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

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SUPPORTING INFORMATIONS:

Contents

1. General consideration

C_6D_6 and $CDCl_3$ were purchased from Cambridge Isotope Laboratory Inc., methyl acrylate (MA), *n*-butyl acrylate (*n*BA), *tert*-butyl acrylate (*t*BA), *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^{II}) 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. ^{1}H 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.

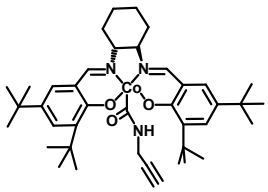
General reaction procedure: The 0.3 ml C_6D_6 solution of catalyst (1.67 mM or 1.25 mM) and monomer (1.0 M) was irradiated by 500W Xe lamp with a 420-780 nm filter 25 °C (3 mW/cm^2). The monomer conversion was determined based on ^{1}H NMR spectra ($M_{n,th} = M_{w(I)} + M_{w(Monomer)} \times$ ratio

×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^{II} (0.09 mmol, 55 mg), Oxone® (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®, added with Na_3PO_4•$12H_2O$ (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, CH_2Cl_2 as eluent) after removing the solvent.

a)

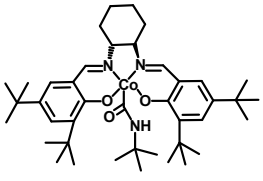


yield: 65%

^{1}H NMR ($CDCl_3$, 400 MHz, 298K, δ): 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) ;

ESI-MS calcd for: 708.363, found: 708.364

b)

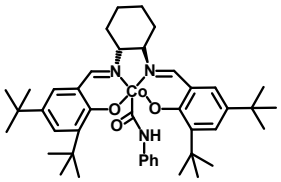


yield:52%

^{1}H NMR ($CDCl_3$, 400 MHz, 298K, δ): 8.03 (s, 1H), 7.38 (d, 1H), 7.38 (d, J = 2.4 Hz, 1H), 7.35 (d, J = 2.4 Hz, 1H), 7.01 (d, J = 2.4 Hz, 1H), 6.94 (d, J = 2.4 Hz, 1H), 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 Hz, 18H), 1.28 (d, J = 11.2 Hz, 18H), 1.04 (s, 3H).

ESI-MS calcd for: 704.419, found: 704.420;

c)

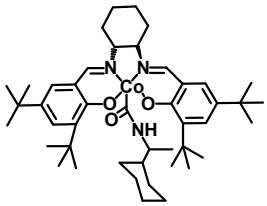


yield:52%

^{1}H NMR ($CDCl_3$, 400 MHz, 298K, δ): 8.77 (s, 1H), 8.07 (d, *J* = 1.7 Hz, 1H), 7.82 (d, *J* = 2.0 Hz, 1H), 7.43 (d, *J* = 2.6 Hz, 1H), 7.35 (d, *J* = 2.6 Hz, 1H), 7.18 (d, *J* = 7.2 Hz, 2H), 7.12 (t, *J* = 7.9 Hz, 2H), 7.02 (d, *J* = 2.6 Hz, 1H), 6.95 (d, *J* = 2.6 Hz, 1H), 6.93 – 6.85 (m, 1H), 3.88 – 3.77 (m, 2H), 3.51 – 3.40 (m, 2H), 2.73 (brs, 2H), 2.05 (d, *J* = 12.2 Hz, 2H), 1.61 (d, *J* = 13.1 Hz, 18H), 1.74-1.46 (m, 4H), 1.28 (d, *J* = 10.4 Hz, 18H).

ESI-MS calcd for: 746.370, found: 746.371;

d)

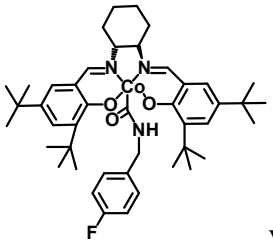


yield:51%

^{1}H NMR ($CDCl_3$, 400 MHz, 298K, δ): 8.05 (s, 1H), 7.76 (s, 1H), 7.38 (d, *J* = 2.4 Hz, 1H), 7.34 (d, *J* = 2.4 Hz, 1H), 6.99 (d, *J* = 2.4 Hz, 1H), 6.94 (d, *J* = 2.4 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 Hz, 18H), 1.43 (s, 3H), 1.28 (d, *J* = 2.4 Hz, 18H), 0.96 (m, 2H), 0.86 (m, 2H), 0.59 (m, 2H), 0.31 (m, 2H).

ESI-MS calcd for: 758.466, found: 758.467;

e)

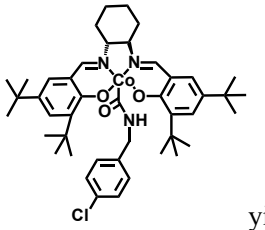


yield:61%

^{1}H NMR ($CDCl_3$, 400 MHz, 298K, δ): 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);

ESI-MS calcd for: 778.377, found: 778.376;

f)

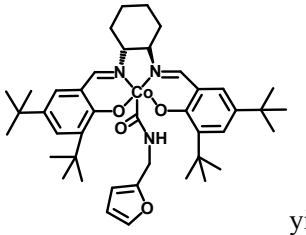


yield: 65%

^{1}H NMR ($CDCl_3$, 400 MHz, 298K, δ): 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)

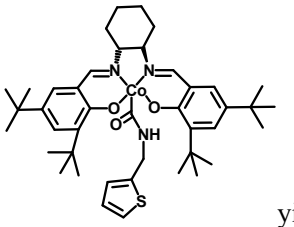


yield: 45%

^{1}H NMR ($CDCl_3$, 400 MHz, 298K, δ): 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)

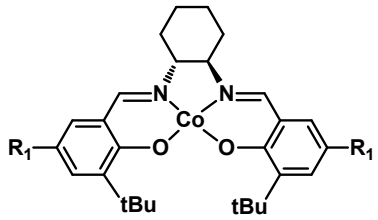


yield: 57%

^{1}H NMR ($CDCl_3$, 400 MHz, 298K, δ): 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), 6.67 (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, *t*Bu, Cl or CF_3 substituted salen Cobalt complex



R_1 = MeO, *t*Bu, Cl, CF_3

Scheme S1 Structures of modified (salen)Co complex

a) Synthesis of MeO(salen)$CoCOOCH_3$

Synthesis of 3-*tert*-butyl-5-methoxysalicylaldehyde: 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 ^oC for 2 h. After disappearance of 3-*tert*-butyl-4-hydroxyanisole was confirmed by TLC, aqueous H_2SO_4 (10 mL, 33%) was added at 75 ^oC. The resulting mixture was heated at 110 ^oC for another 3 h. The mixture was extracted with diethyl ether (25 mL), and the extract was washed with water, saturated Na_2CO_3 solution and saturated NaCl solution. The organic layer was dried over $MgSO_4$, and then the solvent was removed by evaporation under reduced pressure. The crude was further purified by a silica column using CH_2Cl_2 as eluent to yield the title compound as yellow oil.

