

# Hyperbranched Polymer Based on Triphenylamine and Pyridine: Fluorescent Chemosensors for Palladium Ions

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Received 23 April 2010; accepted 3 October 2010

DOI 10.1002/app.33527

Published online 17 February 2011 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** Two new hyperbranched fluorescent conjugated polymers containing pyridine units were synthesized via Heck coupling reaction and Sonogashira coupling reaction, respectively, and characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, FTIR, and GPC. The copolymers are readily soluble in common organic solvents such as chloroform, THF, and DMF. Thermal analysis revealed that the copolymers had good thermal stability. The fluorescence quenching behaviors of the hyperbranched copoly-

mers by metal ions were studied. It was found that the fluorescence of the copolymers can be effectively quenched by  $\text{Pd}^{2+}$ . Moreover, the two hyperbranched copolymers exhibited different quenching efficiency, which may be related to difference in the hindrance for the chelation of pyridine unit with metal ions of the two polymers. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 217–225, 2011

**Key words:** hyperbranched; fluorescence; sensors

## INTRODUCTION

Recently, Pd has been proved to exhibit high levels of biochemical activity, e.g., cytotoxicity and mutagenicity. Chronic exposure even at very low levels to Pd may lead to risks of significant negative effects on human health.<sup>1–5</sup> Therefore, there is an exigent need to develop effective monitoring methods to detect trace amounts of  $\text{Pd}^{2+}$  ions in the environment. Traditional methods for  $\text{Pd}^{2+}$  ion assays such as flame atomic absorption spectrometry (FAAS) and inductively coupled plasma mass spectrometry (ICP-MS) often require sophisticated instruments and skilled professionals,<sup>6</sup> which hindered their practical applications.

Fluorescent conjugated polymers (CPs) are promising chemical sensitive materials developed in recent years. They are featured with high sensitivity and ease of measurement, thus have been successfully utilized for the detection of a variety of analytes ranging from ions,<sup>7</sup> explosives,<sup>8</sup> to biomolecules.<sup>9</sup> In comparison with the small molecule-based fluorescent chemosensors, the electron delocalized backbone structures of CPs allow for more rapid and

efficient in-chain and intrachain exciton migrations, giving rise to enhanced signal outputs with high detection sensitivity.<sup>10,11</sup> By introducing specific ligands such as bipyridine,<sup>12</sup> phenanthroline,<sup>13</sup> quinoline,<sup>14</sup> and dipyrrolylquinoxaline<sup>15</sup> to the polymer backbones or side chains, CPs have been successfully used for metal ion detection.

However, until now, there are few reports on the applications of CP-based fluorescent sensors for the determination of  $\text{Pd}^{2+}$  ions. Herein, we report the synthesis of two new CPs with pyridine units and hyperbranched structure, and investigations on their fluorescent quenching behaviors by  $\text{Pd}^{2+}$  and other interference metal ions. Pyridine was chosen as the binding domain because the monopyridyl group has a great affinity for  $\text{Pd}^{2+}$  ion and could bind selectively.<sup>16,17</sup> While the introduction of hyperbranched structure into CPs was based on the following considerations: it was known that greatly enhanced amplification in CPs (and therefore high sensitivity) can be achieved by simply increasing the diffusional pathways available to the exciton, because the probability that an exciton visits a new receptor and quenches the fluorescent signal is increased accordingly.<sup>18</sup> In this sense, dendrimers with 3D structures may be a good choice compared with the linear polymers. However, their synthesis usually involved with complicated procedures. Instead, hyperbranched polymers (HBPs) provide an excellent alternative since they can be easily synthesized in one reaction while showing comparable

Additional Supporting Information may be found in the online version of this article.

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*Journal of Applied Polymer Science*, Vol. 121, 217–225 (2011)  
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properties.<sup>19</sup> Both polymers were found to exhibit high sensitivity in the fluorescent response to Pd<sup>2+</sup> ion, while the interference of most common metal ions were negligible.

## EXPERIMENTAL

### Materials

Methyl triphenylphosphonium bromide (MTPB), (trimethylsilyl) acetylene (TMSA), and 2,5-dibromopyridine was purchased from Alfa Aesar. Triphenylamine (TPA) was recrystallization from ethanol. DMF was purified by reduced pressure distillation from CaH<sub>2</sub>. Phosphorus oxychloride (POCl<sub>3</sub>) was purified by reduced pressure distillation. Diethylamine (DEA) and triethylamine (TEA) were purified by distillation from CaH<sub>2</sub>. Diisopropylamine (DIPA) was purified by distillation from NaOH. All other reagents were commercially obtained and used without purification.

### Synthesis of monomers

#### Preparation of 4,4'-diformyl triphenylamine (1)

Phosphorus oxychloride (46.6 mL, 0.5 mol) was added dropwise to a stirred 77.4 mL (1 mol) of DMF at 0°C.<sup>20–23</sup> The mixture was stirred at 0°C for 1 h and then stirred at room temperature for another 1 h. After the addition of triphenylamine (10 g, 0.04 mol) dissolved in 10 mL of 1,2-dichloroethane, the mixture was stirred at 80°C for 48 h. After cooling, the solution was poured into cold water. The resulting mixture was neutralized to pH of 7 with 2M NaOH aqueous solution and extracted with dichloromethane. The extract was washed with plenty of brine and the solvent was removed at reduced pressure. The residue was chromatographed on a silica gel column with ethyl acetate/*n*-hexane (v/v, 1/3) to produce 8 g of yellowish solid. Yield: 66%. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ (ppm) 7.12–7.19 (m, 6H), 7.23–7.26 (m, 1H), 7.33–7.37 (m, 2H), 7.71–7.77 (m, 4H), 9.86 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ (ppm) 122.68, 126.20, 126.99, 130.09, 131.17, 131.24, 145.41, 151.94, 190.49; Anal. Calcd. for C<sub>20</sub>H<sub>15</sub>NO<sub>2</sub>: C 79.72; H 5.02; N 4.65. Found: C 79.79; H 4.97; N 4.68.

