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Fluorescent non-linear chiral polymer chemosensor bonded alternatively with 1,4-diethynyl-2,5-dioctyloxybenzene and (*R*,*R*)-salen for Zn^{2+}recognition

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ABSTRACT

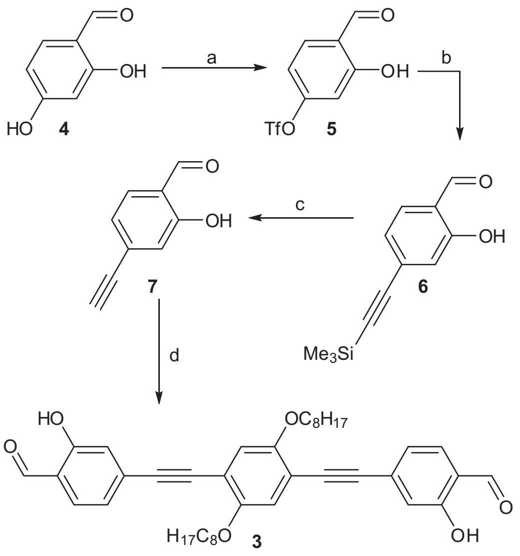
Stereoregular non-linear chiral main chain polymers **1a**–**b** bonded alternatively with (*R*,*R*)-salen and 1,4-diethynyl-2,5-dioctyloxybenzene moieties have been synthesized using palladium catalyzed C–C cross-coupling and Schiff base formation reactions as the key steps. These polymers are soluble in common organic solvents, and act as an effective chemosensor for the detection of Zn^{2+} with respect to other metal ions with enhanced fluorescence. The CD spectra observed for the polymers **1a**–**b** could be attributed to the helical secondary structure with a low degree of inter-strand interactions. This reduced inter-strand interaction has been ascertained from the titration of pyridine to the Zn(II)-polymer **1b** complex, which results in minor changes in the fluorescence emission.

1. Introduction

The study of stereoregular organic polymers is an active topic due to their remarkable electronic and optical properties.[1,2] Much effort has been made to control the bulk properties of these materials by a design strategy based on molecular engineering.[3] Chiral main chain polymers are potentially useful materials. For example, they can be used in areas such as electroluminescence, non-linear optics, chiral sensors, and asymmetric catalysis. These materials can be classified into two types: (i) polymers incorporating the chiral units in the main chain[4] and (ii) polymers having either chiral side chains or chiral dopants.[5] Both types of materials have received growing research attention in recent years. In a continuation of our studies on chiral macromolecules,[6] we herein describe the synthesis of the non-linear chiral main chain polymers **1a**–**b** from the readily accessible dialdehyde **3** and (1*R*,2*R*)-1,2-diamines[7] **2a**–**b** by Schiff base formation. The dialdehyde **3** can be obtained by a palladium catalyzed C–C cross-coupling reaction as a key step.[8] The stereoregular polymers **1a**–**b** are soluble in common organic solvents, and exhibit high specific rotations and a strong negative cotton effect. The polymers **1a**–**b** act as an effective chemosensor for Zn^{2+} recognition with respect to other metal ions with enhanced fluorescence.

2. Results and discussion

The synthesis of the dialdehyde **3** is shown in Scheme 1. The reaction of 2,4-dihydroxybenzaldehyde **4** with Tf_2O in the presence of pyridine gave the triflate **5** in a 60% yield.[9a,b] The C–C cross-coupling of **5** with ethynyltrimethylsilane using $Pd(PPh_3)_2Cl_2$ and CuI afforded the silyl derivative **6** in an 80% yield.[9c] The latter was transformed to the aldehyde **3** via desilylation using K_2CO_3



Scheme 1. Reagents and conditions: (a) Tf_2O (1 equiv), pyridine (1 equiv), CH_2Cl_2, 0–25 °C, 27 h, 60%; (b) Me_3SiC_2H (1.1 equiv), $Pd(PPh_3)_2Cl_2$ (3 mol %), PPh_3 (2 mol %), CuI (4 mol %), Et_3N (2 equiv), THF, rt, 12 h, 80%; (c) K_2CO_3 (1.5 equiv), MeOH, rt, 6 h, 60%; d) 2,5-dibromo-1,4-dioctyloxybenzene **10** (0.5 equiv), $Pd(PPh_3)_2Cl_2$ (3 mol %), PPh_3 (2 mol %), CuI (4 mol %), $(^iPr)_2NH$, THF, reflux, 12 h, 22%.

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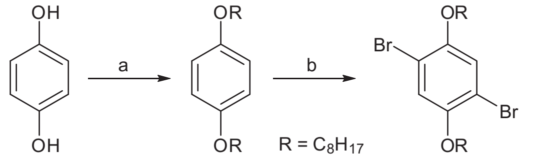
followed by Pd-catalyzed C–C cross-coupling with 1,4-dibromo-2,5-dioctyloxyben-zene **10** (Scheme 2).[6c,9c]



Scheme 2. Reagents and conditions: (a) $C_8H_{17}Br$ (2.5 equiv), K_2CO_3 (2.5 equiv), EtOH, 70 °C, 24 h, 80%; (b) Br_2, $CHCl_3$, 0 °C to rt, 27 h, 90%.

