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Fluorescent OFF–ON polymer chemosensor bonded alternatively with 1,4-dioctyloxybenzene and (*R*,*R*)-salen for cascade Zn^{2+} and chiral recognition

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ABSTRACT

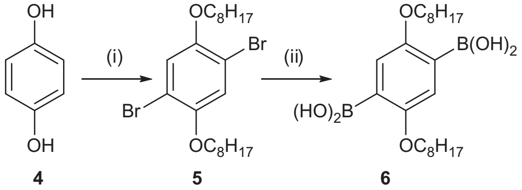
The synthesis of the chiral main chain polymers **1a**–**b** bonded alternatively with (*R*,*R*)-salen and 1,4-dioctyloxybenzene has been described employing a palladium-catalyzed C–C cross-coupling reaction as the key step. They are soluble in common organic solvents and act as a highly selective '*OFF–ON*' fluorescent chemosensors toward Zn^{2+}. The resultant Zn(II)-polymer complexes exhibit significant chiral recognition toward (*R*)- and (*S*)-1-phenyl-*N*-[(pyridin-2-yl)methylene]ethanamines **9** under ambient conditions.

1. Introduction

The detection of metal ions found in biological systems and in the environment has received considerable attention in recent years, as these ions can be either beneficial or toxic to human health.[1] Among them, Zn^{2+} is the second most essential transition metal ion for the human body, and plays an indispensable role in various biological processes, such as gene transcription, cell apoptosis, regulation of metalloenzymes, neural signal transmission, and insulin secretion.[2] The deviation of Zn^{2+} concentration from normal levels causes diabetes and many severe neurological diseases including epilepsy and Alzheimer's disease.[3] Thus, the selective detection of Zn^{2+} in various samples is of vital toxicological and environmental importance. However, unlike other transition metal ions such as Cu^{2+}, Co^{2+}, and Ni^{2+}, Zn^{2+} does not give any spectroscopic or magnetic signals due to its complete valence shell electronic configuration. In this context, the fluorometric detection of Zn^{2+} has been appealing since it is easy to perform with high sensitivity.[4] Numerous scientific endeavors have thus been made in the development of fluorescent Zn^{2+} probes based on small molecules, such as quinolines,[5] rhodamine,[6] bis(benzoxazole),[7] bipyridine,[8] spirobenzopyravarien,[9] anthracene,[10] naphthalimide[11] and tricarbocyanine,[12] peptides,[13] and nanoparticles.[14] More recently, a few studies have focused on the use of stereoregular organic polymers for this purpose,[4a,15] because the selective coordination and binding of certain metal ions to the chromophoric site of the polymers can greatly influence the optical properties of the materials, making them promising candidates for sensors.[16] In conjugated polymers, a small change in the chromophoric site can generate a signal, which can be amplified through the delocalized π-electron cloud of the polymer backbone to produce an effective optical response in comparison to small molecules as chemosensors.[15f,g] In continuation of our studies on stereoregular polymers,[4a,17a,b] we herein report the synthesis and application of new chiral main chain polymers **1a**–**b** for the highly selective recognition of Zn^{2+} as *OFF–ON* fluorescent chemosensors. The resultant Zn(II)-polymer complexes exhibited significant chiral recognition toward (*R*)- and (*S*)-1-phenyl-*N*-[(pyridin-2-yl)methylene]ethanamines **9** under ambient conditions.

2. Results and discussion

The reaction of 1,4-hydroquinone **4** with 1-bromooctane in the presence of K_2CO_3 gave 1,4-dioctyloxybenzene, which could be brominated using Br_2 to afford 1,4-dibromo-2,5-dioctyloxybenzene **5** in 85% yield. Compound **5** was then reacted with trimethoxyborane in the presence of *n*-BuLi followed by acid hydrolysis to give 2,5-dioctyloxyphenyldiboronate **6** in 80% yield (Scheme 1).[17b,c]



Scheme 1. Reagents and conditions: (i) $C_8H_{17}Br$ (2.5 equiv), K_2CO_3 (2.5 equiv), EtOH, 70 °C, 24 h, 80%; (ii) Br_2, $CHCl_3$, 0 °C to rt, 27 h, 90%; (iii) *n*-BuLi (2.3 equiv), $B(OMe)_3$ (2.5 equiv), Et_2O, −20 °C to rt, 12 h, 2 N HCl, rt, 0.5 h, 80%.

The chemoselective reaction of 2,4-dihydroxybenzaldehyde **7** with trifluoromethanesulfonic anhydride in the presence of pyridine gave 4-formyl-3-hydroxyphenyl trifluoromethanesulfonate[4a,18] **8** in 60% yield, which could be C-C cross-coupled with **6**

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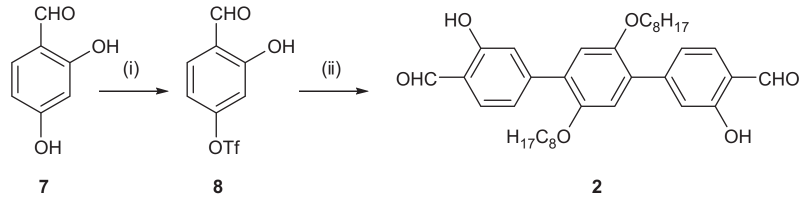


