

The Amplified Circularly Polarized Luminescence Emission Response of Chiral 1,1'-Binaphthol-Based Polymers via Zn(II)-Coordination Fluorescence Enhancement

Fandian Meng,¹ Fei Li,² Lan Yang,² Yuxiang Wang,² Yiwu Quan,¹ Yixiang Cheng²

¹Department of Polymer Science and Engineering, State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, 210093, China

²Key Laboratory of Mesoscopic Chemistry of MOE, Collaborative Innovation Center of Chemistry for Life Sciences, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, 210093, China

Correspondence to: Y. Quan (E-mail: quanyiwu@nju.eu.cn) or Y. Cheng (E-mail: yxcheng@nju.edu.cn)

Received 22 January 2018; accepted 7 March 2018; published online 00 Month 2018 DOI: 10.1002/pola.29009

ABSTRACT: Two kinds of chiral 1,1'-binaphthol (BINOL)-based polymer enantiomers were designed and synthesized by the polymerization of 5,5'-((2,2'-bis (octyloxy)-[1,1'-binaphthalene]-3,3'-diyl)bis(ethyne-2,1-diyl))bis(2-hydroxybenzaldehyde) (**M1**) with alkyl diamine (**M2**) via nucleophilic addition–elimination reaction. The resulting chiral polymers can exhibit mirror image cotton effects either in the absence or in the presence of Zn²⁺ ion. Almost no fluorescence or circularly polarized luminescence (CPL) emission could be observed for two chiral BINOL-based polymer enantiomers in the absence of Zn²⁺. Interestingly, the chiral polymers

INTRODUCTION Normally, circularly polarized luminescence (CPL) can be regarded as the differential emission direction of right- and left-handed circularly polarized light.¹ Various CPL materials with high dissymmetry factors (g_{lum}) have been successfully used as an effective tool to investigate and characterize the chiral features of natural and synthetic molecules.² In the past decade, many strategies have been developed to design CPL emission materials based on chiral organic chromophores.³ In the recent years, the design on excellent CPL materials has been mainly focused on chiral conjugated fluorescence polymers,⁴ metal-containing chiral complexes,⁵ supramolecular selfassembly,⁶ chiral emission nematic liquid crystal,⁷ and so on. Liu and coworkers6^(f) reported a chiral gelator with weak CPL signal via supramolecular self-assemble, but the amplified CPL emission could be detected from blue to green color change when this host gelator co-assembled into nanohelix with the achrial guest BPEA chromophore due to intremolecular chirality and energy transfer. Akagi and coworkers' group $^{7(\mathrm{a})}$ reported a chiral disubstituted liquid-crystalline polyacetylene (di-LCPA), which can be dynamically switched and amplified from left- to

can show strong fluorescence and CPL response signals upon the addition of Zn^{2+} , which can be attributed to Zn^{2+} -coordination fluorescence enhancement effect. This work can develop a new strategy on the design of the novel CPL materials via metal-coordination reaction. © 2018 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2018**, *00*, 000–000

KEYWORDS: 1,1'-binaphthol; circularly polarized luminescence; coordination; fluorescence enhancement; polymer

right-handed CPL. Both circular dichroism (CD) and CPL signal appeared reversable when the temperature was slightly modified, which is due to the Grandjean texture phase change induced by the thermotropic N*-LC cell from the temperature change.

Chiral 1,1'-binaphthol (BINOL) and its derivatives, as one of the most important *C2*-symmetric compounds, can not only exhibit the efficient and stable chiral configuration but also high chiral induction and chiral discrimination.⁸ In the past few years, much attention has been paid to the BINOL-based dyes as CPL emission materials.⁹ Kawai and coworker¹⁰ reported a pair of bichromophoric perylene bisimide enantiomers containing chiral binanphthane diamine unit with weak CPL signal in dilute CHCl₃ solution and the enhanced CPL emission response behavior in the aggregation state due to the effective integration of individual bichromophoric moieties into helical nanofibers. Recently, Zhang et al. also found strong CPL emission response signals of chiral BINOL-based polymers induced by the effective chirality transfer from the

F. Meng and F. Li contributed equally to this article.

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chiral binaphthyl moiety to the conjugated polymer chain backbone via the rigid π -conjugation bond linker.¹¹

