butyl-5-nitrosalicylaldehyde[6c] were prepared according to literature. FTIR spectra were recorded using a Nicolet-410 spectrometer. Optical rotation was measured using a PerkinElmer-343 polarimeter. Elemental analysis was obtained from PerkinElmer 2400 CHNS analyzer. Flash column chromatography was performed using 230−400 mesh silica gel. UV−vis spectra were recorded using PerkinElmer Lambda-25 spectrometer. Thermogravimetric analysis (TGA) was performed using TGA/SDTA-851 Mettler Toledo analyzer. EPR spectrum was recorded using JES-FA-200 spectrometer. Magnetic susceptibility

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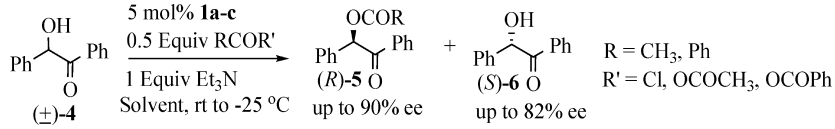
Table 1. Kinetic Resolution of (±)-Benzoin by Acylation[a]



entry	catalyst	solvent	RCOR′	base	temperature (°C)	time (h)	**5** (ee %)[b]	**6** (ee %)[c]	Conv. (%)[d]	s[d]	**5** (Confign)
1	**1a**	CH_2Cl_2	PhCOCl	Et_3N	0	4.5	42	35	45	3.4	*R*
2	**1a**	acetone	PhCOCl	Et_3N	0	4.5	60	56	48	6.9	*R*
3	**1a**	toulene	PhCOCl	Et_3N	0	4.5	41	38	48	3.4	*R*
4	**1a**	Et_2O	PhCOCl	Et_3N	0	4.5	25	17	33	1.9	*R*
5	**1a**	THF	PhCOCl	Et_3N	0	4.5	62	53	46	9.9	*R*
6	**1a**	THF	PhCOCl	Et_3N	−10	6.5	65	58	47	8.3	*R*
7	**1a**	THF	PhCOCl	Et_3N	−25	8	78	75	49	18	*R*
8	**1b**	THF	PhCOCl	Et_3N	−25	8	39	35	47	3.1	*R*
9	**1c**	THF	PhCOCl	Et_3N	−25	8	31	26	46	2.3	*R*
10	**1a**	Et_2O	$(CH_3CO)_2O$	Et_3N	rt	4	49	38	44	4.3	*R*
11	**1a**	acetone	$(CH_3CO)_2O$	Et_3N	−25	9	35	32	48	2.8	*R*
12	**1a**	THF	$(CH_3CO)_2O$	Et_3N	−25	15	68	55	44	8.9	*R*
13	**1a**	toulene	$(CH_3CO)_2O$	Et_3N	−25	9	37	30	45	2.9	*R*
14	**1a**	Et_2O	$(CH_3CO)_2O$	Et_3N	−25	15	90	82	48	50	*R*
15	**1a**	Et_2O	$(CH_3CO)_2O$	Et_3N	−25	15	50	42	46	4.5	*R*
16	**1a**	Et_2O	$(CH_3CO)_2O$	Et_3N	−25	15	41	34	45	3.8	*R*
17	**1a**	Et_2O	CH_3COCl	Et_3N	−25	6	15	9	37	1.5	*R*
18	**1a**	THF	PhCOCl	$^iPr_2NH$	−25	22	43	35	45	3.5	*R*
19	**1a**	THF	PhCOCl	pyridine	−25	25	0				
20	**1a**	THF	PhCOCl	2,6-lutidine	−25	25	35	25	41	2.6	*R*
21	**1a**	THF	$(PhCO)_2O$	Et_3N	−25	10	75	64	46	13.3	*R*

[a] Benzoin (1 mmol), catalyst **1a**−**c** (5 mol%, with respect to monomeric unit), acylating agent (0.5 mmol), and base (1 mmol) were stirred in appropriate solvent (2 mL) and temperature under nitrogen atmosphere. [b] Determined by HPLC using chiralcel OD-H column with *n*-hexane/isopropanol (95:5). [c] Determined by HPLC using chiralcel OD column with *n*-hexane/isopropanol (95:5). [d] Determined according to ref 14c.

data were measured using a Lokshore-8200 magnetometer. HPLC analysis was carried out on Waters-2478 with chiral stationary phase columns (chiralcel OJ, OD, OD-H, and OB-H). NMR spectra were recorded on Mercury plus Varian-400 spectrometer with Me_4Si as an internal standard. The melting point was recorded using Buchi B-540 apparatus and uncorrected. X-ray data were collected on a Bruker SMART APEX equipped with a CCD area detector using Mo Kα radiation. The structures were solved by direct method using *SHELLX-97* (Göttington, Germany).

