

Synthesis of Dendrimer Based Polymeric and Macrocyclic Complexes with a Platinum-Acetylide π -Conjugated Organometallic Core

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Abstract: A three-layered poly(benzyl ether) dendrimer having a bis-ethynylbenzene core was synthesized and characterized with ^1H NMR and MALDI-TOF-MS spectroscopy. The dendrimer was reacted with platinum complexes to obtain platinum-acetylide based organometallic polymers. When the dendrimer was reacted with *trans*- $[\text{PtCl}_2(\text{PEt}_3)_2]$, a high molecular weight polymeric compound was formed, whereas, with *cis*- $[\text{PtCl}_2\text{dppp}]$, a uniform molecular weight compound was formed, which was found to be a dimeric metallacycle by ^1H NMR, ^{31}P NMR and ESI-TOF-MS spectroscopy. Both these complexes exhibited relatively a strong emission around 440 nm, indicating that they could be potential candidates for blue emitting polymer LEDs.

Keywords: dendrimer, platinum-acetylide, metallacycle, supramolecules, π -conjugation.

Introduction

Dendrimers are regularly branched macromolecules with well predictable three-dimensional structures, and have a wide range of potential applicable to the development of functional materials.¹⁻⁴ In recent years, organometallic dendrimers attract increasing attentions as a well-defined nanoscopic object, since they exhibit various characteristics such as redox, photo-functional, and catalytic properties.⁵⁻¹⁰ On the other hand, the synthesis and characterization of organometallic polymers offers opportunity to the tailoring of physicochemical properties of materials by changing of the transition metal and/or the organic spacer. Several types of platinum-acetylide-based π -conjugated polymers and oligomers were reported as a potential scaffold of organic semiconductors in optoelectronic devices such as light-emitting diodes, lasers, photocells, micro-sensor and field-effect transistors.¹¹⁻¹⁵ In this context, novel bis-ethynylbenzene core dendrimer have been synthesized, which was reacted with platinum complexes to obtain platinum-acetylide based organometallic polymers. In present paper, we report the synthesis of poly(benzyl ether) dendrimer having bis-ethynylbenzene core and wish to highlight formation of dendritic supramolecular polymer or macrocyclic complexes with platinum-acetylide-based π -conjugated core structure.

Experimental

Manipulations were performed using standard Schlenk techniques under a nitrogen atmosphere and with previously dried solvents. Tetrahydrofuran (THF), used as a solvent for synthetic reactions, was distilled from sodium benzophenone under Ar just before use. Diethylamine was distilled from LiAlH_4 under Ar just before use. 18-Crown-6 ether was recrystallized from acetonitrile (MeCN). Potassium carbonate (K_2CO_3) and potassium fluoride (KF) were kept in an oven at 130 °C. Commercially available reagents were used as-received from TCI and Aldrich.

Measurements. Recycling preparative HPLC was carried out on a Japan Analytical Industry model LC-908, equipped with a column set consisting of JAIGEL-2H (exclusion limit 5×10^3) combined with JAIGEL-1H (exclusion limit 1×10^3) or JAIGEL-3H (exclusion limit 3×10^4), with CHCl_3 as the eluent at a flow rate of 3.5 mLmin⁻¹. Analytical GPC was carried out on a TOSOH model HLC-8020, equipped with TSKgel-3H and 4H column. MALDI-TOF MS was performed on a Bruker Protein ToF FEFLEX III mass spectrometer with dithranol as the matrix. ESI-TOF-MS was performed on a JEOL JMS-T100LC mass spectrometer. For the mild ionization, 0.1% of silvertrifluoroacetate was added to the THF solution of analyte.