Salen, as a particular chelating Schiff base, can be synthesized by the condensation of salicylaldehydes or salicylaldehyde derivatives with 1,2-diamines. Salen-based ligands can form stable complexes with various metal ions due to the strong tetradentate N_2O_2 donor.¹² Xu et al.¹³ reported Salen-based polymer as fluorescent chemosensor which could exhibit highly sensitive and selective enhancement response on Zn²⁺ recognition. Recently, Nishihara and coworkers observed the amplified CPL emission signals from bis(dipyrrinato)zinc(II) complex chiroptical wires which could be exfoliated into single strands, and g_{lum} could greatly increase as high as 5.9 times larger than that of the corresponding monomer complex.9^(b) In this work, we found the strong CPL emission response behavior of chiral BINOL-based polymers promoted by fluorescence enhancement effect via Salen-Zn(II) coordination reaction. This kind of *in situ* metal-coordination reaction can supply a new design strategy on the novel CPL emission materials.

EXPERIMENTAL

Measures and Materials

All solvents and reagents were commercially available and analytical reagent grade. THF was distilled from sodium. NMR spectra were obtained from a Bruker 400 spectrometer at 400 MHz for ¹H NMR and reported as parts per million (ppm) from the internal standard TMS. UV-vis spectra were recorded on a PerkinElmer Lambda 35 UV/VIS spectrometer. Fluorescence spectra were obtained from an RF-5301PC spectrometer. FT-IR spectra were obtained from a TENSOR27 FT-IR Spectrometer. CD was recorded on a JASCO J-810 spectropolarimeter. Thermogravimetric analyses (TGA) were performed using a PerkinElmer Pyris-1 instrument under an N_2 atmosphere. Molecular weight was determined by gel permeation chromatography (GPC) with a Waters 244 HPLC pump, and THF was used as a solvent relative to polystyrene standards. CPL spectra were obtained on a JASCO CPL-300 Spectrofluoropolarimeter. All optical measurements were investigated in THF with a fixed concentration (1.0 \times 10 $^{-5}$ mol L $^{-1}$ corresponding to the BINOL moiety). The magnitude of circular polarization in the excited state is defined as $g_{lum} = 2(I_L - I_R)/(I_L + I_R)$, where I_L and $I_{\rm R}$ indicate the output signals for left and right circularly polarized light, respectively. Experimentally, the value of g_{lum} is defined as $2\Delta I/I = 2[\text{ellipticity}/(32980/\ln 10)]/$ (unpolarized PL intensity) at the CPL extremum.

Synthesis of Compound *R*-1/*S*-1

2,2'-Bis(methoxymethoxy)-1,1'-binaphthalene (4.28 g, 11.4 mmol) was dissolved in 100 mL of anhydrous Et₂O, 16 mL of *n*-BuLi (2.5 mol L⁻¹ in hexane, 40 mmol) was added by syringe injection at room temperature under N₂ atmosphere. The solution was stirred for 2 h at room temperature, and then the solution of iodine (12 g, 44.7 mmol) was slowly injected to the mixed solution at 0 °C under N₂ atmosphere. The mixture was then stirred overnight while the temperature was gradually warmed to room temperature. The reaction was quenched by

NaHSO₃ saturated solution. After removal of the solvent under reduced pressure, the residue was extracted with ether (2 \times 50 mL), and the combined organic layers were washed with water. The residues were purified by silica gel column chromatography, yielding light yellow powder in 44% yield.

¹H NMR (400 MHz, CDCl₃): 8.54 (s, 2H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.16–7.45 (m, 6H), 4.81 (d, *J* = 5.7 Hz, 2H), 4.70 (d, *J* = 5.7 Hz, 2H,), 2.60 (s, 6H).

Synthesis of Compound R-2/S-2

R/S-3,3'-diiodo-[1,1'-binaphthalene]-2,2'-diol (1.00 g, 1.86 mmol), K₂CO₃ (0.77 g, 5.57 mmol), and 1-bromooctane (0.90 g, 4.65 mmol) were dissolved in 20 mL acetonitrile. After the reaction mixture was refluxed overnight, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate, 100/1, v/v) to get *R*-2/*S*-2 as a yellow oil (1.20 g, 84.5%).