General Procedure for the Preparation of 1a−c. Aldehyde **2a**−**c** (3 mmol), L-*tert*-leucine (3 mmol, 393.5 mg) and Et_3N (3 mmol, 417 μL) were stirred in EtOH (10 mL) at room temperature for 12 h. The resultant yellow solution having **3a**−**c** was treated with $Cu(OAc)_2 \cdot 1H_2O$ (3 mmol, 598 mg), and the stirring was continued for an additional 6−9 h. The solvent was evaporated under reduced pressure, and the residue was purified on silica gel flash column chromatography using CH_2Cl_2 and methanol (19:1) as eluent to afford **1a**−**c** as green-colored crystals.

1a. Yield 85%; $[\alpha]_D^{25}$ +220 (c = 0.02, MeOH); UV−vis (MeOH) λ_{max} (ϵ) = 384 (52076 $mol^{-1}dm^3cm^{-1}$); EPR (X-band, MeOH, liquid N_2) $g_\perp = 2.040$, $g_\parallel = 2.291$, $A_\parallel = 283.11$ G; IR (KBr) ν 2960, 1619, 1585, 1466, 1439, 1379, 1205, 1168, 1096, 1035, 840, 789, 595, 549, 415 cm^{-1}. Anal. Calcd for $(C_{21}H_{31}CuNO_3)_n$: C 72.05, H 8.92, N 4.32. Found: C 72.20, H 8.78, N 4.35.

1b. Yield 88%; $[\alpha]_D^{25}$ +578 (c = 0.02, MeOH); UV−vis (MeOH) λ_{max} (ϵ) = 365 nm (104945 $mol^{-1}dm^3cm^{-1}$); EPR (X-band, MeOH, liquid N_2), $g_\perp = 2.0$, $g_\parallel = 2.25$, $A_\parallel = 286.7$ G; IR (KBr) ν 3838, 3567, 2963, 1638, 1593, 1496, 1468, 1423, 1382, 1222, 1199, 1176, 1114, 1084, 1030, 991, 910, 820, 777, 750, 731, 576, 518 cm^{-1}. Anal. Calcd for $(C_{17}H_{22}CuN_2O_5)_n$: C 51.4, H 5.67, N 7.0. Found: C 50.8, H 5.67, N 6.69.

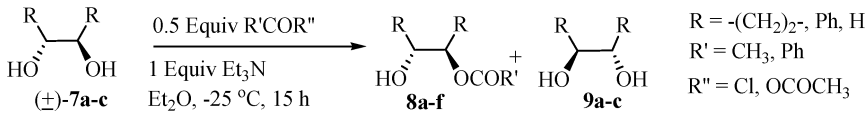
1c. Yield 87%; $[\alpha]_D^{25}$ +121 (c = 0.02, MeOH); UV−vis (MeOH) λ_{max} (ϵ) = 380 nm (39190 mol^{-1} dm^3cm^{-1}); EPR (X-band, MeOH, liquid N_2), $g_\perp = 2.0$, $g_\parallel = 2.26$, $A_\parallel = 285.7$ G; IR (KBr) ν 3854, 3748, 3650, 2953, 2366, 1615, 1569, 1433, 1407, 1371, 1273, 1162, 1086, 866, 775, 723, 575 cm^{-1}. Anal. Calcd for $(C_{17}H_{22}BrCuNO_3)_n$: C 47.2, H 5.1, N 3.2. Found: C 47.13, H 5.8, N 3.15.

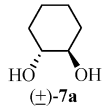
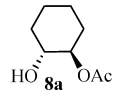
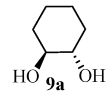
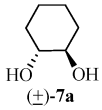
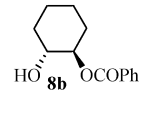
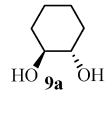
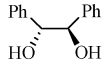
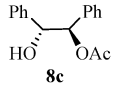
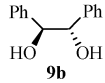
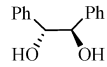
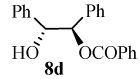
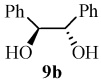
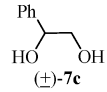
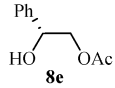
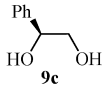
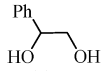
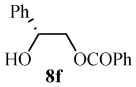
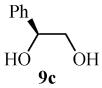
General Procedure for the Acylation Reaction. To a stirred solution of substrate (1 mmol), catalyst **1a**−**c** (5 mol%, with respect to repeating unit), base (1 mmol), solvent (2 mL), and acylating agent (0.5 mmol) were added, and the stirring was continued for the appropriate time (Tables 1–2). The progress of the reaction was monitored by thin layer chromatography (TLC). After completion, the solvent was evaporated under reduced pressure and the residue was dissolved in CH_2Cl_2 (25 mL) and successively washed with saturated $NaHCO_3$ solution (2 × 5 mL) and water (1 × 5 mL). Drying (Na_2SO_4) and evaporation of the solvent afforded a residue that was purified on silica gel flash column chromatography using ethyl acetate and hexane as eluent.

