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PAPER

# Conjugated coordination polymers based on 8-hydroxyquinoline ligands: impact of polyhedral oligomeric silsesquioxanes on solubility and luminescence<sup>†</sup>

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A novel bis(8-hydroxyquinoline) zinc-based conjugated coordination polymer with polyhedral oligomeric silsesquioxanes (POSSs) in the side chains has been synthesized. In contrast to the traditional coordination polymers, this new coordination polymer has good solubility in common organic solvents and can be characterized and processed in solution. The thermal stability of the polymer is also enhanced by POSSs and the fluorescence is not quenched by intermolecular aggregation in the solid state. This fluorescence enhancement is due to the significant effect of the bulky POSS units. Nanoparticles is obtained by a facile self-assembly method of the polymer materials and the nanoparticles show strong fluorescence at 545 nm.

#### Introduction

In recent years, metal-organic coordination polymers have received increasing interest due to their attractive electronic, catalytic, optic, and magnetic properties.<sup>1-4</sup> In comparison with common polymers, coordination polymers are easy to synthesize and possess much greater design flexibility due to their abundant and tunable synthons, e.g. variation in oxidation state, size, and number of center metal atoms or ions, ligand environment, and geometry.<sup>5</sup> Conjugated coordination polymers whose structures consist of conjugated ligands interconnected by metallic nodes have been extensively studied because of their numerous applications including chemical sensors, electroluminescence devices. electrocatalysis, batteries, smart windows, and memory devices.<sup>6-11</sup> Unfortunately, most of the conjugated coordination polymers suffer from poor solubility that limits the ability to characterize the materials in solution and to process them for applications.<sup>7</sup> To resolve this issue, significant efforts have been focused on the synthesis of ligands with pendant organic groups, such as long or bulky alkyl substituents, even with polymer chains. The introduction of a flexible polymer chain into ligands is efficient for enhancing the solubility, however this approach usually yields much increased molecular weight, and the molecular weight of the ligands is difficult to control due to uncontrolled polymerization.<sup>12,13</sup> The incorporation of sterically demanding groups into the conjugated polymers has attracted much attention recently, because it can improve solubility and simultaneously maintain solid state luminescence. For instance, iptycene units are particularly useful in the design of advanced materials because of their three-dimensional, noncompliant structures.<sup>14</sup> Iptycenes can provide steric blocking, which can prevent strong interactions between polymeric chromophores that have a strong tendency to form nonemissive exciplex complexes.

8-Hydroxyquinoline (8-HQ), as a very useful ligand, has often been incorporated into conjugated coordination polymers. These polymers may find potential applications in OLED devices, optical sensors, and dye-sensitized solar cells due to their exceptional optical properties and thermal stability.<sup>5,15-18</sup> However, these polymers usually possess very poor processability due to lack of thermoplasticity and solubility in common solvents.<sup>19,20</sup> Moreover, it was reported that the coordination polymers often exhibit strong fluorescence in solution, but undergo fluorescence quenching in the solid state because of molecular aggregation.<sup>17</sup> These disadvantages have remarkably limited the applications of the coordination polymers in optical and electronic devices.

Recently, polyhedral oligomeric silsesquioxanes (POSSs)<sup>21</sup> have attracted a great deal of attention in the materials field because of their unique nanoscale cage-shaped structures and good solubility in organic solvents. Some of the novel hybrid polymers with promising properties such as thermal and flammability resistance or special surface properties have been prepared by incorporating POSS into polymers.<sup>22–32</sup> In addition, POSS has also been successfully used in the enhancement of solubility, luminescence efficiencies, and colour purities of the conjugated polymers by suppressing undesired excimer

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formation and intermolecular aggregation.<sup>22,23</sup> However, there has not been any paper reporting the conjugated metal coordination polymers with POSS moieties.

In this paper, we report the synthesis and properties of a 8-HQ conjugated coordination polymer with pendant POSS moieties. The new coordination polymer materials have good solubility in common low-boiling point solvents and simultaneously maintain their luminescence in the solid state. Nanoparticles of the polymer materials can be obtained by a facile self-assembly method and the nanoparticles show strong fluorescence at 545 nm.

### Experimental

#### Characterizations

**Nuclear magnetic resonance spectroscopy (NMR).** <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AVANCE II spectrometer (resonance frequency of 400 MHz for <sup>1</sup>H) operated in the Fourier transform mode. CDCl<sub>3</sub> and TMS were used as the solvent and internal standard, respectively.