¹H NMR (400 MHz, CDCl₃): δ 8.53 (s, 2H), 7.80 (d, J = 6.0 Hz, 2H), 7.42(t, J = 6.0 Hz, 2H), 7.28 (d, J = 6.0 Hz, 2H), 7.15 (d, J = 6.0 Hz, 2H), 3.89–3.82 (m, 2H), 3.38–3.80 (m, 2H), 1.37–0.57 (m, 30H); ¹³C NMR (100 MHz, CDCl₃): δ 154.1 139.6 134.0, 132.1, 126.9, 125.9, 125.7, 125.5, 93.2, 73.6, 31.8, 29.7, 29.2, 29.0, 25.5, 22.8, 14.3.

Synthesis of Compound *R*-M1/*S*-M1

R-**2**/*S*-**2** (3.0 g, 4 mmol), **3** (1.31 g, 9 mmol), $Pd(PPh_3)_2Cl_2$ (60 mg, 0.08 mmol, 2 mol %), and CuI (16 mg, 0.08 mmol, 2 mol %) were dissolved in anhydrous THF (30 mL) and Et₃N (30 mL) under N₂ atmosphere. After stirring at 80 °C for 36 h, the mixture were cooled to room temperature and filtered. The filtrate was collected and the solvent was removed under reduced pressure. The residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate, 25/1, *v/v*) to get *R*-**M1**/*S*-**M1** as a yellow oil (0.88 g, 27.5%).

¹H NMR (400 MHz, CDCl₃) δ 11.13 (s, 1H), 9.90 (s, 2H), 8.18 (s, 2H), 7.86 (d, *J* = 8.1 Hz, 2H), 7.78 (d, *J* = 2.0 Hz, 2H), 7.70 (dd, *J* = 8.7, 2.1 Hz, 2H), 7.46–7.36 (m, 2H), 7.33–7.24 (m, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 4.08 (dt, *J* = 8.9, 6.2 Hz, 2H), 3.72 (dt, *J* = 8.9, 6.3 Hz, 2H), 1.40–0.77 (m, 30H). ¹³C NMR (100 MHz, CDCl₃): δ 196.1, 161.5, 155.1, 139.7, 136.6, 134.0, 133.8, 133.1, 127.8, 127.2, 125.9, 125.3, 125.2, 120.6, 117.5, 115.5, 91.5, 86.4, 73.9, 31.8, 30.1, 29.2, 29.1, 25.9, 25.6, 22.7, 14.1.

Synthesis of Polymer *R*-P1/*S*-P1

A Mixture of R-**M1**/S-**M1** (160 mg, 0.2 mmol) and ethylenediamine (12.0 mg, 0.2 mmol dissolved in toluene) was dissolved in 6 mL of toluene. The solution was stirred at 95 °C for 36 h. After removing the solvent under vacuum, a small amount of dichloromethane was added, then dropped into 100 mL of methanol to precipitate the yellow solid R-**P1**/S-**P1**. The resolution R-**P1**/S-**P1** was filtered and washed with methanol and dried in the yield of 63%.

¹H NMR (400 MHz, CDCl₃): δ 8.45–8.28 (m, 2H), 8.20–8.09 (m, 2H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.57–7.33 (m, 6H), 7.30–7.10



SCHEME 1 Synthesis procedures of R-M1/S-M1 and two chiral polymers R-P1/S-P1 and R-P2/S-P2.

(m, 6H), 6.98–6.88 (m, 2H), 4.18–4.02 (m, 2H), 4.04–3.90 (s, 4H), 3.73 (tt, J = 14.4, 7.2 Hz, 2H), 1.40–0.52 (m, 30H). GPC: $M_{\rm w} = 15,570$, $M_{\rm n} = 10,960$, PDI = 1.42. $[\alpha]_{\rm D}^{20} = -292.0$ ($c = 1.0 \text{ mg mL}^{-1}$, THF) for R-**P1**. IR(KBr): 3612(w), 3525(w), 3438(w), 3330(w), 2922(m), 2850(w), 2206(w), 1633(s, C=N), 1488(vs), 1286(m), 1222(w), 1124(m), 889(m), 825(m), 750(m), 464(m).