#### Preparation of tris(4-formyl-phenyl)amine (2)

Phosphorus oxychloride (46.6 mL, 0.5 mol) was added dropwise to a stirred 77.4 mL (1 mol) of DMF at 0°C. The mixture was stirred at 0°C for 1 h and additionally stirred at room temperature for 1 h. After the addition of compound 1 (6 g, 0.02 mol) in 10 mL of 1, 2-dichloroethane, the mixture was stirred at 80°C for 48 h. After cooling, the solution was poured into water. The resulting mixture was neutralized to pH of 7 with 2M NaOH aqueous

solution and extracted with dichloromethane. The extract was washed with plenty of brine and the solvent was removed at reduced pressure. The residue was chromatographed on a silica gel column with ethyl acetate/*n*-hexane (v/v, 1/2) as eluent to produce 1.35 g of yellowish solid. Yield: 20%. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ (ppm) 9.92 (s, 3H), 7.84 (d, 6H), 7.24 (d, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ (ppm) 124.49, 131.46, 132.52, 151.14, 190.46; Anal. Calcd. for C<sub>21</sub>H<sub>15</sub>NO<sub>3</sub>: C 76.58; H 4.59; N 4.25. Found: C 76.45; H 4.65; N 4.42.

#### Preparation of tris(4-vinylphenyl)amine (3)

Potassium *tert*-butoxide (1.8 g, 16 mmol) was added to a solution of methyl triphenylphosphonium bromide (5.36 g, 10 mmol) in 30 mL of THF under cooling and argon atmosphere, during which the solution changed to yellow color. The reaction solution was stirred for another 30 min and then compound 2 (0.7g, 2.1 mmol) dissolved in 2 mL THF was added. The ice bath was removed and the reaction was stirred for 3 days at room temperature. The reaction was quenched by few drops of water. The mixture was then dissolved in dichloromethane and partitioned with water. The organic layer was extracted, washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>. After solvent evaporation the crude product was chromatographed on a silica gel column with petroleum ether/diethyl ether (v/v, 3/1) as eluent to give clear oil. The oil solidified into 0.55 g white solid under vacuum. Yield: 81%. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ (ppm) 7.3 (d, 6H), 7.06 (d, 6H), 6.96 (m, 3H), 5.69 (d, 3H) 5.19 (d, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ (ppm) 147.1, 136.3, 132.5, 127.3, 124.2, 112.6; Anal. Calcd. for C<sub>24</sub>H<sub>21</sub>N: C 89.12; H 6.54; N 4.33. Found: C 89.23; H 6.48; N 4.29.

#### Preparation of tris(4-iodophenyl)amine (4)

TPA (3.92 g, 16 mmol), potassium iodide (5.84 g, 35.2 mmol) and potassium iodate (3.76 g, 17.6 mmol) were dissolved in 240 mL of acetic acid. The mixture was stirred at 110°C for 12 h. After cooling, the formed precipitate was collected. The crude product was thoroughly washed with 200 mL water. The solid was dissolved in 100 mL chloroform and consecutively washed with water, 0.2M aqueous sodium sulfite solution, and NaHCO<sub>3</sub>. The organic layer was dried over anhydrous MgSO<sub>4</sub>. After solvent evaporation, a light gray solid was obtained, which was purified by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/hexane (v/v, 1/2). 8.96 g light gray solid was obtained. Yield: 90%. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ (ppm) 7.54 (m, 6H), 6.81 (m, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ (ppm) 146.8, 138.7, 126.3, 86.9; Anal. Calcd. for C<sub>18</sub>H<sub>12</sub>I<sub>3</sub>N: C 34.70; H 1.94; N 2.25. Found: C 34.66; H 2.01; N 2.46.

### Preparation of 2,5-bis[(trimethylsilyl)ethynyl]pyridine (5)

The 2,5-dibromopyridine (3.60 g, 15.2 mmol), (trimethylsilyl) acetylene (3.03 g, 30.8 mmol), bis(triphenylphosphine) palladium (II) chloride (140 mg), and a catalytic amount of copper (I) iodide (5 mg) were added into a 100 mL Schlenk type flask charged with 50 mL of freshly distilled diethylamine. The solution was stirred for 12 h at room temperature under an atmosphere of argon. Diethylamine was then removed *in vacuo*, and the precipitate was extracted into diethyl ether. The compound was separated by chromatography on silica gel with petroleum ether/diethyl ether (v/v, 3/1) as eluent. The product was further purified by sublimation and recrystallization from hexane, affording 3.41 g white crystalline solid. Yield: 83%.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.60 (s, 1H), 7.66 (d, 1H), 7.36 (d, 1H), 0.20, 0.24 (s, 18H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 152.6, 141.7, 138.8, 126.4, 119.5, 103.3, 101.2, 100.2, 97.04, -0.3; Anal. Calcd. for  $\text{C}_{15}\text{H}_{21}\text{Si}_2\text{N}$ : C 66.36; H 7.80; N 5.16. Found: C 66.49; H 7.84; N 5.24.

### Preparation of 2,5-diethynylpyridine (6)

Compound 5 (1.00 g, 3.7 mmol) was dissolved in 10 mL of methanol in a 100 mL Schlenk type flask. About 4 mL of 1M potassium hydroxide was added into this solution, and the solution was allowed to stir for 1 h. After removing the solvent *in vacuo*, the product was extracted into diethyl ether and washed several times with water and brine solution. The product was separated by column chromatography on silica with petroleum ether/diethyl ether (v/v, 3/1) as eluent and further purified by recrystallization in hexane affording 0.4 g white needles. Yield: 85%.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.64 (s, 1H), 7.70 (d, 1H), 7.41 (d, 1H), 3.28 (s, 1H), 3.23 (s, 1H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 152.9, 141.5, 139.1, 126.6, 119.0, 82.4, 82.3, 79.9, 79.0; Anal. Calcd. for  $\text{C}_9\text{H}_5\text{N}$ : C 85.02; H 3.96; N 11.02. Found: C 84.72; H 4.01; N 10.93.