^1H NMR spectroscopy was performed in CDCl_3 on a JEOL GSX-270 spectrometer operating at 270 MHz. The chemical shifts were determined with respect to CHCl_3 ($\delta = 7.28$) as the internal standard. ^{31}P $\{^1\text{H}\}$ NMR spectroscopy

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was recorded on the Varian Mercury-300 spectrometer with the external standard of aqueous H_3PO_4 solution. Electronic absorption spectra were recorded at 25 °C on a JASCO model V-570 spectrophotometer in a quartz cell of 1 cm path length. Fluorescence spectra were recorded at 25 °C in a quartz cell of 1 cm path length, on a JASCO model FP-777 W spectrophotometer equipped with a temperature controller.

Synthesis. 2: To a tetrahydrofuran (THF) solution (60 mL) of a mixture of 3,5-bis(tert-butyl-diphenylsilyloxy)benzylalcohol (**1**: 9.0 mmol), phthalimide (10.8 mmol), and triphenylphosphine (10.8 mmol), was added 40% toluene solution of diethylazodicarboxylic acid (DEAD; 10.8 mmol) and the resulting mixture was stirred under Ar at 0 °C for 1 h and 25 °C for 11 h. The reaction mixture was then evaporated to dryness, and the residue was chromatographed on silica gel with CH_2Cl_2 as an eluent, where the second fraction was collected and evaporated to give **2** as transparent oil in 87% yield. MALDI-TOF-MS for $C_{47}H_{47}NO_4Si_2$ m/z : calcd: 745 $[M]^+$; found: 745. 1H NMR ($CDCl_3$): δ 0.94 (s, 18H; *tert*-Bu), 4.47 (s, 2H; $-CH_2-$), 6.04 (t, 1H; *p*-H in C_6H_5), 6.30 (d, 2H; *o*-H in C_6H_5), 6.03-7.48 (m, 20H; $-C_6H_5$), 7.69 and 7.76 (m, 4H, C_6H_4 in phthalimide).

3: A acetone solution (20 mL) of a mixture of **2** (0.8 mmol), Fréchet's dendritic bromide (1.6 mmol), and 18-crown-6 (0.2 mmol), containing KF (1.9 mmol), was refluxed under Ar for 3 h. The reaction mixture was poured into water (50 mL) and extracted three times with ethyl acetate (50 mL). The combined extracts were dried over anhydrous $MgSO_4$ and chromatographed on silica gel with CH_2Cl_2 as an eluent, where the third fraction was collected and freeze-dried from benzene to give **3** as white solid in 90% yield. MALDI-TOF-MS for $C_{65}H_{63}NO_{16}$ m/z : calcd: 1153 $[M+K]^+$; found: 1153. 1H NMR ($CDCl_3$): δ 3.76 (s, 24H; $-OMe$), 4.75, 4.91, and 4.94 (s, 2H, 4H, and 8H; $-CH_2-Ph$), 6.30-6.63 (m, 21H; *o*, *p*-H in C_6H_5), 7.67 and 7.80 (m, 4H; $C_6H_4C_6H_4$ in phthalimide).

4: To a THF/EtOH (1:1) solution (20 mL) of **3** (0.72 mmol) was added hydrous hydrazine (10 mL), and the resulting mixture was refluxed for 12 h. Then, insoluble fractions were filtered off from the reaction mixture, and the filtrate was poured into water (100 mL) and extracted three times with ethyl acetate (50 mL). The combined extracts were dried over anhydrous $MgSO_4$ and evaporated to dryness, and then freeze-dried from benzene to give **4** as white solid in quantitative yield. MALDI-TOF-MS for $C_{57}H_{61}NO_{14}$ m/z : calcd: 939 $[M+H]^+$; found: 939. 1H NMR ($CDCl_3$): δ 3.76 (s, 24H; $-OMe$), 4.95 (m, 12H; $-CH_2-Ph$), 6.28-6.65 (m, 21H; *o*, *p*-H in C_6H_5).