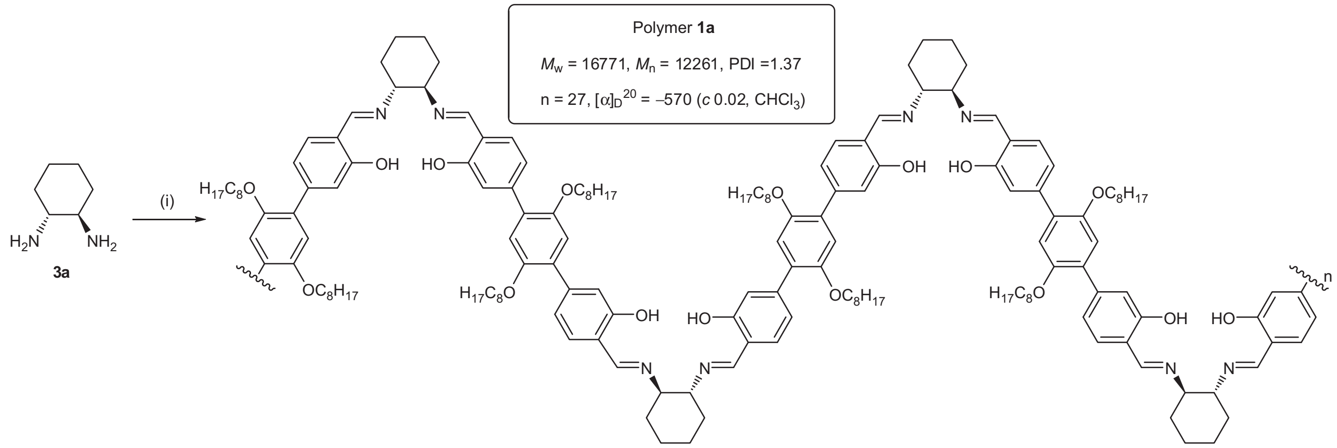
Scheme 2. Reagents and conditions: (i) Tf_2O (1 equiv), pyridine (1 equiv), CH_2Cl_2, 0 °C-rt, 27 h, 60%; (ii) 2,5-dioctyloxyphenyldiboronate **6** (0.5 equiv), $Pd(PPh_3)_2Cl_2$ (3 mol %), PPh_3 (9 mol %), K_2CO_3 (3 equiv), THF, reflux, 24 h, 80%.

using $Pd(PPh_3)_2Cl_2$ to afford the desired dialdehyde **2** in 80% yield (Scheme 2).[19]

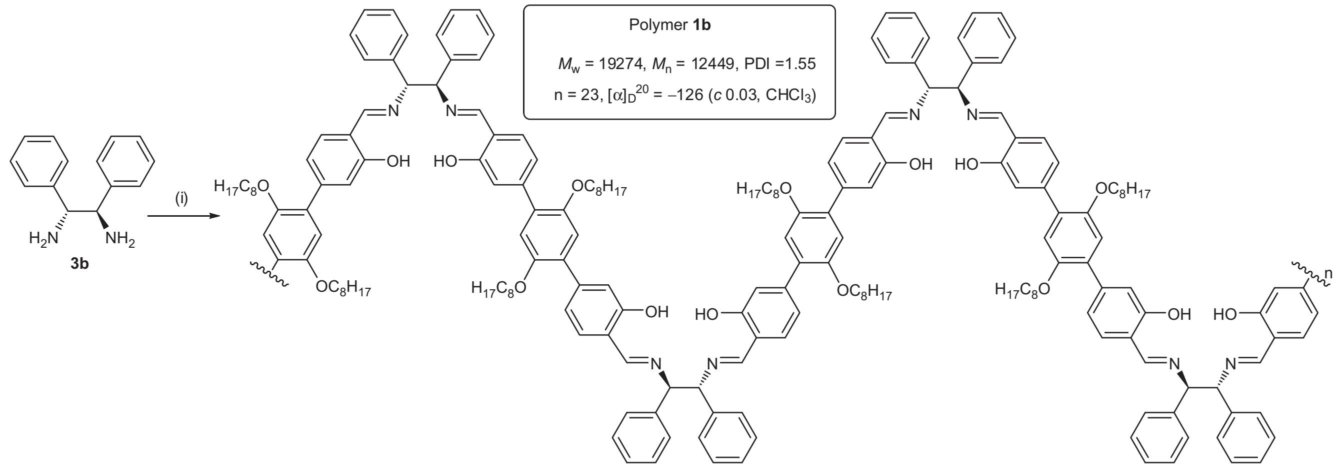
Dialdehyde **2** was then used in a Schiff base formation with (*R*,*R*)-1,2-diaminocyclohexane **3a** and (*R*,*R*)-1,2-diphenylethylenediamine **3b** upon heating in $CHCl_3$ to give the polymers **1a-b** as yellow powders (Schemes 3 and 4).[4a,17a–b,20] The octyloxy substituent on the polymer backbone helps them to be soluble in common organic solvents such as THF, $CHCl_3$, and CH_2Cl_2. GPC analysis, with polystyrene as an internal standard and THF as an eluent, was used to determine their average molecular weights, which corresponded to ca. 27 repeating units for **1a** (M_w = 16771, M_n =12261 and PDI = 1.37) and ca. 23 repeating units for **1b** (M_w = 19274, M_n = 12449 and PDI = 1.55). The ^{1}H NMR spectra recorded at 400 MHz were found to be consistent with their structures.