The synthesis of the polymers **1a**–**b** is shown in Scheme 3. The reactions of **3** with (1*R*,2*R*)-1,2-diaminocyclohexane **2a** and (1*R*,2*R*)-1,2-diphenylethylenediamine **2b** in $CHCl_3$ provided the polymers **1a**–**b** as yellow powder in 76–78% yield. The polymers **1a**–**b** are soluble in common organic solvents such as toluene, THF, CH_2Cl_2, and $CHCl_3$. GPC analysis, with polystyrene as an internal standard and THF as the eluent, exhibited the molecular weights that correspond to ca. 17 repeating units for **1a** (M_w = 12102 and PDI 1.27) and ca. 27 repeating units for **1b** (M_w = 22157 and PDI 1.49). The ^1H NMR spectra recorded at 400 MHz were consistent with the structure of the polymers.

The absorption, emission, thermal and circular dichrosim properties of the polymers **1a**–**b** were studied. The UV-vis spectra showed absorptions at ca. 320 nm (ε = 42325 M^{-1} cm^{-1}) and 384 nm (ε = 57713 M^{-1} cm^{-1}) for **1a**, and at ca. 322 nm (ε = 36461 M^{-1} cm^{-1}) and 388 nm (ε = 50261 M^{-1} cm^{-1}) for **1b**, respectively, due to π–$\pi*$ transition (Fig. 1). With respect to fluorescence, **1a** emitted blue light at 502 nm (λ_{ex} = 380 nm) and **1b** at 503 nm (λ_{ex} = 380 nm). The thermal analysis under N_2 atmosphere showed that the polymers **1a**–**b** are quite stable up to ca. 270 °C, and a total weight loss of ~50% was observed when the temperature was increased to 600 °C (Fig. 2). The CD spectra of the $CHCl_3$ solutions of **1a**–**b** exhibited a strong negative Cotton effect at 406 nm and a weak positive Cotton effect at 276 and 304 nm showing a negative chirality (Fig. 3).[10] The CD spectra may arise from a contribution of the helical secondary structure that might be responsible for the observed low degree of inter-strand interaction in the material.[4e]

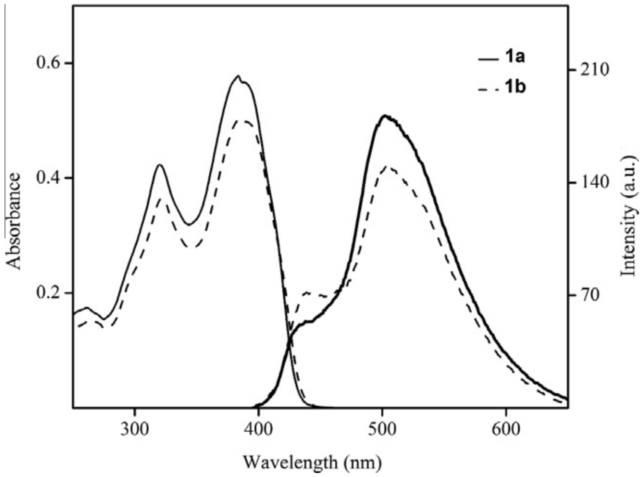


Figure 1. UV–vis and fluorescence spectra of the polymers **1a–b** (1.0 × 10^{-5} M in THF).

The fluorescent nature of the polymers **1a**–**b** led us to investigate their sensor properties with different metal ions.[11] Addition of 1.0 equiv (with respect to the monomeric unit of the polymer) of an aqueous solution of the nitrate salts of Na^+, Ag^+, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Fe^{3+}, Al^{3+} and Ce^{3+} to the THF solution of **1a**–**b** led to change in the fluorescence intensity and the best sensitivity was observed toward Zn^{2+} (Fig. 4). The polymer **1b** containing (*R*,*R*)-1,2-diphenyethylenediamine was found to be superior to **1a** bearing (*R*,*R*)-1,2-diaminicyclohexane exhibiting the best result. These results suggest that the substituent on the salen moiety of the polymer plays an important role in the sensitivity toward Zn^{2+}.

