Visible-light-induced synthesis of polymers with versatile end groups mediated by organocobalt complexes

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1. General consideration

C₆D₆ and CDCl₃ were purchased from Cambridge Isotope Laboratory Inc., methyl acrylate (MA), n-butyl acrylate (nBA), tert-butyl acrylate (tBA), N,N-dimethylacrylamide (DMA) and Potassium peroxymonosulfate (Oxone®) from Alfa Aesar, N,N-diethylacrylamide (DEA), N-acryloylmorpholine (AMO) and (2,4,6-trimethylbenzoyl)diphenylphosphine oxide (TPO) from TCI, and N,N’-bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediamine((salen)Co) from Aldrich. All other chemicals were purchased from Alfa Aesar or J&K Scientific Ltd. and used as received unless otherwise noted. Monomers were all purified by passing through a neutral alumina column, distilled under reduced pressure to remove the inhibitor and stored in the refrigerator before use. ¹H NMR spectra were recorded on a Bruker AVII-400 spectrometer at ambient temperature. ESI-MS results were obtained by a Bruker Apex IV FTMS spectrometer. Light in the irradiation experiments was provided by A 500 W xenon lamp (CEL-S500, Aulight, Beijing, China) which was used as the light source with a 420–780 nm filter to give visible light.

General reaction procedure: The 0.3 ml C₆D₆ solution of catalyst (1.67 mM or 1.25 mM) and monomer (1.0 M) was irradiated by 500W Xe lamp with a 420-780 nm filter 25 °C (3 mW/cm²). The monomer conversion was determined based on ¹H NMR spectra ($M_{n,th} = M_{w(I)} + M_{w(Monomer)} \times \text{ratio}$).
×conv.(%)), where ratio referred to the equivalent of monomer to catalyst; \( M_{n, GPC} \) and PDI were
determined using gel permeation chromatography (GPC) in DMF calibrated against
poly(methylmethacrylate) (PMMA) standard.

2. Preparation of (salen)Co-R (I)

General procedure for synthesis of (salen)Co-COR (I): A 8.0 mL toluene solution of (salen)Co\( \text{II} \) (0.09
mmol, 55 mg), Oxone\( ^\text{®} \) (0.44 mmol, 135mg) and methanol (7.4mmol 0.3 mL) was stirred for 1 hour at
room temperature. Subsequently, the mixture was filtered to remove excess unsolved Oxone\( ^\text{®} \), added
with \( \text{Na}_3\text{PO}_4 \cdot \text{H}_2\text{O} \) (1.71 mmol, 650mg) and corresponding amine (7.4 mmol), then degassed by
three freeze-pump-thaw cycles and refilled with CO (1 atm). The reaction solution was stirred for 24 h
under dark condition at room temperature. The crude product was purified by column chromatography
(basic alumina, \( \text{CH}_2\text{Cl}_2 \) as eluent) after removing the solvent.

a)

\[
\text{yield: 65%}
\]

\( ^1\text{H NMR} \) (CDCl\( _3 \), 400 MHz, 298K, \( \delta \)): 8.03 (s, 1H), 7.79 (s, 1H), 7.40 (s, 1H), 7.37 (s, 1H), 7.02 (s,
1H), 6.95 (s, 1H), 4.13-3.91(m, 2H), 3.71 (br, t, 1H), 3.60(s, 1H), 3.42 (br, t, 1H), 2.71 (m, 2H), 2.04
(m, 2H), 1.86 (m, 2H), 1.54 (s, 9H), 1.46 (m, 2H), 1.30 (s, 18H);

\( \text{ESI-MS} \) calcd for: 708.363, found: 708.364

b)

\[
\text{yield:52%}
\]

\( ^1\text{H NMR} \) (CDCl\( _3 \), 400 MHz, 298K, \( \delta \)): 8.03 (s, 1H), 7.38 (d, 1H), 7.38 (d, \( J = 2.4 \text{ Hz}, 1\text{H} \)), 7.35 (d, \( J
= 2.4 \text{ Hz}, 1\text{H} \)), 7.01 (d, \( J = 2.4 \text{ Hz}, 1\text{H} \)), 6.94 (d, \( J = 2.4 \text{ Hz}, 1\text{H} \)), 3.66 (m, 2H), 3.37 (m, 2H), 2.66 (m,
2H), 2.01 (m, 2H), 1.57 (s, 6H), 1.53 (d, \( J = 5.2 \text{ Hz}, 18\text{H} \)), 1.28 (d, \( J = 11.2 \text{ Hz}, 18\text{H} \)), 1.04 (s, 3H).