^1H NMR($CDCl_3$, 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-methoxysalicylidene)-1,2-cyclohexanediamine (MeO-salen): The compound was prepared via literature procedure.[2] A mixture of (1*R,*2*R*)-1,2-diaminocyclohexane (0.4 g) and 3-*tert*-butyl-5-methoxysalicylaldehyde (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($CDCl_3$, 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)Co^{II}: The compound was prepared by the modification of a published procedure.[3] 25 mL Schlenk flask was loaded with MeO-salen (0.17 g), $Co(OAc)_2{\cdot}4H_2O$ (0.11 g) and ethanol (10 mL), degassed by three freeze-pump-thaw (FPT) cycles on vacuum line and refilled with N_2 in glove box. The solution was heated to 80 ^oC, 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.
ESI-MS Calcd $[M]^+$: 551.23201. Found: 551.23133.

Synthesis of MeO(salen)CoCOOCH$_3$: The compound was prepared via an adaption from a published procedure to synthesize ^{t}Bu(salen)CoCOOCH$_3$.[4] A mixture of MeO(salen)Co^{II} (50 mg), Oxone® (138 mg), methanol (150 μL) and toluene (6 mL) was heated at 50 ^{o}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 $Na_3PO_4 \cdot 12H_2O$ (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_2Cl_2 as eluent) to give the title compound as dark green solid (10%).
^{1}H NMR ($CDCl_3$, 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)CoCOOCH$_3$

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 H_2SO_4 (3.8 mL) was slowly added at 0 ^{o}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 Na_2CO_3 solution and saturated NaCl solution. The organic layer was dried over Na_2SO_4 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%).
^{1}H NMR ($CDCl_3$, 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 N_2. Acetonitrile and triethylamine were distilled over CaH_2 prior to use. Paraformaldehyde was dried over P_2O_5, and $MgCl_2$ was dried in a vacuum oven at 80 ^{o}C overnight. A 100 mL Schlenk charged with 2-*tert*-butyl-4-chlorophenol (1.3 g), $MgCl_2$ (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 N_2 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 Na_2SO_4, 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%).

^{1}H NMR ($CDCl_3$, 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*-butyl-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%).

^{1}H NMR ($CDCl_3$, 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)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 (64%).

ESI-MS Calcd $[M]^+$: 559.13293. Found: 559.13260.

Synthesis of Cl(salen)$CoCOOCH_3$: The compound was prepared via an adaption from a published procedure to synthesize ^{t}Bu(salen)$CoCOOCH_3$.[4] A mixture of Cl(salen)Co^{II} (50 mg), Oxone® (138 mg), methanol (150 μL) and toluene (6 mL) was heated at 50 ^{o}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 $Na_3PO_4{\cdot}12H_2O$ (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, CH_2Cl_2:PE = 1:1 as eluent) to give the title compound as dark green solid (21%).

^{1}H NMR ($CDCl_3$, 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 CF_3(salen)$CoCOOCH_3$

Synthesis of 2-*tert*-butyl-4-trifluoromethylphenol: The compound was prepared via literature procedure.[7] 4-trifluromethylphenol (1 g) was dissolved in CH_3OH (1 mL) and *tert*-butyl alcohol (5 mL) was added at room temperature. Concentrated H_2SO_4 (4.7 mL) was then added at 0 ^oC. After 12 h stirring at room temperature, the reaction mixture was poured into ice blocks and extracted with CH_2Cl_2. The extract was washed by saturated Na_2CO_3 solution, saturated NaCl solution and dried over Na_2SO_4. Solvent was removed by evaporation under reduced pressure. The crude was further purified with column chromatography (silica, CH_2Cl_2:PE = 1:1) to give the title compound as pale yellow oil (71%).

^1H NMR ($CDCl_3$, 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 CH_2Cl_2. The extract was washed with saturated NaCl solution and dried over Na_2SO_4. The solvent was removed by evaporation under reduced pressure. The crude was further purified by column chromatography (silica, $CHCl_3$:PE = 4:1) to give the title compound as a pale yellow oil (10%).

^1H NMR ($CDCl_3$, 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-trifluromethylsalicylidene)-1,2-cyclohexanediamine (CF_3-salen): The compound was prepared via the same procedure as the synthesis of MeO-salen. The title compound precipitated as a yellow solid (80%).

^1H NMR ($CDCl_3$, 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 CF_3(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 CF_3(salen)$CoCOOCH_3$: The compound was prepared via an adaption from a published procedure to synthesize ^{t}Bu(salen)$CoCOOCH_3$.[4] A mixture of CF_3(salen)Co^{II} (50 mg), Oxone® (138 mg), methanol (150 μL) and toluene (6 mL) was heated at 50 ^oC for 2 h, wrapped with aluminum foil to avoid light irradiation. The solution was then filtered to a 25

mL Schlenk flask loaded with $Na_3PO_4 \cdot 12H_2O$ (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_2Cl_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, δ): 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 ^{t}Bu(salen)CoCOOCH$_3$

This compound was prepared via literature procedure[4]. A mixture of ^{t}Bu(salen)Co^{II} (50 mg), Oxone® (138 mg), methanol (150 μL) 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 $Na_3PO_4 \cdot 12H_2O$ (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_2Cl_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, δ): 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); 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 ^{o}C)[a]

Entry	Substituent	T/h	Co^{II} (equiv.)	[b]Conv.(%)	[c]$M_{n,th}$	[d]$M_{n,GPC}$/PDI
1	CF_3	19	16%	21.1	11586	9149/1.21
2	^{t}Bu	19	16%	14.6	8204	7985/1.13
3	MeO	30	16%	11.2	6396	7726/1.13
4	Cl	72	16%	13.7	7696	6579/1.20

[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]$M_{n,th} = M_{w(I(a))} + M_{w(Monomer)} \times$ ratio $\times$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$_a$**) in THF (0.01 mM) was detected by UV-visible detector.

