Tacticity Control Approached by Visible-Light Induced Organocobalt-Mediated Radical Polymerization: the Synthesis of Crystalline Poly(*N*,*N*-dimethylacrylamide) with High Isotacticity

Zhenqiang Wu,[a] Chi-How Peng*[b] and Xuefeng Fu*[a]

[a] Beijing National Laboratory for Molecular Sciences, State Key Lab of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

[b] Department of Chemistry and Frontier Research Center on Fundamental and Applied Sciences of Matters, National Tsing Hua University, Hsinchu 30013, Taiwan

Contents:

1 General experimental section

Materials

N,*N*-dimethylacrylamide (DMA, Alfa Aesar) was distilled under reduced pressure and stored in the refrigerator before use. (salen)Co^{II} ((salen)H_2 = (*R*,*R*)-(-)-*N*,*N*'-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine, Aldrich), potassium peroxymonosulfate (Oxone®, Alfa Aesar), aluminum triflate ($Al(OTf)_3$, Alfa Aesar), scandium triflate ($Sc(OTf)_3$, Aldrich), lutetium triflate ($Lu(OTf)_3$, Energy), yttrium triflate ($Y(OTf)_3$, TCI), lanthanum triflate ($La(OTf)_3$, TCI), benzene (99.8%, Alfa Aesar), and methanol (99.9%, J&K) were used as received. $CDCl_3$, DMSO-d_6 and CD_3OD were purchased from Cambridge Isotope Laboratory Inc.. Spectra/Por(R) dialysis membrane was purchased from Sangon Biotech (Shanghai) Ltd.. All other chemicals were purchased from Alfa Aesar, Aldrich, TCI or J&K Scientific Ltd. and used as received unless otherwise noted.

Light source

A 500 W xenon lamp (CEL-S500, Aulight, Beijing, China) was used as the light source with a 420~780 nm filter to give the visible-light. The intensity of visible-light irradiation was modulated by employing neutral density filters, and measured by a FZ-A radiometer (Photoelectric Instrument Factory of Beijing Normal University) equipped with a 400~1000 nm sensor.

Characterization

NMR spectroscopy and ESI-MS. ^{1}H NMR spectra were recorded on a Bruker 400 MHz FT spectrometer at ambient temperature in $CDCl_3$, DMSO-d_6 or CD_3OD. Electrospray ionization-mass spectrometry (ESI-MS) results were obtained by a Bruker Apex IV FTMS spectrometer.

Single-crystal X-ray diffraction analysis. The single-crystal X-ray diffraction data of complex (TMP-OH)$CoCO_2CH_3$ (**IV**) was collected on a Rigaku XtaLAB PRO 007HF(Mo) single crystal X-ray diffractometer.

GPC measurement. The gel permeation chromatography (GPC) in DMF was performed in an Agilent 1200 series system, equipped with two Agilent PolarGel-M columns (300 × 7.5 mm), an Iso Pump (G1310A), a UV detector, and a differential refractive index detector (RID). The number-average molecular weight (M_n), weight-average molecular weight (M_w), and PDI were measured at 50 °C with a flow rate of 1.0 mL min^{-1}. A series of poly(methyl methacrylate)s (molecular weight range of 2710-298900 g mol^{-1}, from Polymer Laboratories) was used as standards for calibration.

GPC in chloroform was also performed in an Agilent 1200 series system, equipped with three Agilent PLGel columns (pore diameters were 10^5, 10^4, and 10^3 Å, respectively), as well as the same pump and detectors mentioned above. M_n, M_w, and PDI were measured at 35 °C with a flow rate of 1.0 mL min^{-1}. The same series of poly(methyl methacrylate)s was used as standards for calibration.

TGA measurement. The thermogravimetric analysis (TGA) measurement was carried out with a TA Q600 SDT thermal analyzer. The polymer powder (about 4 mg) was weighed into an alumina pan, and placed in the oven of TGA instrument. The sample was heated to 800 °C from room temperature, at a heating rate of 10 °C min^{-1} under the nitrogen or air atmosphere.

DSC measurement. The differential scanning calorimetry (DSC) measurement was carried out with a TA Q100 or TA Q2000 thermal analyzer. The polymer powder (about 2 mg) was weighed into an aluminum, sealed pan, and placed in the oven of DSC instrument. Then, dynamic scans were performed within a temperature range of -20 to 300 °C at heating and cooling rates of 5 °C min^{-1} under the nitrogen atmosphere. Any thermal history difference in the polymer was eliminated by the first cycle: cooling from room temperature to -20 °C, then heating to 300 °C. And, the thermal properties were recorded during the second cycle: cooling from 300 °C to -20 °C, then heating to 300 °C.

PXRD measurement. The powder X-ray diffraction (PXRD) data of polymer before annealing were directly collected on a Philips X Pert Pro diffractometer with Cu Kα radiation (λ = 1.5418 Å) over the 2θ range of 5-30° at room temperature. Then, the polymer powders were annealed under air atmosphere at a specific temperature for about 80 h, and measured at room temperature to obtain the PXRD data of polymer after annealing.

Synthesis procedures for cobalt complexes

Organocobalt complexes (salen)$CoCO_2CH_3$ (**I**)[1] and (TMP)$CoCO_2CH_3$ (**II**, (TMP)H_2 = 5,10,15,20-tetramesitylporphyrin),[2] as well as porphyrins (TDMAP)H_2 (5,10,15,20-tetrakis(2,6-dimethyl-4-methoxylphenyl)porphyrin)[3,4] and (TMP-OH)H_2 (5-(4-hydroxylphenyl)-10,15,20-trimesitylporphyrin)[5] were prepared following the previously reported methods.

Synthesis of (TDMAP)Co^{II}. (TDMAP)H_2 (0.10 mmol, 86 mg) and cobalt acetate tetrahydrate (0.61 mmol, 151 mg) were dispersed in 9.0 mL DMF. The mixture was stirred under the nitrogen atmosphere for 24 h at 140 °C, then cooled to room temperature. After removing solvent under vacuum, the crude product was dissolved in chloroform, and purified by water extraction (yield = 93%). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 15.24(br, 8H, pyrrole-*H*), 8.94(s, 8H, *m*-phenyl-*H*), 5.14(s, 12H, -OC*H*$_3$), 3.51(br, 24H, -C*H*$_3$). ESI-MS *m*/*z* calculated for $[C_{56}H_{52}CoN_4O_4]^+$: 903.331503, found: 903.330718.

Synthesis of (TMP-OH)Co^{II}. (TMP-OH)H_2 (0.10 mmol, 77 mg) and cobalt acetate tetrahydrate (0.20 mmol, 51 mg) were dispersed in 8.0 mL DMF. The mixture was stirred under the nitrogen atmosphere for 5 h at 160 °C, then cooled to room temperature. After removing solvent under vacuum, the crude product was dissolved in chloroform, and purified by water extraction (yield = 99%). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 16.0-14.8(br, 8H, pyrrole-*H*), 12.39(br, 2H, *o*-phenyl-*H*), 9.28(s, 4H, *m*-phenyl-*H*), 9.15(s, 4H, *m*-phenyl-*H*), 6.53(br, 1H, -O*H*), 3.99(s, 6H, *p*-C*H*$_3$), 3.91(s, 3H, *p*-C*H*$_3$), 3.55(br, 12H, *o*-C*H*$_3$), 3.26(br, 6H, *o*-C*H*$_3$). ESI-MS *m*/*z* calculated for $[C_{53}H_{46}CoN_4O]^+$: 813.299809, found: 813.297350.

Synthesis of (TDMAP)CoCO$_2$CH$_3$ (III). A 6.0 mL toluene solution of (TDMAP)Co^{II} (0.023 mmol, 19 mg), Oxone® (0.10 mmol, 32 mg), Na_2HPO_4 (0.42 mmol, 59 mg), and methanol (0.40 mL) was degassed by three freeze-pump-thaw cycles and refilled with CO (1 atm), then stirred for 13 h under dark at room temperature. The crude product was purified by column chromatography (basic alumina, mixture of petroleum ether and CH_2Cl_2 (3:1, *v*/*v*) as eluent) after removing the solvent (yield = 42%). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 8.67(s, 8H, pyrrole-*H*), 7.01(d, 4H, *J* = 2.3 Hz, *m*-phenyl-*H*), 6.95(d, 4H, *J* = 2.4 Hz, *m*-phenyl-*H*), 4.04(s, 12H, -OC*H*$_3$), 2.03(s, 12H, -C*H*$_3$), 1.67(s, 12H, -C*H*$_3$), 1.13(s, 3H, COOC*H*$_3$). ESI-MS *m*/*z* calculated for $[C_{58}H_{55}CoN_4O_6]^+$: 962.344807, found: 962.346346.