Fourier transform infrared spectroscopy (FT-IR). FT-IR spectra were recorded as KBr pellets with a Bruker VECTOR-22 IR spectrometer. The spectra were collected at 64 scans with a spectral resolution of  $4 \text{ cm}^{-1}$ .

**Elemental analyses.** Elemental analyses were performed on a VARIO ELIII C, H, and N analyzer.

**Solubility measurement.** A solubility experiment was performed by gravimetric analysis of the evaporated solvent of saturated solution.

Gel permeation chromatography (GPC). Molecular weights and molecular weight distributions were determined by GPC equipped with a Waters 1515 pump, a Waters 2414 RI detector, and Waters UV/RI detectors (set at 30 °C). It used a series of three linear Styragel columns HR3, HR4, and HR6 at an oven temperature of 45 °C. The eluent was DMF at a flow rate of 1.0 ml min<sup>-1</sup>. A series of low-polydispersity polystyrene (PS) standards were employed for the GPC calibration.

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA). TGA and DTA were carried out on a SDT Q600 V20.9 Build 20 instrument at a heating rate of  $10 \,^{\circ}\text{C} \,^{min^{-1}}$  in air from room temperature to 600  $^{\circ}\text{C}$ .

**Ultraviolet-visible spectroscopy (UV-vis).** UV-Vis spectra of solutions were recorded with a Pgeneral UV-Vis TU-1901 spectrometer.

**Photoluminescence (PL) spectroscopy.** Emission spectra of solutions were measured using a RF-5301PC spectrometer. The quantum yields in solution were determined twice. Quinine bisulfate in  $0.05 \text{ M H}_2\text{SO}_4$  solution was used as the standard. The measurements were averaged. Solid-state emission spectra were measured in powders by JY Fluorolog-3-Tou, equipped with solid state accessories. The PL quantum yields in the solid state were determined as absolute values in an integrating sphere.

Temperature-dependent fluorescence spectra were acquired at a heating rate of 0.2 °C min<sup>-1</sup>.

Transmission electron microscopy (TEM). TEM observations were conducted on a JEM100-SX transmission electron microscope at an acceleration voltage of 200 kV. The sample for TEM observations was prepared by placing 10  $\mu$ L of micellar solution on copper grids coated with thin films of Formvar and carbon successively.

**Dynamic laser light scattering (DLS).** A commercial spectrometer (ALV/DLS/SLS-5022F) equipped with a multi-tau digital time correlator (ALV5000) and a cylindrical 22 mW UNIPHASE He–Ne laser ( $\lambda_0 = 632$  nm) as the light source was employed for DLS measurements. Scattered light was collected at a fixed angle of 90° for duration of ~10 min.

#### Material synthesis

All reagents and solvents were purchased commercially and used without further purification. Aminopropylheptakis (isobutyl) POSS (POSS-NH<sub>2</sub>, 97%) was obtained from Hybrid Plastics. 5-Formyl-8-hydroxyquinoline (denoted as FHQ) was synthesized from 8-hydroxyquinoline according to the reported procedure (ESI†).<sup>33</sup> The main synthesis procedure was illustrated in Scheme 1.

*N*-Propylheptakis(isobutyl) POSS-3,5-dinitrobenzamide (PDNB). Modification of the procedures in the literature was used.<sup>34</sup> POSS-NH<sub>2</sub> (3.5 g, 4 mmol), 3,5-dinitrobenzoic acid (DNBA, 1.3 g, 6 mmol), dry tetrahydrofuran (THF) (30 ml), and *N*,*N'*-dicyclohexylcarbodiimide (DCC, 1.0 g, 5 mmol) were added into a flask and the mixture was stired for 24 h. After the reaction, the precipitate was filtered off, and the filtrate was rotary concentrated. The precipitate was obtained by dropping the solution into acetonitrile, and the precipitation cycle was repeated twice more. PDNB was collected by filtration and dried *in vacuo* at 40 °C for 24 h with a yield of 93%. <sup>1</sup>H NMR  $\delta_{\rm H}$  (400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si):  $\delta = 9.17$  (1H, *ArH*), 8.93 (2H, *ArH*), 6.29 (1H, *NH*), 3.53 (2H, NH*CH*<sub>2</sub>), 1.85 (7H, SiCH<sub>2</sub>*CH*), 1.66 (2H,



Scheme 1 Synthetic procedure of the ligands and polymers.