The blue fluorescence of polymer **1** with Zn^{2+} could be due to the formation of a Zn(II)-polymer complex that can reduce the non-radiative decay of the excited state of the Zn(II)-polymer complex and the quenching contributed from the photoinduced-electron-transfer (PET) of the lone pair of the electrons of nitrogen.[12] Furthermore, a blue shift (~30 nm) in the emitted light was observed that could be attributed to the formation of the Zn(II)-polymer complex with a reduced HOMO energy level of the polymer.[13]

The sensing selectivity of the polymer **1b** with different Zn^{2+} concentrations was studied (Fig. 5). The weakly emissive **1b** (THF, 1.0 × 10^{-5} M) with emission at ca. 503 nm, upon addition of Zn^{2+} (3 × 10^{-4} M), exhibited a blue-shifted emission at 471 nm. The enhancement in the intensity of the emission band was proportional to the Zn^{2+} concentration. When the Zn^{2+}concentration reached 3.0 equiv with respect to the monomeric unit of the polymer **1b**, the fluorescence intensity increased to maximum with a 6.3 fold enhancement. Thereafter, no change in fluorescence intensity was observed upon further addition of Zn^{2+}. Figure 6 illustrates the images of the fluorescence of **1b** without and with Zn^{2+}ion. By applying a Hill plot to this titration data (Fig. 7), the Zn^{2+}: polymer **1b** ratio was found to be 1.3:1 and the stability constant of Zn(II)-polymer **1b** complex was calculated as 6.9502 × 10^6 M^{-1}.[14]

It is well known that a tetracoordinated Zn(II)-complex can chelate with a Lewis base such as pyridine.[15] Since the coordinating ligand can reduce the inter-strand interaction, the degree of inter-strand interactions could be examined using the fluorometric titration of the resultant Zn(II)-polymer **1b** complex with the Lewis base. The Zn(II)-polymer **1b** complex could exist in aggregated form through Zn–O interaction as shown in Scheme 4.[9c,16] Due to this excimer like inter-strand interaction, the fluorescence intensity might be reduced by quenching. The addition of pyridine may enhance the deaggregation of the Zn(II)-polymer **1b** complex that could lead to increase the fluorescence emission (Fig. 8). The slight increase in fluorescence emission observed could be attributed to the helical (or) coil nature of the polymer **1b** inhibiting the self aggregation of Zn(II)-polymer **1b**.[16c]