Synthesis of (TMP-OH)CoCO$_2$CH$_3$ (IV). A 19.0 mL toluene solution of (TMP-OH)Co^{II} (0.082 mmol, 67 mg), Oxone® (0.41 mmol, 125 mg), Na_2HPO_4 (1.63 mmol, 232 mg), and methanol (1.20 mL) was degassed by three freeze-pump-thaw cycles and refilled with CO (1 atm), then stirred for 7 h under dark at room temperature. The crude product was purified by column chromatography (basic alumina, gradient mixture of CH_2Cl_2 and CH_3OH (from 50:1 to 5:1, *v*/*v*) as eluent) after removing the solvent (yield = 47%). Recrystallization using diffusion process of CH_2Cl_2/*n*-hexane gave dark red crystal suitable for single-crystal X-ray diffraction analysis. ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 8.84(d, 2H, *J* = 4.8 Hz, pyrrole-*H*), 8.70(d, 2H, *J* = 4.9 Hz, pyrrole-*H*), 8.66(q, 4H, *J* = 4.8 Hz, pyrrole-*H*), 8.00(d, 2H, *J* = 7.8 Hz, phenyl-*H*), 5.02(s, 1H, -O*H*), 2.60(d, 9H, *p*-C*H*$_3$), 2.04(s, 3H, *o*-C*H*$_3$), 1.95(s, 6H, *o*-C*H*$_3$), 1.74(s, 6H, *o*-C*H*$_3$), 1.59(s, 3H, *o*-C*H*$_3$), 1.16(s, 3H, -COOC*H*$_3$). ESI-MS *m*/*z* calculated for $[C_{55}H_{49}CoN_4O_3]^+$: 872.313113, found: 872.315147.

Synthesis of (TMP-OH)Co-*a*PDMA$_n$ (V$_n$). A certain amount of (TMP-OH)CoCO$_2$CH$_3$ (**IV**) and DMA were mixed in C_6H_6 in a Schlenk flask. After three freeze-pump-thaw cycles, the flask was refilled with nitrogen, then placed in a water bath with room temperature and irradiated by 500 W Xe lamp with a 420~780 nm filter for about 12 h. The DMA conversion and tacticity of polymer were determined by ^{1}H NMR spectra in DMSO-*d*$_6$, then $M_{n,GPC}$ and PDI were determined using GPC analysis in DMF. After removing DMA and solvent under vacuum, the organocobalt complex (TMP-OH)Co-*a*PDMA$_n$ (**V$_n$**) was stored under nitrogen atmosphere in the refrigerator before use.

Typical procedure for visible-light induced stereospecific polymerization.

A certain amount of organocobalt complex **V$_n$** (or other complexes), DMA and Lewis acids were dissolved in the mixed solvent of methanol and benzene (1:1, *v*/*v*) in a Schlenk flask. After three freeze-pump-thaw cycles, the flask was refilled with nitrogen, then placed in a water bath with room temperature (or cold bath with specific temperature) and irradiated by 500 W Xe lamp with a 420~780 nm filter for a specified period of time. The polymer powder was precipitated by adding diethyl ether with ten times volume into the solution, purified by dialysis in water, and then freeze dried on CHRIST Alpha 1-2 LDplus freeze drier for further characterization. The DMA conversion and tacticity of polymer were determined by ^{1}H NMR spectra in DMSO-d_6 and CD_3OD. After dissolving polymers in DMF or chloroform, $M_{\mathrm{n,GPC}}$ and PDI were determined using GPC analysis. The glass transition temperature (T_g), crystallization temperature (T_c) and melting temperature (T_m) of polymer were measured using DSC analysis.

2 Single crystal X-ray diffraction data of (TMP-OH)$CoCO_2CH_3$ (IV)

Table S1 Crystal data and structure refinement for complex **IV**

Deposition number	1972804
Empirical formula	C55 H49 Co N4 O3
Formula weight	872.91 g/mol
Temperature	179.98 K
Wavelength	0.71073 Å
Crystal system	trigonal
Space group	P -3 c 1
Unit cell dimensions	a = 26.2516(5) Å α = 90° b = 26.2516(5) Å β = 90° c = 26.8975(8) Å γ = 120°
Volume	16052.9(8) Å^3
Z	12
Density (calculated)	1.08348 g/cm^3
Absorption coefficient	0.362 mm^{-1}
F(000)	5496.0
Crystal size	0.20 × 0.15 × 0.05 mm^3
Theta range for data collection	1.759 to 25.026°
Index ranges	-25<=h<=31, -30<=k<=30, -32<=l<=32
Reflections collected	51398
Independent reflections	9464 [R(int) = 0.0427]
Completeness to theta = 25.026°	99.9%
Absorption correction	Symmetry-related measurements
Max. and min. transmission	1.00000 and 0.82910
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9464 / 0 / 579
Goodness-of-fit on F2	1.025
Final R indices [I>2sigma(I)]	R1 = 0.0520, wR2 = 0.1205
R indices (all data)	R1 = 0.0872, wR2 = 0.1390
Extinction coefficient	n/a
Largest diff. peak and hole	0.608 and -0.587 e.Å^{-3}

Single crystal of (TMP-OH)$CoCO_2CH_3$ (**IV**) suitable for X-ray diffraction analysis were obtained by recrystallization from CH_2Cl_2 solution. The structure of complex **IV** is shown in Fig. S1. The cobalt atom is almost located in the porphyrin plane and has a five-coordinated, square pyramidal geometry. The Co–N bond lengths at the range of 1.945 to 1.957 Å were similar to those found in the analogue cobalt-vinyl porphyrin complex (1.941 to 1.975 Å).[6] The Co–C bond length was 1.882 Å, which was similar with that of (salen)$CoCO_2CH_3$ (1.863 Å) reported previously.[1]

The deposition number of CCDC is 1972804 for complex **IV**.

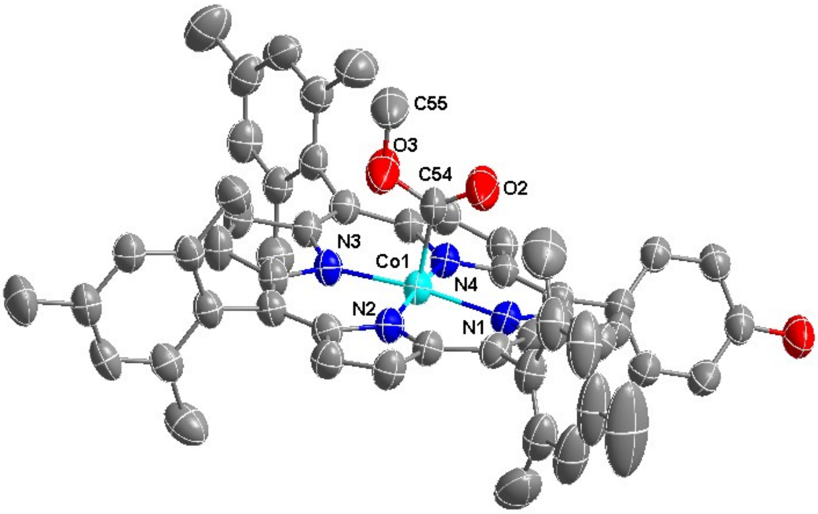

Fig. S1 Solid state structure of organocobalt complex (TMP-OH)$CoCO_2CH_3$ (**IV**) shown with 50% thermal ellipsoids. *n*-hexane and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Co1-N1 1.954(2), Co1-N2 1.949(2), Co1-N3 1.945(2), Co1-N4 1.957(2), Co1-C54 1.882(3), N1-Co1-N2 89.29(9), N2-Co1-N3 90.49(9), N3-Co1-N4 89.50(9), N4-Co1-N1 89.80(9), C54-Co1-N1 92.92(11), O2-C54-Co1 125.6(3), O3-C54-Co1 115.1(2)