6: To a diethylamine solution (10 mL) of methyl-3,5-dibromobenzoate (**5**: 4.6 mmol), $PdCl_2(PPh_3)_2$ (16.1 mmol), and catalytic amount of CuI was added trimethylsilylacetylene, and the reaction mixture was vigorously stirred at 25 °C for 3 h. Insoluble fractions were filtered off from the reac-

tion mixture, and the filtrate was evaporated to dryness. Then, resulting mixture was chromatographed on silica gel with $CHCl_3$ as an eluent, where the first fraction was collected and freeze-dried from benzene to give **6** as white solid in 45% yield. 1H NMR ($CDCl_3$): δ 0.23 (s, 9H; $-Si(CH_3)_3$), 3.82 (s, 3H; $-CO_2CH_3$), 7.72 (m, 1H, *p*-H in C_6H_5), 8.04 (m, 2H; *m*-H in C_6H_5).

7: To a THF solution of **6** was added 1 N NaOH aqueous solution, and the reaction mixture was vigorously stirred at 25 °C for 12 h. Solution thus obtained was poured into 1 N HCl aqueous solution and extracted three times with ethyl acetate (50 mL). The combined extracts were dried over anhydrous $MgSO_4$ and evaporated to dryness, and then freeze-dried from benzene to give **7** as white solid in quantitative yield. 1H NMR ($CDCl_3$): δ 3.15 (s, 2H; $-H$ in acetylene), 7.81 (m, 1H, *p*-H in C_6H_5), 8.14 (m, 2H; *m*-H in C_6H_5).

8: To a CH_2Cl_2 solution (60 mL) of a mixture of **4** (9.0 mmol), **7** (10.8 mmol), and 1-hydroxybenzotriazole (10.8 mmol), was added EDC (10.8 mmol) and the resulting mixture was stirred under Ar at 0 °C for 1 h and 25 °C for 12 h. The reaction mixture was then evaporated to dryness, and the residue was chromatographed on silica gel with CH_2Cl_2 as an eluent, where the second fraction was collected and evaporated to give **8** as transparent oil in 87% yield. MALDI-TOF-MS for $C_{68}H_{65}NO_{15}$ m/z : calcd: 1259 $[M+Na]^+$; found: 1259. 1H NMR ($CDCl_3$): δ 3.05 (s, 2H; $-H$ in acetylene), 3.69 (s, 24H; $-OMe$), 4.43 (d, 2H, $-CH_2-Ph$ in 1st layer of dendron), 4.86 (s, 12H; $-CH_2-Ph$), 6.31-6.55 (m, 21H; *o*, *p*-H in C_6H_5), 7.65 (s, 1H; *p*-H in core unit), 8.03 (s, 2H; *m*-H in core unit).

Polymerization. To a diethylamine/THF (0.5:1) solution of **8** and each platinum chloride precursors (*trans*- $[PtCl_2(PPh_3)_2]$ or *cis*- $[PtCl_2(dppp)]$) was added catalytic amount of CuI and resulting mixture was vigorously stirred under Ar at 25 °C for 3 h. Then, insoluble fractions were filtered off from the reaction mixture, and the filtrate was poured into water (100 mL) and extracted three times with ethyl acetate (50 mL). The combined extracts were dried over anhydrous $MgSO_4$ and evaporated to dryness, and the residue was chromatographed on silica gel with CH_2Cl_2 as an eluent, where the first fraction was collected and freeze dried in benzene to give **A** and **B** as yellow powder in 25% and 45% yields, respectively.

A: 1H NMR ($CDCl_3$): δ 1.32 (t, 18H; $-CH_3$ in triethylphosphine), 2.08 (m, 12H, $-CH_2-$ in triethylphosphine), 3.73 (s, 24H; $-OMe$), 4.51 (br, 2H, $-CH_2-Ph$ in 1st layer of dendron), 4.92 (m, 12H, $-CH_2-Ph$ in 2nd and 3rd layer of dendron), 6.35-6.62 (m, 21H; *o*, *p*-H in C_6H_5), 7.40 (s, 1H; *p*-H in core unit), 7.63 (s, 2H; *m*-H in core unit). ^{31}P $\{^1H\}$ NMR: δ 11.73 (J_{P-Ph} = 1300 Hz), 15.43 (J_{P-Ph} = 1225 Hz).