Figure 1 illustrates the UV-vis, fluorescence and TGA of polymers **1a–b**. The UV–vis spectra showed absorption maxima at *ca.*289 ($\varepsilon = 2.60 \times 10^4$ $M^{-1}cm^{-1}$) and 349 nm ($\varepsilon = 2.98 \times 10^4$ $M^{-1}cm^{-1}$) for **1a**, and 290 ($\varepsilon = 2.77 \times 10^4$ $M^{-1}cm^{-1}$) and 352 nm ($\varepsilon = 3.21 \times 10^4$ $M^{-1}cm^{-1}$) for **1b**, respectively, due to π–π^* transition. Regarding fluorescence, **1a** emitted a weak blue light at 423 and 521 nm (λ_{ex} = 360 nm), and **1b** at 421 and 519 nm (λ_{ex} = 360 nm). Thermal analysis showed that the polymers **1a-b** were thermally stable up to ca. 270 °C and a total weight loss of 58–68% was observed upon a gradual increase in temperature to 600 °C.

The fluorescent nature of polymers **1a**–**b** prompted us to evaluate them as chemosensors for the detection of various common metal ions. Interestingly, polymers **1a**–**b** exhibited the best selectivity toward Zn^{2+} as an *OFF–ON* hemosensor compared with other metal ions such as Na^+, Ag^+, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Al^{3+}, and Ce^{3+} (Fig. 2). Polymer **1b** was found to be superior to **1a** with an enhancement in the fluorescence. Figure 3 illustrates the



Scheme 3. Reagent and conditions: (i) dialdehyde **2** (1 equiv), $CHCl_3$, 45 °C, 3 h, 91%.



Scheme 4. Reagent and conditions: (i) dialdehyde **2** (1 equiv), $CHCl_3$, 45 °C, 3 h, 97%.

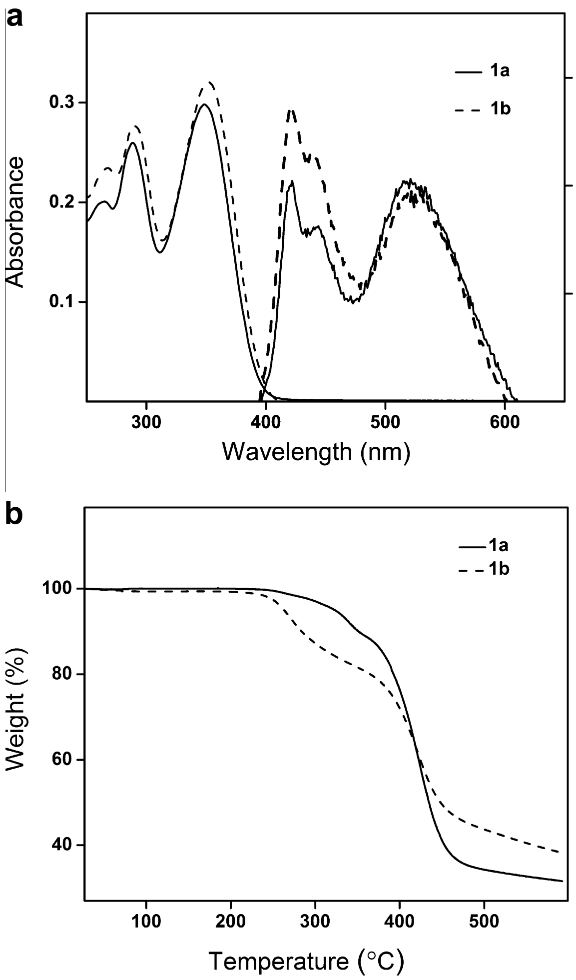


Figure 1. The polymers **1a–b**: (a) UV–vis and fluorescence spectra (1×10^{-5} M in THF) and (b) TGA.

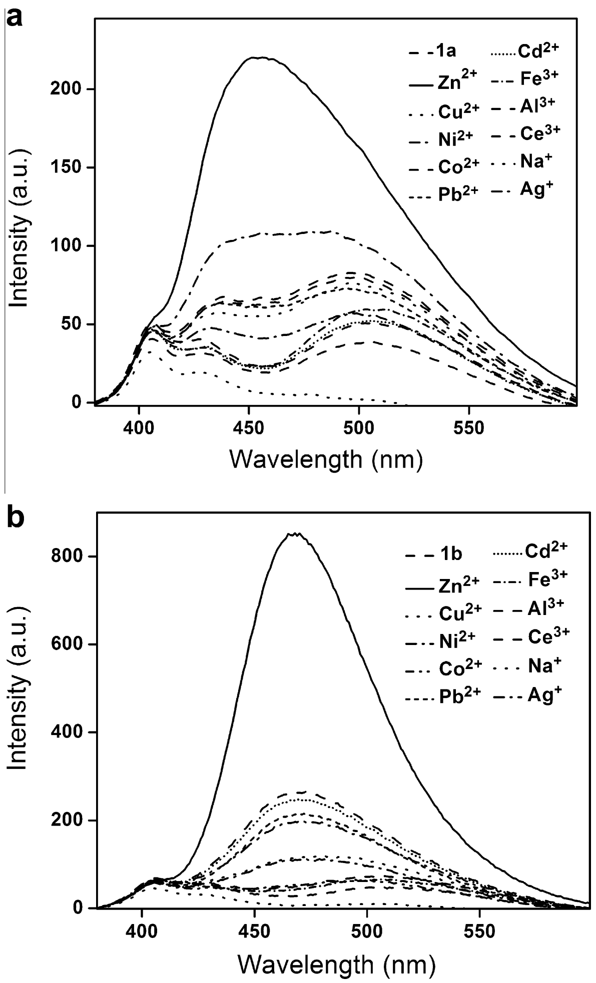


Figure 2. Fluorometric titration: (a) **1a** (λ_{ex} = 360 nm) and (b) **1b** (λ_{ex} = 360 nm) (1×10^{-5} M in THF) with different metal nitrate salts (3×10^{-4} M in water, 1 equiv with respect to the monomeric unit).