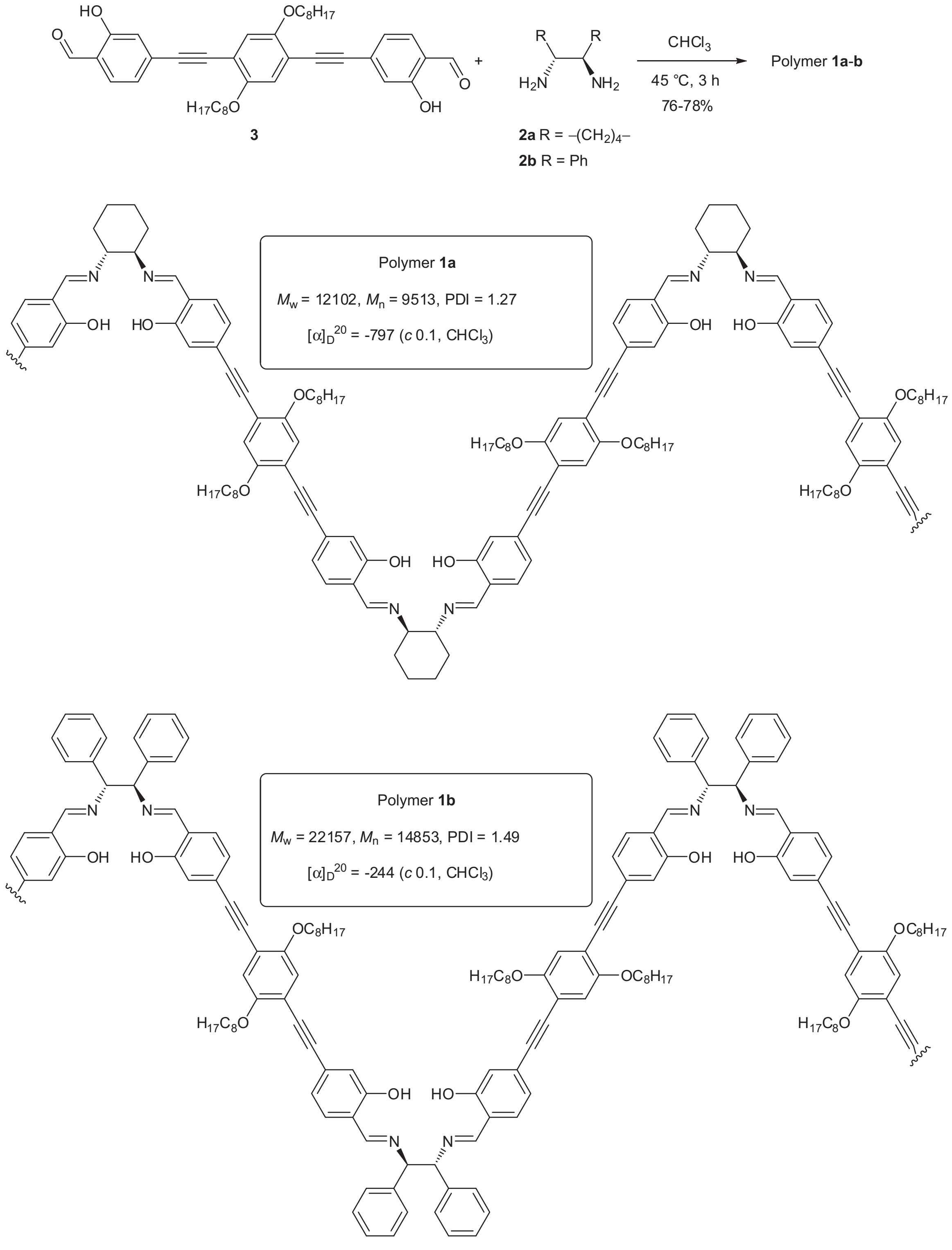
3. Conclusions

In conclusion, we have described the synthesis of chiral main chain polymers **1a**–**b** using a Pd-catalyzed C–C cross-coupling reaction as a key step. These are soluble in common organic solvents and exhibit a strong Cotton effect. They can be used as an effective chemosensor for the recognition of Zn^{2+} ion under ambient conditions.

4. Experimental section

4.1. General

2,4-Dihydroxybenzaldehyde (98%), trifluoromethane-sulfonic anhydride (⩾99%), hydroquinone (⩾99%), (trimethylsilyl)acetylene (98%), octyl bromide (99%), $Pd(PPh_3)_2Cl_2$ (98%), CuI (98%), PPh_3 (99%) $Ce(NO_3)_3{\cdot}6H_2O$ (⩾98%), $Cd(NO_3)_2{\cdot}4H_2O$ (⩾99%) and $Zn(NO_3)_2{\cdot}6H_2O$ (98%) were purchased from Aldrich. $Co(NO_3)_2{\cdot}6H_2O$ (97%), $Cu(NO_3)_2{\cdot}3H_2O$ (⩾99%), $Ni(NO_3)_2{\cdot}6H_2O$ (98%), $Al(NO_3)_3{\cdot}9H_2O$ (⩾95%) and $NaNO_3$ (⩾99%) were purchased from Merck, and $Fe(NO_3)_3{\cdot}9H_2O$ (98%), $Pb(NO_3)_2$(98%) and $AgNO_3$(99%) were obtained from Rankem and used as received without further purification. THF was freshly distilled from sodium and benzophenone under nitrogen prior to use. Column chromatography was carried



Scheme 3. Synthesis of polymers **1a–b.**

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 ^{1}H and 100 MHz for ^{13}C) were recorded using DRX-400 Varian spectrometer using $CDCl_3$ as solvent and Me_4Si as internal standard. Melting points were determined using Buchi B-540 melting point apparatus and are uncorrected. FT-IR spectra were obtained using PerkinElmer spectrum one spectrometer. UV-vis spectra were recorded using PerkinElmer Lambda 25 UV/vis spectrometer. Fluorescence spectra were recorded on Cary Eclipse fluorescence spectrometer. The optical rotation was measured on a PerkinElmer model-343. Thermal gravimetric analysis was performed on SDT Q600 under a nitrogen atmosphere. GPC analysis was performed on a Waters-2414 with stationary phase column Styragel® WAT044221 using polystyrene as an internal standard and THF as eluent. Elemental analysis was carried out using a PerkinElmer-2400 CHNS analyzer

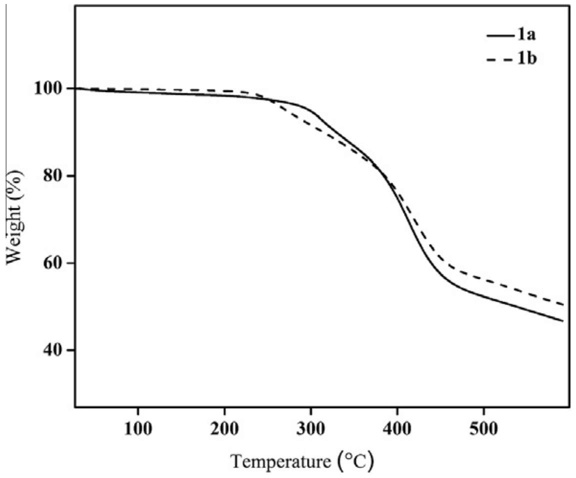


Figure 2. TGA of polymers **1a–b.**

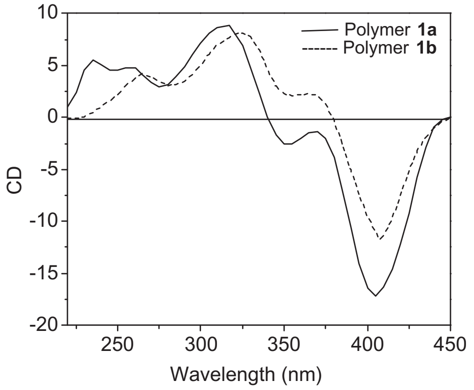


Figure 3. CD Spectra of the polymers in $CHCl_3$ (5.16×10^{-6} M for **1a** and 3.52×10^{-5} M for **1b**).

