π-Conjugated Soluble Palladium Poly-ynes: Synthesis and Fluorescence Properties

MUJIE YANG,[1] ZIQIANG LEI,[1] MEIXIANG WAN,[2] YOUQIN SHEN,[2] JUN WANG,[2] JIANXIN CHEN,[3] HAO WANG,[3] TONG YE[3]

[1] Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China

[2] Laboratory of Organic Solids, Institute of Chemistry, Academia Sinica, Beijing 10080, China

[3] State Key Laboratory for Structural Chemistry of Unstable and Stable Species, Institute of Chemistry, Academia Sinica, Beijing 10080, China

ABSTRACT: Insertion of thiophene-2,5-diyl, or 1,4-phenylene into palladium poly-ynes by the polycondensation of dihalide complexes $PdCl_2(PR_3)_2$ (R = Ph o γ n-butyl) with a di-yne monomer (obtained from the reaction of equimolar quantities of p-diethynyl-benzene with 2,5-diiodothiophene or 1,4-diiodobenzene) affords a series of palladium poly-ynes **1–6**. The polymers/oligomers, soluble in common organic solvents, exhibit strong fluorescence at the excitation of UV-visible light at room temperature. The emission intensity of the polymers/oligomers with thiophene-2,5-diyl is 3–17 times stronger than that of the analogous polymers without thiophene-2,5-diyl. Polymers with phenyl substituted phosphine ligands emit stronger emission than those only with n-butyl phosphine ligands. The effects of molecular weight, ligands, solvents, and concentration on the fluorescence properties are also investigated. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 1657–1665, 1997

Key words: π-conjugated polymers; polladium poly-ynes; fluorescence

INTRODUCTION

Much interest has been stimulated by the potential application of π-conjugated polymers in nonlinear devices as well as in light emitting displays since the first demonstration of organic polymer light-emitting diodes.[1–9] The main issues for light-emitting devices to be addressed are device efficiency and material stability. One approach commonly employed is to limit delocalization length of the polymer by interrupting π-conjugation or synthesizing short-chain oligomers.[8] This effectively increases the rigidity of such systems and reduces relaxation from excited states through
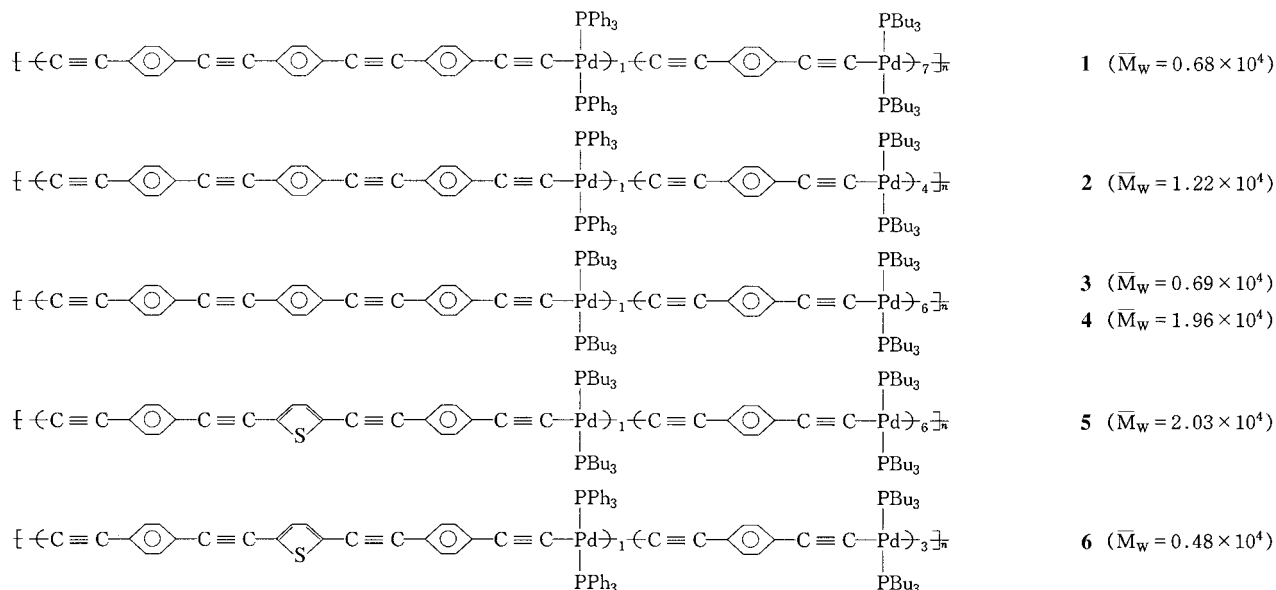
nonradiative processes. Transition metal poly-ynes, which were thoroughly studied for their third-order nonlinearity but were barely investigated for their fluorescence properties,[10–12] possess exactly those structures needed for efficient emission: π-conjugated polymer backbone perturbed by transition metals of which the d orbitals provide a localized electronic system within the polymer chain.