## Synthesis of polymers

### Preparation of hyperbranched copolymer HTPY

The monomer 3 (200 mg, 0.6 mmol) and 2,5-dibromopyridine (213 mg, 0.9 mmol), palladium (II) acetate (20 mg), tri(*o*-tolyl) phosphine (100 mg), anhydrous DMF (2.5 mL) and triethylamine (2.5 mL) were mixed and stirred for 48 h at 90°C under argon. Then the mixture was cooled to room temperature and poured into an amount of methanol. After stirring for several hours, a dark-red precipitate was collected, dissolved in THF, and reprecipitated into methanol. Then the precipitate was extracted with methanol in a Soxhlet apparatus for 48 h. After dry-

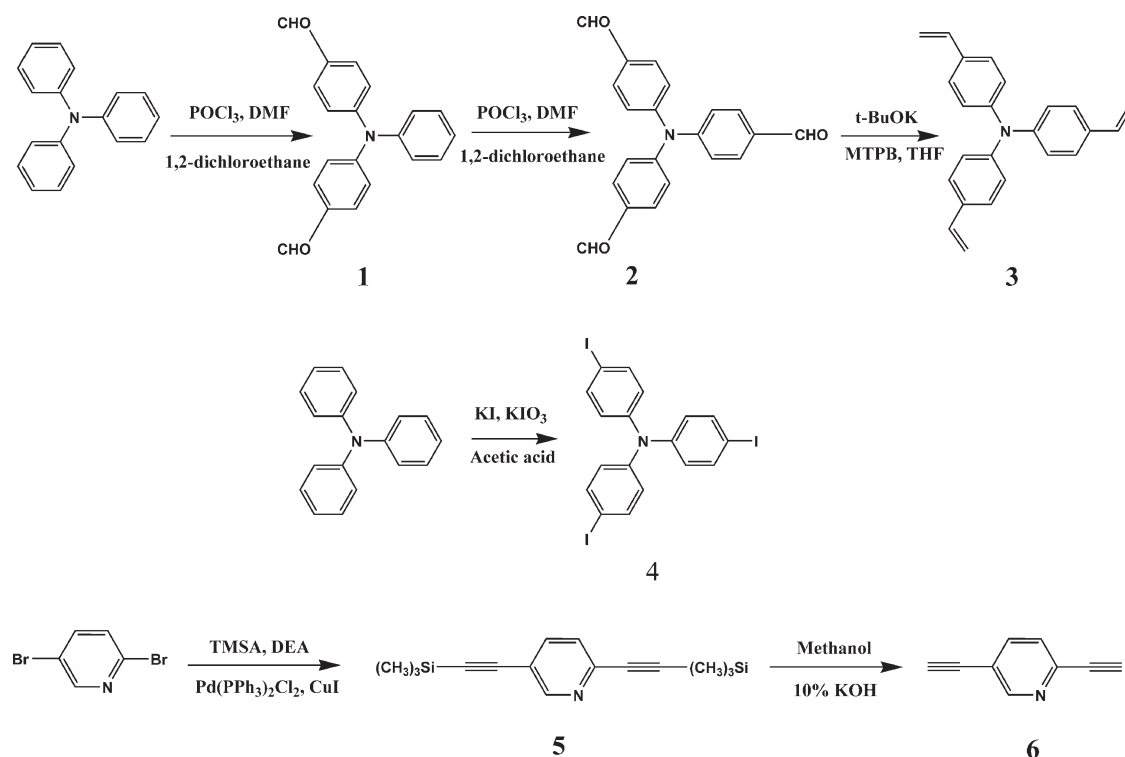
ing under vacuum at 60°C for 12 h, HTPY was obtained. Yield: 142 mg, 53%. FTIR (KBr,  $\text{cm}^{-1}$ ): 3032, 2921, 1595, 1504, 1459, 1322, 1283, 1187, 1092, 833  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ),  $\delta$  (ppm) 8.89 (m, pyridine protons), 8.45 (m, pyridine protons), 8.28 (m, pyridine protons), 6.9–8.1(m, aromatic protons), 6.61–6.74 (dd, end vinyl group (v)-H), 5.63–5.69 (d, v-H), 5.16–5.21 (d, v-H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm) 152.7, 148.1, 146.6, 146.0, 136.5, 135.7, 134.5, 134.2, 133.4, 132.6, 127.5, 126.5, 125.3, 123.9, 123.6, 122.3, 121.9, 121.5, 116.9, 116.7.

### Preparation of hyperbranched copolymer HTPYB

The monomer 4 (305 mg, 0.5 mmol) and 6 (95 mg, 0.75 mmol), bis(triphenylphosphine) palladium(II) chloride (60 mg), and copper(I) iodide (12 mg), anhydrous toluene (20 mL), and diisopropylamine (10 mL) were mixed and stirred for 48h at 70°C under argon. Then the mixture was cooled to room temperature and poured into an amount of methanol. After stirring for several hours, a dark-red precipitate was collected, dissolved in THF, and reprecipitated into methanol. Then the precipitate was extracted with methanol in a Soxhlet apparatus for 48 h. After drying under vacuum at 60°C for 12 h, HTPYB was obtained. Yield: 148 mg, 52%. FTIR (KBr,  $\text{cm}^{-1}$ ): 3033, 2965, 2212, 1581, 1504, 1482, 1316, 1289, 1264, 1181, 1160, 1097, 1060, 1008, 816, 696  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ),  $\delta$  = 8.73 (m, pyridine protons), 8.40 (m, pyridine protons), 8.29 (m, pyridine protons), 6.82–7.87 (m, aromatic protons);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  = 152.6, 147.6, 146.6, 142.1, 138.5, 133.5, 133.2, 128.1, 127.9, 127.4, 126.9, 126.5, 126.3, 123.8, 123.2, 123.1, 122.9, 87.4, 86.2, 78.8, 78.7.

## Instrumentation

FTIR spectra were recorded on a Bruker Vector 22 IR spectrometer. NMR spectra were recorded using a Varin mercury Plus NMR, operating at 300 MHz for  $^1\text{H NMR}$  and at 75 MHz for  $^{13}\text{C NMR}$  (solvent:  $\text{CDCl}_3$ ; internal standard: tetramethylsilane). GPC analysis was conducted with a Waters 2696 separation module equipped with a Waters 410 differential refractometer HPLC system and Waters Styragel HR 4E columns using polystyrene as standard and THF as eluant. Thermogravimetric analyses (TGA) were conducted on a Perkin–Elmer Pyris 6 TGA under a heating rate of 20°C  $\text{min}^{-1}$ . The elemental analyses were performed on ThermoFinnigan Instrument Flash EA1112. The UV–vis spectra were recorded on a Cary 100 Bio UV–vis spectrophotometer. Photoluminescence (PL) measurements were carried out on Perkin–Elmer LS55 Luminescence spectrometer. Cyclic voltammetry was performed on a CHI440 Electrochemical Workstation. It was carried out in



Scheme 1 Synthetic routes of monomers.