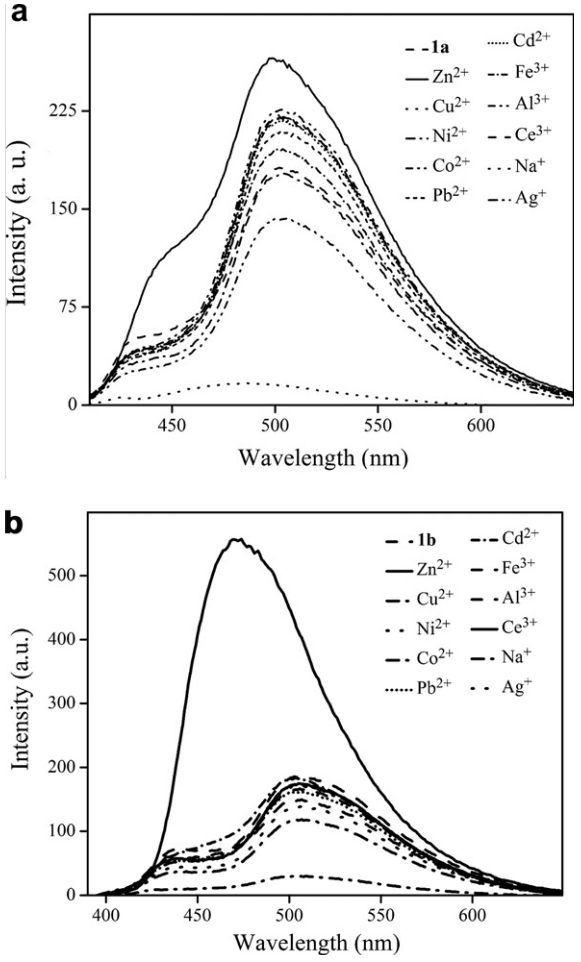


Figure 4. Fluorescence spectra of the polymers **1a** (a) (λ_{ex} = 380 nm) and **1b** (b) (λ_{ex} = 380 nm) (1.0×10^{-5} M in THF) with various metal nitrate salts (3×10^{-4} M in water, 1 equiv with respect to the monomeric unit).

4.2. 4-Trifluoromethanesulfonyl-2-hydroxybenzalde-hyde 5

To a stirred solution of 2,4-dihydroxybenzaldehyde (14.49 mmol, 2.0 g) and pyridine (14.49 mmol, 1.2 mL) in CH_2Cl_2 (15 mL) at 0 °C was added trifluoromethane-sulfonic anhydride (14.49 mmol, 2.4 mL). After 0.5 h, the reaction mixture was allowed to warm to ambient temperature and the stirring was continued for an additional 27 h. The organic layer was separated and the residue was extracted with CH_2Cl_2 (2×15 mL). The combined organic solution was then washed with water (2×10 mL), dried (Na_2SO_4) and evaporated under reduced pressure to give a residue which was purified by silica gel flash column chromatography using ethyl acetate and hexane to afford **5** as a colorless liquid in a 60% (2.3 g) yield. ^1H NMR (400 MHz, $CDCl_3$) δ 11.27 (s, 1H), 9.90 (s, 1H), 7.67 (d, J = 8.4 Hz, 1H), 6.94–6.89 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.2, 163.2, 154.7, 135.9, 120.46, 120.39, 113.2, 111.0; FT-IR (neat) 3406, 3109, 2873, 1706, 1688, 1602, 1432, 1216, 1133, 969, 879, 608 cm^{-1}. Anal. Calcd for $C_8H_5F_3O_5S$: C, 35.56; H, 1.87; S, 11.87. Found. C, 35.62; H, 1.89; S, 11.88.

4.3. 4-Ethynyl-2-hydroxybenzaldehyde 7[9c]