SiCH<sub>2</sub>*CH*<sub>2</sub>), 0.95 (42H, CH(*CH*<sub>3</sub>)<sub>2</sub>), 0.59 (16H, Si*CH*<sub>2</sub>). <sup>13</sup>C NMR  $\delta_{\rm C}$  (100 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si):  $\delta$  = 162.7, 148.8, 138.4, 127.2, 121.1, 43.2, 25.9–22.6, 9.7. Anal. Calcd for C<sub>38</sub>H<sub>73</sub>N<sub>3</sub>O<sub>17</sub>Si<sub>8</sub>: C 42.74%; H 6.84%; N 3.94%. Found: C 42.76%; H 6.87%; N 3.92%.

N-Propylheptakis(isobutyl) POSS-3,5-diaminobenzamide (PDAB). PDNB was reduced with ammonium formate catalyzed by Pd/C.<sup>35</sup> PDNB (3.2 g, 3 mmol), ammonium formate (1.9 g, 30 mmol), 5% palladium on carbon (0.1 g), and ethanol (30 ml) were added into a flask and the mixture was refluxed for 6 h. After the reaction was completed, the precipitate was filtered out, and the filtrate was rotary evaporated. The solid was dissolved in 5 ml THF and precipitation in 50 ml water. PDAB was collected by filtration and dried in vacuo at 50 °C for 48 h with a yield of 95%. <sup>1</sup>H NMR  $\delta_{\rm H}$  (400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si):  $\delta = 6.44$  (2H, ArH), 6.11 (1H, ArH), 5.94 (1H, C(=O)NH), 3.69 (4H, NH<sub>2</sub>), 3.39 (2H, NHCH<sub>2</sub>), 1.85 (7H, SiCH<sub>2</sub>CH), 1.66 (2H, SiCH<sub>2</sub>CH<sub>2</sub>), 0.95 (42H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.59 (16H, SiCH<sub>2</sub>). <sup>13</sup>C NMR  $\delta_{\rm C}$  (100 MHz;  $CDCl_3$ ; Me<sub>4</sub>Si):  $\delta = 168.4$ , 148.0, 137.5, 104.3, 104.1, 42.4, 25.8– 22.6, 9.7. Calcd for C38H77N3O13Si8: C 45.28%; H 7.65%; N 4.17%. Found: C 42.19%; H 7.76%; N 4.14%.

3,5-Bis(8-HQ Schiff base)-N-propyl heptakis(isobutyl) POSS benzamide (1a). PDAB (2.2 g, 2.2 mmol), FHQ (0.76 g, 4.4 mmol), and 100 ml ethanol were refluxed for 30 h under nitrogen. After the reaction, the solution was concentrated to obtain a yellow product **1a**. The product was then filtered off and dried at 30 °C for 24 h under vacuum. Yield = 82%; <sup>1</sup>H NMR  $\delta_{\rm H}$  (400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si):  $\delta = 10.14$  (2H, N=*CH*), 9.68 (2H, 4-H of 8-HQ), 8.85 (2H, 2-H of 8-HQ), 8.01 (2H, 6-H of 8-HQ), 7.65 (2H, 3-H of 8-HQ), 7.29 (2H, 7-H of 8-HQ), 6.44 (2H, ArH), 6.12 (1H, ArH), 5.96 (1H, C(=O)NH), 3.39 (2H, NHCH<sub>2</sub>), 1.85 (7H, SiCH<sub>2</sub>CH), 1.66 (2H, SiCH<sub>2</sub>CH<sub>2</sub>), 0.95 (42H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.59 (16H, SiCH<sub>2</sub>). <sup>13</sup>C NMR  $\delta_{\rm C}$  (100 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si):  $\delta =$ 167.2, 161.7, 158.0, 155.7, 154.0, 148.9, 140.6, 138.5, 134.9,  $127.9-124.8, 116.7, 116.0, 42.4, 25.9-22.6, 9.7. M_{p}(GPC) =$ 1,400;  $M_{\rm w}/M_{\rm n} = 1.09$ ; Anal. Calcd for C<sub>58</sub>H<sub>87</sub>N<sub>5</sub>O<sub>15</sub>Si<sub>8</sub>: C 52.85%; H 6.60%; N 5.32%. Found: C 52.77%; H 6.64%; N 5.19%.