images of fluorescence of **1b** without (a) and with (b) Zn^{2+}, while (c) shows the graphical presentation of the selectivity of **1b** with different metal ions. Polymer **1b** with Zn^{2+}emits a strong blue fluorescence, which could be attributed to the reduced non-radiative decay of the Zn(II)-polymer complex excited state and the quenching contributed from the lone pair of electrons of the nitrogen through internal charge transfer (ICT).[1b,21] In addition, a blue shift (~50 nm) in the emitted light was observed, which could be caused by a decrease in energy of the HOMO of the polymer upon the formation of the Zn(II)-polymer complex.[22]

Polymer **1b** was further studied with various Zn^{2+} concentrations (Fig. 4). The absorption band at 290 nm slightly shifted to 293 nm with a gradual decrease of intensity. The isosbestic points at 296 and 366 nm indicate the formation of a Zn(II)-polymer complex.

Next, the sensing selectivity of polymer **1b** with different Zn^{2+}concentrations was studied (Fig. 5a). The weakly emissive **1b** (THF, 1×10^{-5} M) at ca. 519 nm, upon addition of Zn^{2+} (3×10^{-4} M), exhibited a blue-shifted emission at 471 nm. The enhancement in intensity of the emission band was proportional to the Zn^{2+} concentration. When the Zn^{2+}concentration was 1.1 equiv with respect to the monomer unit of the polymer **1b**, the fluorescence intensity increased to a maximum 22-fold enhancement. Further enhancement in the addition of Zn^{2+} concentration led to no change in the fluorescence intensity. By applying a Hill plot to this titration data (Fig. 5b), the stability constant of Zn(II)-polymer **1b** complex was calculated as 1.62×10^8 M^{-1}.[23]

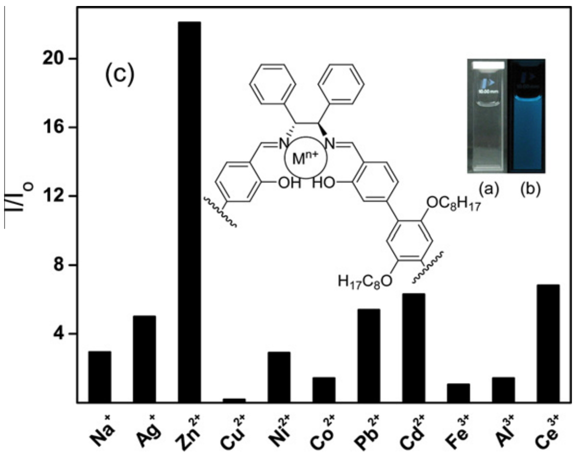


Figure 3. The polymer **1b** (1×10^{-5} M in THF): (a) fluorescence image without Zn^{2+} and (b) fluorescence image with 1 equiv Zn^{2+} (3×10^{-4} M in water) (both are excited using a commercially available UV lamp (λ = 360 nm). (c) The selectivity of **1b** (1×10^{-5}M in THF) with metal ions (3×10^{-4} M in water).

The use of fluorometric titration for the enantioselective recognition of chiral compounds has received considerable attention in recent years.[24] Since the Zn(II)-polymer complexes are optically active and pyridine is known to cause chelation to Zn^{2+} with

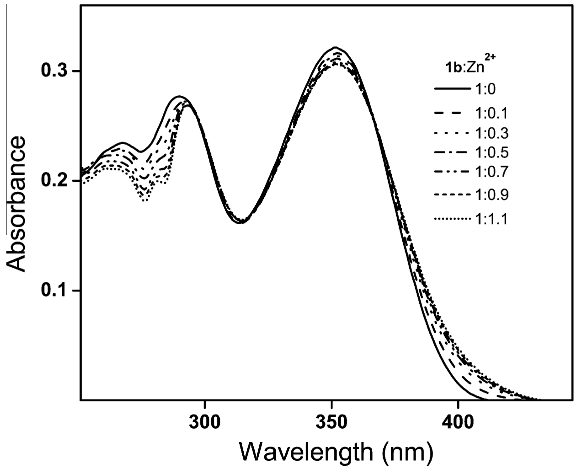


Figure 4. UV–vis titration of **1b** (1×10^{-5} M in THF) with 0.1–1.1 equiv of Zn^{2+} ion (3×10^{-4} M in water with respect to the monomeric unit of **1b**).