To a stirred solution of 4-trifluromethanesulfonyl-2-hydroxybenzaldehyde (1 mmol, 0.270 g), $Pd(PPh_3)_2Cl_2$ (3 mol %, 21.03 mg) and PPh_3 (6 mol %, 5.7 mg) in THF (10 mL) at ambient temperature, Et_3N (2 mmol, 0.25 mL) and trimethylsilyl-acetylene (1.1 mmol, 0.108 g) were added. The resultant orange colored reaction mixture, after 0.5 h, was treated with CuI (4 mol %, 5.7 mg) to afford a dark brown solution. After stirring the reaction mixture for 12 h, the solvent was evaporated under reduced pressure and the residue was dissolved in Et_2O and passed through a short pad of Celite. The solvent was evaporated and the residue was stirred with K_2CO_3 (6.74 mmol, 0.930 g) in MeOH (10 mL) for 6 h at ambient temperature. The solid was filtered and the filtrate was concentrated to afford a residue which was treated with a 1:3 mixture of H_2O and CH_2Cl_2 (5 mL). The organic layer was separated and the aqueous layer was extracted further with CH_2Cl_2 (5×2 mL). The combined organic solution was dried over Na_2SO_4 and evaporated to afford a residue that was purified by silica gel flash column chromatography to afford **6** as a yellow solid in 60% (0.393 g) yield. Mp 63 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 10.98 (s, 1H), 9.86 (s, 1H), 7.49 (d, J = 8.0 Hz, 1H), 7.09–7.07 (m, 2H), 3.27 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.0, 161.4, 133.6, 130.8, 123.6, 121.3, 120.7, 82.5, 81.7; FT-IR (KBr) 3439, 3275, 2961, 2923, 2851, 2098, 1655, 1624, 1555, 1493, 1436, 1364, 1273, 1224, 1195, 1125, 966, 885, 803, 680, 531 cm^{-1}. Anal. Calcd for $C_9H_6O_2$: C, 73.97; H, 4.14. Found. C, 74.04; H, 4.17.

4.4. Preparation of dialdehyde 3[9c]

To a stirred solution of 4-ethynyl-2-hydroxybenzaldehyde **7** (1.5 mmol, 0.230 g), 1,4-dibromo-2,5-dioctyloxybenzene **10** (0.785 mmol, 0.492 g), $Pd(PPh_3)_2Cl_2$ (3 mol %, 33 mg) and PPh_3 (2 mol %,

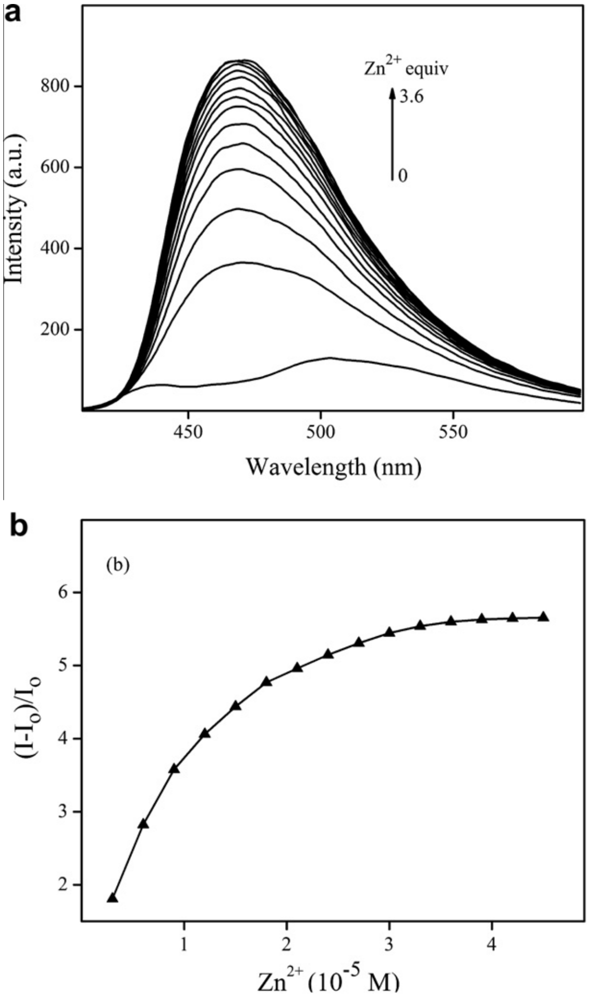


Figure 5. (a) Fluorescence spectra of **1b** (1.0×10^{-5} M in THF, λ_{ex} = 380 nm) with 0.3–3.6 equiv of Zn^{2+} ion (9.0×10^{-4} M in water, with respect to the monomeric unit of **1b**). (b) Plot of 0.3–4.5 equiv of Zn^{2+} (with respect to monomeric unit of **1b**) vs $(I–I_o)/I_o$ (I = fluorescence intensity of **1b**-Zn^{2+}at λ_{em} = 471 nm and I_o = fluorescence intensity of **1b** at λ_{em} = 503 nm).

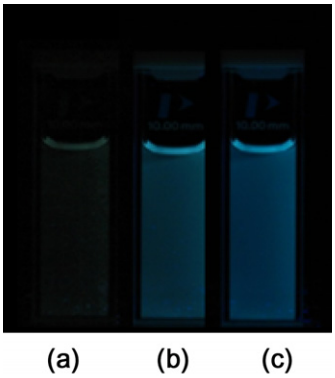


Figure 6. The fluorescence images of **1b** (1×10^{-5} M in THF): without Zn^{2+} (a) and with 1.0 equiv (b) and 3.0 equiv (c) of Zn^{2+} (9×10^{-4} M in water). Both are excited using a commercially available UV lamp.