**Preparation of the coordination polymer 2a.** The zinc-based coordination polymer **2a** was prepared by adding an equivalent amount of  $ZnCl_2$  into a solution of **1a** in DMF under vigorous stirring, and the solution turned from yellow to red color immediately. The reaction mixture was poured into methanol and a precipitate was formed. The red precipitate was washed with absolute methanol and dried *in vacuo* at 40 °C. Yield = 80%;  $M_n$ (GPC) = 220 000;  $M_w/M_n = 1.34$ ; Anal. Calcd for (C<sub>58</sub>H<sub>85</sub>N<sub>5</sub>O<sub>15</sub>Si<sub>8</sub>Zn)<sub>n</sub>: C 50.43%; H 6.16%; N 5.07%. Found: C 49.70%; H 6.34%; N 5.01%.

*N*-Dodecyl-3,5-dinitrobenzamide (DDNB). Dodecylamine (0.74 g, 4 mmol) and triethylamine (0.6 ml, 4.2 mmol) were added to 30 ml dry THF (30 ml). Then 3,5-dinitrobenzoyl chloride (0.92 g, 4 mmol) in 20 ml THF was added dropwise at 0 °C. After the addition, the mixture was warmed to room temperature and stirred overnight. After having been filtered, THF was rotary evaporated and the solid was dissolved in  $CH_2Cl_2$ . The  $CH_2Cl_2$ 

solution was washed by dilute muriatic acid and dilute sodium hydroxide three times, respectively. The organic solution was dried with sodium sulfate and subsequently passed through a neutral alumina column to move the salts. DDNB was obtained by rotary evaporation and drying *in vacuo* at 40 °C. Yield = 95%; <sup>1</sup>H NMR  $\delta_{\rm H}$  (400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si):  $\delta$  = 9.16 (1H, *ArH*), 8.94 (2H, *ArH*), 6.34 (1H, *NH*), 3.54 (2H, NH*CH*<sub>2</sub>), 1.68 (2H, NCH<sub>2</sub>*CH*<sub>2</sub>), 1.41–1.26 (18H, NCH<sub>2</sub>CH<sub>2</sub>(*CH*<sub>2</sub>)<sub>9</sub>), 0.88 (3H, *CH*<sub>3</sub>). <sup>13</sup>C NMR  $\delta_{\rm C}$  (100 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si):  $\delta$  = 162.6, 148.5, 138.4, 127.3, 121.0, 43.1, 32.0, 29.6, 27.0, 22.7, 14.7. Anal. Calcd for C<sub>19</sub>H<sub>29</sub>N<sub>3</sub>O<sub>5</sub>: C 60.14%; H 7.70%; N 11.07%. Found: C 60.13%; H 7.73%; N 11.06%.

*N*-Dodecyl-3,5-diaminobenzamide (DDAB). DDAB was prepared similar to PDAB with a yield of 91%. <sup>1</sup>H NMR  $\delta_{\rm H}$  (400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si):  $\delta = 6.45$  (2H, *ArH*), 6.12 (1H, *ArH*), 5.97 (1H, *NH*), 3.70 (4H, *NH*<sub>2</sub>), 3.40 (2H, NH*CH*<sub>2</sub>), 1.56 (2H, NCH<sub>2</sub>*CH*<sub>2</sub>), 1.32–1.25 (18H, NCH<sub>2</sub>CH<sub>2</sub>(*CH*<sub>2</sub>)<sub>9</sub>), 0.88 (3H, *CH*<sub>3</sub>). <sup>13</sup>C NMR  $\delta_{\rm C}$  (100 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si):  $\delta = 168.1$ , 148.2, 137.4, 104.3, 104.4, 40.0, 31.9, 29.7, 29.6, 29.4, 27.0, 22.7, 14.9. Anal. Calcd for C<sub>19</sub>H<sub>33</sub>N<sub>3</sub>O<sub>1</sub>: C 71.43%; H 10.41%; N 13.15%. Found: C 71.33%; H 10.50%; N 13.11%.