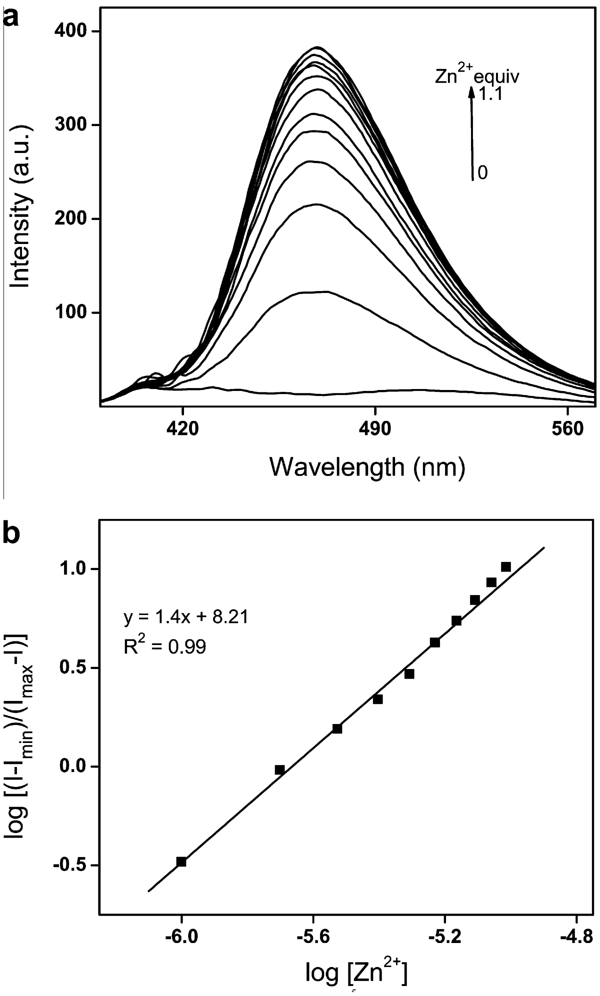


Figure 5. (a) Fluorometric titration of **1b** (1×10^{-5} M in THF, λ_{ex} = 360 nm) with 0.1–1.1 equiv of Zn^{2+} ion (3×10^{-4} M in water, with respect to the monomeric unit of **1b**). (b) Hill plot of **1b** with 0.1–1.1 equiv of Zn^{2+} (with respect to monomeric unit of **1b**).

enhanced fluorescence,[4a,25] the in situ generated Zn(II) complexes of polymers **1a–b** with Zn^{2+} were studied for the selective recognition of chiral imines (*R*)-**9** and (*S*)-**9** bearing the pyridine moiety (Figs. 6 and 7 and Table 1).

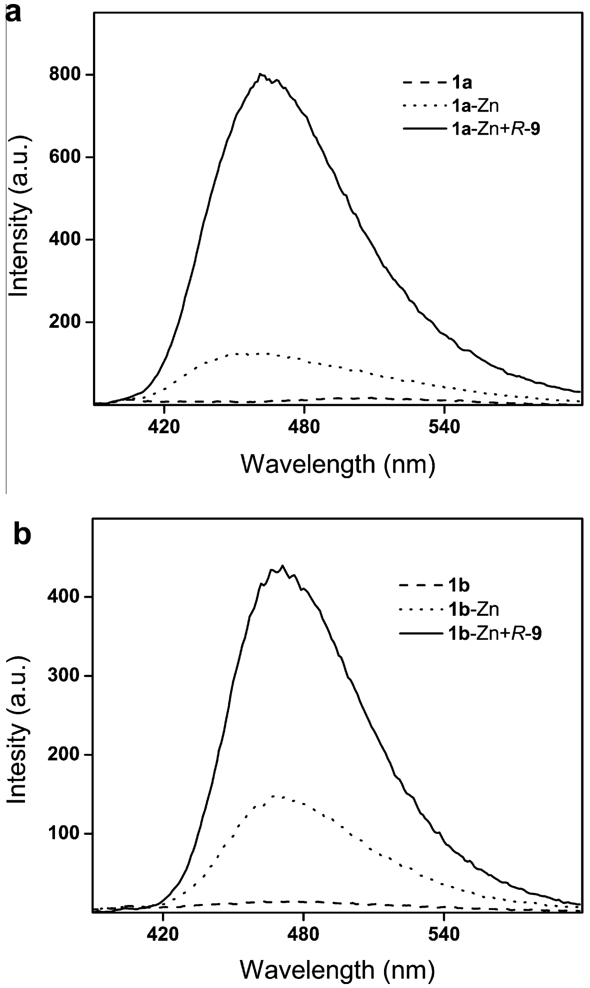


Figure 6. Fluorescence spectra (λ_{ex} = 360 nm): (a) **1a**, **1a** + Zn^{2+} and **1a** + Zn^{2+}**+** *R*-**9** and (b) **1b**, **1b** + Zn^{2+} and **1b** + Zn^{2+}**+** *R*-**9** (1×10^{-5} M in THF) [12 equiv of (*R*)-**9** with respect to Zn(II)-polymer complex].

The Zn(II)-polymer complexes exhibited significant enantioselective recognition toward (*R*)-1-phenyl-*N*-[(pyridin-2-yl)methylene] ethanamine (*R*)-**9** and (*S*)-1-phenyl-*N*-[(pyridin-2-yl)- methylene]ethanamine (*S*)-**9**. In these experiments, an excess of imines (*R*)- or (*S*)-**9** (1–18 equiv) could drive the equilibrium toward the right to ensure enantiomeric differentiation through distinct enhanced fluorescence difference (Scheme 5).[25b] Thus, the fluorescent '*OFF*' polymers **1a**–**b** may form complexes with Zn^{2+} to give fluorescent '*ON*' Zn(II)-polymer complexes that could enantioselectively recognize (*R*)-**9** and (*S*)-**9** to afford enhanced fluorescent Zn(II)-polymer-**9** complexes. Experiments with (*R*)-**9** ($(I_R/I_o)_{max}$ = 6.78 and 3.19, respectively, for **1a** and **1b**) showed higher fluorescence intensity compared to that with (*S*)-**9** [$(I_S/I_o)_{max}$ = 5.94 and 2.58, respectively, for **1a** and **1b**]. The enhancement in the fluorescence of the Zn(II)-polymer-**9** complex was due to the reduced secondary Zn—O interactions between the salen unit.[4a,26] The $\Delta(I/I_o)_{max}$ corresponds to 0.91 and 0.61 for the Zn(II)-polymer **1a** and Zn(II)-polymer **1b** complexes, respectively, which suggests that the Zn(II)-polymer **1a** complex could strongly discriminate between enantiomers (*R*)-**9** and (*S*)-**9** compared with Zn(II)-polymer **1b** complex.