We report here the synthesis and steady-state fluorescence properties of a series of soluble palladium poly-ynes **1–6** (Scheme 1).

These polymers/oligomers emit strong fluorescence at the excitation of UV or visible light at room temperature. We found that the palladium-containing polymers or oligomers with thiophene-2,5-diyl in the repeat units exhibit stronger emission than those of the analogous polymers without

PPh$_3$ … PBu$_3$

$\{ \{C \equiv C - \langle \bigcirc \rangle - C \equiv C - \langle \bigcirc \rangle - C \equiv C - \langle \bigcirc \rangle - C \equiv C - Pd \}_1 \{C \equiv C - \langle \bigcirc \rangle - C \equiv C - Pd \}_7 \}_n$ **1** ($\overline{M}_W = 0.68 \times 10^4$)

PPh$_3$ … PBu$_3$

PPh$_3$ … PBu$_3$

$\{ \{C \equiv C - \langle \bigcirc \rangle - C \equiv C - \langle \bigcirc \rangle - C \equiv C - \langle \bigcirc \rangle - C \equiv C - Pd \}_1 \{C \equiv C - \langle \bigcirc \rangle - C \equiv C - Pd \}_4 \}_n$ **2** ($\overline{M}_W = 1.22 \times 10^4$)

PPh$_3$ … PBu$_3$

PBu$_3$ … PBu$_3$

$\{ \{C \equiv C - \langle \bigcirc \rangle - C \equiv C - \langle \bigcirc \rangle - C \equiv C - \langle \bigcirc \rangle - C \equiv C - Pd \}_1 \{C \equiv C - \langle \bigcirc \rangle - C \equiv C - Pd \}_6 \}_n$ **3** ($\overline{M}_W = 0.69 \times 10^4$)   **4** ($\overline{M}_W = 1.96 \times 10^4$)

PBu$_3$ … PBu$_3$

PBu$_3$ … PBu$_3$

$\{ \{C \equiv C - \langle \bigcirc \rangle - C \equiv C - \langle \substack{\bigcirc \\ S} \rangle - C \equiv C - \langle \bigcirc \rangle - C \equiv C - Pd \}_1 \{C \equiv C - \langle \bigcirc \rangle - C \equiv C - Pd \}_6 \}_n$ **5** ($\overline{M}_W = 2.03 \times 10^4$)

PBu$_3$ … PBu$_3$

PPh$_3$ … PBu$_3$

$\{ \{C \equiv C - \langle \bigcirc \rangle - C \equiv C - \langle \substack{\bigcirc \\ S} \rangle - C \equiv C - \langle \bigcirc \rangle - C \equiv C - Pd \}_1 \{C \equiv C - \langle \bigcirc \rangle - C \equiv C - Pd \}_3 \}_n$ **6** ($\overline{M}_W = 0.48 \times 10^4$)

PPh$_3$ … PBu$_3$

Scheme 1

the thiophene-2,5-diyl. The intense photoluminescence indicates that these polymers/oligomers may be potential electroluminescence materials.