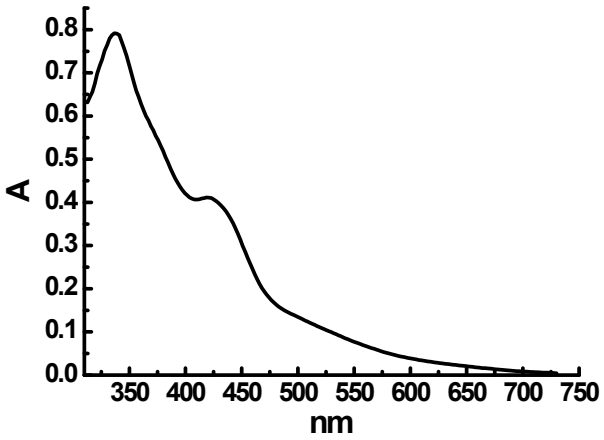


Figure S1 UV-visible spectrum of (salen)Co-CONHCH$_2$CCH (**I$_a$**)

b) 0.35 mL C_6D_6 solution of **I$_a$** (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 ^1H NMR (Figure S2). Sharp signals at 1.2-2.2 ppm were assigned to the *t*Bu group of **I$_a$**, 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$_a$**. 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$_a$** in the presence of TEMPO was also obtained (Figure S3).

c)

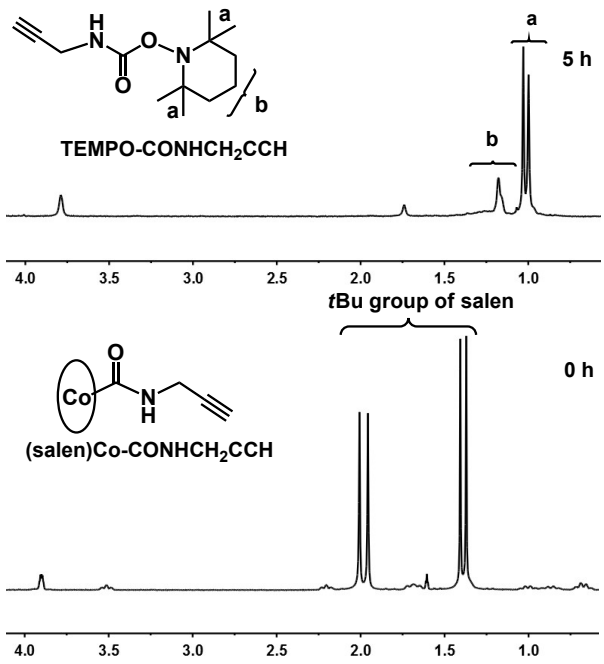


Figure S2 ^{1}H NMR spectrum of $\mathbf{I_a}$ (4 mM) and TEMPO (40.0 mM) in C_6D_6 under visible light irradiation (in the range of 0.2-4.0 ppm) for 5h

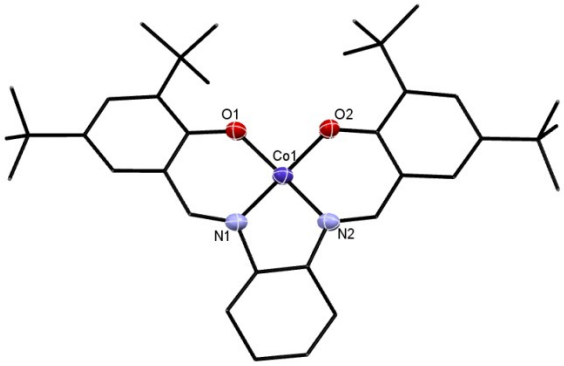
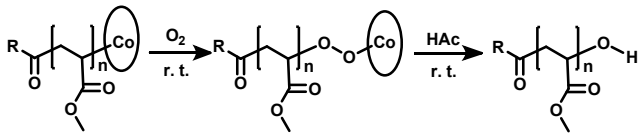


Figure S3. Solid state structure of (salen)Co^{II}. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (^{o}): Co-O1 1.849, Co-O2 1.847, Co-N1 1.855, Co-N2 1.856; O1-Co-O2 87.30, O1-Co-N1 92.89, N2-Co-O2 93.75, N2-Co-N1 86.09.

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 $\mathbf{I_a}$ 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 $HC{\equiv}CCH_2NHCO$- at the α end and HO- at the ω end, plus a sodium ion from externally added salt for ionization.

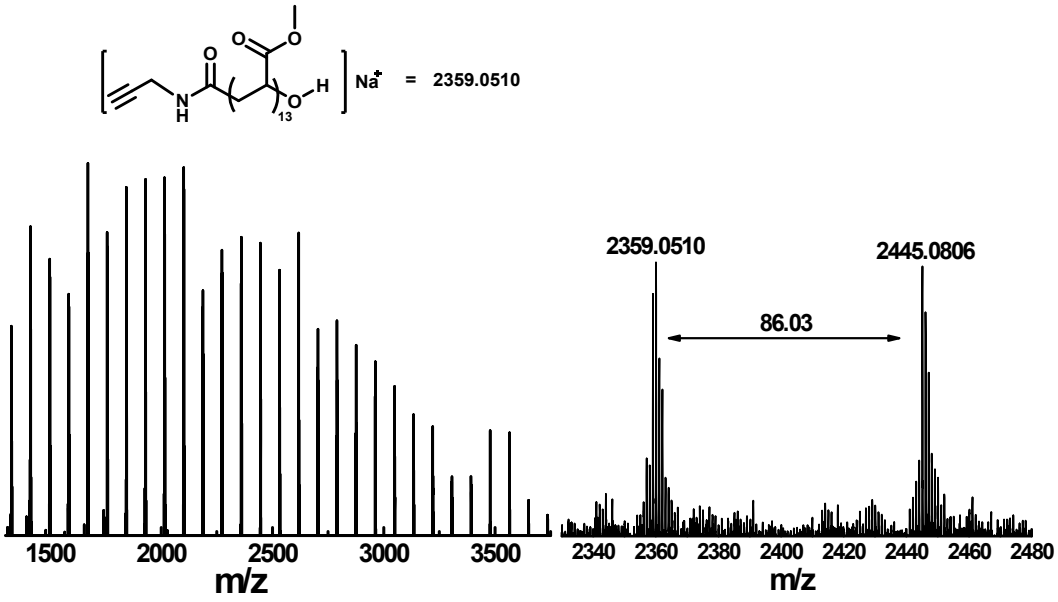
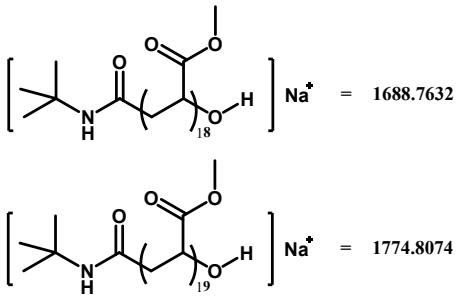


Figure S4. MALDI-TOF-MS spectroscopy of PMA obtained from photo-LRP mediated by $\mathbf{I_a}$;