\( \text{ESI-MS} \) calcd for: 704.419, found: 704.420;

c)
\[ \text{yield: 52\%} \]

\[ ^1H \text{ NMR (CDCl}_3, 400 \text{ MHz, 298K, } \delta): \ 8.77 (s, 1H), 8.07 (d, } J = 1.7 \text{ Hz, 1H}), 7.82 (d, } J = 2.0 \text{ Hz, 1H), 7.43 (d, } J = 2.6 \text{ Hz, 1H), 7.35 (d, } J = 2.6 \text{ Hz, 1H), 7.18 (d, } J = 7.2 \text{ Hz, 2H), 7.12 (t, } J = 7.9 \text{ Hz, 2H), 7.02 (d, } J = 2.6 \text{ Hz, 1H), 6.95 (d, } J = 2.6 \text{ Hz, 1H), 6.93 \text{ – } 6.85 \text{ (m, 1H), 3.88 – 3.77 (m, 2H), 3.51 – 3.40 (m, 2H), 2.73 (brs, 2H), 2.05 (d, } J = 12.2 \text{ Hz, 2H), 1.61 (d, } J = 13.1 \text{ Hz, 18H), 1.74-1.46 (m, 4H), 1.28 (d, } J = 10.4 \text{ Hz, 18H).} \]

\[ \text{ESI-MS calcd for: 746.370, found: 746.371;} \]

d)

\[ \text{yield: 51\%} \]

\[ ^1H \text{ NMR (CDCl}_3, 400 \text{ MHz, 298K, } \delta): \ 8.05 (s, 1H), 7.76 (s, 1H), 7.38 (d, } J = 2.4 \text{ Hz, 1H), 7.34 (d, } J = 2.4 \text{ Hz, 1H), 6.99 (d, } J = 2.4 \text{ Hz, 1H), 6.94 (d, } J = 2.4 \text{ Hz, 1H), 3.85 (m, 2H), 3.70 (m, 2H), 3.43 (m, 2H), 2.68 (m, 2H), 2.01 (m, 2H), 1.53 (d, } J = 5.6 \text{ Hz, 18H), 1.43 (s, 3H), 1.28 (d, } J = 2.4 \text{ Hz, 18H), 0.96 (m, 2H), 0.86 (m, 2H), 0.59 (m, 2H), 0.31 (m, 2H).} \]

\[ \text{ESI-MS calcd for: 758.466, found: 758.467;} \]

e)

\[ \text{yield: 61\%} \]

\[ ^1H \text{ NMR (CDCl}_3, 400 \text{ MHz, 298K, } \delta): \ 8.04 (s, 1H), 7.82 (s, 1H), 7.40 (m, 2H), 7.04 (s, 1H), 7.00 (s, 1H), 6.98 (s, 1H), 6.75-6.63 (m, 4H), 4.51-4.19 (m, 2H), 3.76 (br, t, 1H), 3.47 (br, t, 1H), 2.70 (m, 2H), 2.04 (m, 2H), 1.54 (s, 9H), 1.46 (m, 2H), 1.31 (s, 9H), 1.30 (s, 9H);} \]

\[ \text{ESI-MS calcd for: 778.377, found: 778.376;} \]

f)
**yield: 65%**

\[ ^1H \text{NMR (CDCl}_3, 400 MHz, 298K, } \delta \text{): 8.04 (s, 1H), 7.82 (s, 1H), 7.40 (m, 2H), 7.04 (s, 1H), 7.00 (s, 1H), 6.98 (s, 1H), 6.93 (d, 2H), 6.70 (d, 2H), 4.51-4.16(m, 2H), 3.76 (br, t, 1H), 3.47 (br, t, 1H), 2.70 (m, 2H), 2.04 (m, 2H), 1.54 (s, 9H), 1.46 (m, 2H), 1.31 (s, 9H), 1.30 (s, 9H); \]

**ESI-MS** calcd for: 794.344, found: 794.347;

g) 

**yield: 45%**

\[ ^1H \text{NMR (CDCl}_3, 400 MHz, 298K, } \delta \text{): 8.06 (s, 1H), 7.86 (s, 1H), 7.40 (s, 1H), 7.36 (s, 1H), 7.07 (m, 1H), 7.02 (s, 1H), 6.98 (s, 1H), 6.04 (dd, 1H), 5.77 (d, 1H), 4.53-4.27(m, 2H), 3.76 (br, t, 1H), 3.45 (br, t, 1H), 2.70 (m, 2H), 2.04 (m, 2H), 1.54 (s, 9H), 1.46 (m, 2H), 1.31 (s, 9H), 1.30 (s, 9H); \]

**ESI-MS** calcd for: 794.344, found: 794.347;

h) 

**yield: 57%**

\[ ^1H \text{NMR (CDCl}_3, 400 MHz, 298K, } \delta \text{): 8.06 (s, 1H), 7.86 (s, 1H), 7.40 (s, 1H), 7.36 (s, 1H), 7.19-7.13 (br, m, 1H), 7.02 (s, 1H), 6.98 (s, 1H), 6.77 (dd, 1H), 6.42 (d, 1H), 4.67-4.43(m, 2H), 3.75 (br, t, 1H), 3.47 (br, t, 1H), 2.70 (m, 2H), 2.04 (m, 2H), 1.54 (s, 9H), 1.46 (m, 2H), 1.30 (s, 18H); \]

**ESI-MS** calcd for: 766.343, found: 766.342

3. Preparation of MeO, tBu, Cl or CF\textsubscript{3} substituted salen Cobalt complex
Scheme S1 Structures of modified (salen)Co complex

a) Synthesis of MeO(salen)CoCOOCH₃

Synthesis of 3-tert-butyl-5-methoxsalicylaldehyde: The compound was prepared via literature procedure.¹ A mixture of 3-tert-butyl-4-hydroxyanisole (1.8 g) and hexamethylenetetramine (2.8 g) dissolved in glacial acetic acid (10 mL) was heated at 110 °C for 2 h. After disappearance of 3-tert-butyl-4-hydroxyanisole was confirmed by TLC, aqueous H₂SO₄ (10 mL, 33%) was added at 75 °C. The resulting mixture was heated at 110 °C for another 3 h. The mixture was extracted with diethyl ether (25 mL), and the extract was washed with water, saturated Na₂CO₃ solution and saturated NaCl solution. The organic layer was dried over MgSO₄, and then the solvent was removed by evaporation under reduced pressure. The crude was further purified by a silica column using CH₂Cl₂ as eluent to yield the title compound as yellow oil.