EXPERIMENTAL

Instrumentation

Infrared (IR) spectra were obtained on a PE 983 infrared spectrophotometer. X-ray photoelectron spectroscopy (XPS) analysis was performed at room temperature on a Kratos ES 300 spectrometer with the use of Mg K$_\alpha$ radiation ($h\upsilon = 1254$ eV). The typical X-ray power was 15 kV · 10 mA. All XPS spectra were energy-referenced to the C1s photoemission peak at 284.6 eV. UV-visible spectra were taken using a Beckman DU-50 spectrophotometer. Fluorescence and excitation spectra were measured at room temperature with a Hitachi F-300 fluorescence spectrophotometer. Molecular weight determination was carried out on a Waters 208 gel permeation chromatograph versus polystyrene standard.

Materials

Diethylamine was distilled from calcium hydride and stored under N$_2$. Triphenylphosphine was purified by a standard method.[13] Diethynylbenzene was prepared by the reported method.[14] The palladium complexes were prepared by procedure in

the literature: bis (triphenylphosphine) palladium (II) dichloride,[15] bis(tri-n-butylphosphine) palladium (II) dichloride.[16] 2,5-Diiodothiophene was prepared by modifying a reported method.[17] Tri-n-butyl-phosphine was purchased from Tokyo Chemical Industry Co. Ltd. All other chemicals were purchased from Shang-hai Chemical Reagent Company.

PREPARATION OF 3, 4, AND 5

A mixture of p-diiodobenzene (or 2,5-diiodothiophene) (1 mmol) and p-diethynylbenzene (2 mmol) was stirred at 25°C in 30 mL of distilled diethylamine in the presence of PdCl$_2$(PPh$_3$)$_2$ (0.025 mmol) and CuI (0.025 mmol) under N$_2$ for 2.5 h (for p-diiodobenzene) or 5 h (for 2,5-diiodothiophene) in a manner similar to the method in the literature.[18,19] A solution of PdCl$_2$(PBu$_3$)$_2$ (1 mmol) and CuI (0.015 mmol) in dry diethylamine (7 mL) was then injected to the reacted mixture and stirred at 5–10°C for 6 h (polymers **3** and **5**) or 15 h (polymer **4**). The mixture was filtered to removal insoluble residue, and the solution was concentrated to dryness at reduced pressure with a cold trap of liquid nitrogen. The product was dissolved in about 3 mL of THF and precipitated into methanol, washed with methanol, and dried under vacuum at room temperature for 24 h to give yellow polymers **3**, **4**, and

Table I   Elemental[a] and GPC Analysis Data for Polymers/Oligomers 1–6

Polymer/Oligomer	C (%)	H (%)	$\bar{M}_w$ (10^4)	D
1	65.92 (66.70)	8.01 (8.36)	0.68	1.62
2	66.80 (68.02)	6.61 (7.90)	1.22	2.37
3	64.34 (65.66)	8.93 (8.98)	0.69	2.11
4	65.34 (65.66)	9.04 (8.98)	1.96	2.91
5	65.33 (65.06)	9.24 (8.93)	2.03	5.60
6	66.73 (67.87)	6.56 (7.52)	0.48	1.70

[a] Calculated values in parentheses.

5 with the yield of 37.9, 26.0, and 61.3%, respectively. The IR, XPS, gel permeation chromatography (GPC), and elemental analysis results are shown in Tables I–III.

PREPARATION OF POLYMERS 1, 2, AND 6

To a reacted mixture of *p*-diiodobenzene (or 2,5-diiodothiophene) (1 mmol) and *p*-diethynylbenzene (2 mmol) described above was injected a solution of $PdCl_2(PBu_3)_2$ (0.7 mmol) and CuI (0.015 mmol) in dry diethylamine (5 mL), stirred at 5–10°C for 6 h. $PdCl_2(PPh_3)_2$ (0.3 mmol) was added, and the mixture was stirred for 3 h at 5–10°C. The resulting mixture was filtered, and the solution was concentrated to dryness at reduced pressure. The polymers were then dissolved in THF (3 mL) and precipitated into methanol and washed and dried as described above to give orange products **1** and **6**. The residue from the reacted mixture of *p*-diiodobenzene, *p*-diethnyylbenzene, $PdCl_2(PBu_3)_2$, and $PdCl_2(PPh_3)_2$ was dissolved in 3 mL of THF and precipitated into methanol and filtered, washed, and dried as described above to obtain orange polymer **2**. The IR, UV, XPS, and elemental analysis results are also shown in Tables I–III.