3 Visible-light induced stereospecific polymerization of DMA

Table S2 Visible-light induced polymerization of DMA mediated by organocobalt complexes in polar solvents[a]

Entry	Cobalt mediator	$[DMA]_0/[Co]_0$	Time (h)	Conv.[b] (%)	$M_{n,th}$[c] (g mol^{-1})	$M_{n,GPC}$[d] (g mol^{-1})	M_w/M_n[d]	m[b] (%)
1	**I**	600:1	10.1	58	35200	30400	1.47	49
2	**II**	600:1	20.3	90	54400	48000	1.44	50
3	**III**	600:1	18.0	74	45000	39400	1.42	52
4[e]	**IV**	600:1	95.0	45	27600	26600	1.15	49

[a] The concentration of DMA was 1.0 mol L^{-1}, solvent was mixture of methanol and benzene (1:1, *v*/*v*), using 500 W xenon lamp with filter of 420~780 nm, light intensity was 3 mW cm^{-2}, reaction temperature was around 25 °C. [b] Determined based on ^{1}H NMR spectra. [c] $M_{n,th} = M_{w(Mediator)} + M_{w(DMA)} \times [DMA]_0/[Co]_0 \times Conv.(DMA)$. [d] Determined using gel permeation chromatography (GPC) in DMF calibrated against the poly(methyl methacrylate) (PMMA) standard. [e] The solvent was methanol.

Table S3 Visible-light induced stereospecific polymerization of DMA mediated by organocobalt complexes[a]

Entry	Lewis acid	Cobalt mediator[b]	$[DMA]_0/[Co]_0$ $/[LA]_0$	Time (h)	Conv.[c] (%)	$M_{n,th}$[d] (g mol^{-1})	$M_{n,GPC}$[e] (g mol^{-1})	M_w/M_n[e]	*m*[c] (%)	m_2[f] (%)	*mm*[c] (%)	mm_2[f] (%)
1	Al(OTf)$_3$	**IV**	600:1:10	115.6	29	18100	26400	1.44	50	-	-	-
2	Sc(OTf)$_3$	$\mathbf{V_{34}}$	600:1:20	69.4	85	54800	53500	1.47	70	71	47	48
3	Lu(OTf)$_3$	$\mathbf{V_{50}}$	600:1:20	15.2	68	46300	50100	1.28	81	85	68	73
4	Y(OTf)$_3$	$\mathbf{V_{50}}$	600:1:20	7.3	58	40300	45200	1.26	81	86	67	73
5[h]	La(OTf)$_3$	$\mathbf{V_{48}}$	600:1:20	8.0	63	43100	62000[g]	1.19[g]	85	90	75	81

[a] The concentration of DMA was 1.0 mol L^{-1}, solvent was mixture of methanol and benzene (1:1, *v*/*v*), using 500 W xenon lamp with filter of 420~780 nm, light intensity was 3 mW cm^{-2}, reaction temperature was around 25 °C. [b] $\mathbf{V_{34}}$: $M_{n,GPC} = 5500$, $M_w/M_n = 1.22$, $m = 50\%$. $\mathbf{V_{50}}$: $M_{n,GPC} = 6800$, $M_w/M_n = 1.21$, $m = 50\%$. $\mathbf{V_{48}}$: $M_{n,GPC} = 6700$, $M_w/M_n = 1.28$, $m = 50\%$. [c] Determined based on ^{1}H NMR spectra. [d] $M_{n,th} = M_{w(Mediator)} + M_{w(DMA)} \times [DMA]_0/[Co]_0 \times \mathrm{Conv.(DMA)}$. [e] Determined using GPC in DMF calibrated against the PMMA standard. [f] $m_2 = [(m \times DP) - (m_1 \times DP_1)]/DP_2$, and $mm_2 = [(mm \times DP) - (mm_1 \times DP_1)]/DP_2$, where DP_1 was determined by complex $\mathbf{V_n}$, $DP_2 = [DMA]_0/[Co]_0 \times \mathrm{Conv.}$, and $DP = DP_1 + DP_2$. [g] Determined using GPC in $CHCl_3$ calibrated against the PMMA standard. [h] Reaction temperature was -10 °C.

4 ^{1}H NMR spectra of isotactic homopolymers

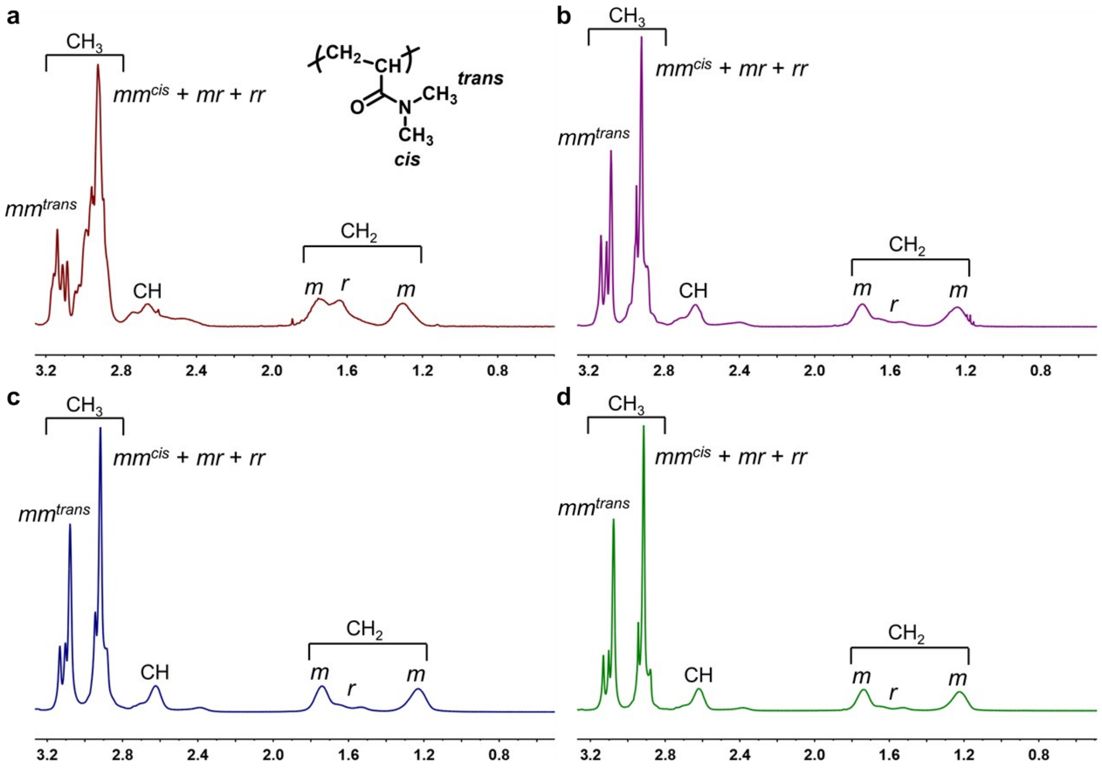

Fig. S2 ^{1}H NMR spectra (400 MHz, CD_3OD) of PDMAs synthesized by visible-light induced radical polymerization mediated by complex **IV** at ambient temperature. **a)** $[Sc(OTf)_3]_0/[DMA]_0 = 10:600$. **b)** $[La(OTf)_3]_0/[DMA]_0 = 10:600$. **c)** $[La(OTf)_3]_0/[DMA]_0 = 40:600$. **d)** $[La(OTf)_3]_0/[DMA]_0 = 80:600$.

5 Kinetic study of visible-light induced polymerization of DMA

The linear first order kinetic plots of the visible-light induced stereospecific radical polymerizations mediated by complex **V$_{46}$** were observed in the presence of various Lewis acids (Fig. S3). Since the organocobalt(III) species was directly used to mediate the DMA polymerization, no induction period was observed.[1,2] The slopes of the kinetic plots, which represent the polymerization rates, were significantly affected by the Lewis acids. In the absence of Lewis acid, the polymerization showed the slowest rate with the apparent rate constant (k_{app}) as (0.39 ± 0.01) ×10^{-3} min^{-1}. The addition of La(OTf)$_3$ caused the increasing of polymerization rate with the trend that the more La(OTf)$_3$ was added, the faster polymerization was observed. The k_{app} was enhanced to (1.64 ± 0.03) ×10^{-3}, (3.06 ± 0.09) ×10^{-3} and (6.78 ± 0.16) ×10^{-3} min^{-1}, when the [La(OTf)$_3$]/[DMA] ratio was 5/600, 10/600 and 20/600, respectively.