¹H NMR(CDCl₃, 400 MHz, 298 k, δ): 11.51 (s, 1H); 9.84 (s, 1H); 7.18 (d, J=3.09 Hz, 1H); 6.82 (d, J=3.11 Hz, 1H); 3.81 (s, 3H); 1.41 (s, 9H).

Synthesis of [(R,R)-N,N’-bis(3-tert-butyl-5-methoxsalicylidene)-1,2-cyclohexanediamine] (MeO-salen): The compound was prepared via literature procedure.² A mixture of (1R,2R)-1,2-diaminocyclohexane (0.4 g) and 3-tert-butyl-5-methoxsalicylaldehyde (1.5 g) dissolved in ethanol (50 mL) was heated at refluxing temperature for 5 h. The solution was then cooled to room temperature to give the title compound as a yellow solid (68%), which was utilized for the following reactions without further purification.

¹H NMR(CDCl₃, 400 MHz, 298 K, δ): 13.45(s, 2H); 8.23 (s, 2H); 6.89 (d, J=3.12 Hz, 2H); 6.47 (d, J=3.00 Hz, 2H); 3.68 (s, 6H); 3.31 (m, 2H); 1.98 (m, 2H), 1.88 (m, 2H); 1.75 (m, 2H); 1.47 (m, 2H); 1.39 (s, 18H)

Synthesis of MeO(salen)Co²⁺: The compound was prepared by the modification of a published procedure.³ 25 mL Schlenk flask was loaded with MeO-salen (0.17 g), Co(OAc)₃·4H₂O (0.11 g) and ethanol (10 mL), degassed by three freeze-pump-thaw (FPT) cycles on vacuum line and refilled with N₂ in glove box. The solution was heated to 80 °C, refluxing for 4 h. The resulting solution was then cooled to room temperature to give the title compound as a dark
red solid (80%), which was purified by being washed with ethanol and methanol.


Synthesis of MeO(salen)CoCOOCH₃: The compound was prepared via an adaption from a published procedure to synthesize ‘Bu(salen)CoCOOCH₃.⁴ A mixture of MeO(salen)Co II (50 mg), Oxone® (138 mg), methanol (150 μL) and toluene (6 mL) was heated at 50 °C for 2 h, wrapped with aluminum foil to avoid light irradiation. The solution was then filtered to a 25 mL Schlenk flask loaded with Na₃PO₄·12H₂O (800 mg) to remove excess unsolved Oxone®, degassed by three FPT cycles and refilled with carbon monoxide (1 atm). The mixture was wrapped with aluminum foil and stirring for 8 min at room temperature. After the solvent was removed under reduced pressure, the crude was purified by column chromatography (basic alumina, CH₂Cl₂ as eluent) to give the title compound as dark green solid (10%).

¹H NMR (CDCl₃, 400 MHz, 298 K, δ): 8.02 (br s, 1H); 7.81 (br s, 1H); 7.05 (br d, J=2.23 Hz, 2H); 6.51 (d, J=2.95 Hz, 1H); 6.48 (d, J=3.32 Hz, 1H); 3.77 (s, 3H); 3.76 (s, 3H); 3.67 (s, 3H); 3.44 (m, 2H); 2.73 (m, 2H); 2.04 (m, 2H); 1.63 (m, 2H); 1.55 (s, 9H); 1.51 (s, 9H); 1.26 (m, 2H)

b) Synthesis of Cl(salen)CoCOOCH₃

Synthesis of 2-tert-butyl-4-chlorophenol: The compound was prepared via literature procedure.⁵ 4-chlorophenol (4 g) was dissolved in a solution of tert-butyl alcohol (6.4 mL), and concentrated H₂SO₄ (3.8 mL) was slowly added at 0 °C, turning the solution from a pale yellow to a light red orange. The solution was stirred for 2 d at room temperature, and subsequently poured into ice blocks. The mixture was extracted with diethyl ether, and the extract was washed with saturated Na₂CO₃ solution and saturated NaCl solution. The organic layer was dried over Na₂SO₄ and solvent was removed by evaporation under reduced pressure. The crude was further purified by column chromatography (silica, PE:EA = 95:5 as eluent) to give the title compound as a pale yellow oil (63%).

¹H NMR (CDCl₃, 400 MHz, 298 K, δ): 7.20 (d, J=2.44 Hz, 1H); 7.01 (dd, J=2.76, 8.40 Hz, 1H); 6.64 (d, J=8.50 Hz, 1H); 1.39 (s, 9H).