0.1M tetrabutylammonium perchlorate (TBAP)/dichloromethane, where the polymer concentration was 2–4 mg mL<sup>-1</sup>, with platinum wires as both counter and working electrodes, and Hg/Hg<sup>2+</sup> as a reference electrode. The ionization potential (IP) and electron affinity (EA) of the polymer were estimated using the following relations<sup>24,25</sup>:  $[E_{\text{on}}]^{\text{ox}} = \text{IP}/e - 4.71$  and  $[E_{\text{on}}]^{\text{red}} = \text{EA}/e - 4.71$ , where  $e$  is the primary electron charge, the  $[E_{\text{on}}]^{\text{ox}}$  and  $[E_{\text{on}}]^{\text{red}}$  are the onset potentials for the oxidation and reduction of polymers versus the reference electrode.

## RESULTS AND DISCUSSION

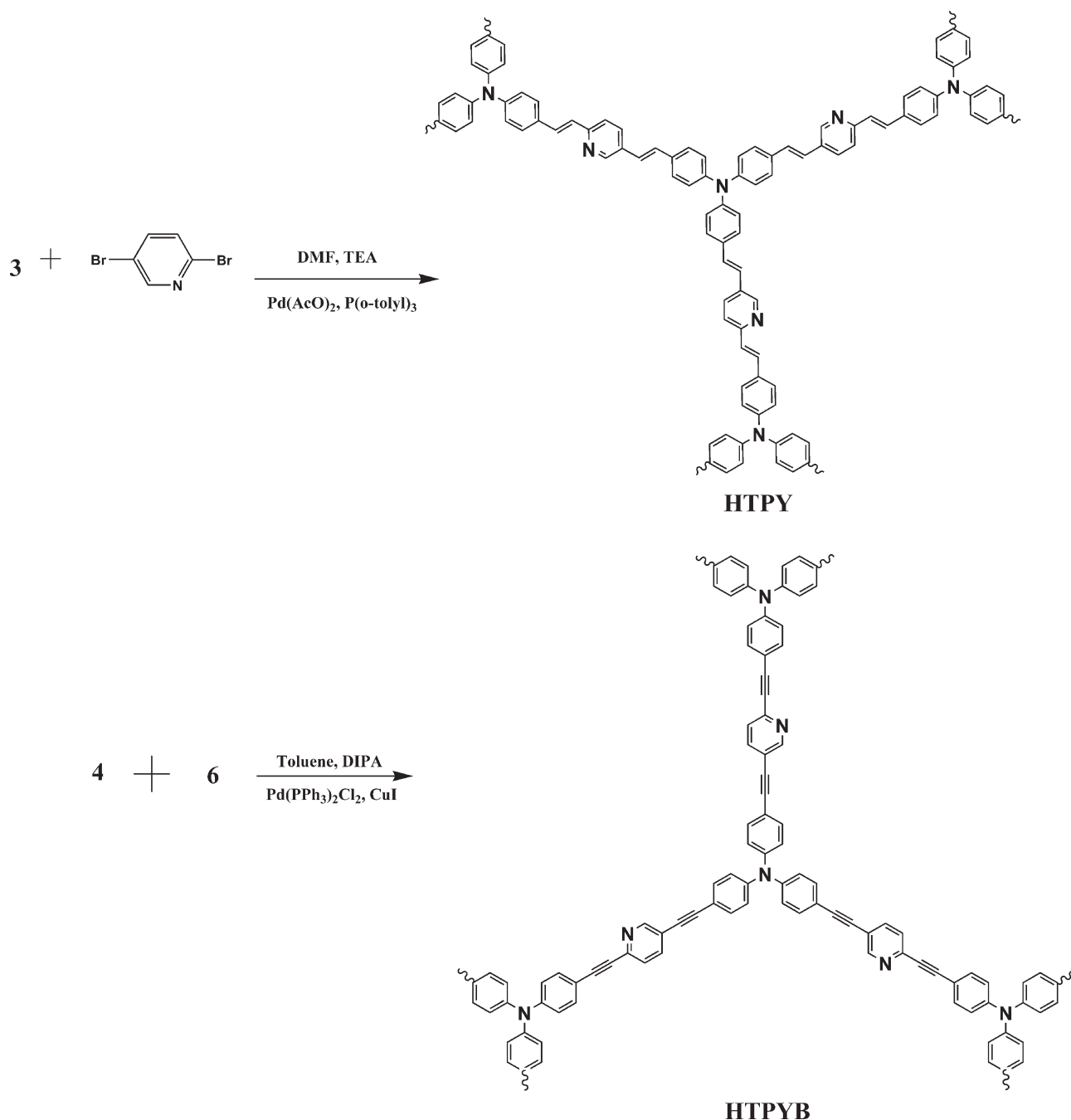
### Synthesis and characterization

Hyperbranched copolymers (HTPY and HTPYB) containing triphenylamine and pyridine units were synthesized via Heck coupling reaction and Sonogashira coupling reaction, respectively. The monomers, polymers, and their synthetic routes are illustrated in Schemes 1 and 2. Pyridine was chosen as the binding domain because the monopyridyl group has a great affinity for the Pd<sup>2+</sup> ion and should selectively bind by self-assembly.