The type of Lewis acid influenced not only the polymerization rate, but also the isotacticity of stereoblock copolymer, similar to the trend observed in the DMA polymerization mediated by complex **IV**. With the same ratio of [Lewis acid]/[DMA] as 20/600, Sc(OTf)$_3$ that has the smallest ionic radius induced the slowest polymerization rate with k_{app} as (0.89 ± 0.01) ×10^{-3} min^{-1}, and the lowest isotacticity with the contents of m_2 and mm_2 as 71% and 48% (Table S3, entry 2). Lewis acids with larger ionic radii than Sc^{3+}, such as Lu(OTf)$_3$ and Y(OTf)$_3$,[7] elevated the polymerization rates, thus the k_{app} as (2.64 ± 0.20)×10^{-3} and (2.97 ± 0.07)×10^{-3} min^{-1}, respectively. Meanwhile, Lu(OTf)$_3$ and Y(OTf)$_3$ also improved the isotacticity, leading to the contents of m_2 = 85%, mm_2 = 73%, and m_2 = 86%, mm_2 = 73%, respectively (Table S3, entries 3-4).

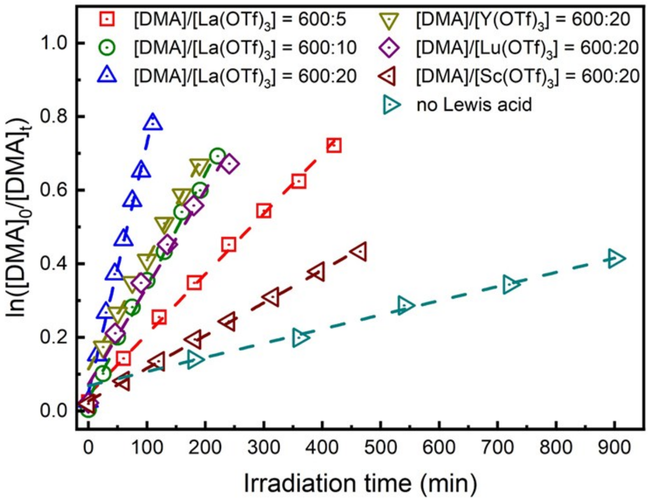

Fig. S3 Kinetic studies of visible-light induced radical polymerization of DMA in mixed solvent of methanol and benzene (1:1, v/v) at 25 °C. (Cobalt mediator was complex **IV** in the absence of Lewis acid, and complex **V$_{46}$** ($M_{n,GPC}$ = 6500, M_w/M_n = 1.23, m = 50%) in the presence of Lewis acids. [DMA]$_0$ = 1.0 mol L^{-1}, [DMA]$_0$/[Co]$_0$ = 600:1, light intensity was 3 mW cm^{-2})

6 GPC traces of stereoblock copolymers

After polymerization, all complexes $\mathbf{V_n}$ completely converted into stereoblock copolymers, based on GPC traces (Fig. S4 and S5), indicating high initiation efficiency.

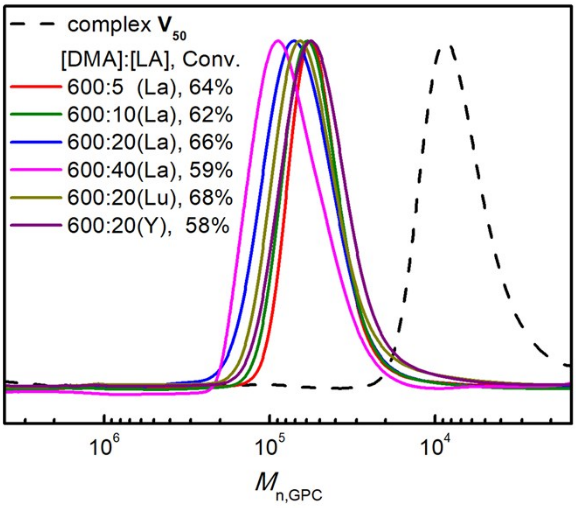

Fig. S4 The GPC traces of stereoblock copolymers (Cobalt mediator was $\mathbf{V_{50}}$: $M_{n,GPC}$ = 6800, M_w/M_n = 1.21, m = 50%.)

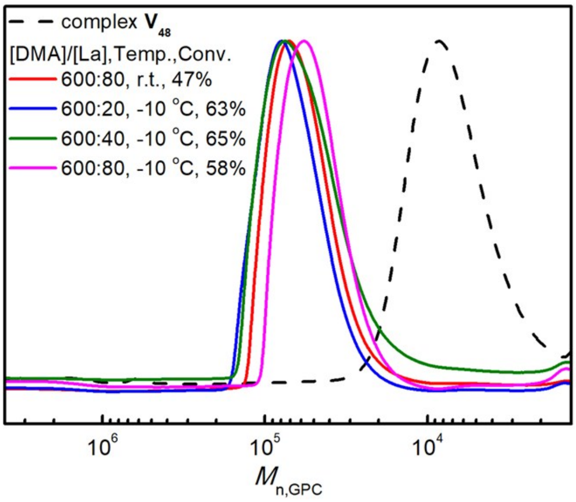

Fig. S5 The GPC traces of stereoblock copolymers (Cobalt mediator was $\mathbf{V_{48}}$: $M_{n,GPC}$ = 6700, M_w/M_n = 1.28, m = 50%.)

7 TGA analysis of PDMA

Under the nitrogen atmosphere, the decomposition temperature (T_d) of atactic PDMA was 396 °C with 84% loss of weight (Fig. S6a), and T_d of bPDMA-91 was 392 °C with 86% loss of weight (Fig. S6b). Under the air atmosphere, T_d of atactic PDMA was 373 °C with 94% loss of weight (Fig. S6c), and T_d of bPDMA-91 was 384 °C with 98% loss of weight (Fig. S6d). Therefore, PDMA was thermally stable when temperature was lower than 300 °C, under both nitrogen and air atmosphere.

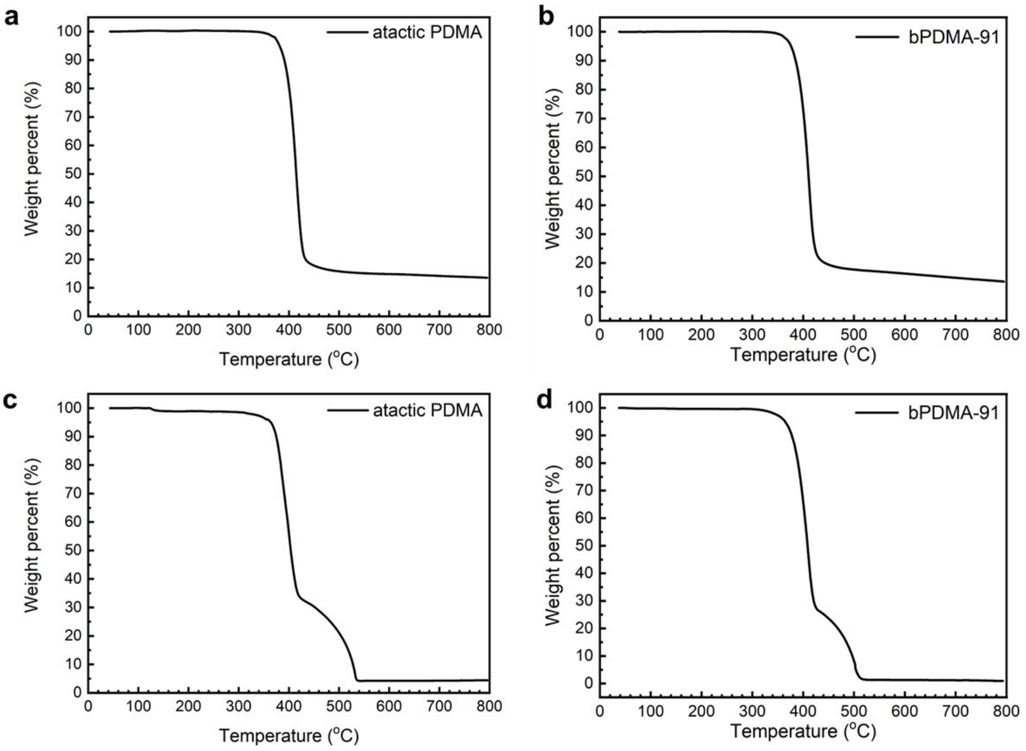

Fig. S6 TGA curves of PDMAs. **a)** and **b)** under the nitrogen atmosphere, **c)** and **d)** under the air atmosphere. **a)** and **c)** atactic PDMA, **b)** and **d)** bPDMA-91.