(*R*)-Benzoic acid 2-oxo-1,2-diphenyl-ethyl ester 5.[7a] Colorless solid; mp 116−117 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12−8.09 (m, 2H), 7.98−7.96 (m, 2H), 7.57−7.34 (m, 11H), 7.07 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.94, 166.26, 134.89, 133.94, 133.71, 133.57, 130.38, 130.19, 129.52, 129.34, 129.05, 128.88, 128.66, 128.61, 78.14; IR (KBr) ν 3420, 2959, 2925, 1716, 1690, 1598, 1356, 1279, 1247, 1177, 1232, 957, 762, 696 cm^{-1}; HPLC: Chiralcel OD-H column, *n*-hexane: isopropanol (95:5), wavelength 254 nm, flow rate 0.7 mL/min, 78% ee; $[\alpha]^{20}_D$ −176 (c = 1.0, acetone).

(*R*,*R*)-Benzoic acid 2-hydroxy-cyclohexyl ester 8b.[7a] Colorless solid; mp 93−94 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04−7.98 (d, J = 9.0 Hz, 2 H), 7.57−7.49 (m, 1 H), 7.45−7.36 (m, 2 H), 4.86−4.75 (m, 2 H), 3.78−3.64 (m, 1 H), 2.21−2.02 (m, 2 H), 1.77−1.67 (m, 2 H), 1.50−1.20 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.96, 133.26, 130.50, 129.86, 128.57, 78.91, 73.01, 33.18, 30.20, 24.09, 23.92; IR (KBr) ν 2939, 2862, 1718, 1603, 1453, 1281 cm^{-1}. HPLC: Chiralcel OJ column, *n*-hexane: isopro-

Table 2. Kinetic Resolution of (±)-1,2-diols by Acylation[a,b,c,d,e,f,g,h]



Entry	(±)-7a-c	R'COR"	8a-f	ee (%)	9a-c	ee (%)	Conv. (%)[g]	s[g]	8a-f (Confign)
1	 (±)-7a	Ac_2O	 8a	72[b]	 9a	68[b]	48	12.3	*1R,2R*
2	 (±)-7a	PhCOCl	 8b	62[b]	 9a	56[b]	47	7.2	*1R,2R*[h]
3	 (±)-7b	Ac_2O	 8c	64[c]	 9b	55[d]	46	7.8	*1R,2R*
4	 (±)-7b	PhCOCl	 8d	50[e]	 9b	44[d]	47	4.6	*1R,2R*[h]
5	 (±)-7c	Ac_2O	 8e	22[c]	 9c	18[f]	45	1.9	*R*
6	 (±)-7c	PhCOCl	 8f	18[e]	 9c	15[f]	45	1.6	*R*[h]

[a] Substrate (1 mmol), catalyst **1a** (5 mol% with respect to repeating unit), acylating agent (0.5 mmol), and Et_3N (1 mmol) were stirred in Et_2O (2 mL). [b] Determined by HPLC using chiralcel OJ column with hexane and isopropanol (97:3) after converting to monobenzoylated product. [c] Determined by HPLC using chiralcel OD-H column with *n*-hexane and isopropanol (90:10). [d] Determined by HPLC using chiralcel OJ column with hexane and isopropanol (90:10). [e] Determined by HPLC using chiralcel OJ column with *n*-hexane and isopropanol (90:10). [f] Determined by HPLC using chiralcel OB-H column with hexane and isopropanol (90:10). [g] Determined according to ref 14c. [h] THF was used as solvent.

panol (97:3), wavelength: 254 nm, flow rate: 1.0 mL/min, 62% *ee*, $[\alpha]^{20}_D$ −50.5 (c = 1.37, CH_3OH).