All the intermediates were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, and element analysis. The polymers were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, and FTIR. In the <sup>1</sup>H NMR spectrum of HTPY [Fig. 1(a)], the three signals in the lower field at 8.89, 8.45, and 8.28 ppm, respectively, are attributed to the three

kinds of different protons on the pyridine ring, the signals between 6.9 and 8.1 ppm belong to the protons on the triphenylamine ring, and other signals at 6.61, 5.69, and 5.16 ppm, respectively, are assigned to the vinyl protons of end groups. In the <sup>1</sup>H NMR spectrum of HTPYB [Fig. 1(b)], the three signals in the lower field at 8.73, 8.40, and 8.29 ppm, respectively, are attributed to the three kinds of different protons on the pyridine ring, the signals between 6.82 and 7.87 ppm belong to the protons on the triphenylamine ring, and other signals at 3.72 ppm are assigned to the ethynyl protons of end groups. FTIR analysis revealed that both HTPY and HTPYB have the same characteristic absorptions in the range of 1430–1595 cm<sup>-1</sup> for pyridyl and benzene rings (see the Supporting Information Fig. S1). There is an absorption peak at 959 cm<sup>-1</sup> for HTPY, corresponding to the out-of-plane bending mode of the *trans*-vinylene groups, indicating that the newly formed vinylene double bonds are mainly in the *trans* configuration. The FTIR spectrum of HTPYB shows a very weak  $\nu_{\text{C}\equiv\text{C}}$  band around 2212 cm<sup>-1</sup>.

The copolymers are readily soluble in common organic solvents such as chloroform, THF, and DMF. The molecular weight and its distribution were measured by GPC to be  $M_n = 1903$ ,  $M_w = 2054$  and PDI = 1.08 for HTPY, and  $M_n = 2249$ ,  $M_w = 2750$  and PDI = 1.22 for HTPYB (Table I, Supporting Information Fig. S2 and 3). It is worth noting that the molecular weight value of polymer HTP



**Scheme 2** Synthetic routes of HTPY and HTPYB.

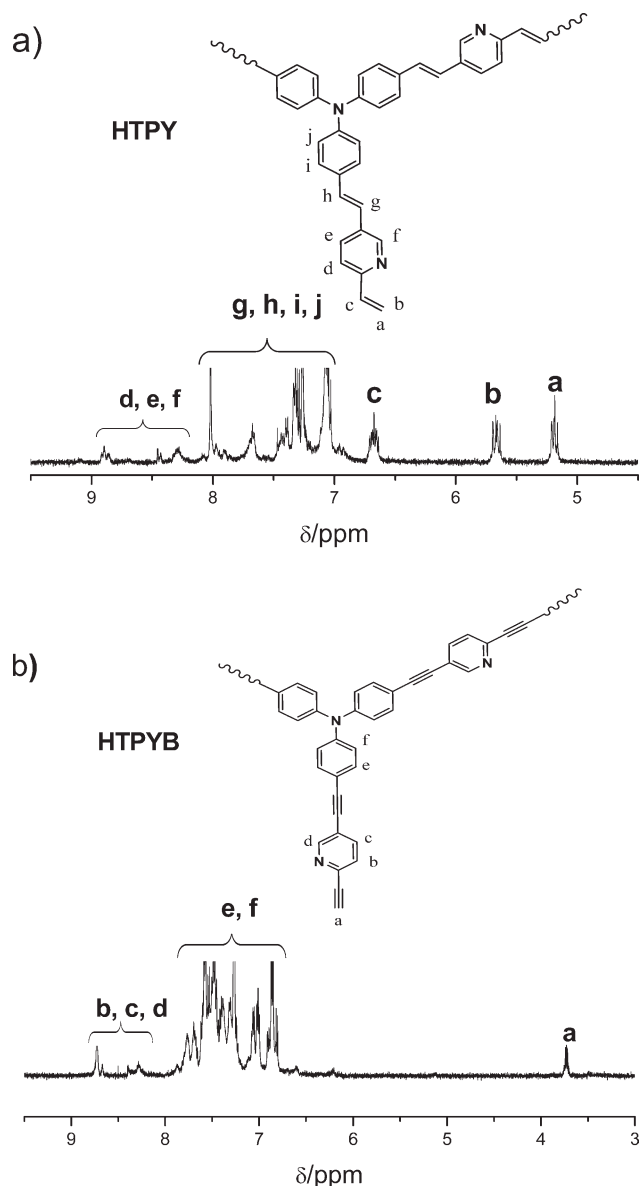
obtained by GPC should be treated as rough estimate due to the big differences in hydrodynamic radius between the hyperbranched polymers and polystyrene standard.<sup>26,27</sup> The narrow polydispersity is probably a result of extensive purification of the samples due to fractionation.

#### Thermal properties, UV-vis, and photoluminescence spectroscopic studies

Thermogravimetric analysis of the polymers revealed a maximum decomposition rate around 371°C and an

onset with 10% mass loss at around 324°C for HTPY, and a maximum decomposition rate around 407°C and an onset with 10% mass loss at around 358°C for HTPYB, respectively, (Fig. 2).

The spectroscopic properties of HTPY and HTPYB were measured both in solution (THF) and as thin films (spin-cast from chloroform solutions). The UV-visible absorption and photoluminescence (PL) spectra of HTPY and HTPYB in the THF solution ( $\sim 1.0 \times 10^{-6}$  M) are shown in Figure 3. HTPY exhibits the maximum absorption wavelength at 426 nm. Its PL spectrum peaks at 498 nm with one shoulder at



**Figure 1**  $^1\text{H}$  NMR spectra of (a) HTPY and (b) HTPYB.

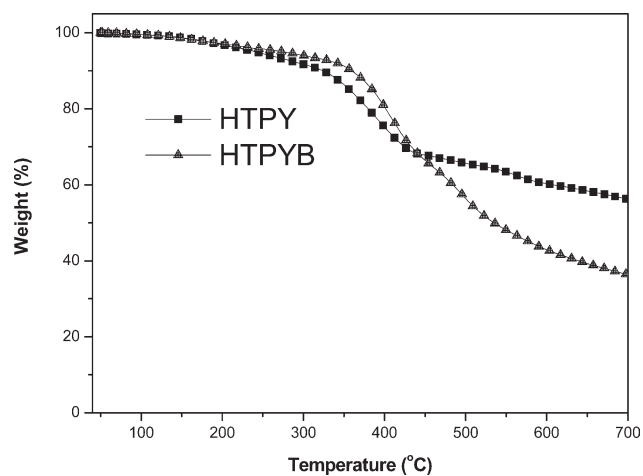
579 nm. Compared with HTPY, HTPYB shows obvious spectral hypsochromic shifts, both in absorption ( $\Delta = 30$  nm) and in emission ( $\Delta = 28$  nm). This obvious spectral difference could be

**TABLE I**  
Basic Properties of HTPY and HTPYB

Polymer	Yield (%)	$M_n^a$	$M_w^a$	PDI <sup>a</sup>	$T_d$ ( $^{\circ}\text{C}$ ) <sup>b</sup>
HTPY	53%	1903	2054	1.08	324
HTPYB	52%	2249	2750	1.22	358

<sup>a</sup> The weight-average molecular weight ( $M_w$ ), number-average molecular weight ( $M_n$ ), and polydispersity index (PDI) were determined for HTP by GPC with polystyrene standards in THF.