8 DSC analysis of stereoblock copolymers

If fixing the degree of polymerization (DP) of atactic block, and the tacticity of isotactic block, the stereoblock copolymers with low molecular weight and middle molecular weight both underwent cold crystallization with similar T_c and T_m (Fig. S7).

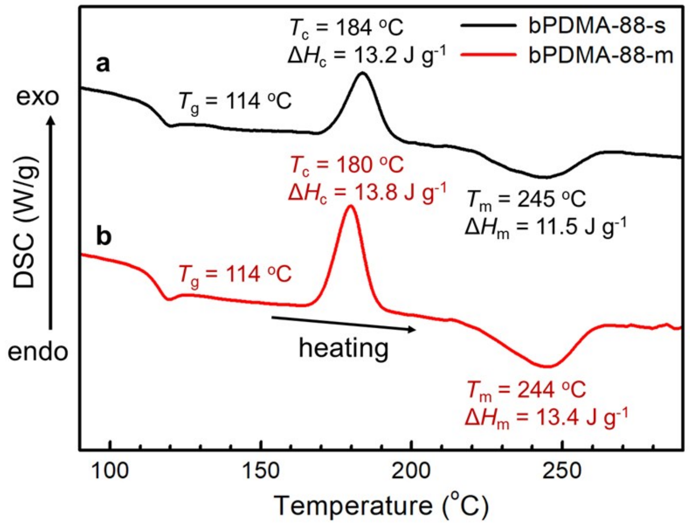

Fig. S7 DSC thermograms of stereoblock copolymers. **a)** bPDMA-88-s, **b)** bPDMA-88-m.

When m_2 content of stereoblock copolymer was less than 88%, neither crystallization nor melting peaks could be observed in DSC thermogram, even the heating and cooling rates were as low as 2.5 °C min^{-1} (Fig. S8).

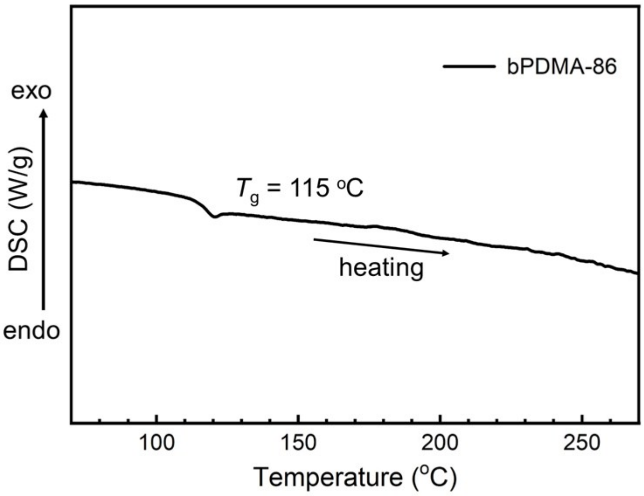

Fig. S8 DSC thermogram of bPDMA-86 with the heating and cooling rates as 2.5 °C min^{-1}.

The DSC result could be influenced by the heating rate during the measurement, especially the crystallization process. The sample of bPDMA-88-l showed the higher T_c as 201 °C, and remarkably lower enthalpies of crystallization (ΔH_c) and melting (ΔH_m) as less than 3 J g^{-1} when the heating rate was 10 °C min^{-1}. If the heating rate was further raised to 20 °C min^{-1}, the crystallization and melting peaks both disappeared in DSC thermogram (Fig. S9).

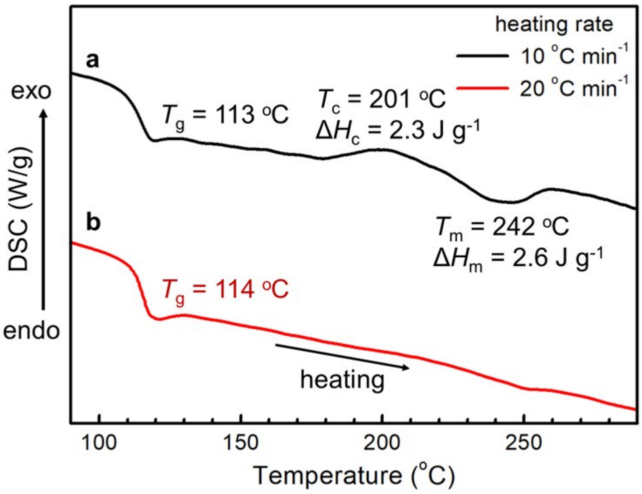

Fig. S9 DSC thermograms of stereoblock copolymer of bPDMA-88-l with different heating and cooling rates. **a)** 10 °C min^{-1}, **b)** 20 °C min^{-1}.

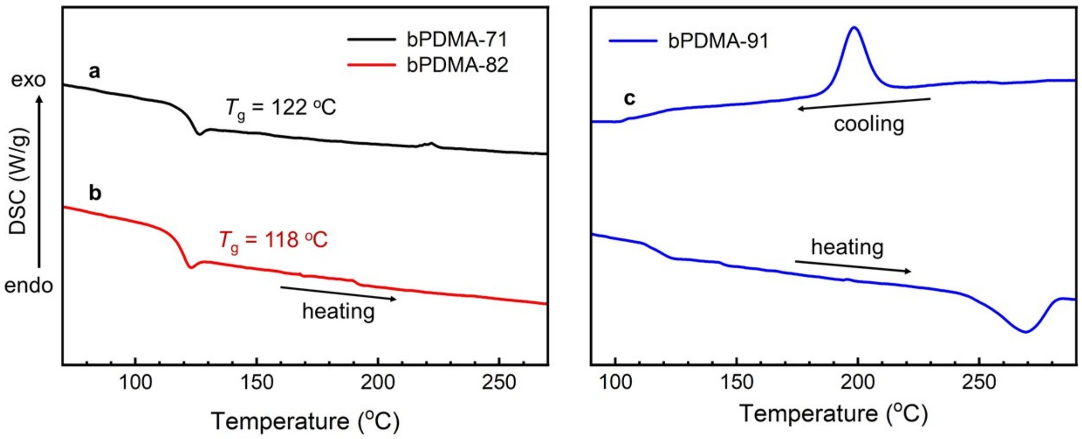

Fig. S10 DSC thermograms of stereoblock copolymers. **a)** bPDMA-71, **b)** bPDMA-82, **c)** bPDMA-91.

9 DSC analysis of isotactic homopolymers

Table S4 Thermal properties of isotactic homopolymers synthesized by stereospecific visible-light induced polymerization of DMA mediated by complex **IV**[a]

Entry	Polymer	$M_{n,GPC}$[b] (g mol^{-1})	M_w/M_n[b]	m[c] (%)	mm[c] (%)	T_g (°C)	T_c (°C)	ΔH_c (J g^{-1})	T_m (°C)	ΔH_m (J g^{-1})
1	hPDMA-65	33200	1.33	65	41	123	-	-	-	-
2	hPDMA-83	51400	1.43	83	68	115	-	-	-	-
3	hPDMA-86	50700	1.46	86	72	115	-	-	-	-
4	hPDMA-88	63600	1.72	88	78	114	179[d]	14.6[d]	243	11.9
5	hPDMA-89	136900[e]	1.85[e]	89	79	116	179[f]	15.8[f]	254	13.8
6	hPDMA-91	153500[e]	1.67[e]	91	83	116	190[f]	16.5[f]	267	15.5

[a] The heating and cooling rates of DSC measurement were both 5 °C min^{-1}. [b] Determined using GPC in DMF calibrated against the PMMA standard. [c] Determined based on ^{1}H NMR spectra. [d] Observed in heating process. [e] Determined using GPC in $CHCl_3$ calibrated against the PMMA standard. [f] Observed in cooling process.