**3,5-Bis(8-HQ Schiff base)-***N***-dodeyl benzamide (1b). 1b** was synthesized similar to **1a** with a yield of 77%. <sup>1</sup>H NMR  $\delta_{\rm H}$  (400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si):  $\delta = 10.14$  (2H, N=*CH*), 9.67 (2H, 4-H of 8-HQ), 8.85 (2H, 2-H of 8-HQ), 8.00 (2H, 6-H of 8-HQ), 7.65 (2H, 3-H of 8-HQ), 7.30 (2H, 7-H of 8-HQ), 6.44 (2H, *ArH*), 6.11 (1H, *ArH*), 5.99 (1H, C(=O)*NH*), 3.40 (2H, NH*CH*<sub>2</sub>), 1.56 (2H, NCH<sub>2</sub>*CH*<sub>2</sub>), 1.32–1.25 (18H, NCH<sub>2</sub>CH<sub>2</sub>(*CH*<sub>2</sub>)), 0.88 (3H, *CH*<sub>3</sub>). <sup>13</sup>C NMR  $\delta_{\rm C}$  (100 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si):  $\delta = 167.1, 161.5, 158.3, 156.1, 154.1, 148.9, 140.7, 138.3, 135.1, 127.9, 127.1, 126.7, 124.8, 116.5, 116.0, 40.4, 31.9, 29.7, 29.6, 29.4, 27.0, 22.7, 14.9. Anal. Calcd for C<sub>39</sub>H<sub>43</sub>N<sub>5</sub>O<sub>3</sub>: C 82.98%; H 7.62%; N 12.41%. Found: C 82.73%; H 7.66%; N 12.37%.$ 

**Preparation of the coordination polymer 2b. 2b** was synthesized similar to **2a** with a yield of 87%. Anal. Calcd for  $(C_{39}H_{41}N_5O_3Zn)$ : C 74.64%; H 6.54%; N 11.16%. Found: C74.57%; H 6.61%; N 11.07%.

#### **Results and discussion**

Ligand 1a was obtained as yellow powder from the reaction of FHQ and amine derivatives bearing a POSS moiety, according to the literature.<sup>5,36</sup> The molecular structure was verified using NMR spectroscopy, as shown in the ESI<sup>†</sup>. The coordination polymer 2a was synthesized using an equimolar ratio of the ligands and ZnCl<sub>2</sub> in DMF via a standard approach.<sup>19</sup> UV-Vis absorption spectra were performed to track the polymerization. As shown in Fig. 1, a new absorption peak appears at 385 nm after the polymerization, which is attributed to the  $\pi$ - $\pi$ \* transition of the metal complex, indicating the complexation of the ligands to Zn<sup>2+</sup>. The FT-IR spectra for 1a and 2a are shown in Fig. 2. For comparison's sake, the FT-IR spectrum of FHQ was also measured. The characteristic stretching vibration band of C=O in FHO is clearly observed at 1663 cm<sup>-1</sup>. The reaction of FHQ and PDAB can be confirmed by the following three bands: the sharp band of C=N bond (Schiff's base) at 1639  $\text{cm}^{-1}$  with



Fig. 1 UV-Vis absorption spectra of 1a and 2a in ethanol with  $4.0 \times 10^{-5}$  M (repeat units).



Fig. 2 FT-IR spectra (KBr) of FHQ, 1a and 2a.

a red-shift relative to the C=O absorption in FHQ;<sup>37</sup> a group of bands at 2800–3000 cm<sup>-1</sup> of C–H vibration stretching on the eight pendant organic arms of POSS, and the Si–O–C stretching band of the cubic cores of POSS located at 1111 cm<sup>-1</sup>. The FT-IR spectra further demonstrate that ligand **1a** has been successfully synthesized. The FT-IR spectrum of the coordination polymer **2a** is also shown in Fig. 2. In comparison to **1a**, the strong C=N band (aromatic ring) in **2a** shifts to 1659 cm<sup>-1</sup>,<sup>19</sup> and a new band appears at 1334 cm<sup>-1</sup>, associated with C–O vibrations of C–O–Zn,<sup>38</sup> indicating the complexation of the ligands to Zn<sup>2+</sup>. The molecular weights and molecular weight distributions of polymer **2a** were 220 000 and 1.34, as determined by GPC in DMF.

Compared to 3,5-bis(8-HQ Schiff base)-benzoic acid reported by Shi's group,<sup>5</sup> which showed poor solubility in common solvents, both **1a** and **2a** are readily soluble in most polar organic solvents, such as ethanol, THF, and DMF. Further, the solubility of **2a** in ethanol was measured as 17 mg ml<sup>-1</sup>. Meanwhile, we also synthesized another bis(8-HQ) ligand **1b** which bears dodecyl instead of POSS. However, unlike ligand **1a**, its zinc complex **2b** shows poor solubility in common low-boilingpoint solvents such as ethanol and THF, and it is only slightly soluble in DMF. These results obviously indicate that POSS is an efficient building block for the solubility enhancement of the coordination polymers due to the bulky and unique nanoscale cage-shaped structure with eight isobutyl groups.