RESULTS AND DISCUSSION

IR and XPS Analysis

The IR data for polymers/oligomers **1–6** are listed in Table II. By the polycondensation, the strong terminal $\nu_{(C\equiv C-H)}$ band of the diethynylbenzene at 3264 cm^{-1} is shifted to a higher frequency to about 3272–3310 cm^{-1} and becomes weak. The result indicates that the products were formed but not with sufficient molecular weight to be polymers. The GPC analysis shows that these poly-

mers/oligomers have $\bar{M}_w$ ranging from 0.48×10^4 to 2.03×10^4 (Table I) conformed with the IR result. The IR spectra of **1–6** show that the $\nu_{(C\equiv C)}$ band of the diethynylbenzene at 2110 cm^{-1} is shifted to 2185–2200 cm^{-1}, which is consistent with a known trend that disubstituted acetylenes give rise to the $\nu_{(C\equiv C)}$ band at a frequency higher than monosubstituted acetylenes.[20] The IR spectra of **1–6** exhibit sharp intense $\nu_{(MC\equiv C)}$ bands at about 2065–2090 cm^{-1}. This also shows that the poly-ynes containing σ-bond metals are formed.

Table III summarizes the XPS analysis data for **1–6**. The binding energy for the Pd $3d_{5/2}$ in **1**, **3**, **5**, **6** is 337.8, 338.3, 337.9, and 337.8 eV, respectively, similar to the values obtained for the reference compounds $PdCl_2(PPh_3)_2$ and $PdCl_2(PBu_3)_2$. The similarity of the binding energy for Pd $3d_{5/2}$ and P 2p between **1**, **3**, **5**, **6** and $PdCl_2(PPh_3)_2/PdCl_2(PBu_3)_2$ reveals that the charge on these two atoms is changed little when polymers are formed. This suggests that only σ-bond Pd(II) exists. A narrow signal of Pd $3d_{5/2}$ is observed, also suggesting that only one species of Pd(II) exists. The result is in accordance with the IR analysis. The binding energy for $Cl_{2p_{3/2}}$ in **1**, **3**, **5**, and **6** is not detected, indicating that the content of chlorine in polymers/oligomers is less than 0.3%.

The Solubility of the Polymers/Oligomers 1–6

The solubility of these materials could be enhanced by varying the substituents on the phosphine ligands. Polymers with *n*-butyl-substituted phosphine ligands are more soluble than those with phenyl phosphine ligands. Polymers/oligomers **1–6** possess good solubility in common organic solvents such as DMF (dimethylformamide), DMSO (dimethylsulfoxide), THF (tetrahydrofuran), toluene, and chloroform. Solubility

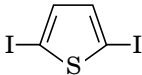**Table II   IR and UV Data for Polymers/Oligomers and Monomers**

Compound	IR (cm^{-1})						UV (nm)
	$\nu(\equiv$C—H)	ν(MC$\equiv$C)	ν(ArC$\equiv$CAr)	δ(C—H, para-phenylene)	δ(C—H, meta-phenylene)	δ(C—H, thiophene)	
I–thiophene–I						785 (s)	
HC≡C–phenylene–C≡CH	3264 (s)		2110 (w)	830 (vs)			
1	3282 (w)	2084 (s)	2195 (w)	834 (vs)	743 (s) 690 (vs)		383.0
2	3272 (w)	2079 (s)	2185 (w)	836 (vs)	745 (s) 687 (s)		386.0
3	3296 (w)	2088 (vs)	2200 (w)	833 (vs)			382.5
4	3290 (w)	2090 (vs)	2195 (w)	832 (vs)			395.0
5	3310 (w)	2065 (vs)	2195 (w)	830 (vs)		795 (s)	382.0
6	3272 (w)	2070 (vs)	2200 (w)	833 (vs)	743 (s) 690 (s)	800 (s)	415.0