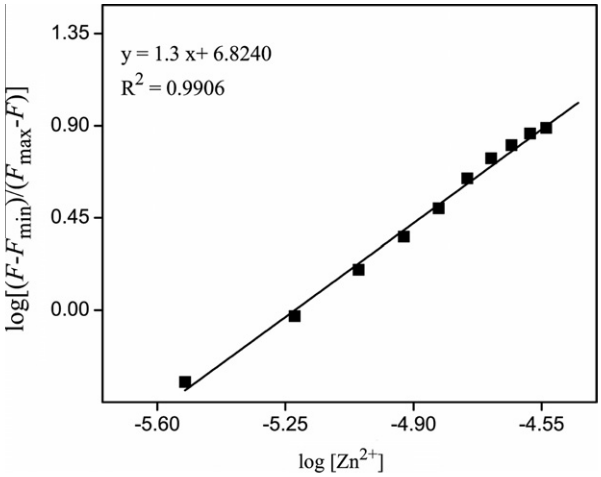
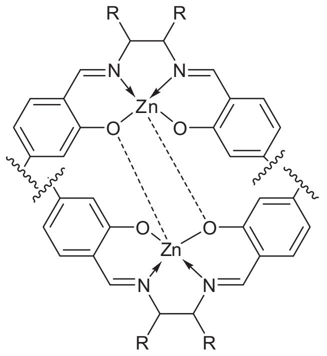


Figure 7. Hill plot of **1b** (1.0×10^{-5} M in THF) with 0.3–3.0 equiv of Zn^{2+} ion (9.0×10^{-4} M in water with respect to the monomeric unit of **1b**).



Scheme 4. Illustration for inter-strand interactions between the Zn(II)-polymer complexes.[9c,16]

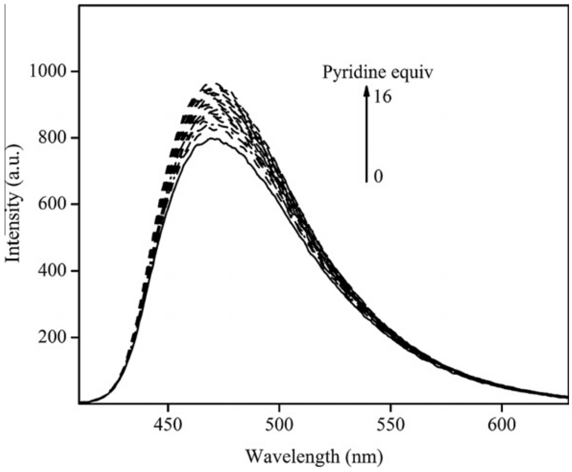


Figure 8. Fluorescence spectra of Zn(II)-polymer **1b** (1.0×10^{-5} M in THF, λ_{ex} = 380 nm) with 1–16 equiv of pyridine (3.0×10^{-3} M in THF, with respect to the monomeric unit of **1b**).

8.4 mg) in THF (12 mL) at ambient temperature, $(^{i}Pr)_2NH$ (35 mmol, 2.5 mL) was added. After 0.2 h, the reaction mixture was treated with CuI (4 mol %, 11.9 mg) and the resultant brown colored solution was heated at reflux for 16 h. The solvent was then evaporated under reduced pressure and the residue was dissolved in $CHCl_3$ (5×2 mL). The solution was passed through a short pad of silica gel and concentrated under reduced pressure and purified by flash chromatography to afford **3** as an orange solid in 22% (122.2 mg) yield. Mp 102 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.06 (s, 2H), 9.88 (s, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.15–7.13 (m, 4H), 7.01 (s, 2H), 4.03 (t, *J* = 6.4 Hz, 4H), 1.88–1.81 (m, 4H), 1.57–1.53 (m, 4H), 1.38–1.25 (m, 16 H), 0.87–0.84 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.9, 161.5, 154.2, 133.6, 132.2, 123.2, 120.4, 120.2, 117.1, 114.1, 94.3, 90.7, 69.8, 32.0, 29.6, 26.3, 22.8, 14.2; FT-IR (KBr) 3435, 2923, 2853, 2211, 1648, 1622, 1491, 1323, 1261, 1215, 1106, 973, 804, 744, 542 cm^{-1}. Anal. Calcd for $C_{40}H_{46}O_6$: C, 77.14; H, 7.44; Found. C, 77.22; H, 7.47.