Synthesis of 3-tert-butyl-5-chlorosalicylaldehyde: The compound was prepared via literature procedure.⁶ The reaction was carried out under N₂. Acetonitrile and triethylamine were distilled over CaH₂ prior to use. Paraformaldehyde was dried over P₂O₅, and MgCl₂ was dried in a vacuum oven at 80 °C overnight. A 100 mL Schlenk charged with 2-tert-butyl-4-chlorophenol (1.3 g), MgCl₂ (1.0 g), triethylamine (3.7 mL) and acetonitrile (25 mL) was stirred for 15 minutes under room temperature. The mixture was degassed three FPT cycles
and refilled with N₂ in glove box, and paraformaldehyde (1.4 g) was added. The solution was heated to reflux for 3.5 h. Subsequently, the solution was cooled to room temperature and poured into aqueous HCl solution (60 mL, 5%), stirring for another 30 min. The mixture was extracted with diethyl ether and the extract was washed with saturated NaCl solution. The organic layer was dried over Na₂SO₄, and solvent was removed by evaporation under reduced pressure. The crude was further purified by recrystallization from heptane to give the title compound as a yellow solid (72%).

¹H NMR (CDCl₃, 400 MHz, 298 K, δ): 11.64 (s, 1H); 9.74 (s, 1H); 7.38 (d, J=2.66 Hz, 1H); 7.29 (d, J=2.66 Hz, 1H); 1.33 (s, 9H).

Synthesis of \((R,R)\)-N,N’-bis(3-tert-buty1-5-chlorosalicylidene)-1,2-cyclohexanediamine (Cl-salen): The compound was prepared via the same procedure as the synthesis of MeO-salen. The title compound precipitated as a yellow solid (63%).

¹H NMR (CDCl₃, 400 MHz, 298 K, δ): 13.80 (s, 2H); 8.18 (s, 2H); 7.18 (d, J=2.84 Hz, 2H); 6.94 (d, J=2.64 Hz, 2H); 3.32 (m, 2H); 1.98 (m, 2H); 1.89 (m, 2H); 1.76 (m, 2H); 1.54 (s, 9H); 1.48 (m, 2H); 1.38 (s, 9H); 1.25 (m, 2H).

Synthesis of Cl(salen)Coᴵᴵ: The compound was prepared via the same procedure as the synthesis of MeO(salen)Coᴵᴵ. The title compound precipitated as a red solid (64%).


Synthesis of Cl(salen)CoCOOCH₃: The compound was prepared via an adaption from a published procedure to synthesize tBu(salen)CoCOOCH₃.⁴ A mixture of Cl(salen)Coᴵᴵ (50 mg), Oxone® (138 mg), methanol (150 μL) and toluene (6 mL) was heated at 50 °C for 2 h, wrapped with aluminum foil to avoid light irradiation. The solution was then filtered to a 25 mL Schlenk flask loaded with Na₃PO₄·12H₂O (800 mg) to remove excess unsolved Oxone®, degassed by three FPT cycles and refilled with carbon monoxide (1 atm). The mixture was wrapped with aluminum foil and stirring for 24 h at room temperature. After the solvent was removed under reduced pressure, the crude was purified by column chromatography (basic alumina, CH₂Cl₂:PE = 1:1 as eluent) to give the title compound as dark green solid (21%).

¹H NMR (CDCl₃, 400 MHz, 298 K, δ): 7.91 (d, J=1.57 Hz, 1H); 7.77 (d, J=1.63 Hz, 1H); 7.25 (m, 1H); 7.23 (d, J=2.80 Hz, 1H); 7.09 (d, J=2.73 Hz, 1H); 7.05 (d, J=2.76 Hz, 1H); 3.70 (s, 3H); 3.40 (m, 2H); 2.72 (m, 2H); 2.06 (m, 2H); 1.62 (m, 2H); 1.52 (s, 9H); 1.49 (s, 9H); 1.46 (m, 2H).

c) Synthesis of CF₃(salen)CoCOOCH₃
Synthesis of 2-tert-butyl-4-trifluoromethylphenol: The compound was prepared via literature procedure. 7 4-trifluoromethylphenol (1 g) was dissolved in CH₃OH (1 mL) and tert-butyl alcohol (5 mL) was added at room temperature. Concentrated H₂SO₄ (4.7 mL) was then added at 0 °C. After 12 h stirring at room temperature, the reaction mixture was poured into ice blocks and extracted with CH₂Cl₂. The extract was washed by saturated Na₂CO₃ solution, saturated NaCl solution and dried over Na₂SO₄. Solvent was removed by evaporation under reduced pressure. The crude was further purified with column chromatography (silica, CH₂Cl₂:PE = 1:1) to give the title compound as pale yellow oil (71%). 

\(^1\)H NMR (CDCl₃, 400 MHz, 298 K, δ): 7.51 (d, J=1.48 Hz, 1H); 7.33 (dd, J=1.74, 8.40 Hz, 1H); 6.72 (d, J=8.29 Hz, 1H); 1.42 (s, 1H).