Synthesis of Polymer R-P2/S-P2

A Mixture of *R*-**M1**/*S*-**M1** (160 mg, 0.2 mmol) and 1,4-butanediamine (17.6 mg, 0.2 mmol dissolved in toluene) was dissolved in 6 mL of toluene. The solution was stirred at 95 °C for 36 h. After removing the solvent under vacuum, a small amount of dichloromethane was added, then dropped into 100 mL of methanol to precipitate the yellow solid *R*-**P2**/*S*-**P2**. The resolution *R*-**P2**/*S*-**P2** was filtered and washed with methanol and dried in the yield of 67%.

¹H NMR (400 MHz, CDCl₃) δ 8.31 (d, 2H), 8.16 (d, 2H), 7.81 (t, 2H), 7.59–7.42 (m, 4H), 7.38 (t, 2H), 7.31–7.20 (m, 4H), 7.17 (d, 2H), 7.03–6.87 (m, 2H), 4.08 (m, 4H), 3.84–3.55 (m, 6H), 1.83 (s, 4H), 1.40–0.51 (m, 28H). GPC: $M_{\rm w} = 11,220, M_{\rm n} = 8090$, PDI = 1.38. $[\alpha]_{\rm D}^{20} = -310.0$ (c = 1.0 mg mL⁻¹, THF) for *R*-**P2**. IR(KBr): 3525(w), 3442(w), 2929(m), 2850(w), 2407(w), 2206(w), 1633(s, C=N), 1488(vs), 1286(m), 1222(m), 1126(m), 887(m), 827(m), 750(m), 460(m).

RESULTS AND DISCUSSION

The synthesis procedures of monomers and chiral polymers are outlined in Scheme 1. The compounds **1**--**3** and chiral monomers *R*-**M1**/*S*-**M1** could be synthesized according to the reported literatures.¹⁴ Two chiral BINOL-based polymer enantiomers could be synthesized by nucleophilic additionelimination polymerization reaction of the linker alkyl diamine

ethylenediamine or butanediamine (M2) with chiral monomers *R*-M1/*S*-M1 at about 65% yield. In all the ¹H NMR spectra of P1-P2 (Supporting Information † 1), the peak at 9.90 and 11.13 ppm from salicylaldehyde group almost disappeared, and a new peak at 8.30–8.50 ppm from N=C—H of Schiff base appeared, which could demonstrate the successful polymerization of the target monomers. Both two polymers were soluble in common organic solvents (THF, DCM, DMF, acetone, and toluene) due to the flexible *n*-octyl group substituent in the polymer side chain. The TGA curves reveal that the degradation temperature (T_d) of 5% weight loss of all these polymers was above 370 °C, indicating that the polymers can provide considerable thermal property for practical applications for optical materials.

UV-Vis and Fluorescence Behaviors of Polymers

In this article, we first investigated their UV-vis absorption and fluorescence emission in THF at the fixed concentration (1.0 imes 10^{-5} mol L⁻¹ corresponding to the BINOL moiety). UV-vis spectra of the polymers have similar absorption two bands situated at about 320 and 336 nm in THF [Fig. 1(a)]. As shown in Figure 1(b) and Supporting Information Figure S6, the orginal absorbance two peaks of **P1** disappear upon addition of Zn^{2+} up to 1 equiv, and a new peak appears at 337 nm with a little reduction and red shift. On the other hand, the shoulder absorption peak at 370 nm of the long wavelength region shows obvious enhancement at 1:1 molar ratio of Zn²⁺, which can be regarded as the conjugated structure between the binaphthyl moiety and Salen-Zn(II) complex. As further increase in Zn²⁺ molar ratio up to 4.0 equiv, almost no change in UV-vis absorption can be observed, which indicates the formation of 1:1 polymer-Zn(II) complex. Meanwhile, P2 has similar change feature with P1 (Supporting Information Fig. S6).

Almost no fluorescent emissions could be detected for **P1– P2** in THF solution. Interestingly, obvious fluorescent signals