3. Conclusion

The synthesis of chiral main chain polymers **1a–b** with (*R*,*R*)-salen and 1,4-dioctyloxybenzene moieties has been accomplished via a C–C cross-coupling reaction as the key step. These chiral mate-

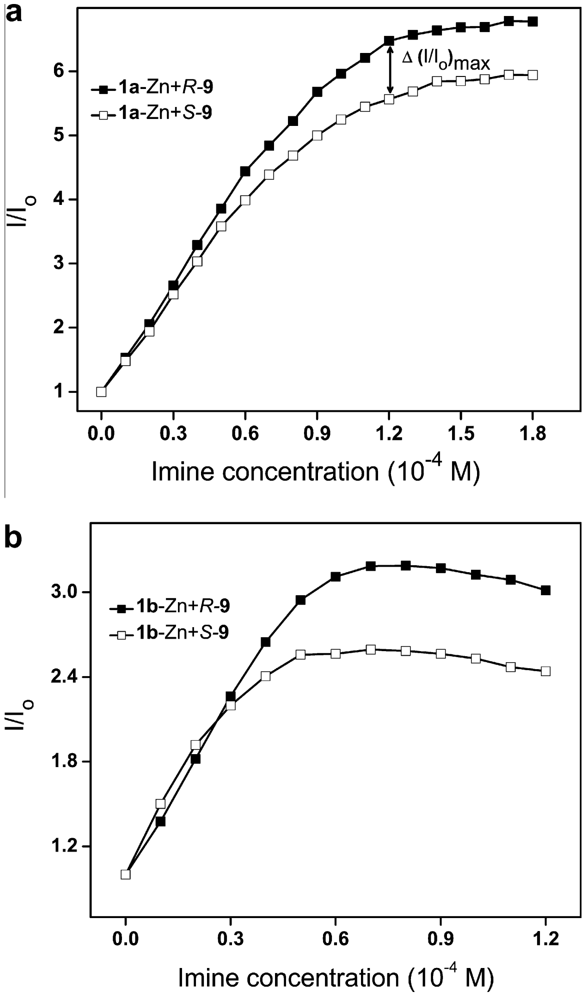
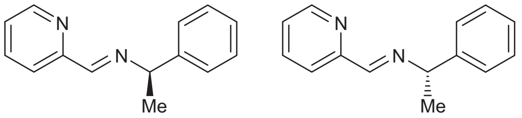


Figure 7. Chiral recognition of the Zn(II)-polymer **1a–b** complexes (generated *in situ* from 1×10^{-5} M of **1a–b** in THF and 12×10^{-4} M of Zn^{2+}in water (1:1.1)) with 1–18 equiv of (*R*)-**9** and (*S*)-**9** (6×10^{-3} M in THF). $\Delta(I/I_o)_{max}$ corresponds to 0.91 and 0.61, respectively, for (a) and (b).

Table 1

Chiral recognition of (*R*)-**9** and (*S*)-**9** with Zn^{2+}-polymer complexes



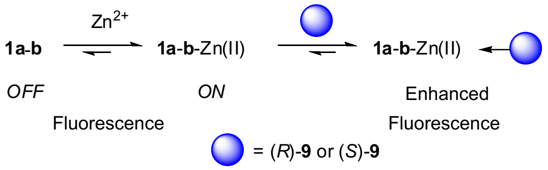
(*R*)-**9** (*S*)-**9**

Zn^{2+}-polymer [c_1][a]	Enantiomer	$(I/I_o)_{max}$	K (M^{-1})[b]
Zn^{2+}-**1a**	(*R*)-**9**	6.78	3.02×10^4
Zn^{2+}-**1a**	(*S*)-**9**	5.94	2.04×10^4
Zn^{2+}-**1b**	(*R*)-**9**	3.19	6.60×10^4
Zn^{2+}-**1b**	(*S*)-**9**	2.58	5.62×10^4

[a] [c_1] = 1×10^{-5} M in THF.

[b] K = stability constant calculated from a linear Hill plot with 1:1 binding model to the fluorescence enhancement.

rials are soluble in common organic solvents and serve as highly selective fluorescent chemosensors toward Zn^{2+}. Polymer **1b** with (*R*,*R*)-1,2-diphenylethylenediamine and Zn^{2+} exhibited the best fluorescence enhancement as an *OFF–ON* chemosensor. In addition, the resultant Zn(II)-polymer complexes showed significant enantioselective discrimination toward (*R*)- and (*S*)-1-phenyl-*N*-[(pyridin-2-yl)methylene]ethanamines under ambient conditions.



Scheme 5. Plausible mechanism for fluorescence chiral recognition.