(*R,R*)-Benzoic acid 2-hydroxy-1,2-diphenyl-ethyl ester 8d.[7a] Colorless solid; mp 147−148 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13−8.10 (m, 2H), 7.62−7.55 (m, 1 H), 7.51−7.44 (m, 2 H), 7.30−7.16 (m, 10H), 6.11 (d, J = 7.4 Hz, 1H), 5.10 (d, J = 7.4 Hz, 1 H), 2.73−2.56 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.38, 139.19, 136.36, 133.43, 130.14, 129.33, 128.66, 128.44, 125.40, 125.32, 125.28, 127.46, 127.32, 80.74, 77.42; IR (KBr) ν 3472, 3034, 1721, 1453, 1273, 1113, 704 cm^{-1}. HPLC: Chiralcel OJ column, *n*-hexane: isopropanol (90:10), wavelength: 254 nm, flow rate: 1.0 mL/min, 50% ee; $[\alpha]^{20}_D$ −48 (c = 1.37, CH_3OH).

(*R*)-Benzoic acid 2-hydroxy-2-phenyl-ethyl ester 8f.[7b] Colorless solid; mp 50−52 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04−8.02 (m, 2H), 7.60−7.54 (m, 1 H), 7.45−7.31 (m, 7H), 5.09 (m, 1H), 4.53−4.49 (dd, J = 11.2, 3.2 Hz, 1H), 4.43−4.38 (dd, J = 11.6, 8.4 Hz, 1H);^{13}C NMR (100 MHz, $CDCl_3$) δ 166.96, 140.07, 133.45, 129.92, 128.84, 128.65, 128.48, 128.41,72.79, 70.01; IR (KBr) ν 3480, 1709, 1451, 1318, 1281, 1096, 703, 698 cm^{-1}; HPLC: Chiralcel OD-H column, *n*-hexane: isopropanol (95:5), wavelength: 254 nm, flow rate: 0.7 mL/min, 18% ee; $[\alpha]^{20}_D$ −6 (c = 0.2, $CHCl_3$).

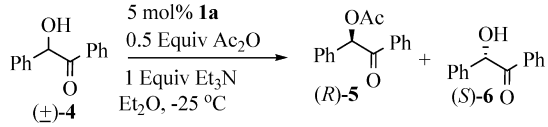
(*R*)-2-Acetyloxy-1,2-diphenylethanone 5.[8a] Colorless solid; mp 82−83 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94−7.92 (m, 2H), 7.53−7.34 (m, 8 H), 6.86 (s, 1 H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.92, 170.72, 134.73, 133.71, 129.57, 129.36, 129.00, 128.92, 128.85, 77.85, 21.00; IR (KBr) ν 3472, 3034, 1721, 1453, 1273, 1113, 704 cm^{-1}; HPLC: Chiralcel OD-H column, *n*-hexane: isopropanol (95:5), wavelength: 254 nm, flow rate: 0.7 mL/min, 90% ee; $[\alpha]^{20}_D$ −217.9 (c = 1.0, benzene).

(*R,R*)-2-Acetoxycyclohexan-1-ol 8a.[8b] Colorless solid; mp 57−59 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.57 (m, 1H), 3.55 (m, 1 H), 2.09 (s, 3 H), 2.07−2.02 (m, 2H) 1.69 (m, 2H) 1.39−1.25 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.67, 78.28, 72.79, 33.17, 30.13, 24.00, 23.92, 21.49; IR (KBr) ν IR: 3432, 2936, 2896, 1732, 1384, 1232,1080, 1040 cm^{-1}. **8a** was transformed to **8b** using aqueous K_2CO_3 followed by monobenzoylation with benzoyl chloride, Et_3N and $Cu(OAc)_2 \cdot 1H_2O$ (5 mol%) in THF. HPLC analysis of the monobenzoylated product **8b**: Chiralcel OJ column, *n*-hexane: isopropanol (97:3), wavelength: 254 nm, flow rate: 1.0 mL/min, 72% ee; $[\alpha]^{25}_D$ −30.9 (c = 1.0, $CHCl_3$).

(*R,R*)-1-Acetoxy-2-hydroxy-1,2-diphenylethane 8c.[8c] Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20−7.12 (m, 6H), 7.07−7.02 (m, 4 H), 5.78−5.76 (d, J = 7.6 Hz, 1H), 4.85−4.83 (d, J = 7.6 Hz, 1H) 2.6 (bs, OH), 2.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.47, 139.22, 137.04, 128.38, 128.34, 127.45, 127.22, 80.30, 21.37; IR (KBr) ν 3472, 3034, 1721, 1453, 1273, 1113, 704 cm^{-1}; HPLC: Chiralcel OD-H column, *n*-hexane: isopropanol (95:5), wavelength: 254 nm, flow rate: 0.7 mL/min, 64% ee; $[\alpha]^{20}_D$ +15 (c = 0.1, MeOH).