Synthesis of 3-tert-butyl-5-trifluoromethylsalicylaldehyde: The compound was prepared via literature procedure. 8 The solution of 2-tert-butyl-4-trifluoromethylphenol (1.5 g) in trifluoroacetic acid (30 mL) was added hexamethylenetetramine (1.1 g). The reaction mixture was stirred at reflux for 16 h. Then it was cooled to room temperature and poured into water (30 mL). The solution was then cooled and extracted with CH₂Cl₂. The extract was washed with saturated NaCl solution and dried over Na₂SO₄. The solvent was removed by evaporation under reduced pressure. The crude was further purified by column chromatography (silica, CHCl₃:PE = 4:1) to give the title compound as a pale yellow oil (10%). 

\(^1\)H NMR (CDCl₃, 400 MHz, 298 K, δ): 12.11 (s, 1H); 9.93 (s, 1H); 7.71 (m, 2H); 1.44 (s, 9H).

Synthesis of \((R,R)\)-N,N’-bis(3-tert-butyl-5-trifluoromethylsalicylidene)-1,2-cyclohexanediamine (CF₃-salen): The compound was prepared via the same procedure as the synthesis of MeO-salen. The title compound precipitated as a yellow solid (80%). 

\(^1\)H NMR (CDCl₃, 400 MHz, 298 K, δ): 14.35 (s, 2H); 8.30 (s, 2H), 7.44 (d, J=2.09 Hz, 2H); 7.25 (m, 2H); 3.37 (m, 2H); 2.04 (m, 2H); 1.93 (m, 2H); 1.79 (m, 2H); 1.54 (s, 9H); 1.44 (m, 2H); 1.39 (s, 9H).

Synthesis of CF₃(salen)Co\(^{II}\): The compound was prepared via the same procedure as the synthesis of MeO(salen)Co\(^{II}\). The title compound precipitated as a red solid (68%). 

ESI-MS Calcd [M]\(^+\): 627.18565. Found: 627.18462.

Synthesis of CF₃(salen)CoCOOCH₃: The compound was prepared via an adaption from a published procedure to synthesize ‘Bu(salen)CoCOOCH₃. 4 A mixture of CF₃(salen)Co\(^{II}\) (50 mg), Oxone® (138 mg), methanol (150 μL) and toluene (6 mL) was heated at 50 °C for 2 h, wrapped with aluminum foil to avoid light irradiation. The solution was then filtered to a 25
mL Schlenk flask loaded with Na$_3$PO$_4$$\cdot$12H$_2$O (800 mg) to remove excess unsolved Oxone®, degassed by three FPT cycles and refilled with carbon monoxide (1 atm). The mixture was wrapped with aluminum foil and stirring for 5 d at room temperature. After the solvent was removed under reduced pressure, the crude was purified by column chromatography (basic alumina, CH$_2$Cl$_2$:PE = 1:1 as eluent) to give the title compound as dark green solid (25%).

$^1$H NMR (CDCl$_3$, 400 MHz, 298 K, $\delta$): 8.09 (s, 1H); 7.89 (s, 1H); 7.49 (s, 1H); 7.46 (s, 1H); 7.44 (s, 1H); 7.40 (s, 1H); 3.73 (s, 3H); 3.46 (m, 2H); 2.76 (m, 2H); 2.08 (m, 2H); 1.86 (m, 2H); 1.70 (m, 2H); 1.51 (s, 9H); 1.43 (s, 9H).

d) Synthesis of Bu(salen)CoCOOCH$_3$

This compound was prepared via literature procedure. A mixture of Bu(salen)Co$^{II}$ (50 mg), Oxone® (138 mg), methanol (150 $\mu$L) and toluene (6 mL) was heated at room temperature for 1 h, wrapped with aluminum foil to avoid light irradiation. The solution was then filtered to a 25 mL Schlenk flask loaded with Na$_3$PO$_4$$\cdot$12H$_2$O (800 mg) to remove excess unsolved Oxone®, degassed by three FPT cycles and refilled with carbon monoxide (1 atm). The mixture was wrapped with aluminum foil and stirring for 8 min at room temperature. After the solvent was removed under reduced pressure, the crude was purified by column chromatography (basic alumina, CH$_2$Cl$_2$:PE = 1:1 as eluent) to give the title compound as dark green solid (60%~85%).

$^1$H NMR (CDCl$_3$, 400 MHz, 298 K, $\delta$): 8.06 (s, 1H); 7.86 (d, $J$=1.33 Hz, 1H); 7.40 (t, $J$=2.44 Hz, 2H); 7.02 (d, $J$=2.51 Hz, 1H); 6.98 (d, $J$=2.56 Hz, 1H); 3.67 (s, 3H); 3.44 (m, 2H); 2.76 (m, 2H); 2.05 (m, 2H); 1.64 (m, 4H); 1.57 (s, 9H); 1.53 (s, 9H); 1.30 (s, 9H).