4. Experimental section

4.1. General

2,4-Dihydroxybenzaldehyde (98%), trifluoromethane-sulfonic anhydride ($\geqslant$99%), hydroquinone ($\geqslant$99%), (trimethylsilyl)acetylene (98%), octyl bromide (99%), trimethyl borate ($\geqslant$98%), *n*-BuLi (2.0 M in cyclohexane), $Pd(PPh_3)_2Cl_2$ (98%), CuI (98%), PPh_3 (99%) $Ce(NO_3)_3{\cdot}6H_2O$ ($\geqslant$98%), $Cd(NO_3)_2{\cdot}4H_2O$ ($\geqslant$99%) and $Zn(NO_3)_2{\cdot}6H_2O$ (98%) were purchased from Aldrich. $Co(NO_3)_2{\cdot}6H_2O$ (97%), $Cu(NO_3)_2{\cdot}3H_2O$ ($\geqslant$99%), $Ni(NO_3)_2{\cdot}6H_2O$ (98%), $Al(NO_3)_3{\cdot}9H_2O$ ($\geqslant$95%) and $NaNO_3$ ($\geqslant$99%) were purchased from Merck. $Fe(NO_3)_3{\cdot}9H_2O$ (98%), $Pb(NO_3)_2$ (98%) and $AgNO_3$ (99%) were purchased from Rankem and used as received without further purification. Et_2O and THF were freshly distilled from sodium and benzophenone under nitrogen prior to use. Column chromatography was carried out with Rankem 60–120 mesh silica gel. Analytical TLC was performed with Rankem silica gel G and GF 254 plates. NMR spectra (400 MHz for ^1H and 100 MHz ^{13}C) were recorded on a DRX-400 Varian spectrometer using $CDCl_3$ as solvent and Me_4Si as an internal standard. Chemical shifts (δ) are reported in ppm and spin–spin coupling constants (*J*) are given in Hz. Melting points were determined using a Buchi B-540 and are uncorrected. IR spectra were recorded using a Perkin–Elmer spectrum one spectrometer. UV-vis spectra were recorded on Perkin–Elmer Lambda 25 UV/vis spectrometer. Fluorescence spectra were recorded on a Varian Carey Eclipse fluorescence spectrophotometer. GPC analysis was performed with the stationary phase column Styragel® WAT044221 using polystyrene as an internal standard and THF as eluent. The optical rotation was measured on a PerkinElmer model-343. Thermal gravimetric analysis was performed on SDT Q600 under a nitrogen atmosphere. Elemental analysis was carried out using a Perkin–Elmer 2400 CHNS analyzer.

4.2. Preparation of the dialdehyde 2

4-Formyl-3-hydroxyphenyl trifluoromethanesulfonate **8** (7.2 mmol, 1.94 g), 2,5-di(octyloxy)phenyldiboronate **6** (3.4 mmol, 1.44 g), $Pd(PPh_3)_2Cl_2$ (6 mol %), PPh_3(18 mol%) and K_2CO_3 (20.4 mmol, 2.8 g) were stirred at reflux for 24 h in THF (30 mL) under a nitrogen atmosphere. The solvent was then evaporated on a rotary evaporator to give a residue, which was dissolved in EtOAc (30 mL) and washed with brine (5 mL) and water (2×10 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a solid, which was purified by silica gel column chromatography using EtOAc and hexane as eluent to give **2** as a yellow solid in 80% yield. Mp 115 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 11.07 (s, 2H), 9.92 (s, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.27 (t, *J* = 8.0 Hz, 2H), 7.19 (s, 2H), 6.96 (s, 2H), 3.93 (t, *J* = 6 Hz, 4H), 1.69 (t, *J* = 6.8 Hz, 4H), 1.35–1.23 (m, 20H) 0.85 (t, *J* = 6.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2, 161.5, 150.5, 147.4, 133.2, 130.3, 121.8, 119.6, 118.5, 115.8, 69.7, 32.0, 29.4, 26.2, 22.8, 14.3; FT-IR (KBr) 3055, 2923, 2853, 1645, 1621, 1557, 1520, 1493, 1467, 1434, 1392, 1371, 1317, 1266, 1211, 1198, 1134, 1055, 1030, 971, 939, 904, 883, 818, 741, 717, 587, 513 cm^{-1}. Anal. Calcd for $C_{36}H_{46}O_6$: C, 75.23; H, 8.07. Found: C, 75.19; H, 8.11.

4.3. Synthesis of polymers 1a–b

4.3.1. Polymer 1a

To a stirred solution of dialdehyde **2** (1.8 mmol, 1.04 g) in $CHCl_3$ (5 mL) was added (1*R*,2*R*)-diamino-cyclohexane **3a** (1.8 mmol, 0.205 g) and the resultant mixture was stirred at 45 °C for 3 h. The reaction mixture was then concentrated (ca. 2 mL) and treated with MeOH (3 mL). The resultant precipitate **1a** was collected by filtration as a yellow powder in 91% (1.06 g) yield. GPC: M_w = 16771, M_n = 12261 (PDI 1.37); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 2H), 7.21–7.07 (m, 6H), 6.91 (s, 2H), 3.84 (t, *J* = 8.6 Hz, 4H), 3.35 (s, 2H), 1.92–1.20 (m, 32 H), 0.83 (t, *J* = 7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 160.8, 150.4, 142.6, 131.0, 130.4, 120.4, 117.8, 117.6, 116.1, 72.8, 69.6, 33.4, 31.9, 29.3, 26.1, 24.4, 22.8, 14.3; FT-IR (KBr) 3440, 2926, 2855, 1622, 1563, 1491, 1468, 1367, 1205, 1142, 1037, 936, 863, 813 cm^{-1}; UV-vis ($CHCl_3$): λ_{max} (ε) = 289 (2.60×10^4), 349 (2.98×10^4) nm ($M^{-1}cm^{-1}$); fluorescence (THF): λ_{ex} = 360 nm; λ_{em} = 423, 521 nm; $[\alpha]_D^{20} = -570$ (*c* 0.02, $CHCl_3$). Anal. Calcd for $(C_{42}H_{56}N_2O_4)_n$: C, 77.26; H, 8.65; N, 4.29. Found: C, 77.19; H, 8.67; N 4.23.