B: 1H NMR ($CDCl_3$): δ 0.90 (m, 2H; $P-CH_2CH_2CH_2-P$), 1.22 (m, 4H; $P-CH_2CH_2CH_2-P$), 1.32 (t, 18H; $-CH_3$ in triethylphosphine), 2.08 (m, 12H, $-CH_2-$ in triethylphosphine), 3.75 (s, 24H; $-OMe$), 4.44 (d, 2H, $-CH_2-Ph$ in 1st layer of

dendron), 4.89 and 4.93 (s, 8H and 4H, $-\text{CH}_2\text{-Ph}$ in 3rd and 2nd layer of dendron, respectively), 5.92 (br, 1H; N-H) 6.36-6.62 (m, 21H; *o*, *p*-H in C_6H_5), 7.20 (m, 13H; *m*, *p*-H in C_6H_5 and *o*-H in core unit), 7.58 (m, 8H; *o*-H in C_6H_5), 7.92 (s, 1H; *p*-H in core unit). ^{31}P $\{^1\text{H}\}$ NMR: δ - 6.28 ($J_{\text{P-Pt}}=1095$ Hz).

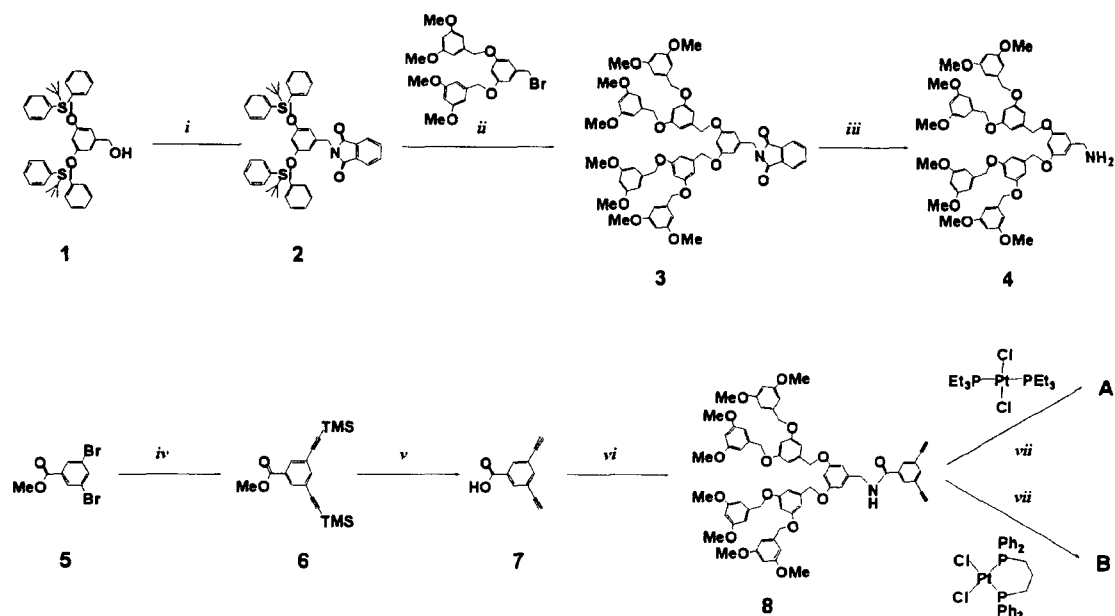
Results and Discussion

A three-layered poly(benzyl ether) dendrimer having bisethynylbenzene core unit (**8**; Scheme I) was synthesized as following and characterized by ^1H NMR and MALDI-TOF-MS spectroscopy. 3,5-di-*tert*-butyldiphenylsilyloxybenzyl alcohol (**1**) was reacted with phthalimide using Mitsunobu's coupling reaction,¹⁶ **2** thus obtained was reacted with Fréchet type two-layered dendritic bromide¹⁷ to get a phthalimide anchored dendrimer (**3**). Then, **3** was converted quantitatively into an amine anchored dendrimer (**4**) by the reaction with hydrazine monohydrate in THF/EtOH (1:1) under reflux for 12 h. Methyl-3,5-bis(trimethylsilylethynyl) benzoate core functionality (**6**) was prepared from methyl 3,5-dibromobenzoate (**5**), which was reacted with trimethylsilyl acetylene at 25 °C in the presence of a $\text{PdCl}_2(\text{PPh}_3)_2/\text{CuI}$ catalyst in diethylamine. Desilylation and hydrolyzation was performed simultaneously using 1 N NaOH aqueous solution in THF to give 3,5-diethynylbenzoic acid (**7**). Finally, **4** and **7** were coupled each other using EDC and HOBT to get the bisethynylbenzene core dendrimer (**8**).

For a preparation of platinum-acetylide based organometallic polymers, **8** was independently reacted with two