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



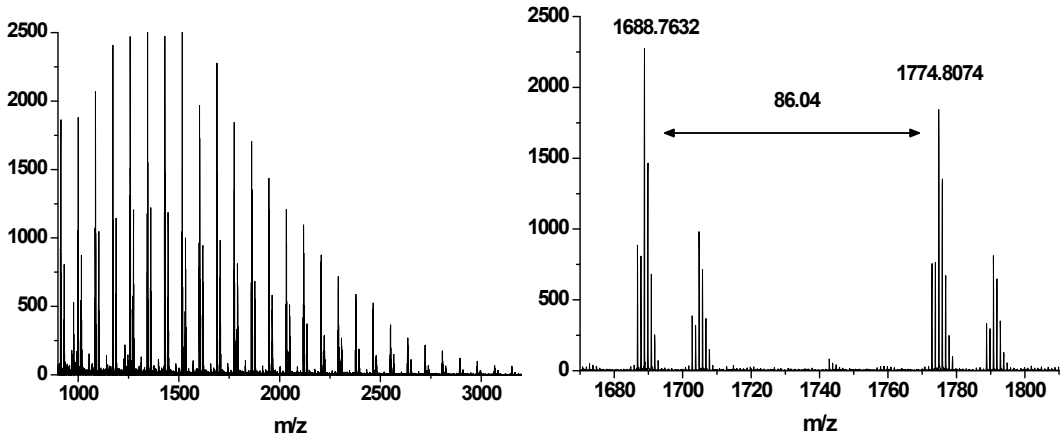


Figure S5. MALDI-TOF-MS spectroscopy of PMA obtained from photo-LRP mediated by $\mathbf{I_b}$; **The other series of molecular ion peaks agreed well with the theoretical values of *t*BuNHCO- at the α end and HO- at the ω end, plus a potassium ion from externally added salt for ionization**

c) When $\mathbf{I_c}$ worked as the photocatalyst, the MALDI results showed Figure S6:

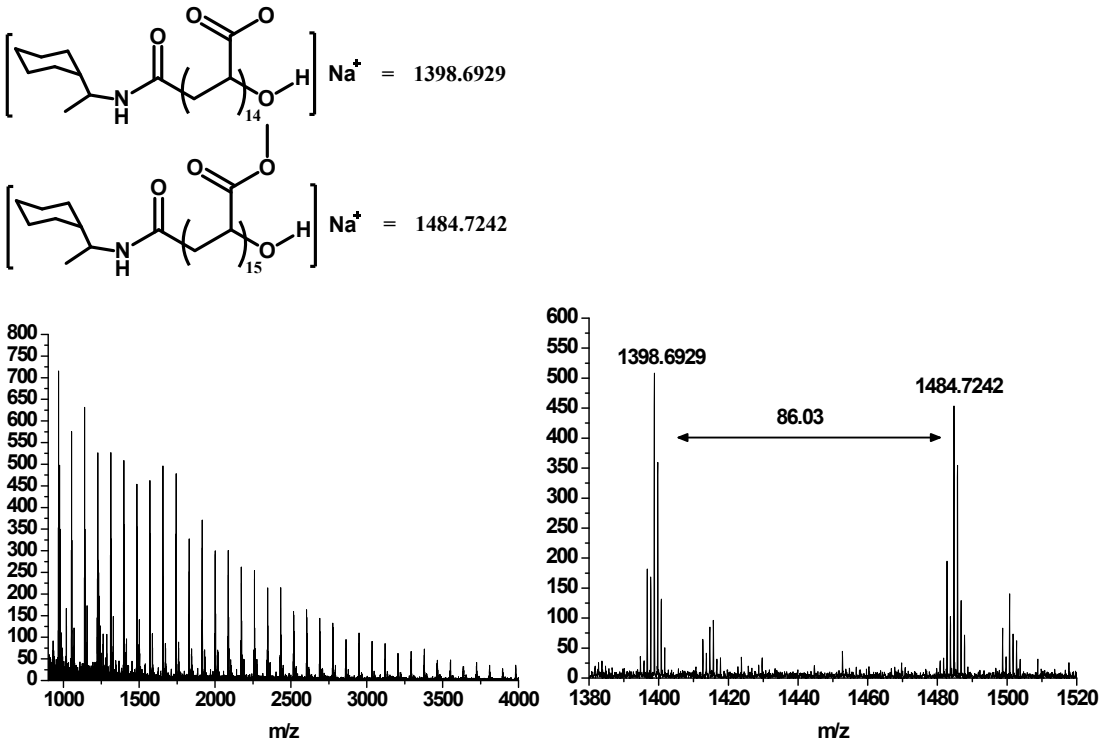


Figure S6. MALDI-TOF-MS spectroscopy of PMA obtained from photo-LRP mediated by $\mathbf{I_c}$; **The other series of molecular ion peaks agreed well with the theoretical values of corresponding chain ends, plus a potassium ion from externally added salt for ionization**

d) When $\mathbf{I_d}$ worked as the photocatalyst, the MALDI results showed Figure S7:

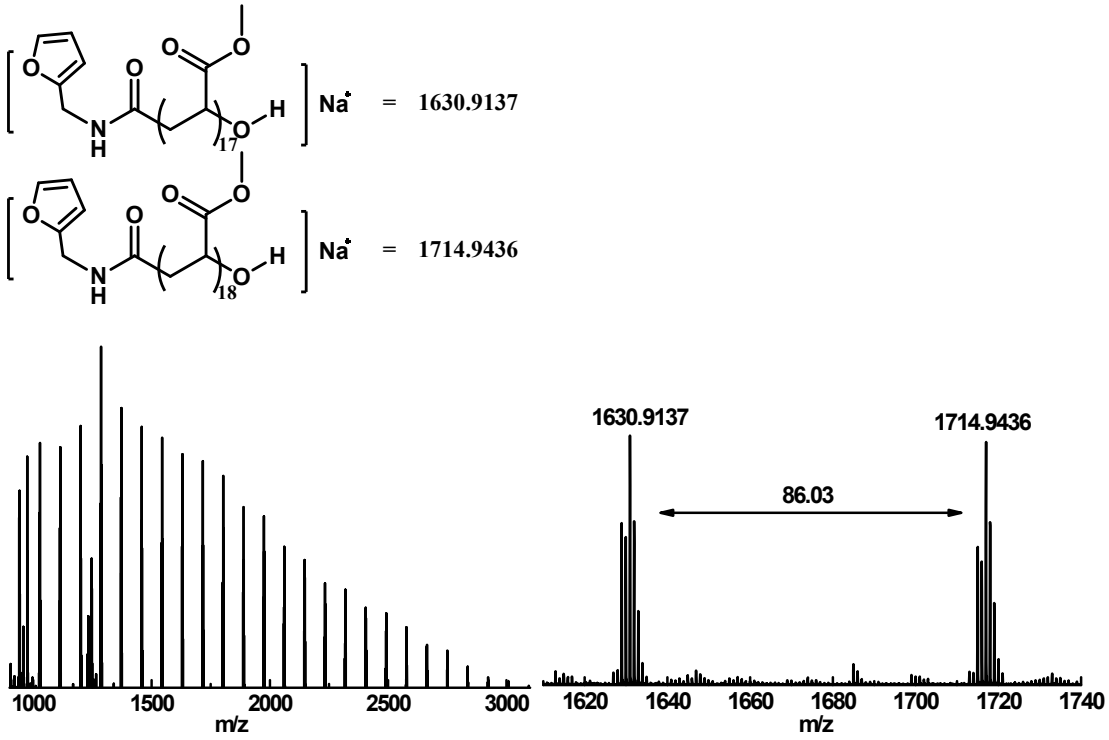


Figure S7. MALDI-TOF-MS spectroscopy of PMA obtained from photo-LRP mediated by $\mathbf{I_d}$.

e) When $\mathbf{I_e}$ worked as the photocatalyst, the MALDI results showed Figure S8:

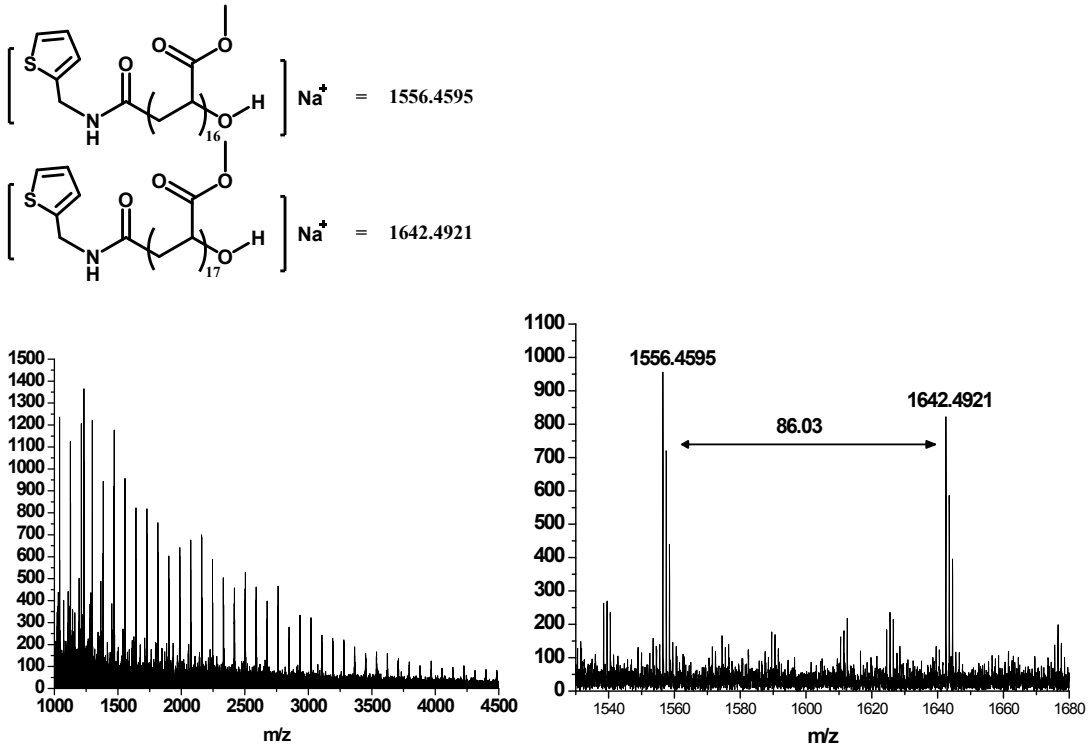


Figure S8. MALDI-TOF-MS spectroscopy of PMA obtained from photo-LRP mediated by $\mathbf{I_e}$.

f) When $\mathbf{I_f}$ worked as the photocatalyst, the MALDI results showed in Figure S9:

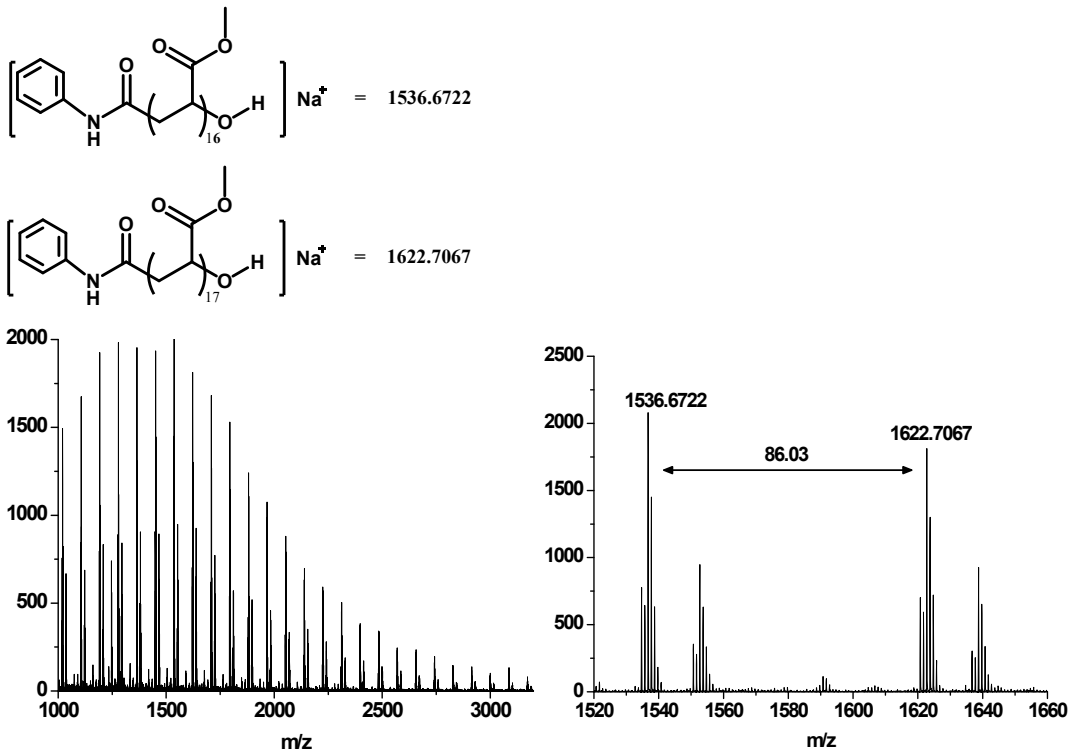
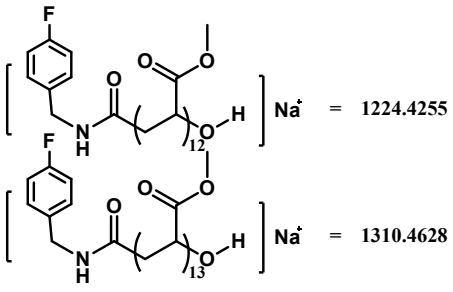