Table S1. Visible Light initiated LRP of of MA Using Substituted (salen)CoCOOCH$_3$ as Both Initiator and Mediator at Room Temperature (25.0 °C)$^a$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substituent</th>
<th>T/h</th>
<th>Co$^{II}$ (equiv.)</th>
<th>$^b$Conv. (%)</th>
<th>$^c$M$_{n,th}$</th>
<th>$^d$M$_{n,GPC}$/PDI</th>
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</thead>
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<tr>
<td>1</td>
<td>CF$_3$</td>
<td>19</td>
<td>16%</td>
<td>21.1</td>
<td>11586</td>
<td>9149/1.21</td>
</tr>
<tr>
<td>2</td>
<td>t-Bu</td>
<td>16</td>
<td>16%</td>
<td>14.6</td>
<td>8204</td>
<td>7985/1.13</td>
</tr>
<tr>
<td>3</td>
<td>MeO</td>
<td>30</td>
<td>16%</td>
<td>11.2</td>
<td>6396</td>
<td>7726/1.13</td>
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<tr>
<td>4</td>
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<td>16%</td>
<td>13.7</td>
<td>7696</td>
<td>6579/1.20</td>
</tr>
</tbody>
</table>

$^a$[MA]$_0$=1.0M, [MA]$_0$ :[(salen)CoCOOCH$_3$]$_0$=600:1, Solvent was benzene-$d_6$, 500W Xe lamp was used as initiating light source, while polymerization going without extraneous light source; $^b$The monomer conversion was determined based on $^1$H NMR spectra; $^c$M$_{n,th}$ = M$_w$(II) + $M_w$(Monomer) × ratio ×conv(%), where ratio referred to the equivalent of monomer to (salen)CoCOOCH$_3$; $^d$Determined using gel permeation chromatography in DMF calibrated against poly(methylmethacrylate) standard.
4. 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) trapped experiments
   a) The solution of (salen)Co-CONHCH$_2$CCH ($I_\text{a}$) in THF (0.01 mM) was detected by UV-visible detector.

![Graph](image)

**Figure S1** UV-visible spectrum of (salen)Co-CONHCH$_2$CCH ($I_\text{a}$)

b) 0.35 mL C$_6$D$_6$ solution of $I_\text{a}$ (4 mM) and TMEPO (40.0 mM) was irradiated for 5 hours under visible light at room temperature (3 mW/cm$^2$), and monitored by $^1$H NMR (Figure S2). Sharp signals at 1.2-2.2 ppm were assigned to the tBu group of $I_\text{a}$, after exposing the reaction solution to visible light for 5 hours, the sharp signals disappeared, indicating the cleavage of the Co-C bond in $I_\text{a}$. In addition, the organo radical segment could be trapped by TEMPO, which was evidenced by the signals at 0.8-1.3 ppm. The single crystal structure of (salen)Co$^{II}$ generated by photolysis of $I_\text{a}$ in the presence of TEMPO was also obtained (Figure S3).

c)
**Figure S2** $^1$H NMR spectrum of $I_a$ (4 mM) and TEMPO (40.0 mM) in C$_6$D$_6$ under visible light irradiation (in the range of 0.2-4.0 ppm) for 5h.

**Figure S3.** Solid state structure of (salen)Co$^{II}$. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Co-O1 1.849, Co-O2 1.847, Co-N1 1.855, Co-N2 1.856; O1-Co-O2 87.30, O1-Co-N1 92.89, N2-Co-O2 93.75, N2-Co-N1 86.09.

5. MALDI analysis

General procedure for MALDI analysis: After polymerization of MA to desired conversion mediated by photocatalyst $I$ under visible light irradiation (3 mW/cm$^2$), the solvent and excess MA were removed by reduced pressure. The resulting PMA was dissolved in CHCl$_3$ and exposed to air for 1 h, then excess acetic acid was added. The solvent and acetic acid were removed after 1 h and the resulting product was analyzed by MALDI-TOF-MS.
Scheme S2. The strategy of PMA modification of ω end of (salen)Co to OH group

a) When $I_a$ worked as the photocatalyst, the MALDI results showed in Figure S4:

The results indicated that there were a series of peaks separated by MA unit. The experimental isotopic mass values of the main peak series agreed well with the theoretical values that HC≡CCH$_2$NHCO- at the α end and HO- at the ω end, plus a sodium ion from externally added salt for ionization.

\[
\text{Na}^+ = 2359.0510
\]

Figure S4. MALDI-TOF-MS spectroscopy of PMA obtained from photo-LRP mediated by $I_a$.

b) When $I_b$ worked as the photocatalyst, the MALDI results showed in Figure S5:

\[
\text{Na}^+ = 1688.7632
\]

\[
\text{Na}^+ = 1774.8074
\]
Figure S5. MALDI-TOF-MS spectroscopy of PMA obtained from photo-LRP mediated by I₆.
The other series of molecular ion peaks agreed well with the theoretical values of iBuNHCO- at the α end and HO- at the ω end, plus a potassium ion from externally added salt for ionization.

c) When I₉ worked as the photocatalyst, the MALDI results showed Figure S6:

\[
\begin{align*}
\text{Na}^+ & = 1398.6929 \\
\text{Na}^+ & = 1484.7242
\end{align*}
\]

Figure S6. MALDI-TOF-MS spectroscopy of PMA obtained from photo-LRP mediated by I₉.
The other series of molecular ion peaks agreed well with the theoretical values of corresponding chain ends, plus a potassium ion from externally added salt for ionization.
d) When I_d worked as the photocatalyst, the MALDI results showed Figure S7:

![MALDI-TOF-MS spectrum](image)

Figure S7. MALDI-TOF-MS spectroscopy of PMA obtained from photo-LRP mediated by I_d.

e) When I_e worked as the photocatalyst, the MALDI results showed Figure S8:

![MALDI-TOF-MS spectrum](image)

Figure S8. MALDI-TOF-MS spectroscopy of PMA obtained from photo-LRP mediated by I_e.
f) When $I_f$ worked as the photocatalyst, the MALDI results showed in Figure S9:

![Figure S9](attachment:image)

The other series of molecular ion peaks agreed well with the theoretical values of PhNHCO-at the $\alpha$ end and HO- at the $\omega$ end, plus a potassium ion from externally added salt for ionization.

g) When $I_g$ worked as the photocatalyst, the MALDI results showed Figure S10:

![Figure S10](attachment:image)
Figure S10. MALDI-TOF-MS spectroscopy of PMA obtained from photo-LRP mediated by \( I_g \).

h) When \( I_h \) worked as the photocatalyst, the MALDI results showed Figure S11:

\[
\text{Na}^+ = 1842.5867
\]

Figure S11. MALDI-TOF-MS spectroscopy of PMA obtained from photo-LRP mediated by \( I_h \).

6. Possible mechanism

In our system, polymerization underwent exclusively reversible termination mechanism mediated by \( I \). The chain growth procedure could be simplified as monomer insertion to the cobalt carbon bond in \( I \).
**Scheme S3.** Reversible termination mechanism in cobalt mediated radical polymerization

**Figure S12.** GPC traces for photo-polymerization of MA in C₆D₆ mediated by Iₐ under different conversion at room temperature (Xe lamp irradiation (3 mw/cm²)). Experimental conditions: [MA]₀ = 1.0 M; [MA]₀/[Iₐ]₀ = 600/1;

GPC traces of the PMA catalyzed by Iₐ were also detected by both refractive index and UV-visible detector;
PMA obtained in our system was also characterized by $^1$H NMR (Figure S16).

7. Discussion of chain end effect on the polymerization rate

The propagation rate is calculated via eq $R_p = k_p[M][R^*]$ which indicates any factors affecting terms on the right side of the equation would be expected to have an influence on the propagation rate. When it comes to the chain end effect, in our system, the α ends of the obtained polymers were expected to be the R group of starting cobalt complexes (R, from I), and ω ends were (salen)Co complexes. The dormant species (PMA-Co, PrBA-Co, or PDMA-Co) propagated the monomer by the
continual homolysis of Co-C bond and subsequent addition reaction between propagating chain radical (PMA radical, PrBA radical, or PDMA radical) and monomer. So the $\alpha$ ends of the obtained polymers, which is the R group of initiator $I$, could affect the initiation rate. However, it would not significantly affect the propagation rate because with DP grows the effect due to the structure difference of R groups attenuates rapidly.

Compare to the effect to R group to the propagation rate, the $\omega$ ends of (salen)Co complexes is expected to be more effective to influence the polymerization process. Three types of (salen)CoCOOCH$_3$ with substituent groups CF$_3$, tBu, and MeO on the salen ligand were prepared. The polymerization process initiated by the three different complexes was also investigated and was added in supporting information.

\[
\text{Different substituent groups would have different impacts on Co-C bond, characterized by the change of equilibrium constant } ((\text{salen})\text{Co-R} - (\text{salen})\text{Co}^{\text{II}} + R^\text{•}, K_{\text{eq}} = \frac{[(\text{salen})\text{Co}^{\text{II}}]_{\text{eq}} \times [R^\text{•}]}{[(\text{salen})\text{Co-R}]_{\text{eq}}}, \text{resulting in the change of the concentration of propagating chain radicals } [R^\text{•}]. \text{As a result, the } \omega \text{ end effect on the propagation rate would be revealed. By employing the thermal living radical polymerization of MA by (salen)CoCOOCH$_3$ as model reaction, the equilibrium constant of dissociation of (salen)CoPMA was determined with injection of extraneous persistent radical (salen)Co$^{\text{II}}$. The equilibrium concentration of } [(\text{salen})\text{CoPMA}]_{\text{eq}} \text{ and } [(\text{salen})\text{Co}^{\text{II}}]_{\text{eq}} \text{ could thus be assumed to be equal to the initial concentration of } [(\text{salen})\text{CoCOOCH$_3$}]_0 \text{ and } [(\text{salen})\text{Co}^{\text{II}}]_0. \text{To determine the } K_{\text{eq}}, \text{different loading of (salen)Co$^{\text{II}}$ to (salen)CoCOOCH$_3$ ratio was exploited before the irradiation and the polymerization kinetics were measured to give the concentration of } [R^\text{•}]. \text{The equilibrium constant } K_{\text{eq}} \text{ was shown in the following scheme. However, different initiators ((salen)CoCOOCH$_3$) varies slightly in the equilibrium constant.}
\]
The polymerization rate was also evaluated when the polymerization is initiated by different substituted (salen)CoCOOCH$_3$ in the presence of the same loading of (salen)Co$^{II}$ (in the following scheme). The polymerization rate increased with the increasing electronegativity of the substituted groups in (salen)CoCOOCH$_3$ (-CF$_3$>-tBu>-OMe), which could be explained by the decrease in the density of electron cloud of Co-C bond resulted from the electron withdrawing effect. Thus, the specific chain end effect to the polymerization rate is expected to be less or comparable to the effect induced by the substitution groups of salen ligand, and surely is under investigation.