The thermal stability of the coordination polymers was evaluated by TGA and DTA in air with a heating rate of 10 °C min<sup>-1</sup>. The onset of the thermal degradation was determined to be 205 °C and the  $T_d$  was about 213 °C for **2b** (Fig. S16 in the ESI†). In the case of **2a**, we observed an increase of 35 °C in the value of  $T_d$  as compared to **2b**, and the onset of the thermal degradation was determined as 214 °C (Fig. 3). Moreover, the ceramic yield of **2a** is approximately 18% higher than theory (19%), suggesting incomplete decomposition of the polymer at 600 °C. This result indicates that the grafted bulky POSS can enhance the thermal stability and reduce the flammability of the coordination polymer, as expected in most cases.<sup>23</sup>

The fluorescent properties of 2a and 2b have been studied. In dilute DMF solution, both 2a and 2b show similarly high emission bands with maxima around 500 nm under the same conditions (Fig. 4). The quantum yields of 2a and 2b in DMF are determined to be 0.43 and 0.41, respectively. However, the fluorescence of 2b is strongly quenched by intermolecular aggregation in the solid state as shown in Fig. 5. By contrast with 2b, 2a shows a well resolved band at 613 nm, indicating only weakly interacting  $\pi$ -stacks of chromophores in the solid state. Polymer 2a shows a much higher quantum yield (0.26) in the solid state as compared to polymer 2b (0.02). This enhancement of solid-state luminescence efficiencies has been widely reported for conjugated polymers.<sup>22,23</sup> The reason may attribute to the bulky POSS groups of 2a on the side chains, as optically inactive spacers,<sup>39</sup> which reduce the packing density of the chromophores in the solid state. To the best of our knowledge, this is the first example of the introduction of POSS units into the conjugated coordination polymers to prepare solid state fluorescent materials.

Motivated by the attractive potentials of fluorescent polymer nanoparticles particularly for the nanosized optoelectronic devices applications, researchers have engaged in developing



Fig. 3 TGA and DTA curves of 2a measured in air.



Fig. 4 Fluorescence spectra of 2a and 2b in dilute DMF solution excited at 385 nm.



Fig. 5 Fluorescence spectra of 2a and 2b in the solid state.

a new class of strongly fluorescent organic materials, *i.e.*, aggregation-induced emission conjugated polymer, for preparation of fluorescent polymer nanoparticles,<sup>40,41</sup> because of the factor that the fluorescence of polymers is generally decreased or quenched in their aggregation state. Herein, the new coordination polymer **2a** has good solubility in common organic solvents and can be processed in solution. We found that **2a** could form a micellar solution spontaneously with green fluorescence when it was dispersed in CHCl<sub>3</sub> by sonication, but **2b** kept undissolved in CHCl<sub>3</sub> even vigorously sonicated for a long time. The TEM image in Fig. S18 (ESI<sup>†</sup>) clearly reveals that spherical nanoparticles of **2a** are formed in CHCl<sub>3</sub>.

The self-assembly behavior of **2a** in CHCl<sub>3</sub> and the fluorescent properties of the nanoparticles have been studied. The critical micelle concentration (CMC) of **2a** in CHCl<sub>3</sub> was measured by fluorescence spectrophotometry. As shown in Fig. 6, the CMC is determined to be about 5  $\mu$ M (repeat units). In dilute CHCl<sub>3</sub> solution, **2a** displays maximum emission at 485 nm with 385 nm excitation, and the 15 nm blue-shift from DMF solution is attributed to the lower polarity of CHCl<sub>3</sub>. When the concentrations exceed the CMC, nanoparticles are formed as demonstrated from the appearance of a new peak at a higher