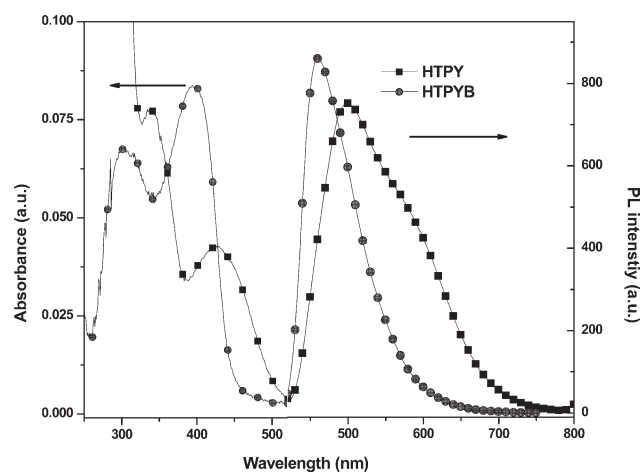
<sup>b</sup> Temperature at the 10% weight loss recorded by TGA at a heating rate of  $20\text{ C min}^{-1}$ .



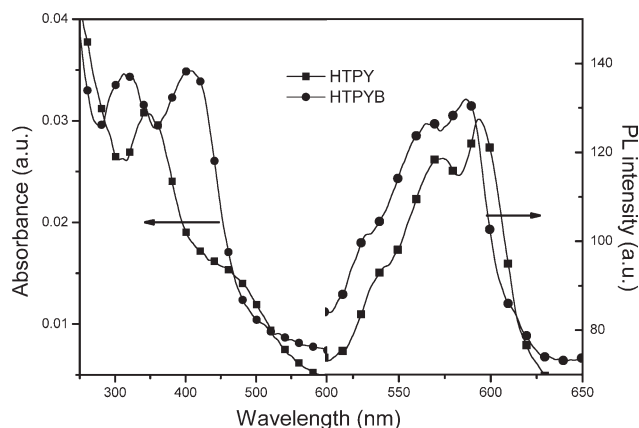
**Figure 2** TGA curves of HTPY and HTPYB (heating rate:  $20^{\circ}\text{C min}^{-1}$ ).

understood in terms of the better conjugation along the HTPY main chain than that in HTPYB.

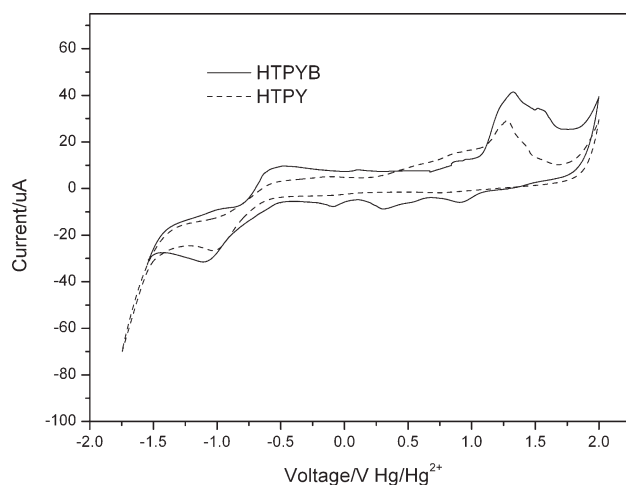
Transparent and uniform film of the polymer was prepared on quartz plates by spin-casting their solutions in chloroform at room temperature. The absorption spectrum of HTPY film shows a peak at 466 nm with an onset wavelength of 556 nm (Band gap of 2.23 eV, Fig. 4). In comparison with its solution emission at 498 nm, the main emission peak of HTPY in the solid film is at 593 nm which shifted about 95 nm toward the longer wavelength. This may be due to the strong intrachain and/or interchain interactions of excited states in the solid state. Compared with HTPY, HTPYB shows obvious spectral hypsochromic shifts, both in absorption ( $\Delta = 60$  nm) and in emission ( $\Delta = 8$  nm). The fluorescence quantum yields were measured and summarized in Table II.



**Figure 3** UV-visible absorption spectra and photoluminescence spectra of HTPY and HTPYB measured from the THF solutions ( $\sim 1.0 \times 10^{-6}$  M) at room temperature ( $\lambda_{\text{ex}} = 405$  nm for HTPY and 398 nm for HTPYB).



**Figure 4** UV-visible absorption spectra and photoluminescence spectra of HTPY and HTPYB measured from the spin-coated films on quartz plates at room temperature ( $\lambda_{\text{ex}} = 398$  nm for HTPY and 391 nm for HTPYB).



**Figure 5** Cyclic voltammetry at  $50 \text{ mV s}^{-1}$  of HTPY and HTPYB in  $\text{CH}_2\text{Cl}_2 + \text{TBAP}$  (0.1 M).