FIGURE 1 (a) UV-vis spectra of chiral polymers **P1** and **P2** in the absence of Zn^{2+} . (b) UV-vis spectra of the chiral polymers **P1** in THF (1.0 × 10⁻⁵ mol L⁻¹) in the presence of Zn^{2+} (from 0.1 to 4 equiv). [Color figure can be viewed at wileyonlinelibrary.com]

at about 466 nm can be observed for both two polymers $\ensuremath{\textbf{P1}}$ and P2 upon the addition of Zn^{2+} as shown in Figure 2. As further increase in Zn^{2+} up to 1:1 molar ratio, the fluorescent intensity of Zn²⁺-containing polymer complex shows gradual enhancement as high as 6.71-fold for P1 and 8.94fold for **P2** [Inset; Fig. 2(a,b)]. The Zn²⁺-polymer solution can emit bright blue fluorescence, which can be visually observed by the naked eye (Inset; Figure 2(a,b), left: in the absence of Zn^{2+} , right: in the presence of Zn^{2+} of 1.0 equiv). The fluorescence curve of the polymer sensor with Zn²⁺ reveals that the fluorescent enhancement value $(I/I_0 - 1)$ can exhibit the good linear relationship on the Zn²⁺ molar ratio versus chiral polymers from 0.1 to 1.0. Only a little increase can be detected from 1.0 to 4.0 equiv, which further demonstrates that both two chiral polymers P1 and P2 can form a 1:1 Zn²⁺-coordinated polymer complex. The fluorescence enhancement phenomenon can be attributed to two reasons. On the one hand, the suppressed photoinduced electron transfer (PET) effect can lead to fluorescence enhancement response while Zn²⁺ coordinates with the nitrogen atoms of the Schiff-base ligand since the lone pair of electrons from -CH=N- group is no longer available for PET upon the formation of Salen-Zn(II) complex. On the other hand, the formation of Zn^{2+} -polymer can enhance the planarity and rigidity of the conjugated segment of the chiral polymer, which can prevent the free rotation of alkyl amine chain and reduce the nonradiative decay of the excited state.^{13,15} Interestingly, the fluorescence of 1:1 Zn^{2+} -coordinated polymer complex almost turned off upon the addition of EDTA (Supporting Information Fig. S7), which can be attributed to the release of Zn^{2+} ion from Zn^{2+} -coordinated polymer complex since EDTA shows stronger binding ability for Zn^{2+} than Salen ligand.

CD and CPL Behaviors of Polymers

The CD spectra of polymers **P1** and **P2** were recorded using a JASCO J-810 spectropolarimeter in THF solution at the fixed concentration 1.0×10^{-5} mol L⁻¹). As is evident from Figure 3(a), both the resulting chiral polymers **P1** in THF solution can exhibit the same CD response signals as **P2**



FIGURE 2 Fluorescence spectra of the chiral polymers **P1** (a) and **P2** (b) in THF $(1.0 \times 10^{-5} \text{ mol L}^{-1})$ in the presence of Zn^{2+} (from 0.1 to 4.0 equiv) at the excitation wavelength of 365 nm. [Color figure can be viewed at wileyonlinelibrary.com]

40

30

20

10

0

-10

CD /mdeg



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FIGURE 3 (a) CD spectra of *R*-**P1**/*S*-**P1** and *R*-**P2**/*S*-**P2** in THF solution $(1.0 \times 10^{-5} \text{ mol } L^{-1})$ in the absence of Zn²⁺. (b) CD spectra of *R*-**P1** in THF solution $(1.0 \times 10^{-5} \text{ mol } L^{-1})$ in the presence of Zn²⁺ (from 0 to 2.0 equiv). [Color figure can be viewed at wileyonlinelibrary.com]

with clear mirror image due to similar polymer structure. The strong Cotton effects situated at 255 and 285 nm can be assigned to chiral BINOL moiety. Meanwhile, the long wavelength CD absorption peak appears at 335 nm, which can be regarded as the extended conjugated structure between chiral binaphthyl moiety and Salen group. Upon addition of Zn^{2+} , the Cotton effect of *R*-**P1** at 285 nm shows obvious decrease, but a new peak appears at 365 nm of long wavelength and gradually enhances as the increase of Zn²⁺ molar ratio up to 1:1 [Fig. 3(b); Supporting Information Fig. S8], which can be attributed to the formation of the π -conjugated structure system between the binaphthyl moiety and Salen-Zn(II) complex and the effective chiral transfer from the binaphthyl moiety to Salen-Zn(II) complex. The g_{abs} (365 nm) values can reach as high as 8.3×10^{-4} for **P1** and 1.0×10^{-3} for **P2** at 1:1 molar ratio of Zn²⁺.