different kind of platinum chloride precursors (*trans*- $[\text{PtCl}_2(\text{PEt}_3)_2]$ or *cis*- $[\text{PtCl}_2\text{dppp}]$) at 25 °C in the presence of catalytic amount of CuI in THF/diethylamine. The feed molar ratio of **8** and the platinum chloride precursors was fixed to 1:1. Purification of polymeric complexes was accomplished by a silica column chromatography using CH_2Cl_2 as an eluent and they were obtained in high purity by collection of the first fraction. Platinum complexes thus obtained were air-stable and readily dissolve in aprotic solvents such as THF, CH_2Cl_2 , CHCl_3 , acetone, or benzene.

^1H NMR spectra of both complexes exhibited peaks originated from the phosphane ligand group bound to Pt atoms in addition to the peaks of dendritic building blocks. Integration of each peaks indicated that **8** was almost stoichiometrically reacted with platinum chloride precursors. On the other hand, the result of ^{31}P $\{^1\text{H}\}$ NMR spectroscopy exhibited quite different aspects to each complexes. ^{31}P $\{^1\text{H}\}$ NMR spectrum of the complex **A** exhibited two singlet peaks at $\delta=11.73$ ($J_{\text{P-Pt}}=1300$ Hz) and 15.43 ($J_{\text{P-Pt}}=1225$ Hz) in an integral ratio of 43:1, which correspond to the phosphane groups bound to internal and terminal Pt atoms, respectively. In case of the complex **B**, ^{31}P $\{^1\text{H}\}$ NMR spectrum showed an only one peak at $\delta=-6.28$ ($J_{\text{P-Pt}}=1095$ Hz), indicating the formation of a homogenous supramolecular structure. Molecular weights of the both polymeric complexes were determined in CH_3Cl by GPC using polystyrene as a standard to give average molecular weights. As a result, the two polymeric complexes exhibited quite different aspects. The complex **A** (Figure 1) exhibited a relatively broad elution



Scheme I. Reagents and reaction conditions: (i) DEAD, PPh_3 , phthalimide, in THF at 0 °C for 1 h and 25 °C for 11 h; (ii) K_2CO_3 , 18-crown-6 ether, in THF reflux 12 h; (iii) $\text{H}_2\text{NNH}_2\cdot\text{H}_2\text{O}$ in THF/EtOH (1/1) reflux 12 h; (iv) TMS-acetylene, $\text{PdCl}_2(\text{PEt}_3)_2$, CuI, in Et_2NH at 25 °C for 3 h; (v) NaOH, in $\text{H}_2\text{O}/\text{THF}$ at 25 °C for 12 h; (vi) EDC, HOBT, **4**, in CH_2Cl_2 at 0 °C for 1 h and 25 °C for 12 h; (vii) CuI, in $\text{Et}_2\text{NH}/\text{THF}$ at 25 °C for 3 h.