Figure S9. MALDI-TOF-MS spectroscopy of PMA obtained from photo-LRP mediated by $\mathbf{I_f}$; **The other series of molecular ion peaks agreed well with the theoretical values of PhNHCO- at the α end and HO- at the ω end, plus a potassium ion from externally added salt for ionization**

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



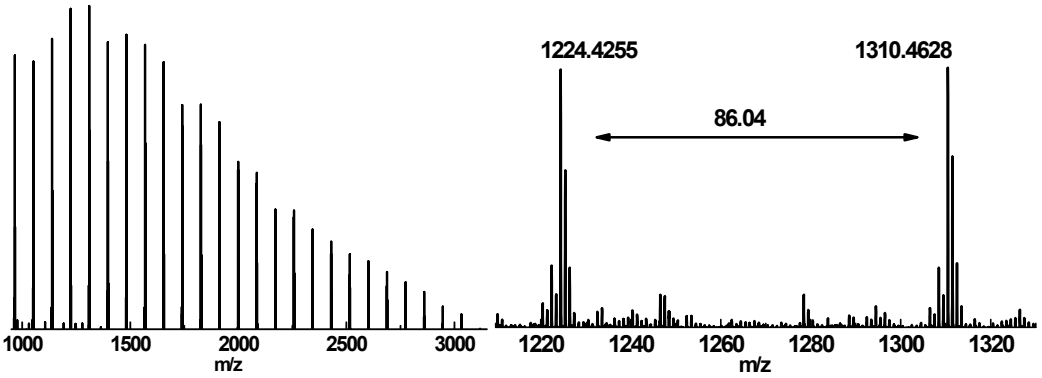


Figure S10. MALDI-TOF-MS spectroscopy of PMA obtained from photo-LRP mediated by $\mathbf{I_g}$.

h) When $\mathbf{I_h}$ worked as the photocatalyst, the MALDI results showed Figure S11:

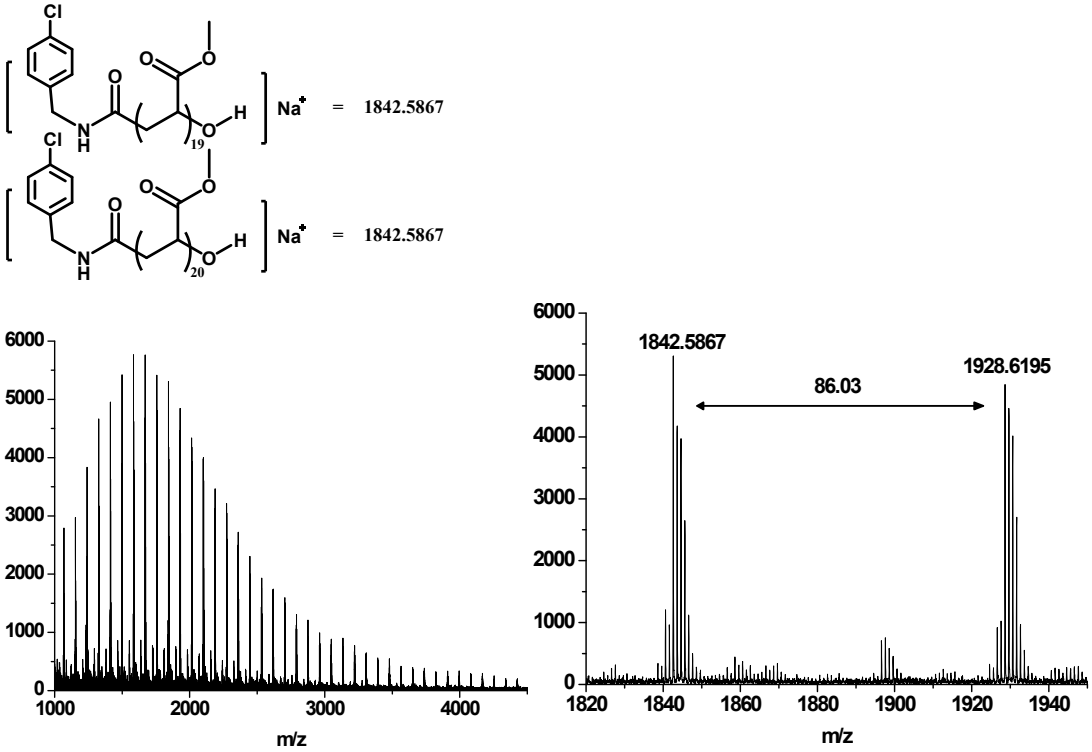
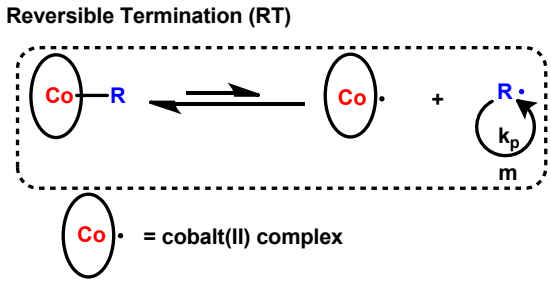


Figure S11. MALDI-TOF-MS spectroscopy of PMA obtained from photo-LRP mediated by $\mathbf{I_h}$.