### Electrochemical properties

The electrochemical properties of the polymer solution were studied by cyclic voltammetry. Figure 5 shows the cyclic voltammogram of HTPY and HTPYB solution. The corresponding electrochemical data are summarized in Table II. As shown, the polymers show irreversibility in both *n*-doping and *p*-doping processes. The reduced electrochemical reversibility of the polymer could be attributed to the enhancement of electron affinity of the polymers through the introduction of the pyridine segments, which are electron deficient and prefer *n*-doping. On sweeping the polymer cathodically, the onset of the *n*-doping process occurred at the potential of  $-0.68$  and  $-1.01$  V for HTPY and HTPYB, respectively, ( $[E_{\text{on}}]^{\text{red}}$ ). In the anodic scan, the *p*-doping process onset at  $1.11$  and  $1.07$  V for HTPY and HTPYB, respectively, ( $[E_{\text{on}}]^{\text{ox}}$ ). According to the difference between IP and EA (or  $[E_{\text{on}}]^{\text{ox}}$  and  $[E_{\text{on}}]^{\text{red}}$ ), the corresponding electrochemical band gap of HTPY and HTPYB were  $1.79$  and  $2.08$  eV, respectively.

### Fluorescence quenching properties by metal ions

The fluorescent responsive properties of the polymers toward metal ions were investigated in THF solution at concentration of  $1.0 \times 10^{-6}$  M [based on the moles of the repeat unit (RU)].

Figure 6(a) shows the emission spectra of HTPY in THF upon successive addition of  $\text{Pd}^{2+}$  ions ( $[\text{Pd}^{2+}] = (0-35) \times 10^{-6}$  M) with an excitation wavelength of  $448$  nm. It is clearly seen that the addition of  $\text{Pd}^{2+}$  ion leads to a significant quenching of the emission of HTPY. Furthermore, both dynamic and static quenching follow a linear Stern-Volmer plot ( $I_0/I$  versus  $[\text{Pd}^{2+}]$ , where  $I$  and  $I_0$  are the fluorescence intensity measured with and without the addition of  $\text{Pd}^{2+}$  ions).<sup>18</sup> However, if the dynamic quenching and static quenching exist simultaneously, an upward curve is observed.<sup>28</sup> The quenching of HTPY shows an upward nonlinear curvature in the Stern-Volmer plot at high  $\text{Pd}^{2+}$  ion concentration ( $\geq 35 \times 10^{-6}$  M) [Fig. 6(b)]. At a lower concentration of  $\text{Pd}^{2+}$  ions ( $0-30 \times 10^{-6}$  M), a linear Stern-Volmer plot is obtained with a Stern-Volmer constant ( $K_{\text{SV}}$ )

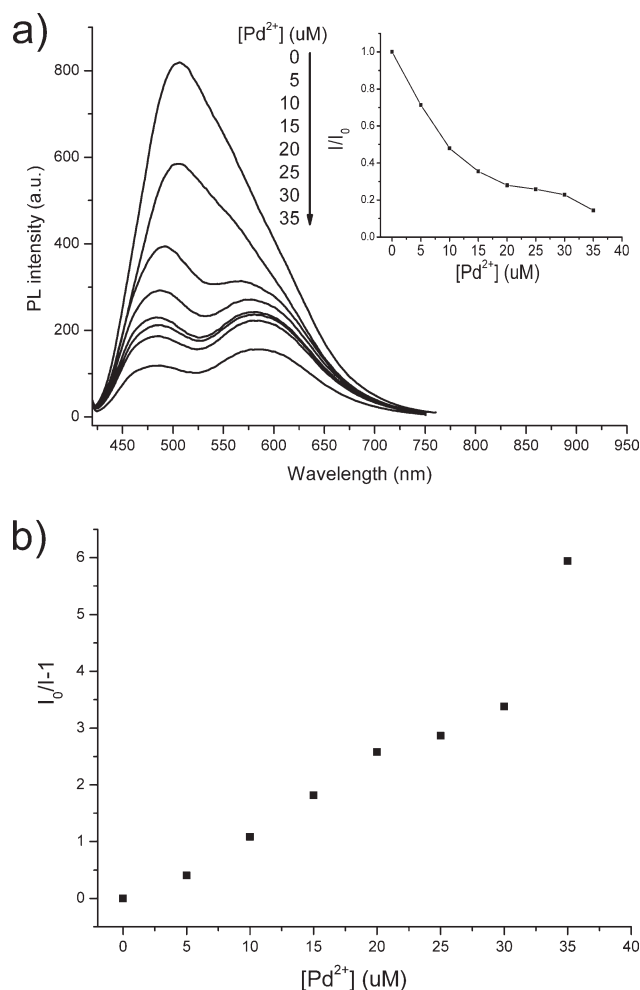
**TABLE II**  
Optical and Electrochemical Data of HTPY and HTPYB

Polymer	$\lambda_{\text{max}}$ (solution) (nm)		$\lambda_{\text{max}}$ (film) (nm)		Quantum yields <sup>a</sup>	Redox potential (V vs. $\text{Hg}/\text{Hg}^{2+}$ )		Band gap (eV)	
	abs	em	abs	em		$[E_{\text{on}}]^{\text{red}}$	$[E_{\text{on}}]^{\text{ox}}$	$E_g^{\text{b}}$	$E_g^{\text{c}}$
HTPY	426	498	466	593	0.21	$-0.68$	$1.11$	$2.23$	$1.79$
HTPYB	396	470	406	575	0.85	$-1.01$	$1.07$	$2.58$	$2.08$

<sup>a</sup> Quantum yields were determined relative to RhB in ethanol with a quantum yield of 0.69.

<sup>b</sup> Band gaps were estimated from the onset wavelength of optical absorption of solid-state film:  $E_g = 1240/\lambda_{\text{onset}}$ .

<sup>c</sup> Band gaps were determined from electrochemical data in  $\text{CH}_2\text{Cl}_2$  solution.