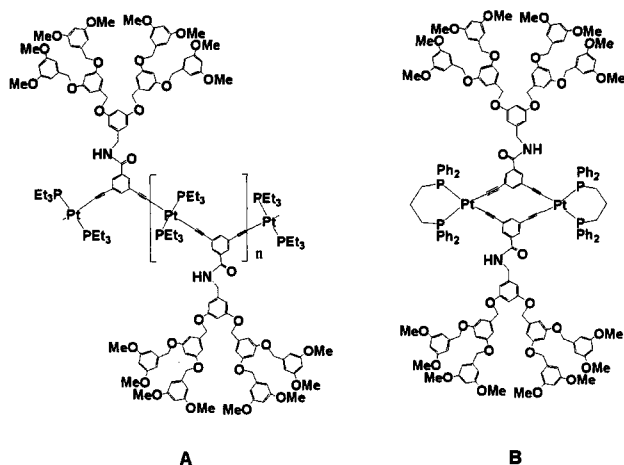


Figure 1. Structures of complex A and B.

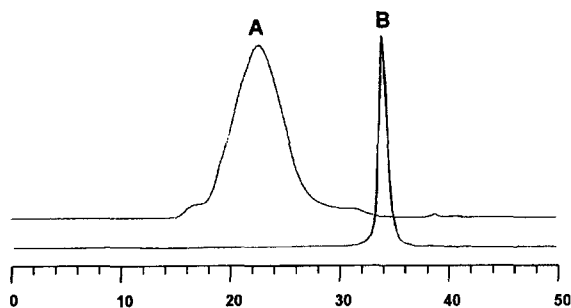


Figure 2. GPC profiles of complexes.

peak with a number average molecular weight of 62,700 and M_w/M_n of 9.4 (Figure 2). The average degree of polymerization would be 41. Considering the integral ratio of phosphane groups, average molecular weight of the **A** obtained by GPC measurement is quite reasonable. The complex **B** (Figure 1) exhibited a very sharp peak with a number average molecular weight of 3,200 and M_w/M_n of 1.2 (Figure 2). Based on this information, the complex **B** was subjected to ESI-TOF-MS to determine the exact molar mass. As shown in Figure 3, ESI-TOF-MS spectrum of the **B** exhibits dicationic peaks at $m/z=1848.61$. From the molecular weight of monomeric unit, the peak is well corresponding to the Ag adduct of dimeric compound ($[M+2Ag]^{2+}$) as shown in Figure 3, indicating that the polymerization reaction of the **8** with $[PtCl_2dppp]$ result in a dimeric macrocyclic complex. This kind of metallacycle has attracted increasing attention in recent supramolecular chemistry.^{9,13,14}

On the other hand, optoelectronic properties of Pt-acetylacetonate complex are attracting interest because of their potential application for the organic semiconductors.⁶⁻⁸ Recent research reveals that dendritic substitution to the π -electronic conjugation system exhibits unique dendrimer effects.¹⁸⁻²⁰ From this sense of view, dendrimer frameworks have a possibility to provide very interesting aspect such as energy transduction event or isolation effect of core Pt-acetylacetonate structures. For the brief exploration, absorption and photoluminescence spectra of the complexes were taken at room temperature in CH_2Cl_2 . Both complexes showed strong absorption at 277 nm, absorption of dendritic wedge, and weak broad absorp-