### Table 1: Polymerization Rate Evaluation

<table>
<thead>
<tr>
<th>Substituted group</th>
<th>[Co$^{II}$]/[Co$^{III}$] (%)</th>
<th>$K_{\text{dis}}$(10$^{-11}$M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF$_3$</td>
<td>20%, 30%</td>
<td>2.70±0.03</td>
</tr>
<tr>
<td>tBu</td>
<td>8%, 12%</td>
<td>2.39±0.04</td>
</tr>
<tr>
<td>MeO</td>
<td>12%, 16%</td>
<td>1.44±0.05</td>
</tr>
</tbody>
</table>

8. Characterization of I$_a$, I$_d$, I$_g$ by single crystal X-ray diffraction

Single crystals suitable for X-ray diffraction analysis were obtained by slow volatilization of
CH$_2$Cl$_2$ solution of $I_a$, $I_d$, $I_g$ respectively.

The deposition number of CCDC is 1510372 for $I_a$.
The deposition number of CCDC is 1510383 for $I_c$.
The deposition number of CCDC is 1510373 for $I_d$.
The deposition number of CCDC is 1510374 for (salen)Co$^{II}$.

### Crystal data and structure refinement for complex $I_a$

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<th>Value</th>
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<td>Wavelength</td>
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<tr>
<td>Crystal system</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P - 1</td>
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<tr>
<td>Unit cell dimensions</td>
<td>$a = 10.784(3)$ Å, $a= 98.614(5)^\circ$</td>
</tr>
<tr>
<td></td>
<td>$c = 14.442(2)$ Å, $g = 105.985(5)^\circ$</td>
</tr>
<tr>
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<td>1841.6(9) Å$^3$</td>
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<tr>
<td>Z</td>
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<td>Density (calculated)</td>
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<td>F(000)</td>
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<td>Crystal size</td>
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<td>Reflections collected</td>
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<td>Independent reflections</td>
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<td>Extinction coefficient</td>
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<tr>
<td>Largest diff. peak and hole</td>
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Crystal data and structure refinement for complex Ic

Empirical formula  
Formula weight  
Temperature  
Wavelength  
Crystal system  
Space group  
Unit cell dimensions  
Volume  
Z  
Density (calculated)  
Absorption coefficient  
F(000)  
Crystal size  
Theta range for data collection  
Index ranges  
Reflections collected  
Independent reflections  
Completeness to theta = 26.000°  
Absorption correction  
Max. and min. transmission  
Refinement method  
Data / restraints / parameters  
Goodness-of-fit on F^2  
Final R indices [I>2sigma(I)]  
R indices (all data)  
Extinction coefficient  
Largest diff. peak and hole

Crystal data and structure refinement for complex Id

Empirical formula  
Formula weight  

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<td>Crystal system</td>
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<tr>
<td>Space group</td>
<td>P -1</td>
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<td>Unit cell dimensions</td>
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</tr>
<tr>
<td>Volume</td>
<td>2142.4(9) Å³</td>
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<td>Z</td>
<td>2</td>
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<td>Density (calculated)</td>
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<td>Crystal size</td>
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<tr>
<td>Largest diff. peak and hole</td>
<td>3.744 and -0.843 e.Å⁻³</td>
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**Crystal data and structure refinement for complex (salen)Co²⁺.**

<table>
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<th>Description</th>
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<td>Temperature</td>
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<td>Wavelength</td>
<td>0.71073 Å</td>
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<td>Crystal system</td>
<td>Orthorhombic</td>
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<tr>
<td>Space group</td>
<td>P 2 1 2 1</td>
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<tr>
<td>Unit cell dimensions</td>
<td>a = 10.1542(10) Å, a = 90°. b = 26.460(3) Å, b = 90°. c = 26.744(3) Å, g = 90°.</td>
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</tbody>
</table>
Volume 7185.6(13) Å³
Z 4
Density (calculated) 1.226 Mg/m³
Absorption coefficient 0.622 mm⁻¹
F(000) 2832
Crystal size 0.45 x 0.12 x 0.06 mm³
Theta range for data collection 1.706 to 27.477°.
Index ranges -13<=h<=11, -28<=k<=34, -34<=l<=21
Reflections collected 29857
Independent reflections 16356 [R(int) = 0.0464]
Completeness to theta = 26.000° 99.9 %
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 1.0000 and 0.6881
Refinement method Full-matrix least-squares on F²
Data / restraints / parameters 16356 / 0 / 799
Goodness-of-fit on F² 1.079
Final R indices [I>2sigma(I)] R1 = 0.0684, wR2 = 0.1367
R indices (all data) R1 = 0.0808, wR2 = 0.1473
Absolute structure parameter 0.037(10)
Extinction coefficient n/a
Largest diff. peak and hole 0.402 and -0.457 e.Å⁻³

References