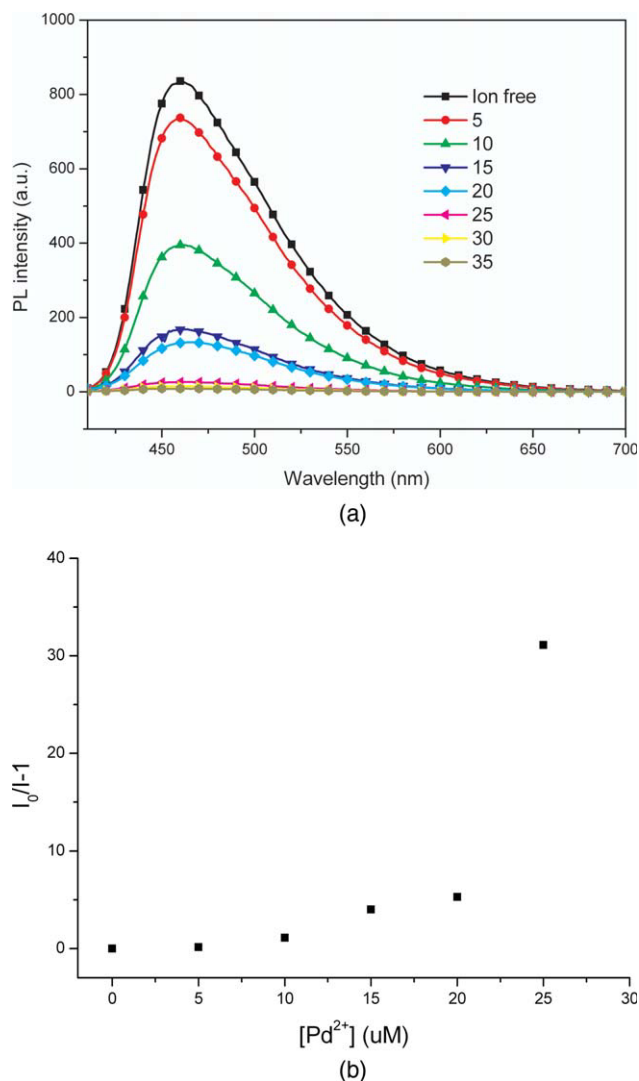
**Figure 6** (a) Fluorescence spectra and plot of the fluorescence intensity at 507 nm (inset) (b)  $K_{SV}$  plot of HTPY upon addition of variable concentrations of  $\text{Pd}^{2+}$  ions in THF.  $[\text{HTPY}] = 1 \times 10^{-6} \text{ M}$  in RU,  $[\text{Pd}^{2+}] = 0\text{--}35 \times 10^{-6} \text{ M}$ ,  $\lambda_{\text{ex}} = 405 \text{ nm}$ .

of  $1.16 \times 10^5 \text{ M}^{-1}$ , suggesting its good sensitivity to  $\text{Pd}^{2+}$  ions.

For the polymer HTPYB, the addition of  $\text{Pd}^{2+}$  ions also leads to a significant quenching of its emission (Fig. 7). At a lower concentration of  $\text{Pd}^{2+}$  ions ( $0\text{--}25 \times 10^{-6} \text{ M}$ ), a linear Stern-Volmer plot [Fig. 7(b)] is obtained with a Stern-Volmer constant ( $K_{SV}$ ) of  $2.36 \times 10^5 \text{ M}^{-1}$ , which is higher than that of HTPY. The results show clearly that both of the hyperbranched CPs exhibit high sensitivity in their fluorescent response to  $\text{Pd}^{2+}$ . Moreover, it is expected that such a difference in chelation caused by different linking bonds will be more pronounced in the interaction with metal ions having a stronger coordinating ability with pyridine moieties. The different  $K_{SV}$  obtained for the two polymers implied that the vinylene bond between the triphenylamine unit and the pyridine unit in HTPY provided stronger hindrance for the chelation of pyridine unit with metal ions than the ethynylene linker in HTPYB.

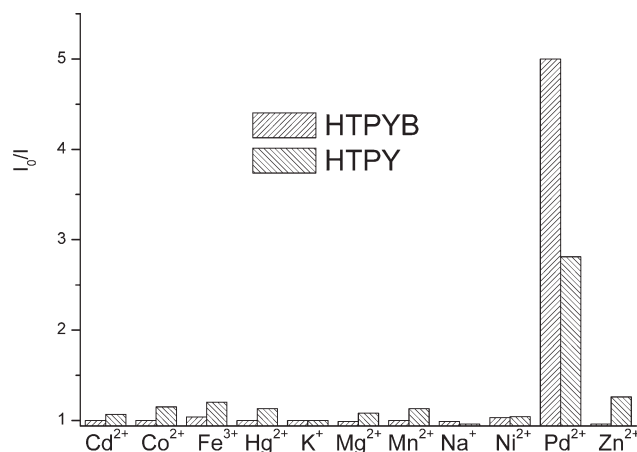
This phenomenon may be also associated with different efficiencies of the energy and/or electron transfer between the backbone and ion receptors.

The fluorescent responsive properties of the polymers toward a series of metal ions apart from  $\text{Pd}^{2+}$  ion were also investigated. Figure 8 presents the relative changes in fluorescence intensities of the two polymers upon addition of different metal ions ( $[\text{metal ion}] = 1.5 \times 10^{-5} \text{ M}$ ). Compared with high quenching efficiency by  $\text{Pd}^{2+}$ , the fluorescence of the polymers is only slightly influenced by the addition of  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Hg}^{2+}$  ions. Moreover, HTPYB exhibits higher selective response towards  $\text{Pd}^{2+}$  than HTPY. The results suggest that the polymers HTPY and HTPYB both have specific recognition ability for  $\text{Pd}^{2+}$  ion.



**Figure 7** (a) Fluorescence spectra (b)  $K_{SV}$  plot of HTPYB upon addition of variable concentrations of  $\text{Pd}^{2+}$  ions in THF.  $[\text{HTPYB}] = 1 \times 10^{-6} \text{ M}$  in RU,  $[\text{Pd}^{2+}] = 0\text{--}30 \times 10^{-6} \text{ M}$ ,  $\lambda_{\text{ex}} = 398 \text{ nm}$ . [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.wileyonlinelibrary.com).]





**Figure 8** Fluorescence response of the polymers to various metal ions in THF solution. [HTPY] = [HTPYB] =  $1 \times 10^{-6}$  M in RU, [metal ion] =  $1.5 \times 10^{-5}$  M.

### CONCLUSIONS

Two new hyperbranched fluorescent conjugated polymers HTPY and HTPYB with pyridine units have been synthesized via Heck coupling reaction and Sonogashira coupling reaction, respectively. The fluorescence of both HTPY and HTPYB can be efficiently quenched by Pd<sup>2+</sup> ion, suggesting their potentials as highly sensitive fluorescent chemical sensitive materials for the detection of Pd<sup>2+</sup> ion.

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