(*R*)-2-hydroxy-2-phenylethyl acetate 8e.[8d] Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30−7.22 (m, 5H), 4.88−4.85 (dd, J = 8.4, 3.2 Hz, 1H), 4.21−4.17 (dd, J = 7.6, 3.2 Hz, 1H), 4.10−4.05 (dd, J = 11.6, 4.4 Hz, 1H), 2.7 (bs, OH) 2.02 (s, 3H); ^{13}C NMR

Table 3. Recyclability of Catalyst **1a**[a]



run	recoverability (%)	**5** ee (%)	**6** ee (%)	Conv. (%)
1	90	90	82	48
2[b]	87	89	80	47
3[b]	82	89	81	48

[a] Benzoin (1 mmol), catalyst **1a** (5 mol%, with respect to monomeric unit), Ac_2O (0.5 mmol), and Et_3N (1 mmol) were stirred at −25 °C for 15 h in Et_2O (2 mL). [b] Recovered catalyst used.

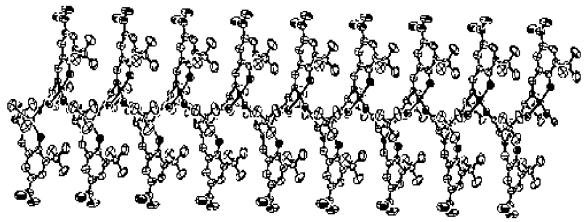


Figure 1. ORTEP view of **1a** (growing form). Thermal ellipsoid set to 50% probability and hydrogen atoms are omitted for clarity.

(100 MHz, $CDCl_3$) δ 171.45, 139.95, 128.77, 128.42, 126.32, 72.54, 69.49, 21.09; IR (KBr) ν 3472, 3034, 1721, 1453, 1273, 1113, 704 cm^{-1}; HPLC: OD-H column, *n*-hexane: isopropanol (95:5), wavelength: 254 nm, flow rate: 0.7 mL/min, 22% ee; $[\alpha]^{20}_D$ −8 (c = 1.1, $CHCl_3$).

Recycling Experiment. To a stirred solution of benzoin (1 mmol, 212 mg), catalyst **1a** (5 mol%, 20 mg), Et_3N (1 mmol, 101 mg) in Et_2O (2 mL), and acetic anhydride (0.5 mmol, 51 mg) were added, and the stirring was continued for 15 h (Table 3). The reaction mixture was then treated with Et_2O (25 mL) and successively washed with a saturated $NaHCO_3$ solution (2 × 5 mL) and water (1 × 5 mL). Drying (Na_2SO_4) and evaporation of the solvent afforded a residue that was treated with CH_3CN. The insoluble catalyst was filtered and recycled for the fresh reaction of benzoin with acetic anhydride in the presence of Et_3N. This process was repeated up to three runs, and no loss of activity was observed.

Results and Discussion

Reaction of the salicylaldehyde derivatives **2a**−**c** with L-*tert*-leucine in the presence of Et_3N provided Schiff bases **3a**−**c**, which were reacted in situ with $Cu(OAc)_2 \cdot 1H_2O$ to afford the polymers **1a**−**c** as green colored crystals in 85−88% yield.[9] Recrystallization of the polymers **1a**−**c** in MeOH, and CH_2Cl_2 gave single crystals that were analyzed by X-ray analysis. ORTEP diagram and crystal packing of **1a** are shown in Figure 1 and Figure 2, respectively (Supporting Information for ORTEP diagram and crystal packing of **1b**−**c**). Polymers **1a**−**c** are stereoregular, and the repeating units having O−H interaction are connected to each other in a perpendicular fashion.[10−12] The copper(II) atoms are pentacoordinated with distorted square-pyramidal geometry for **1a**−**b** and square-planar geometry for **1c**.[5,13]

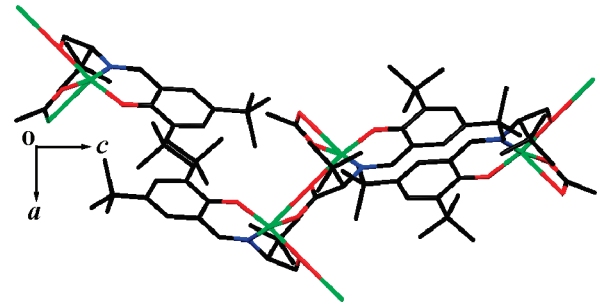


Figure 2. Crystal packing of **1a**.