In situ Zn(II)-containing chiral polymer complexes could exhibit strong fluorescence enhancement emission and CD absorption in the long wavelength region, which inspired us



FIGURE 4 (a) CPL spectra of *R*-**P1**/*S*-**P1** and *R*-**P2**/*S*-**P2** in THF $(1.0 \times 10^{-5} \text{ mol } \text{L}^{-1})$ in the presence of Zn^{2+} (1 equiv), (b,c) CPL spectra of *R*-**P1** and *R*-**P2** in THF $(1.0 \times 10^{-5} \text{ mol } \text{L}^{-1})$ in the presence of Zn^{2+} (from 0.3 to 2.0 equiv). [Color figure can be viewed at wileyonlinelibrary.com]

to further investigate their CPL behaviors. As the essential parameter of CPL, the optical dissymmetry factors (g_{lum}) can be obtained from $g_{lum} = 2(I_L - I_R)/(I_L + I_R)$, where I_L and I_R are the emission intensities of left and right circularly polarized luminescence, respectively. We found that almost no



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CPL emission signal could be detected for either P1 or P2 in the absence of Zn^{2+} and lower molar ratios at 1:0.1 or 1:0.2 due to very weak fluorescence emission. But we found that the strong CPL emission with clear mirror image can be detected as the increase of Zn^{2+} molar ratio up to 1:0.3, and CPL emission wavelengths at about 465 nm are similar with that of their fluorescence. We assume that the CPL response behavior of chiral BINOL-based polymers can be ampified by fluorescence enhancement effect of Salen-Zn(II) coordination reaction. The $g_{\rm lum}$ can reach as high as 8.5 \times 10⁻³ for **P1** and 8.0 \times 10⁻³ for **P2**. No obvious g_{lum} enhancement can be observed as the increase in Zn^{2+} molar ratio from 0.3 to 4.0 equiv as shown in Figure 4(a,b). Meanwhile, we also found that CPL emission signal almost disappears upon the addition of EDTA due to the degradation of Salen-Zn(II) complex unit and fluorescence quenching. This research work could provide a strategy to develop a higher g_{lum} value of CPLactive polymer materials by metal-coordination fluorescence enhancement.

CONCLUSIONS

Two chiral BINOL-based polymer enantiomers incorporating Salen moiety in the main chain backbone can exhibit "off-on" CPL response signals only in the present of Zn^{2+} ion, which can be attributed to the fluorescence enhancement effect of Salen-Zn(II) coordination reaction and the effective chiral transfer from the binaphthyl moiety to Salen-Zn(II) complex. This work can provide a new design strategy on the amplified CPL materials promoted by metal-coordination chiral complexes.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (21474048, 21674046, and 51673093).

REFERENCES AND NOTES

1 (a) A. Montali, C. Bastiaansen, P. Smith, C. Weder, *Nature* **1998**, *392*, 261; (b) Y. J. Zhang, T. Oka, R. Suzuki, J. T. Ye, Y. Iwasa, *Science* **2014**, *344*, 725; (c) B. A. S. Jose, S. Matsushita, K. Akagi, *J. Am. Chem. Soc.* **2012**, *134*, 19795; (d) M. Li, H. Y. Lu, C. Zhang, L. Shi, Z. Y. Tang, C. F. Chen, *Chem. Commun.* **2016**, *52*, 9921.

2 (a) W. Li, D. Huang, J. Wang, W. Shen, L. Chen, S. Yang, M. Zhu, B. Tang, G. Liang, Z. Xu, *Polym. Chem.* 2015, *6*, 8194; (b) F. Guo, W. Gai, Y. Hong, B. Tang, J. Qin, Y. Tang, *Chem. Commun.* 2015, *51*, 17257; (c) E. M. Sánchez-Carnerero, L. Gartzia-Rivero, F. Moreno, B. L. Maroto, A. R. Agarrabeitia, M. J. Ortiz, J. Bañuelos, I. López-Arbeloa, S. de la Moya, *Chem. Commun.* 2014, *50*, 12765; (d) G. D. Sampedro, E. Palao, A. R. Agarrabeitia, S. de la Moya, N. Boens, M. J. Ortiz, *RSC Adv.* 2014, *4*, 19210; (e) B. He, H. Nie, L. Chen, X. Lou, R. Hu, A. Qin, Z. Zhao, B. Tang, *Org. Lett.* 2015, *17*, 6174; (f) T. Hirano, S. Sugihara, Y. Maeda, *J. Phys. Chem. B* 2013, *117*, 16356