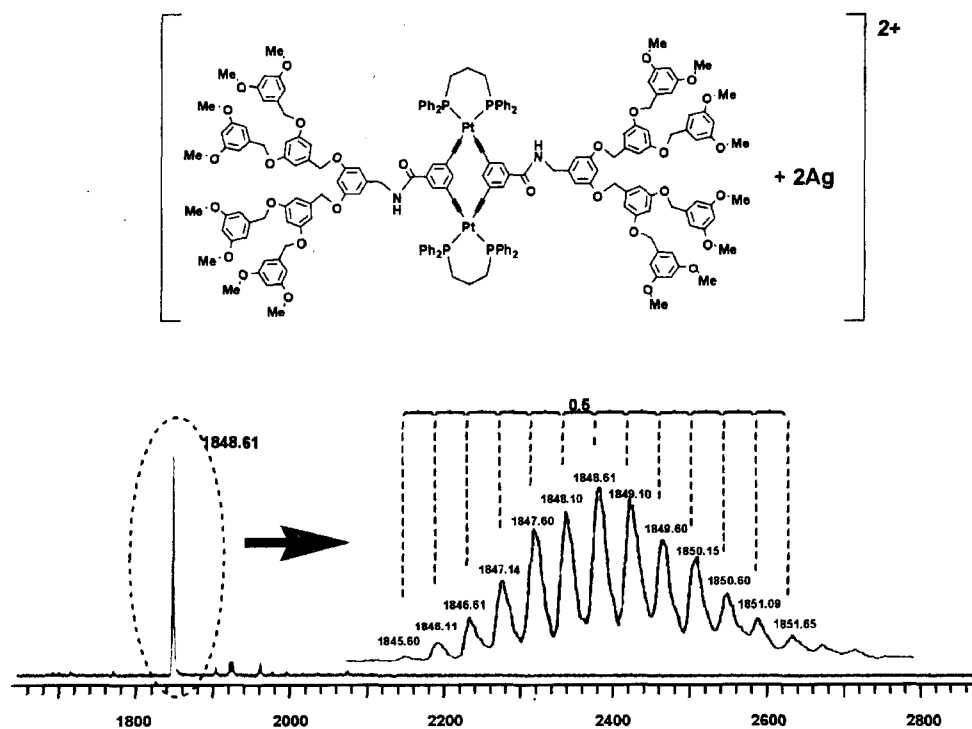


Figure 3. ESI-TOF-MS spectrum of complex B.

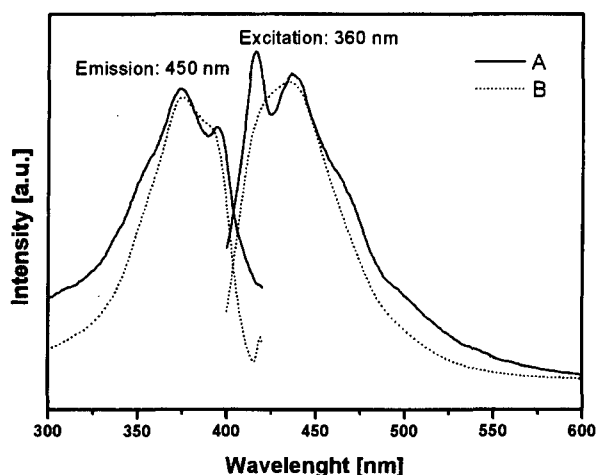


Figure 4. Emission and excitation spectra of complexes.

tion around 350 nm, which are attributable to the absorption of π - π^* transition and MLCT band of Pt-acetylide. Figure 4 shows excitation and emission spectra of both complexes. Both complexes show relatively strong emissions around 440 nm, suggesting that they could be possible candidates for blue emitting polymer LEDs.

Conclusions

A bis-ethynylbenzene core dendrimer was successfully synthesized and polymerized to form platinum-acetylide complexes. Polymerization reaction of the dendritic bis-ethynylbenzene with the *trans*-[PtCl₂(PEt₃)₂] forms a linear high molecular weight polymeric compound, and with the *cis*-[PtCl₂dppp] predominantly forms a dimeric macrocyclic compound. Both complexes exhibit high solubility to various organic solvent and relatively strong emissions around 440 nm.

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