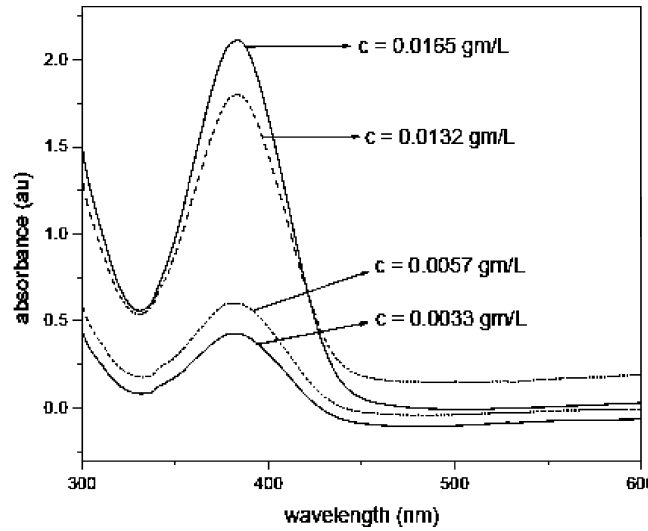


Figure 3. UV−vis spectra of **1a** at different concentrations.

Because the polymers **1a**−**c** are stereoregular, we were interested to study them for asymmetric catalysis. First, we examined the kinetic resolution of secondary alcohols by acylation.[14] The reaction of benzoin was studied as a model substrate with different acylating agents (Table 1). We were pleased to find that the reaction occurred to afford the desired acylated product with up to 62% ee when the substrate was

(10) Crystal data for **1a**: $C_{21}H_{31}CuNO_3$, MW = 409.06, orthorhombic; $P2_12_12_1$; a = 6.2168(7) Å, b = 16.4734(18) Å, c = 21.668(2) Å; α = 90°, β = 90°, γ = 90°; V = 2219.0(4) Å^3; Z = 2, D_{calcd} = 1.224 mgm^{-3}; T = 296 (2) K; Scan range 6.26° < θ < 28.32°; cryst dimension 0.50 × 0.16 × 0.10 mm^3; 5416 reflns, 4428 unique reflections; ($I > 2\sigma(I)$); R_1 = 0.0360; wR_2 = 0.0785 (all data); GOF (on F^2) = 1.016.

(11) Crystal data for **1b**: $C_{17}H_{22}CuN_2O_5$, MW = 397.92, orthorhombic; $P2_1$; a = 10.92(3) Å, b = 6.47(1) Å, c = 13.84(3) Å; α = 90°, β = 100°, γ = 90°; V = 963.68 (4) Å^3; Z = 2, D_{calcd} = 1.371 mgm^{-3}, T = 296(2) K; Scan range 1.6° < θ < 28.59°; cryst dimension 0.45 × 0.20 × 0.08 mm^3; 4297 reflns; 3347 unique reflns; ($I > 2\sigma(I)$); R_1 = 0.0336, wR_2 = 0.0733 (all data); GOF (on F^2) = 1.001.

(12) Crystal data for **1c**: $C_{17}H_{22}CuBrNO_3$, MW = 431.81, orthorhombic, $P2_1$; a = 11.65(8) Å, b = 7.29(6) Å, c = 12.03(9) Å; α = 90°, β = 113°, γ = 90°; V = 935.29(12) Å^3; Z = 2, D_{calcd} = 1.45 mgm^{-3}; T = 296(2) K; Scan range 1.57° < θ < 28.85°; cryst size 0.50 × 0.12 × 0.07 mm^3; 4139 reflns; 3317 unique reflns; ($I > 2\sigma(I)$); R_1 = 0.1330; wR_2 = 0.3824, (all data), GOF (on F^2) × 1.603.

(13) (a) Drago, R. S. *Physical Methods in Chemistry*; Saunders Company: Eastbourne, England, 1977. (b) Peisach, J. In *Bioinorganic Chemistry of Copper*; Karlin, K. D., Tyeklár, Z., Eds.; Chapman and Hall: New York, 1993. (c) Hathaway, B. J. In *Comprehensive Coordination Chemistry*; Vol. 5, Wilkinson, S. G., Gillard, R. D., McCleverty, J. A., Eds., Pergamon Press: England, 1987; p 533.