3 (a) S. Ito, K. Ikeda, S. Nakanishi, Y. Imai, M. Asami, *Chem. Commun.* **2017**, *53*, 6323; (b) T. Imagawa, S. Hirata, K. Totani, T. Watanabea, M. Vacha, *Chem. Commun.* **2015**, *51*, 13268; (c)

H. Sakai, S. Shinto, J. Kumar, Y. Arak, T. Sakanoue, T. Takenobu, T. Wada, T. Kawai, T. Hasobe, *J. Phys. Chem. C* **2015**, *119*, 13937; (d) D. Q. He, H. Y. Lu, M. Li, C. F. Chen, *Chem. Commun.* **2017**, *53*, 6093; (e) L. Fang, M. Li, W.B. Lin, Y. Shen, C.F. Chen, *J. Org. Chem.* **2017**, *82*, 7402.

4 (a) Y. Kawagoe, M. Fujiki, Y. Nakanoa, *New J. Chem.* **2010**, *34*, 637; (b) S. T. Duonga, M. Fujiki, *Polym. Chem.* **2017**, *8*, 4673; (c) Y. J. Jin, K. U. Seo, Y. G. Choi, M. Teraguchi, T. Aoki, G. Kwak, *Macromolecules* **2017**, *50*, 6433; (d) Y. Wang, Y. Li, S. Liu, F. Li, C. Zhu, S. Li, Y. Cheng, *Macromolecules* **2016**, *49*, 5444; (e) C. Zhang, M. Li, H. Y. Lu, C. F. Chen, *RSC Adv.* **2018**, *8*, 1014; (f) A. Satrijo, S. C. J. Meskers, T. M. Swager, *J. Am. Chem. Soc.* **2006**, *128*, 9030.

5 (a) T. Ikeda, M. Takayama, J. Kumar, T. Kawai, T. Haino, *Dalton Trans.* **2015**, *44*, 13156; (b) T. Harada, Y. Nakano, M. Fujiki, M. Naito, T. Kawai, Y. Hasegawa, *Inorg. Chem.* **2009**, *48*, 11242; (c) R. Carr, N. H. Evansa, D. Parkera, *Chem. Soc. Rev.* **2012**, *41*, 7673.

6 (a) H. Jintoku, M. T. Kao, A. D. Guerzo, Y. Yoshigashima, T. Masunaga, M. Takafujiac, H. Ihara, *J. Mater. Chem. C* 2015, *3*, 5970; (b) Z. Shen, T. Wang, L. Shi, Z. Tang, M. Liu, *Chem. Sci.* 2015, *6*, 4267; (c) R. B. Alnoman, S. Rihn, D. C. O'Connor, F. A. Black, B. Costello, P. G. Waddell, W. Clegg, R. D. Peacock, W. Herrebout, J. G. Knight, M. J. Hall, *Chem. Eur. J.* 2016, *22*, 93; (d) F. Salerno, J. A. Berrocal, A. T. Haedler, F. Zinna, E. W. Meijer, L. D. Bari, *J. Mater. Chem. C* 2017, *5*, 3609; (e) D. Venkatakrishnarao, C. Sahoo, E. A. Mamonov, V. B. Novikov, Nikolai V. Mitetelo, S. Ram, G. Naraharisetty, T. V. Murzina, R. Chandrasekar, *J. Mater. Chem. C* 2017, *5*, 12349; (f) D. Yang, P. Duan, L. Zhang, M. Liu, *Nat. Commun.*, DOI: 10.1038/ ncomms15727.

7 (a) B. A. S. Jose, J. Yan, K. Akagi, *Angew. Chem.* **2014**, *126*, 10817; (b) J. Park, T. Yu, T. Inagaki, K. Akagi, *Macromolecules* **2015**, *48*, 1930; (c) J. Fan, Y. Li, H. K. Bisoyi, R. S. Zola, D. Yang, T. J. Bunning, D. A. Weitz, Quan Li, *Angew. Chem. Int. Ed.* **2015**, *54*, 2160; (d) A. Bobrovsky, K. Mochalov, V. Oleinikov, A. Sukhanova, A. Prudnikau, M. Artemyev, V. Shibaev, I. Nabiev, *Adv. Mater.* **2012**, *24*, 6216.