4.3.2. Polymer 1b

To a stirred solution of dialdehyde **2** (1.8 mmol, 1.04 g) in $CHCl_3$ (5 mL) was added (1*R*,2*R*)-diphenylethylenediamine **3b** (1.8 mmol, 0.382 g) and the resultant mixture was stirred at 45 °C for 3 h. The isolation of **1b** was carried out as described for **1a** as a yellow powder in 97% (1.26 g) yield. GPC: M_w = 19274, M_n = 12449 (PDI 1.55); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 2H), 7.19–7.08 (m, 16H), 6.92 (s, 2H), 4.77 (s, 2H), 3.84 (t, *J* = 6.4 Hz, 4H), 1.62–1.19 (m, 24 H), 0.80 (t, *J* = 6.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 160.8, 150.4, 143.1, 139.8, 131.2, 130.4, 128.5, 128.1, 127.8, 120.7, 117.9, 117.6, 116.1, 80.4, 69.7, 31.9, 29.4, 26.2, 22.8, 14.3; FT-IR (KBr) 3435, 3029, 2924, 2853, 1622, 1561, 1490, 1467, 1454, 1367, 1260, 1207, 1137, 1027, 935, 865, 812, 766, 698, 603 cm^{-1}; UV-vis ($CHCl_3$): λ_{max} (ε) = 290 (2.77×10^4), 352 (3.21×10^4) nm ($M^{-1}cm^{-1}$); fluorescence (THF): λ_{ex} = 360 nm; λ_{em} = 421, 519 nm; $[\alpha]_D^{20} = -126$ (*c* 0.03, $CHCl_3$). Anal. Calcd for $(C_{50}H_{58}N_2O_4)_n$: C, 79.96; H, 7.78; N, 3.73. Found: C, 79.91; H, 7.81; N, 3.76.

4.4. Metal ion titration

The solutions of polymers **1a-b** (3 mL, 1×10^{-5} M in THF with respect to the monomeric unit) and metal nitrate salts (100 μL, 3×10^{-4} M in water, 1 equiv) were thoroughly mixed at ambient temperature to produce the corresponding metal-polymer complexes (Fig. 2). After 5 min, the fluorescent properties of the solution with the in situ generated metal-polymer complexes were measured.

4.5. Preparation of 1-phenyl-*N*-[(pyridin-2-yl)methyl-ene]ethanamines (*R*)-9 and (*S*)-9[27a–b]

To a stirred solution of pyridine-2-carboxaldehyde (1 mmol, 107 mg) in CH_3OH (1 mL), (*R*)- or (*S*)-1-phenylethanamine (1 mmol, 121 mg) was added and the resulting solution was stirred at room temperature for 3 h. The solvent was evaporated on a rotary evaporator to give a residue, which was dissolved in EtOAc (10 mL) and washed with brine (5 mL) and water (2×10 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue, which was purified on basic silica gel column chromatography using EtOAc and hexane as eluent to give (*R*)-**9** or (*S*)-**9** as a yellow liquid in 97% (203 mg) yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.62 (d, *J* = 4.8 Hz, 1H), 8.47 (s, 1H), 8.08 (d, *J* = 8 Hz, 1H), 7.71 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.39–7.23 (m, 4H), 4.65 (q, *J* = 13.2, 6.8 Hz, 1H), 1.62 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 154.8, 149.4, 144.6, 136.6, 128.6, 127.1, 126.8, 124.8, 121.5, 69.6, 24.6; FT-IR (neat) 3060, 2972, 2926, 2861, 1587, 1567, 1467, 1436, 1371, 1080, 993, 908, 762, 699, 549 cm^{-1}; (*R*)-enantiomer (*R*)-**9** $[\alpha]_D^{20} = -34.1$ (*c* 1.05, $CHCl_3$). Anal. Calcd for $C_{14}H_{14}N_2$: C, 79.97; H, 6.71; N, 13.32. Found: C, 79.90; H, 6.73; N, 13.37. (*S*)-enantiomer (*S*)-**9** $[\alpha]_D^{20} = +34.8$ (*c* 1.04, $CHCl_3$); lit.[27b] $[\alpha]_D^{20} = +85$ (*c* 0.6, $CHCl_3$). Anal. Calcd for $C_{14}H_{14}N_2$: C, 79.97; H, 6.71; N, 13.32. Found: C, 79.92; H, 6.73; N, 13.35.

4.6. Enantioselective fluorescent recognition

A solution of polymers **1a–b** (3 mL, 1×10^{-5} M in THF with respect to monomeric unit) and $Zn(NO_3)_2{\cdot}6H_2O$ (28 μL, 12×10^{-4} M in H_2O, 1.1 equiv) was thoroughly mixed at ambient temperature to produce the respective Zn(II)-polymer complexes. After 5 min, they were treated with (*R*)-**9** or (*S*)-**9** (5–90 μL (1–18 equiv), 6×10^{-3} M in THF). The solutions were mixed and left for 5 min at ambient temperature to generate the corresponding Zn(II)-polymer-(*R*)-**9** or (*S*)-**9** complexes. The fluorescence of the respective solutions was measured with λ_{ex} = 360 nm.

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