**Fig. 6** Concentration dependence of the emission of **2a** in CHCl<sub>3</sub> excited at 385 nm: concentration of repeat units:  $C1 = 2.5 \times 10^{-6}$  M,  $C2 = 5.0 \times 10^{-6}$  M,  $C3 = 7.5 \times 10^{-6}$  M,  $C4 = 1.0 \times 10^{-5}$  M,  $C5 = 2.5 \times 10^{-5}$  M,  $C6 = 5.0 \times 10^{-5}$  M,  $C7 = 7.5 \times 10^{-5}$  M,  $C8 = 1.0 \times 10^{-4}$  M,  $C9 = 2.0 \times 10^{-4}$  M.

wavelength in the PL spectra. We notice that with the increase of concentration, the new emission band shifts to a higher wavelength. The interesting concentration-dependent emissions can be attributed to the superposition of fluorescence of the unimers and the nanoparticles. The nanoparticles show strong fluorescence at 545 nm, which is strongly blue-shifted as compared to the solid-state emission. This indicates that the packing density of the chromophores in the nanoparticles is much lower than that in the solid state.

The formation of the nanoparticles was also investigated with DLS at different concentrations. In Fig. 7, a bimodal (two peaks) distribution can be observed at lower concentrations, indicating the unimers and the nanoparticles coexist in the solution. The  $\langle R_h \rangle$  of the unimer is about 3 nm, tracked by DLS. The size of the nanoparticles does not show obvious augmentation at higher concentrations, which suggests that there is only one kind of micellar aggregate.<sup>42</sup> Beside the bimodal distribution, the changes of their relative intensities are also in excellent agreement



Fig. 7 Hydrodynamic radius distributions obtained for CHCl<sub>3</sub> solution of **2a** at different concentrations.  $C1 = 2.5 \times 10^{-5}$  M,  $C2 = 7.5 \times 10^{-5}$  M,  $C3 = 2.0 \times 10^{-4}$  M.



**Fig. 8** Temperature-dependent fluorescence spectra obtained for  $10^{-4}$  M (repeat units) CHCl<sub>3</sub> solution of **2a**.

with the PL spectra. The disappearance of the unimers at  $10^{-4}$  M indicates a completed self-assembly of **2a**.

To test the stability of the fluorescent nanoparticles, temperature-dependent fluorescence measurements of the nanoparticles dispersed in CHCl<sub>3</sub> ( $10^{-4}$  M repeat units) were carried out below 60 °C, and the results are shown in Fig. 8. It can be seen that the emission maxima was resistant towards the change of temperature. It is worthy to point out that strong fluorescence of the nanoparticles can also be observed without the self-quenching of aggregation because of the incorporation of POSS moieties.

## Conclusions

In summary, this work reports a new kind of soluble bis(8hydroxyquinoline) zinc-based conjugated coordination polymer. The experimental results demonstrate that incorporation of POSS moieties not only effectively improves the solubility of the bis(8hydroxyquinoline) coordination polymers, but also prevents the fluorescence quenching effect caused by intermolecular aggregation. Both the solubility enhancement and the prevention of the fluorescence self-quenching will promote the application of 8hydroxyquinoline-based conjugated coordination polymer as electrooptic material. Moreover, this research provides a facile approach for the design and preparation of soluble conjugated metal coordination polymers as advanced materials.

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## References

- 1 X. Wang and R. McHale, Macromol. Rapid Commun., 2010, 31, 331.
- 2 A. O. Moughton and R. K. O'Reilly, *Macromol. Rapid Commun.*, 2010, **31**, 37.