4.5. Synthesis of polymers 1a–b

4.5.1. Polymer 1a

To a stirred solution of the dialdehyde **3** (0.08 mmol, 50 mg) in $CHCl_3$ (3 mL), (1*R*,2*R*)-1,2-diaminocyclohexane **2a** (0.080 mmol, 9.12 mg) was added and the resulting solution was heated at 45 °C for 3 h. The reaction mixture was then cooled to room temperature, concentrated (ca. 2 mL) and treated with MeOH (3 mL). The resultant precipitate **1a** was collected by filtration as a yellow powder in a 78% (43.80 mg) yield. GPC: M_w = 12102, M_n = 9513 (PDI 1.27); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 2H), 7.09 (d, *J* = 7.6, 2H), 7.02 (s, 2H), 6.97–6.92 (m, 4H), 3.96 (t, *J* = 6.4 Hz, 4H), 3.28 (s, 2H), 1.91–1.60 (m, 16H), 1.47–1.45 (m, 6H), 1.31–1.22 (m, 10H), 0.80 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 160.9, 153.9, 131.4, 127.3, 122.2, 119.7, 118.7, 117.1, 114.1, 94.9, 88.0, 72.7, 69.8, 33.2, 31.9, 29.4, 26.2, 24.3, 22.8, 14.3; FT-IR (KBr) 3463, 2961, 2928, 2862, 2373, 2071, 1629, 1462, 1262, 1215, 1091, 1028, 801, 697 cm^{-1}; UV–vis (THF): λ_{max} (ε) = 320 (42325), 382 (57713) nm (M^{-1} cm^{-1}); fluorescence (λ_{ex} = 380 nm, THF): 502 nm; $[\alpha]_D^{20} = -797$ (*c* 0.1, $CHCl_3$). Anal. Calcd for $(C_{46}H_{56}N_2O_4)_n$: C, 78.82; H, 8.05; N, 4.00. Found: C, 78.88; H, 8.07; N, 4.05.

4.5.2. Polymer 1b

To a stirred solution of the dialdehyde **3** (0.08 mmol, 50 mg) in $CHCl_3$ (3 mL), (1*R*,2*R*)-1,2-diphenylethylene-diamine **2b** (0.080 mmol, 16.90 mg) was added and the resulting solution was heated at 45 °C for 3 h. The reaction mixture was then cooled to room temperature, concentrated (*ca.* 2 mL) and treated dropwise with MeOH (3 mL). Isolation of **1b** was performed as described for **1a** as a yellow powder in a 76% (48.76 mg) yield. GPC: M_w = 22157, M_n = 14853 (PDI 1.49); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 2H), 7.18–6.93 (m, 18H), 4.71 (s, 2H), 3.97 (t, *J* = 6.4 Hz, 4H), 1.80 (t, *J* = 6.8 Hz, 4H), 1.59–1.47 (m, 8H), 1.23 (s, 12H), 0.81 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 160.8, 153.9, 139.3, 131.7, 128.6, 128.0, 127.7, 122.3, 119.8, 118.6, 117.1, 114.1, 94.8, 88.3, 80.4, 69.8, 31.9, 29.5, 26.2, 22.8, 14.3; FT-IR (KBr) 3452, 2961, 2923, 2857, 2362, 2093, 1627, 1377, 1262, 1212, 1102, 1023, 973, 697 cm^{-1}; UV-vis (THF): λ_{max} (ε) = 322 (36461), 381 (50261) nm (M^{-1} cm^{-1}); fluorescence (λ_{ex} = 380 nm, THF): 503 nm; $[\alpha]_D^{20}$ = -244 (*c* 0.1, $CHCl_3$). Anal. Calcd for $(C_{54}H_{58}N_2O_4)_n$: C, 81.17; H, 7.32; N, 3.51. Found: C, 81.25; H, 7.33; N, 3.55.

4.6. Fluorometric titration

4.6.1. Metal ion titration

The solutions of the polymers **1a**–**b** (3 mL, 1×10^{-5} M in THF with respect to the monomeric unit) and metal nitrate salts (3.0×10^{-4} M in water, 1 equiv) were thoroughly mixed at ambient temperature to produce the corresponding metal-polymer complexes (Fig. 4). After 5 min, the fluorescent properties of the solution having the in situ generated metal–polymer **1a**–**b** complexes were measured.

4.6.2. Zinc titration

The solutions of the polymer **1b** (3 mL, 1×10^{-5} M in THF with respect to the monomeric unit) and zinc nitrate salt (9.0×10^{-4} M in water) were thoroughly mixed at ambient temperature to produce the corresponding Zn(II)-polymer **1b** complex (Figure 5). After 5 min, the fluorescent properties of the solution having the in situ generated Zn(II)-polymer **1b** complex were measured.

4.6.3. Pyridine titration

To the solutions of the Zn(II)-polymer complex (3 mL, 1×10^{-5} M in THF with respect to the monomeric unit, Zn^{2+} and polymer ratio was 3:1), derived from $Zn(NO_3)_2$ (9.0×10^{-4} M in water, 1 equiv) and **1b** (3 mL, 1×10^{-5} M in THF with respect to the monomeric unit) for 1 h, was added the solutions of pyridine in THF (3.0×10^{-3} M in THF, 1–16 equiv). The resulting solutions were mixed thoroughly. After 5 min, the fluorescence of the respective solutions was measured (Fig. 8).

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