The isotactic homopolymers synthesized *via* the mediation of complex **IV** showed a decreasing of T_g from 123 °C to 114 °C when *m* content increased from 65% to 88% (Table S4, entries 1-4). Similar with stereoblock copolymer, isotactic homopolymer also transformed to crystalline polymer when the contents of *m* and *mm* approached to 88% and 78% (Table S4, entry 4, and Fig. S11c). In addition, when heating rate of DSC measurement was decreased from 5 °C min^{-1} to 2.5 °C min^{-1}, there were also no crystallization or melting peaks observed for hPDMA-86 (Fig. S12). Different to the stereoblock copolymer of bPDMA-89, isotactic homopolymer of hPDMA-89 whose *m* content was also 89% went through melt crystallization rather than cold crystallization with higher T_c as 179 °C and similar T_m as 254 °C (Table S4, entry 5, and Fig. S11d). The isotactic homopolymer of hPDMA-91, which had the higher *m* and *mm* contents as 91% and 83%, demonstrated the increased T_c as 190 °C, ΔH_c as 16.5 J g^{-1}, T_m as 267 °C, and ΔH_m as 15.5 J g^{-1} (Table S4, entry 6, and Fig. S11e).

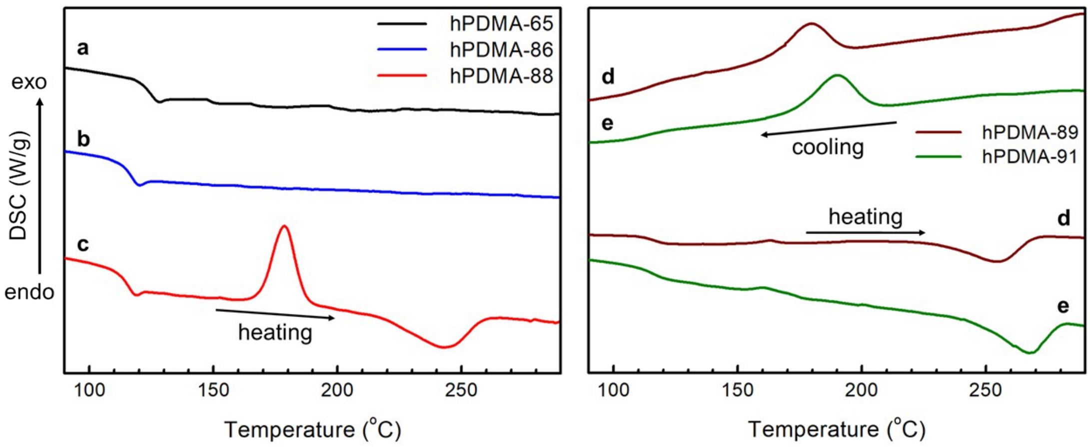

Fig. S11 DSC thermograms of isotactic homopolymers. **a)** hPDMA-65, **b)** hPDMA-86, **c)** hPDMA-88, **d)** hPDMA-89, **e)** hPDMA-91.

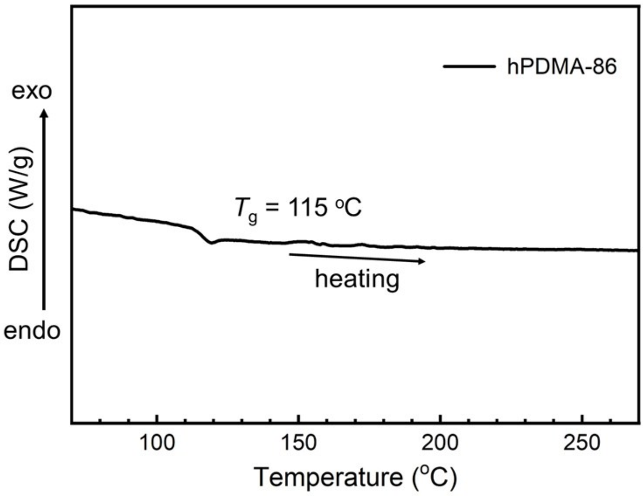

Fig. S12 DSC thermogram of hPDMA-86 with the heating and cooling rates as 2.5 °C min^{-1}.

10 PXRD plots of isotactic homopolymers

Similar with stereoblock copolymers, the crystalline isotactic homopolymers also exhibited sharp peaks (*d* spacing: 0.78 and 0.50 nm) in powder X-ray diffraction (PXRD) plots after annealing treatment (Fig. S13), which was consistent with isotactic PDMA synthesized by coordination polymerization.[8]

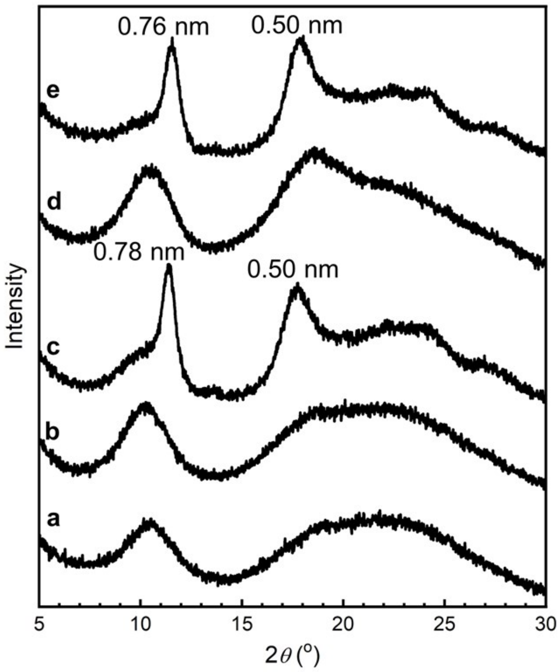

Fig. S13 PXRD plots of isotactic homopolymers. **a)** hPDMA-86, **b)** hPDMA-88, **c)** hPDMA-88 annealed at 170 °C for 85 h, **d)** hPDMA-91, **e)** hPDMA-91 annealed at 180 °C for 84 h.