Table III   XPS Analysis of Complexes PdCl$_2$(PPh$_3$)$_2$ and PdCl$_2$(PBu$_3$)$_2$ and Polymers/Oligomers 1, 3, 5, and 6

Compound	Binding Energy E_b (eV)					Molar Ratio	
	Pd 3d$_{3/2}$	Pd 3d$_{5/2}$	P 2p	Cl 2p	S 2p	Pd/S	Pd/P
PdCl$_2$(PPh$_3$)$_2$	343.2	337.8	131.6	198.3			
PdCl$_2$(PBu$_3$)$_2$	343.1	337.7	131.1	198.5			
1	342.9	337.8	131.6, 130.9				1 : 2.84
3	344.3	338.3	131.0				1 : 2.34
5	343.0	337.9	131.1		164.8	1 : 0.49	1 : 3.20
6	343.0	337.8	131.7, 131.2		164.6	1 : 0.90	1 : 3.02

is an important factor to consider of in making films or devices for photo-/electroluminescence.

Absorption, Excitation, and Emission Properties

The absorption, excitation, and fluorescence spectra of **1**−**6** were recorded. The excitation and emission from **3** are illustrated in Figure (A) and (B). The emission spectrum of **3** in THF (0.1 mg/mL) exhibits a main peak at 401.2 nm and a subpeak at 431.4 nm. The transition energy [$E(\pi\pi^*)$] of the absorption band of **3** is 3.25 eV, and the band gap Eg (3.08 eV) estimated from the onset position of the absorption consistent with the main emission band (3.10 eV) are shown in Table IV, indicating that the fluorescence takes place by mi-

gration of electrons in the conduction band to the valence band. The emission band of **3** at 431.4 nm may be attributed to the excimer-like emission coupled with a vibration.

The excitation spectrum of **3** in THF (0.1 mg/mL) shows bands at 387 and 366 nm monitored with the emission at 401.2 nm. The peak position (387 nm) of the excitation spectrum agrees with the peak position (Table II, 382.5 nm) as usually observed with various fluorescence molecules. Other samples of this system possess a similar fluorescence process, as described above. The optical properties are summarized in Table IV and Figure 2. As shown in Table IV, the apparent Stokes shift is comparatively small except for 4 (0.25 eV for **1**, 0.29 eV for **2**, 0.15 eV for **3**, 0.63 eV for **4**, 0.37 eV
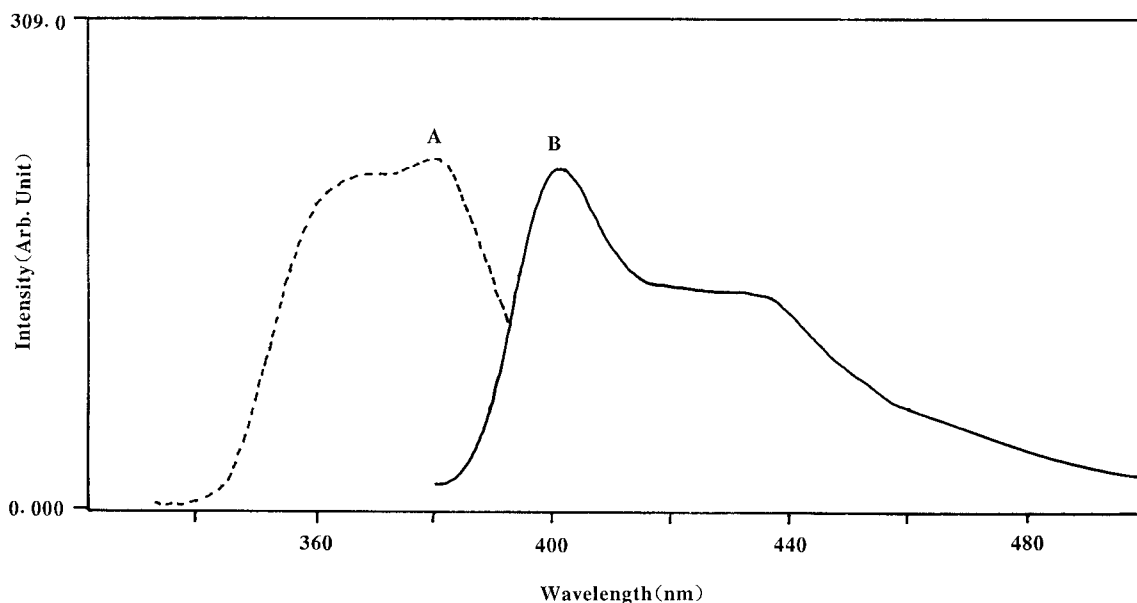