(14) (a) Matsumura, Y.; Maki, T.; Murakami, S.; Onomura, O. *J. Am. Chem. Soc.* **2003**, *125*, 2052. (b) Gissibl, A.; Padie, C.; Hager, M.; Jaroschik, F.; Rasappan, R.; Cuevas-Yanez, E.; Turrin, C.-O.; Caminade, A.-M.; Majoral, J.-P.; Reiser, O. *Org. Lett.* **2007**, *9*, 2895. (c) Mazet, C.; Roseblade, S.; Koehler, V.; Pfaltz, A. *Org. Lett.* **2006**, *8*, 1879. (d) Iwasaki, F.; Maki, T.; Onomura, O.; Nakashima, W.; Matsumura, Y. *J. Org. Chem.* **2000**, *65*, 996. (e) Demizu, Y.; Matsumoto, K.; Onomura, O.; Matsumura, Y. *Tetrahedron Lett.* **2007**, *48*, 7605. (f) Roseblade, S. J.; Pfaltz, A. *Synthesis* **2007**, 3751. (g) Takayoshi, A.; Tomoe, M.; Akira, Y. *Org. Lett.* **2007**, *9*, 1145.

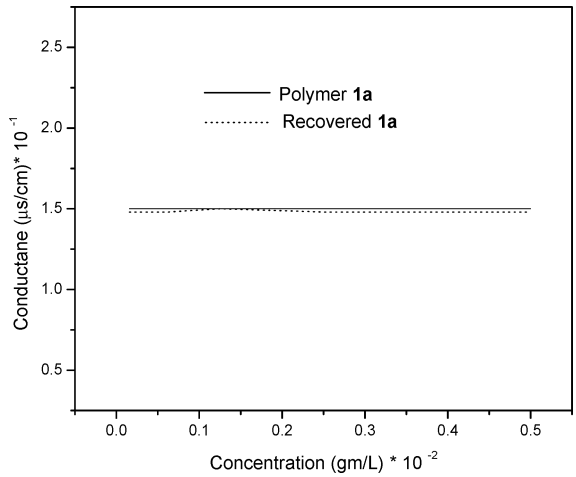
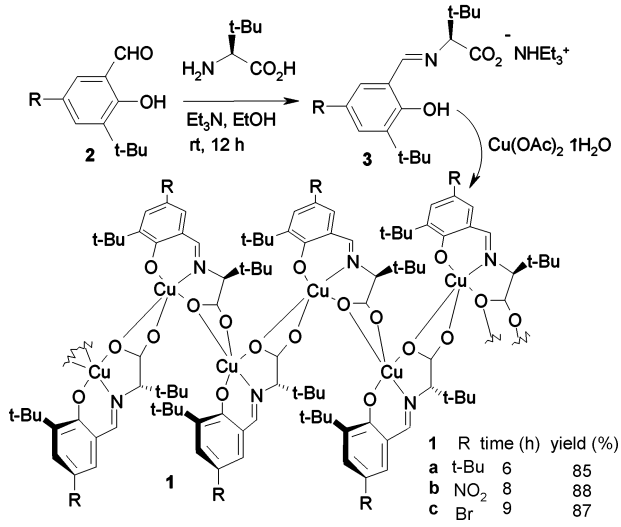


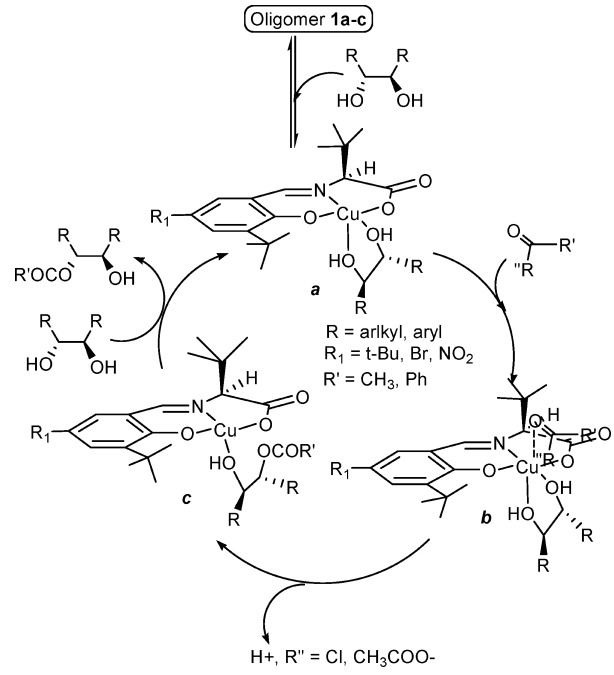
Figure 4. Conductivity of **1a** and recovered catalyst at different concentrations.