8 (a) J. F. Cui, M. Ko, K. P. Shing, J. R. Deng, N. C. H. Lai, M. K. Wong, *Angew. Chem. Int. Ed.* **2017**, *56*, 3074; (b) G. Mirri, S. D. Bull, P. N. Horton, T. D. James, L. Male, J. H. R. Tucker, *J. Am. Chem. Soc.* **2010**, *132*, 8903; (c) A. P. Smalley, J. D. Cuthbertson, M. J. Gaunt, *J. Am. Chem. Soc.* **2017**, *139*, 1412; (d) J. H. Tay, A. J. Arguelles, P. Nagorny, *Org. Lett.* **2015**, *17*, 3774; (e) Z. B. Li, L. Pu, *Org. Lett.* **2004**, *6*, 1065.

9 (a) E. M. Sánchez-Carnerero, F. Moreno, B. L. Maroto, A. R. Agarrabeitia, M. J. Ortiz, B. G. Vo, G. Muller, S. de la Moya, J. Am. Chem. Soc. 2014, 136, 3346; (b) R. Aoki, R. Toyoda, J. F. Koğel, R. Sakamoto, J. Kumar, Y. Kitagawa, K. Harano, T. Kawai, H. Nishihara, J. Am. Chem. Soc. 2017, 139, 16024; (c) S. Feuillastre, M. Pauton, L. Gao, A. Desmarchelier, A. J. Riives, D. Prim, D. Tondelie, B. Geffroy, G. Muller, G. Clavier, J. Am. Chem. Soc. 2016, 138, 3990; (d) S. Nakanishi, N. Hara, N. Kuroda, N. Tajima, M. Fujiki, Y. Imai, Org. Biomol. Chem. 2018, 16, 1093; (e) M. S. Sundar, H. R. Talele, H. M. Mande, A. V. Bedekar, R. C. Tovar, G. Muller, Tetrahedron Lett. 2014, 55, 1760; (f) F. Song, Z. Xu, Q. Zhang, Z. Zhao, H. Zhang, W. Zhao, Z. Qiu, C. Qi, H. Zhang, H. H. Y. Sung, I. D. Williams, J. W. Y. Lam, Z. Zhao, A. Qin, D. Ma, B. Z. Tang, Adv. Funct. Mater. DOI: 10.1002/adfm.201800051.

10 (a) J. Kumar, H. Tsumatori, J. Yuasa, T. Kawai, T. Nakashima, *Angew. Chem.* **2015**, *127*, 6041; (b) T. Ikeda, T. Masuda, T. Hirao, J. Yuasa, H. Tsumatori, T. Kawai, T. Haino, *Chem. Commun.* **2012**, *48*, 6025.

11 (a) S. Zhang, Y. Sheng, G. Wei, Y. Quan, Y. Cheng, C. Zhu, *Polym. Chem.* **2015**, *6*, 2416; (b) F. Meng, Y. Li, W.Zhang, S. Li, Y. Quan, Y. Cheng, *Polym. Chem.* **2017**, *8*, 1555.

12 P. G. Cozzi, Chem. Soc. Rev. 2004, 33, 410.

13 Y. Xu, J. Meng, L. Meng, Y. Dong, Y. Cheng, C. Zhu, *Chem. Eur. J.* **2010**, *16*, 12898.

14 (a) F. R. Michailidis, M. R. Michaelides, M. Pupier, A. Alexakis, *Chem. Eur. J.* **2015**, *21*, 5561; (b) M. Vidal, A.

Schmitzer, *Chem. Eur. J.* **2014**, *20*, 9998; (c) M. S. More, S. B. Pawal, S. R. Lolage, S. S. Chavan, *J. Mol. Struct.* **2017**, *1128*, 419.

15 (a) Z. Xu, K. H. Baek, H. N. Kim, J. Cui, X. Qian, D. R. Spring, I. Shin, J. Yoon, *J. Am. Chem. Soc.* **2010**, *132*, 601; (b) J. N. Ngwendson, A. Banerjee, *Tetrahedron Lett.* **2007**, *48*, 7316. (c) J. Hou, F. Song, L. Wang, G. Wei, Y. Cheng, C. Zhu, *Macromolecules* **2012**, *45*, 7835; (d) L. Pu, *Chem. Rev.* **1998**, *98*, 2405.