11 ^{1}H NMR spectra of ligands and organocobalt complexes

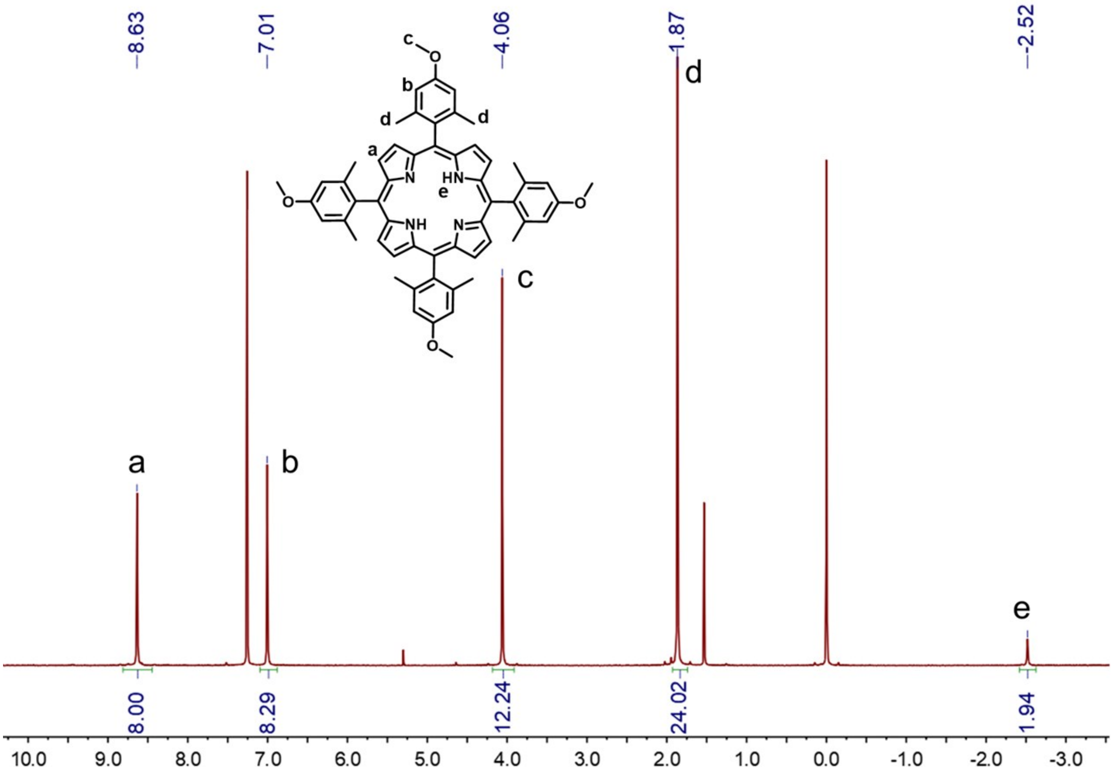

Fig. S14 ^{1}H NMR spectrum (400 MHz, CDCl$_3$) of (TDMAP)H$_2$

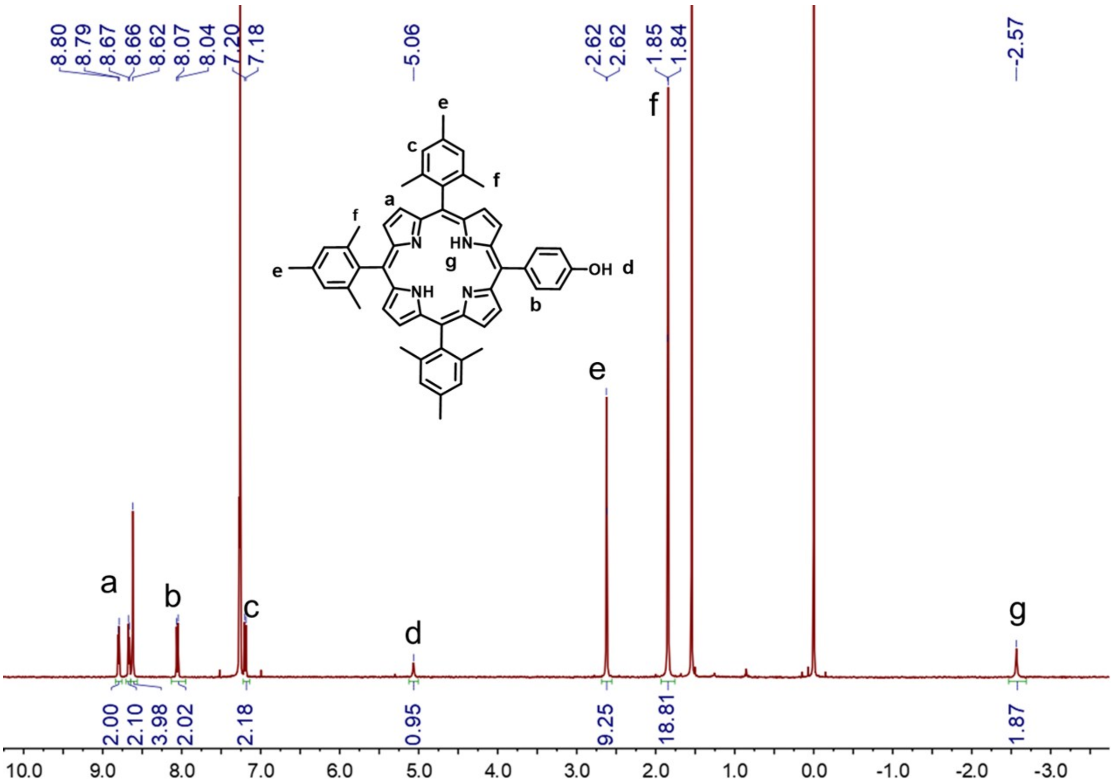

Fig. S15 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (TMP-OH)H_2

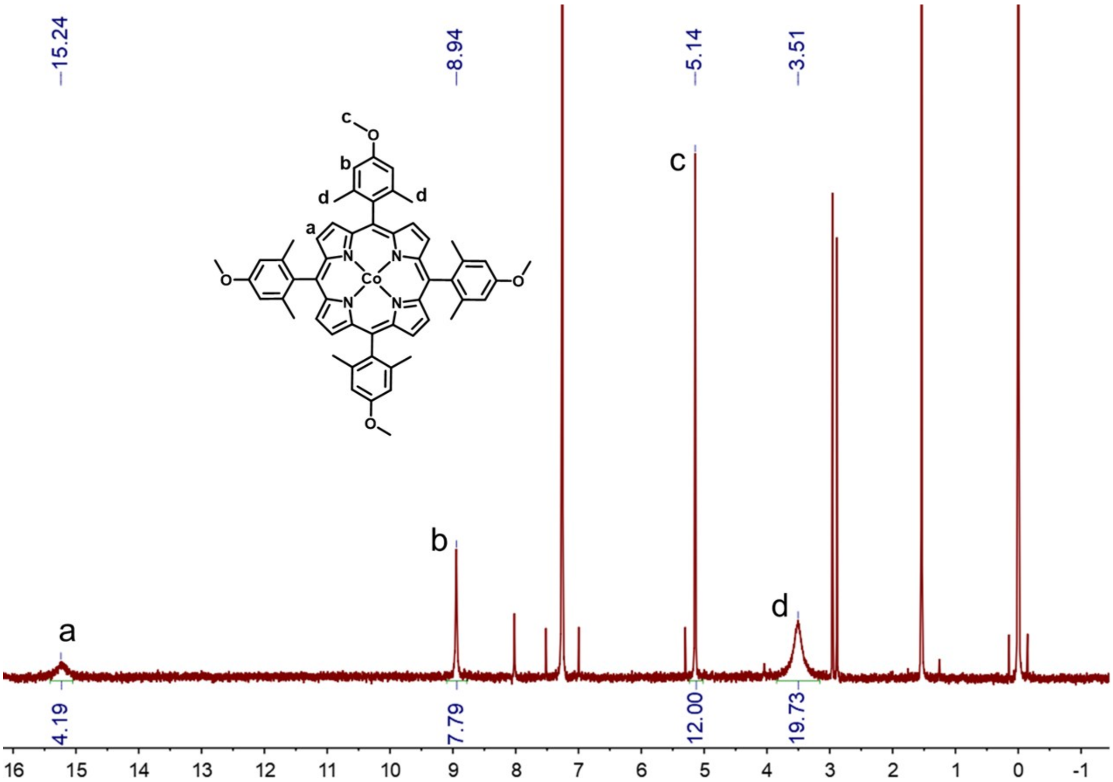

Fig. S16 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (TDMAP)Co^{II}

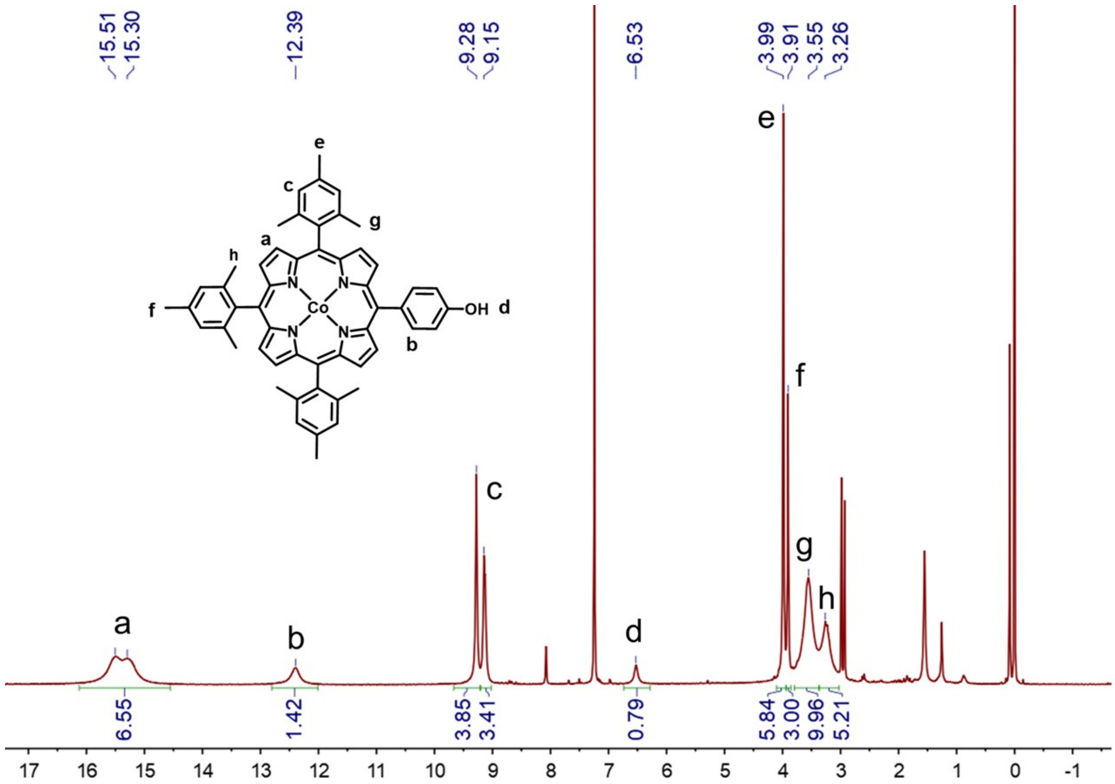

Fig. S17 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (TMP-OH)Co^{II}

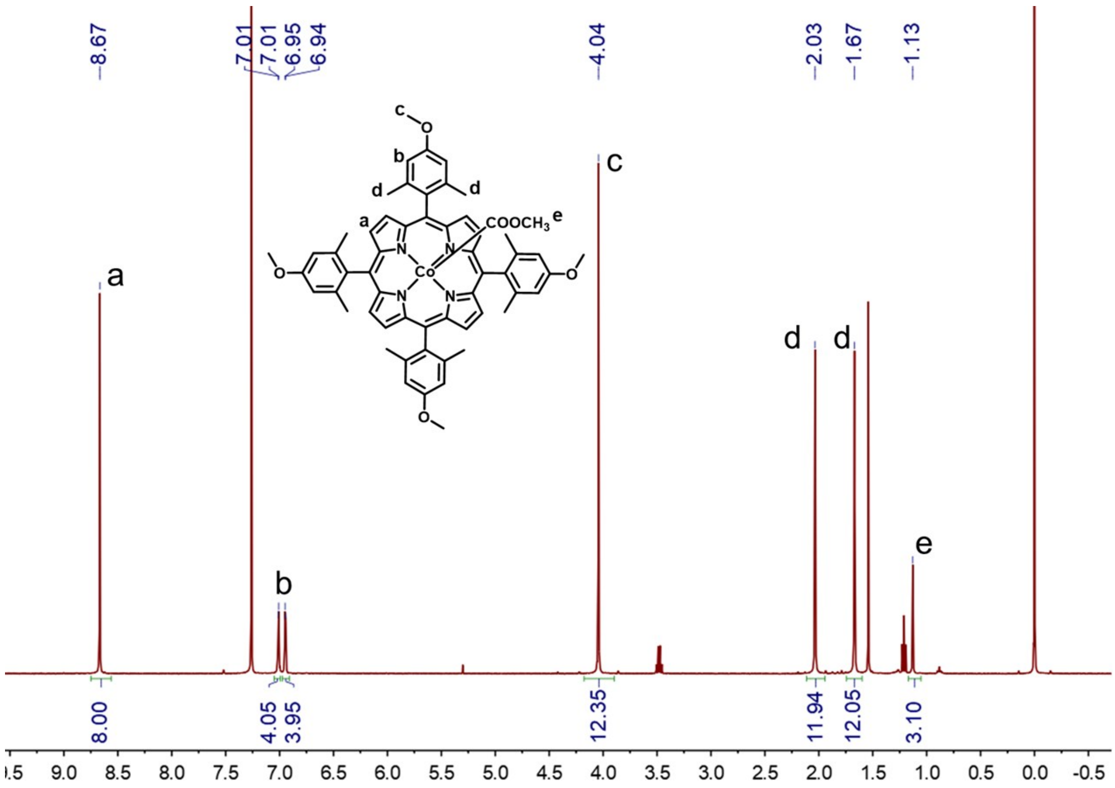

Fig. S18 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (TDMAP)$CoCO_2CH_3$ (**III**)

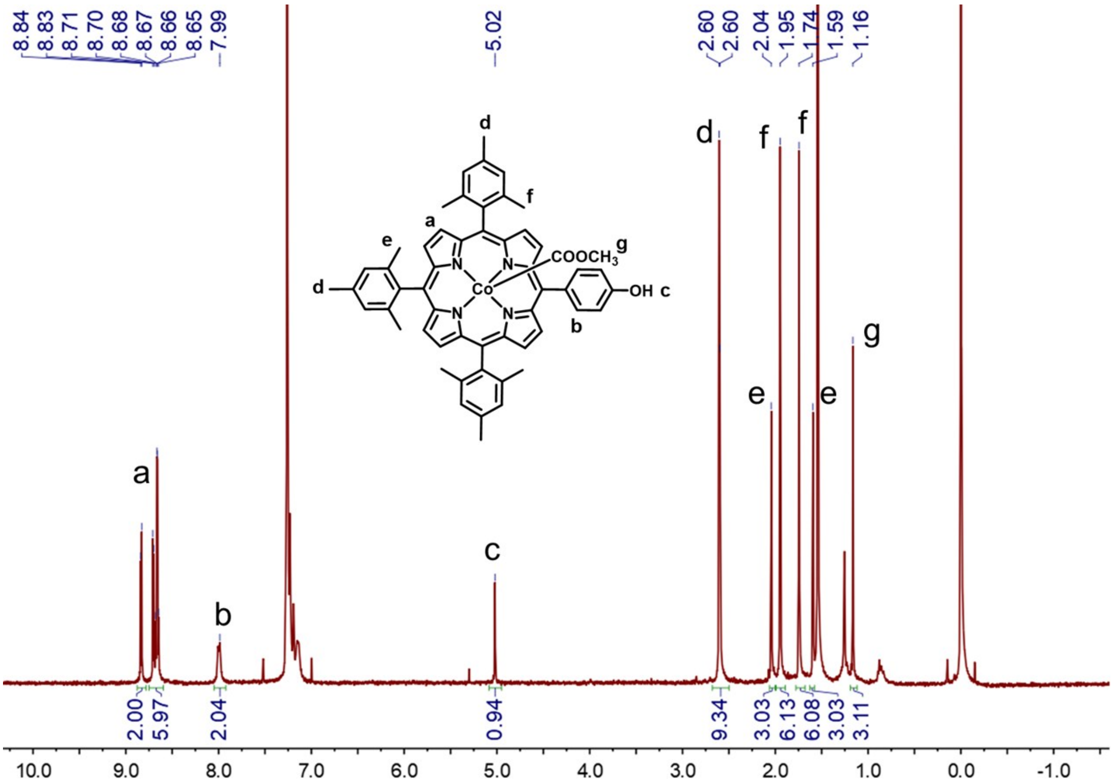

Fig. S19 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (TMP-OH)$CoCO_2CH_3$ (**IV**)

References

1 Y. Zhao, M. Yu, S. Zhang, Z. Wu, Y. Liu, C.-H. Peng and X. Fu, *Chem. Sci.*, 2015, **6**, 2979–2988.

2 Y. Zhao, M. Yu, S. Zhang, Y. Liu and X. Fu, *Macromolecules*, 2014, **47**, 6238–6245.

3 A. D. Adler, J. D. Finarelli, F. R. Longo, J. Goldmacher, J. Assour and L. Korsakoff, *J. Org. Chem.*, 1966, **32**, 476.

4 M. Góngora-Benítez, L. Mendive-Tapia, I. Ramos-Tomillero, A. C. Breman, J. Tulla-Puche and F. Albericio, *Org. Lett.*, 2012, **14**, 5472–5475.

5 Y. Zhao, H. Dong, Y. Li and X. Fu, *Chem. Commun.*, 2012, **48**, 3506–3508.

6 H. Lu, W. I. Dzik, X. Xu, L. Wojtas, B. de Bruin and X. P. Zhang, *J. Am. Chem. Soc.*, 2011, **133**, 8518–8521.

7 P. W. Atkins, T. L. Overton, J. P. Rourke, M. T. Weller, F. A. Armstrong and M. Hagerman, *Inorganic Chemistry*, Oxford University Press, New York, Fifth Edition., 2010.

8 W. R. Mariott and E. Y.-X. Chen, *Macromolecules*, 2004, **37**, 4741–4743.