Scheme 1. Preparation of Polymers **1a**−**c**



stirred at 0 °C in the presence of 0.5 equiv of acylating agent, 1 equiv of base, and 5 mol% of copper(II) polymer **1a**−**c** (with respect to the monomeric unit). When the reaction temperature was further lowered to −25 °C, the enantioselectivity of the acylated product was enhanced up to 90% ee ($s = 50$). Of the acylating agents studied, benzoyl chloride, benzoic anhydride, acetic anhydride, and acetyl chloride, the latter was less effective, affording the acylated product with 15% ee. The reactions with benzoyl chloride and benzoic anhydride showed similar results, providing the benzoylated product with up to 78% ee. Whereas the reaction with acetic anhydride exhibited up to 90% ee, among the bases screened, Et_3N, $^iPr_2NH$, pyridine, and 2,6-lutidine, the former provided the best result. Of the solvents examined, THF, Et_2O, CH_2Cl_2, acetone, and toluene, THF provided the highest ee for benzoylation, whereas Et_2O was found to be the choice for acetylation. In catalysts, **1a** was found to superior to **1b** and **1c**, exhibiting the highest ee. These results suggest that the success of the reactions depends on the combination of solvent, acylating agent, and catalyst.

Scheme 2



Next, to study the scope of the procedure, **1a** was investigated for the monoacylation of (±)-*trans*-1,2-diols **7**, using acetic anhydride and benzoyl chloride as acylating agents (Table 2). (±)-*trans*-1,2-cyclohexanediol **7a** underwent a reaction to give the monoacylated products **8a** and **8b** in 72% and 62% ee, respectively. Similar results were observed with (±)-*trans*-1,2-diphenylethane-1,2-diol **7b**, providing the monoacylated products **8c** and **8d** in 64% and 50% ee. Under these conditions, (±)-1-phenyl-1,2-ethanediol **7c** was selectively acylated with the primary hydroxy group without affecting secondary OH group in 22% and 18% ee, respectively. The reactions were selective, and no diacetylated product was obtained.

The catalyst is recyclable without loss of activity (Table 3). After completion of the acetylation of benzoin with polymer **1a**, the reaction mixture was successively washed with saturated $NaHCO_3$ solution and water. Drying (Na_2SO_4) and evaporation of the solvent provided a residue that was treated with CH_3CN (0.5 mL for 0.05 mmol of catalyst). The insoluble green-colored copper(II) catalyst was filtered and re-used for the fresh reaction of acetylation of benzoin. This process was repeated up to three runs, and the reactions occurred to afford the desired **5** and **6** without loss of activity and selectivity. The recovered catalyst was further examined by optical rotation, UV−vis and conductivity experiments. The observed specific rotation, $[\alpha]_D^{25}$ +219 ($c = 0.02$, MeOH), UV−vis absorption and conductance data were identical to that of the polymer **1a** (before the reaction) (Figure 3–4). These studies reveal that the recovered catalyst and polymer **1a** are same.

To reveal the nature of these polymers in solution, MALDI TOF MS of **1a** in $CHCl_3$ was studied. Peaks corresponding to dimer, trimer, tetramer, and pentamer were observed, suggesting that the polymer undergoes dissociation into oligomers in solution (Supporting Information). Thus, these

oligomers may be dissociated into monomers during the reaction process and catalyze the reaction (Scheme 1 and Scheme 2). Reaction of the oligomers with 1,2-diol may give the monomeric **a** that could react with the acylating agent to give intermediate **b**. The latter **b** could be transformed to intermediate **c** by intramolecular acylation of the OH group with acylating agent. The intermediate **c** can complete the catalytic cycle by replacing the acylated product with fresh 1,2-diol.

Conclusions

Chiral copper(II) polymers **1a**−**c** have been prepared in one-pot with high yield. Single-crystal X-ray analysis showed that they are stereoregular, and the repeating units are connected to each other by perpendicular fashion through a carboxylate linker. The polymers **1a**−**c** are found to catalyze efficiently the kinetic resolution of secondary alcohols by acylation with 90% ee. Further investigations of **1a**−**c** on the mechanism and application to other reactions are currently being pursued.

Acknowledgment. This work was supported by Department of Science and Technology, New Delhi, and Council of Scientific and Industrial Research, New Delhi. We thank Mr. Babulal Das for X-ray analysis.

Supporting Information Available: Crystal data, EPR and UV−vis spectra for **1a**−**c**, TGA, magnetic susceptibility and MALDI-TOF MS for **1a** and the UV−vis of reaction mixture, and NMR spectra of acylated products **5** and **8a**−**f**. This material is available free of charge via the Internet at http://pubs.acs.org.

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