- 3 S. Noro, S. Kitagawa, T. Akutagawa and T. Nakamura, *Prog. Polym. Sci.*, 2009, **34**, 240.
- 4 W. Lin, W. J. Rieter and K. M. L. Taylor, Angew. Chem., Int. Ed., 2009, 48, 650.
- 5 P. Jiang, W. Huang, J. Li, D. Zhuang and J. Shi, J. Mater. Chem., 2008, 18, 3688.
- 6 J. Crassous and R. Réau, Dalton Trans., 2008, 6865.
- 7 M. O. Wolf, J. Inorg. Organomet. Polym. Mater., 2006, 16, 189.
- 8 W. K. Chan, *Coord. Chem. Rev.*, 2007, 251, 2104.
  9 B. J. Holliday and T. M. Swager, *Chem. Commun.*, 2005, 23.
- 10 I. Manners, *Science*, 2001, **294**, 1664.
- 11 K. A. Williams, A. J. Boydston and C. W. Bielawski, *Chem. Soc. Rev.*, 2007, **36**, 729.
- 12 M. Sukwattanasinitt, A. Nantalaksakul, A. Potisatityuenyong, T. Tuntulani, O. Chailapakul and N. Praphairakait, *Chem. Mater.*, 2003, **15**, 4337.
- 13 Z. Yang, J. M. Lu and L. H. Wang, Polym. Bull., 2005, 53, 249.
- 14 T. M. Swager, Acc. Chem. Res., 2008, 41, 1181-1189.
- 15 P. Jiang, W. Zhu, Z. Gan, W. Huang, J. Li, H. Zeng and J. Shi, J. Mater. Chem., 2009, 19, 4551.
- 16 M. A. Palacios, Z. Wang, V. A. Montes, G. V. Zyryanov and P. Anzenbacher, Jr., J. Am. Chem. Soc., 2008, 130, 10307.
- 17 V. A. Montes, G. V. Zyryanov, E. Danilov, N. Agarwal, M. A. Palacios and P. Anzenbacher, Jr., J. Am. Chem. Soc., 2009, 131, 1787.
- 18 L. Xiao, Y. Liu, Q. Xiu, L. Zhang, L. Guo, H. Zhang and C. Zhong, J. Polym. Sci., Part A: Polym. Chem., 2010, 48, 1943.
- 19 H. Huang, C. Zhong and Y. Zhou, Eur. Polym. J., 2008, 44, 2944.
- 20 L. Xiao, Y. Liu, Y. Zhou, H. Huang, L. Li and C. Zhong, J. Coord. Chem., 2010, 63, 3117.
- 21 D. B. Cordes, P. D. Lickiss and F. Rataboul, *Chem. Rev.*, 2010, **110**, 2081.
- 22 K. L. Chan, P. Sonar and A. Sellinger, J. Mater. Chem., 2009, 19, 9103.
- 23 F. Wang, X. Lu and C. He, J. Mater. Chem., 2011, 21, 2775.
- 24 J. Wu and P. T. Mather, Polym. Rev., 2009, 49, 25.
- 25 J. Q. Zhao, Y. Fu and S. M. Liu, Polym. Polym. Compos., 2008, 16, 483.
- 26 S. H. Philips, T. S. Haddad and S. J. Tomczak, Curr. Opin. Solid State Mater. Sci., 2004, 8, 21.
- 27 P. D. Lickiss and F. Rataboul, *Adv. Organomet. Chem.*, 2008, 57, 1.
- 28 M. Joshi and B. S. Butola, Polym. Rev., 2004, 44, 389.
- 29 G. Li, L. Wang, H. Ni and C. U. Pittman Jr., J. Inorg. Organomet. Polym., 2001, 11, 123.
- 30 R. Y. Kannan, H. J. Salacinski, P. E. Butler and A. M. Seifalian, Acc. Chem. Res., 2005, 38, 879.
- 31 E. A. Quadrelli and J.-M. Basset, Coord. Chem. Rev., 2010, 254, 707.
- 32 D. Gnanasekaran, K. Madhavan and B. S. R. Reddy, J. Sci. Ind. Res., 2009, 68, 437–464.
- 33 C. Jiang, W. He, Z. Tai and J. Ouyang, Spectrochim. Acta, Part A, 2000, 56, 1399.
- 34 A. Hari and B. L. Miller, Tetrahedron Lett., 1999, 40, 245.
- 35 K. Takahashi, S. Sulaiman, J. M. Katzenstein, S. Snoblen and R. M. Laine, Aust. J. Chem., 2006, 59, 564.
- 36 A. Meyers and M. Weck, Macromolecules, 2003, 36, 1766.
- 37 H. Zeng, W. Huang and J. Shi, Chem. Commun., 2006, 880.
- 38 J. Cheng, C. H. Chen and C. H. Liao, Chem. Mater., 2004, 16, 2862.
- 39 M. Brinkmann, G. Gadret, M. Muccini, C. Taliani, N. Masciocchi and A. Sironi, J. Am. Chem. Soc., 2000, 122, 5147.
- 40 R. Deans, J. Kim, M. R. Machacek and T. M. Swager, J. Am. Chem. Soc., 2000, 122, 8565.
- 41 B. K. An, S. K. Kwon, S. D. Jung and S. Y. Park, J. Am. Chem. Soc., 2002, 124, 14410.
- 42 H. Hussain, B. H. Tan, G. L. Seah, Y. Liu, C. B. He and T. P. Davis, *Langmuir*, 2010, 26, 11763.