Figure 1   Excitation (A) and emission (B) spectra of polymer **3** in THF (0.1 mg/mL) at room temperature. Slit (em/ex): 5/5 nm.
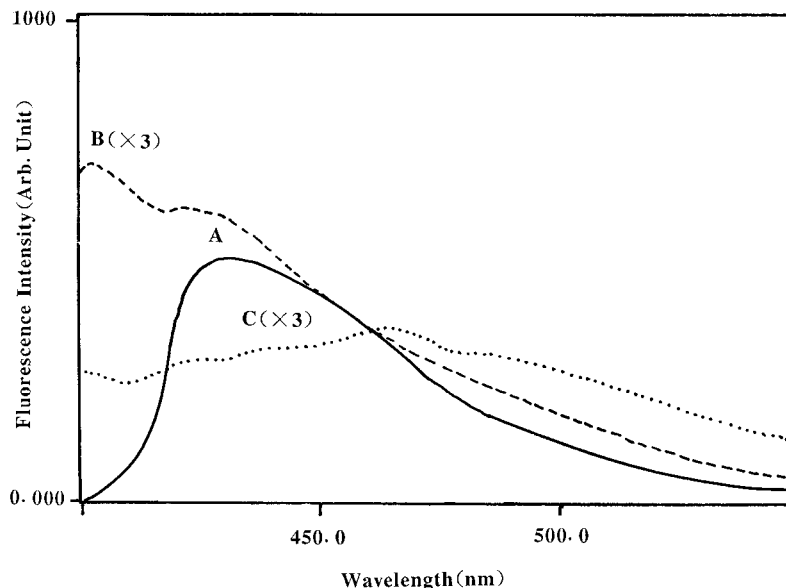
Figure 2   Emission spectra of polymer **2** (A), **3** (B), and **4** (C) in THF (0.1 mg/mL) at room temperature. Slit (ex/em): 5/5 nm.

for **5**, and 0.23 eV for **6**), indicating a limited degree of coupling to vibrational states in these materials. This is an important point to emphasize since such a coupling process may give rise to excessive heating in polymeric light-emitting diodes.[9]

The Effects of Inserted Thiophene-2,5-diyl and 1,4-Phenylene into Main Chain on Emission Intensity

As seen by comparing **5** with **4** and **6** with **2** in Table IV, the intensity of the emission from the solution of **5** (or **6**) is stronger than that from the solution of **4** (or **2**) at the same concentration. The strength of the emission from solution of **6** is about four times that of **2** and 18 times that of **4** at the same concentration. The results suggest that polymers having a thiophene ring in the main chain exhibit stronger fluorescence than those having only benzene rings in this system. Also, as seen by comparing **2** with **1**, the fluorescence is enhanced with the increase of 1,4-phenylene in the polymer repeat unit.

Table IV   Fluorescence,[a] Excitation,[b] $E(\pi\pi^*)$,[c] and E_g^d Data for Polymers/Oligomers 1–6