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

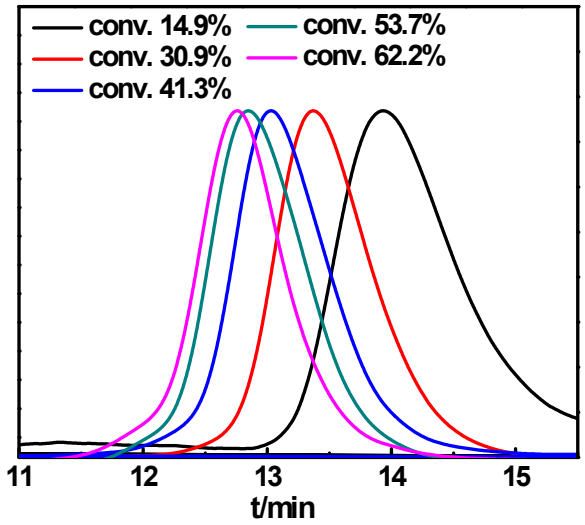


Figure S12. GPC traces for photo-polymerization of MA in C_6D_6 mediated by $\mathbf{I_a}$ under different conversion at room temperature (Xe lamp irradiation (3 mw/cm^2)). Experimental conditions: $[MA]_0$ = 1.0 M; $[MA]_0/[\mathbf{I_a}]_0$ = 600/1;

GPC traces of the PMA catalyzed by $\mathbf{I_a}$ were also detected by both refractive index and UV-visible detector;

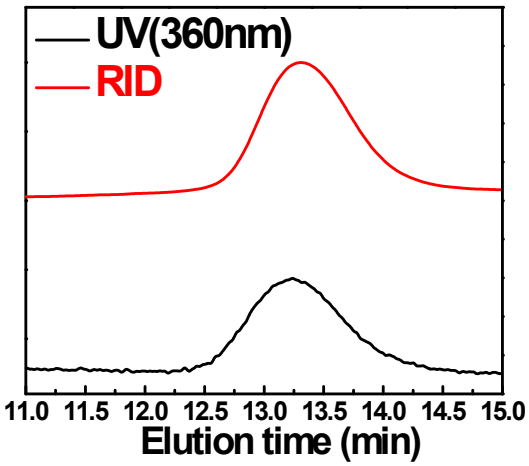


Figure S13. Gel permeation chromatography (GPC) traces of the PMA produced by photo-LRP mediated by $\mathbf{I_a}$ ($M_{n,\,th}$= 22033, $M_{n,\,GPC}$ = 23396; M_w/M_n = 1.18). Black line indicated the UV-visible (360 nm) detection trace, and red line indicated the refractive index detection trace.

PMA obtained in our system was also characterized by ^{1}H NMR (Figure S16).

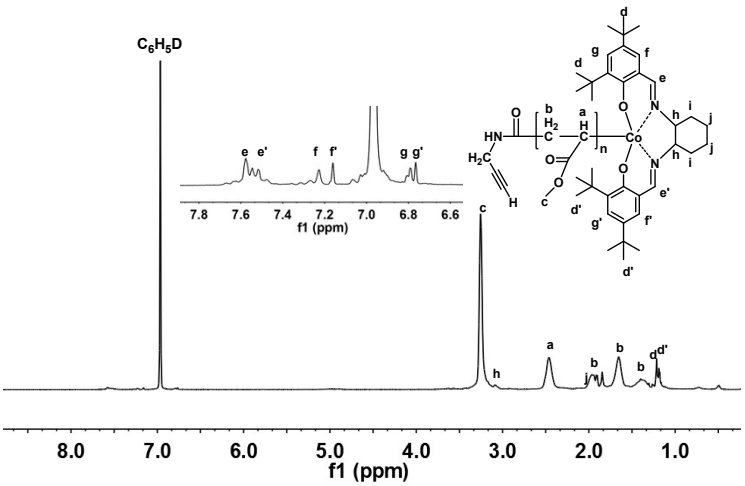


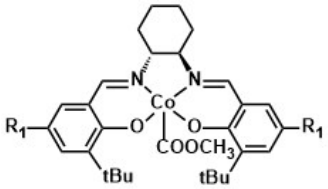
Figure S14. ^{1}H NMR spectrum of PMA, C_6D_6 was used as the solvent. Experimental conditions: $[MA]_0$ = 1.0 M; $[MA]_0/[\mathbf{I_a}]_0$ = 600/1; The solution was irradiated with 420-780 nm filter (3 mW/cm^2), conversion = 41%, $M_{n,\,th}$ = 22033, $M_{n,\,GPC}$ = 23396; M_w/M_n = 1.18.

7. Discussion of chain end effect on the polymerization rate

The propagation rate is calculated via eq $R_p = k_p[M][R\bullet]$ 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, P*t*BA-Co, or PDMA-Co) propagated the monomer by the

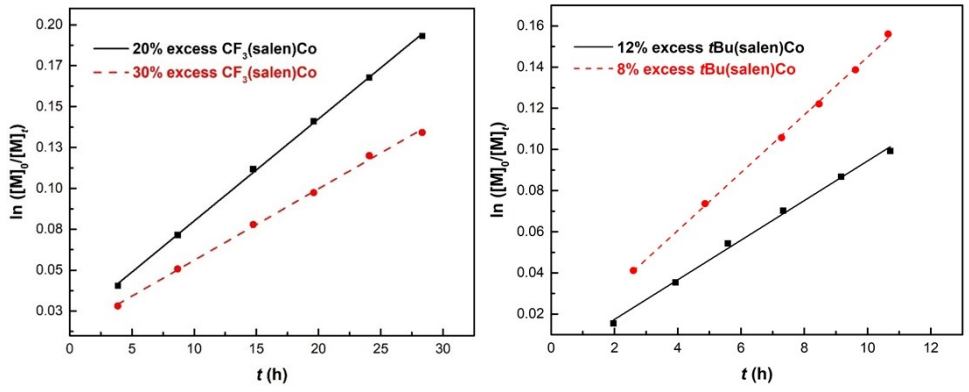
continual homolysis of Co-C bond and subsequent addition reaction between propagating chain radical (PMA radical, P*t*BA radical, or PDMA radical) and monomer. So the α ends of the obtained polymers, which is the R group of initiator **I**, could affect the initiation rate. However, it would not significantly affect the propagation rate because with DP grows the effect due to the structure difference of R groups attenuates rapidly.

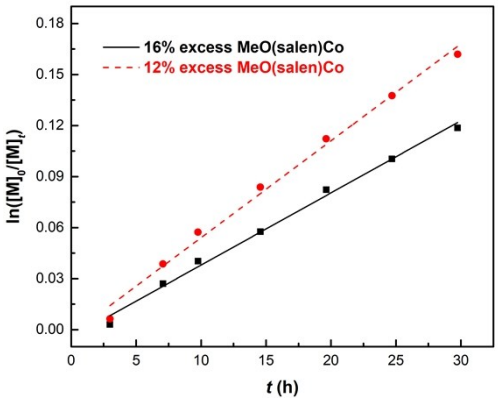
Compare to the effect to R group to the propagation rate, the ω ends of (salen)Co complexes is expected to be more effective to influence the polymerization process. Three types of (salen)CoCOOCH$_3$ with substituent groups CF$_3$, *t*Bu, and MeO on the salen ligand were prepared. The polymerization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



R_1 = CF_3, *t*Bu, MeO

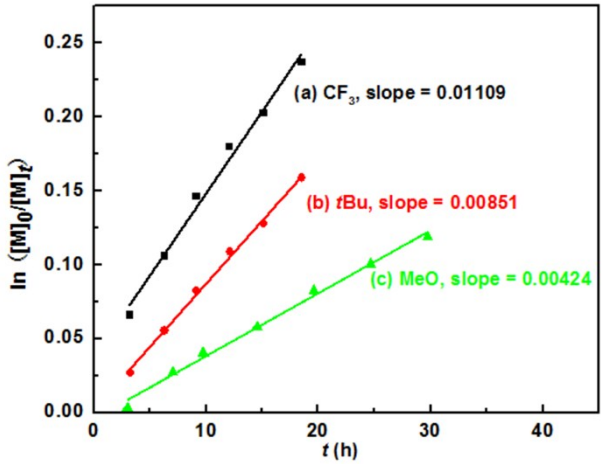
Different substituent groups would have different impacts on Co-C bond, characterized by the change of equilibrium constant ((salen)Co-R $\rightleftharpoons$ (salen)Co^{II} + R•, K_{eq} = [(salen)Co^{II}]$_{eq}$ × [R•]/ [(salen)Co-R]$_{eq}$), resulting in the change of the concentration of propagating chain radicals [R•]. As a result, the ω 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^{II}. The equilibrium concentration of [(salen)CoPMA]$_{eq}$ and [(salen)Co^{II}]$_{eq}$ could thus be assumed to be equal to the initial concentration of [(salen)CoCOOCH$_3$]$_0$ and [(salen)Co^{II}]$_0$. To determine the K_{eq}, different loading of (salen)Co^{II} to (salen)CoCOOCH$_3$ ratio was exploited before the irradiation and the polymerization kinetics were measured to give the concentration of [R•]. The equilibrium constant K_{eq} was shown in the following scheme. However, different initiators ((salen)CoCOOCH$_3$) varies slightly in the equilibrium constant.





Substituted group	[Co^{II}]/[Co^{III}] (%)	K_{dis}(10^{-11}M)
CF_3	20%, 30%	2.70±0.03
^{t}Bu	8%, 12%	2.39±0.04
MeO	12%, 16%	1.44±0.05

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>-*t*Bu>-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.



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_2Cl_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

Empirical formula	C40 H56 Co N3 O3	
Formula weight	685.80	
Temperature	173.1500 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 10.784(3) Å	a= 98.614(5)°.
	b = 12.609(4) Å	b= 96.546(3)°.
	c = 14.442(2) Å	g = 105.985(5)°.
Volume	1841.6(9) $Å^3$	
Z	2	
Density (calculated)	1.237 Mg/m^3	
Absorption coefficient	0.506 mm^{-1}	
F(000)	736	
Crystal size	0.37 x 0.11 x 0.05 mm^3	
Theta range for data collection	1.991 to 27.479°.	
Index ranges	-13<=h<=13, -16<=k<=16, -18<=l<=18	
Reflections collected	23756	
Independent reflections	8385 [R(int) = 0.0470]	
Completeness to theta = 26.000°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.7528	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8385 / 0 / 473	
Goodness-of-fit on F^2	1.220	
Final R indices [I>2sigma(I)]	R1 = 0.0763, wR2 = 0.1735	
R indices (all data)	R1 = 0.0780, wR2 = 0.1744	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.482 and -0.711 $e.Å^{-3}$	

Crystal data and structure refinement for complex I_c

Empirical formula	C45 H68 Co N3 O3	
Formula weight	757.95	
Temperature	173.1500 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 16.383(3) Å	a= 90°.
	b = 10.7067(18) Å	b= 90.313(3)°.
	c = 23.844(4) Å	g = 90°.
Volume	4182.3(12) $Å^3$	
Z	4	
Density (calculated)	1.204 Mg/m^3	
Absorption coefficient	0.452 mm^{-1}	
F(000)	1640	
Crystal size	0.28 x 0.14 x 0.05 mm^3	
Theta range for data collection	2.107 to 27.483°.	
Index ranges	-21<=h<=20, -13<=k<=13, -30<=l<=20	
Reflections collected	29483	
Independent reflections	9525 [R(int) = 0.0607]	
Completeness to theta = 26.000°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.7629	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9525 / 38 / 539	
Goodness-of-fit on F^2	1.253	
Final R indices [I>2sigma(I)]	R1 = 0.1231, wR2 = 0.2472	
R indices (all data)	R1 = 0.1290, wR2 = 0.2500	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.702 and -0.695 $e.Å^{-3}$	

Crystal data and structure refinement for complex I_d

Empirical formula	C42 H56 Co N3 O4
Formula weight	725.82

Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 10.733(2) Å	a= 92.40(3)°.
	b = 12.501(3) Å	b= 104.50(3)°.
	c = 17.319(4) Å	g = 106.39(3)°.
Volume	2142.4(9) $Å^3$	
Z	2	
Density (calculated)	1.125 Mg/m^3	
Absorption coefficient	0.440 mm^{-1}	
F(000)	776	
Crystal size	? x ? x ? mm^3	
Theta range for data collection	1.223 to 27.472°.	
Index ranges	-13<=h<=13, -16<=k<=16, -22<=l<=22	
Reflections collected	19256	
Independent reflections	9718 [R(int) = 0.0516]	
Completeness to theta = 26.000°	99.1 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9718 / 0 / 500	
Goodness-of-fit on F^2	2.272	
Final R indices [I>2sigma(I)]	R1 = 0.1216, wR2 = 0.3487	
R indices (all data)	R1 = 0.1311, wR2 = 0.3546	
Extinction coefficient	n/a	
Largest diff. peak and hole	3.744 and -0.843 $e.Å^{-3}$	

Crystal data and structure refinement for complex (salen)Co^{II}.

Empirical formula	C73 H105 Cl3 Co2 N4 O4	
Formula weight	1326.81	
Temperature	173.1500 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 10.1542(10) Å	a= 90°.
	b = 26.460(3) Å	b= 90°.
	c = 26.744(3) Å	g = 90°.

Volume	7185.6(13) $Å^3$
Z	4
Density (calculated)	1.226 Mg/m^3
Absorption coefficient	0.622 mm^{-1}
F(000)	2832
Crystal size	0.45 x 0.12 x 0.06 mm^3
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 F^2
Data / restraints / parameters	16356 / 0 / 799
Goodness-of-fit on F^2	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 $e.Å^{-3}$

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