Polymer/Oligomer	λ_{max}^{ex} (nm)	λ_{max}^{em} (nm)	I	$E(\pi\pi^*)$ (eV)	E_g (eV)	Apparent Stokes Shift (eV)
1	383.1	416.0 (2.99 eV)	315.0	3.24	2.91	0.25
2	389.6	423.4 (2.93 eV)	508.6	3.22	2.91	0.29
3	387.0	401.2 (3.10 eV)	216.7	3.25	3.08	0.15
		431.4 (2.88 eV)	138.0			
4	389.6	463.6 (2.68 eV)	109.6	3.31	2.75	0.63
		480.0 (2.59 eV)	93.20			
5	390.4	431.4 (2.88 eV)	614.1	3.25	2.95	0.37
		452.0 (2.75 eV)	185.7			
6	423.6	450.0 (2.76 eV)	1942	2.99	2.81	0.23
		468.0 (2.65 eV)	1520			

[a] In THF (0.1mg/mL) at room temperature. Slit (ex/em) : 5/5 nm. Energy corresponding to λ_{max}^{em} is given in parentheses.
[b] Measured at λ_{max} of the emission in the same condition indicated by footnote a.
[c] $\pi - \pi^*$ transition energy estimated from maximum absorption.
[d] Band gap estimated from the position of the absorption band.
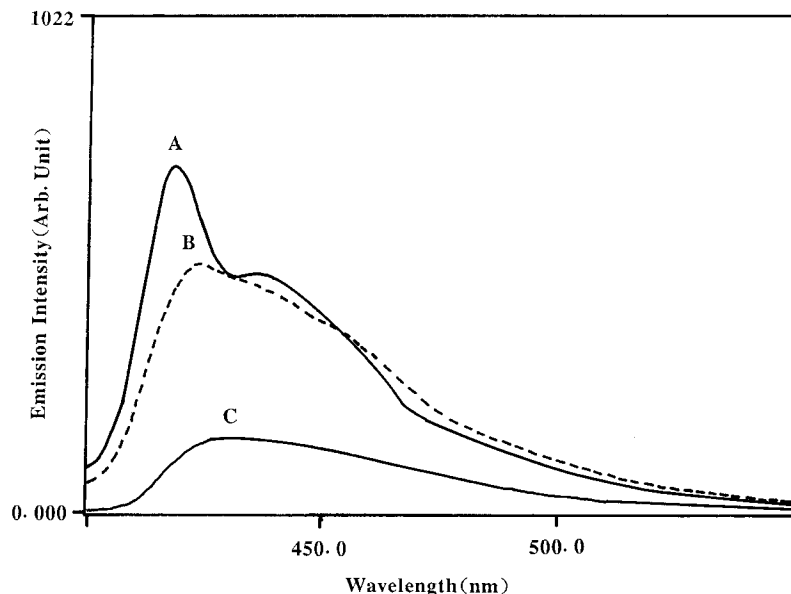[e] Energy separation between absorption and fluorescence maxima.

Figure 3 Fluorescence spectra of polymer 2 in different organic solvents (0.1 mg/mL; (A) toluene, (B) THF, (C) CHCl$_3$) at room temperature. Slit (ex/em) 5/5 nm.

The Effects of Ligands and Molecular Weight on the Optical Properties

Comparison of **4** with **3** (Table IV) shows differences both in emission position and intensity. The solution of **4** in THF emits the fluorescence peak at a position much different (at a longer wavelength by 62.4 nm) from that of **3** at the same concentration. The emission spectrum from solution of **3** ($\bar{M}_w = 0.69 \times 10^4$) in THF exhibits stronger emission at shorter wavelength than that of **4** ($\bar{M}_w = 1.96 \times 10^4$), indicating that polymers possessing higher molecular weight (ranges from $\bar{M}_w = 0.69 \times 10^4$ to 1.96×10^4) emit weaker fluorescence at longer wavelength. This may be due to the fact that the longer polymer chain possesses higher carrier mobility and lack of rigidity. Comparison of **1** with **3** or **2** with **4** (Table IV and Figure 2) suggests that polymers with phenyl-substituted phosphine ligands exhibit stronger emission than those with n-butyl phosphine ligands. This may also be attributed to the rigidity of the polymers.

The Effects of Solvents on the Fluorescence

Figure 3 shows the fluorescence spectra of 2 in toluene [Fig. 3(A)], THF [Fig. 3(B)], and CHCl$_3$ [Fig. 3(C)]. The emission intensity and the peak position are different with the different solvents at the same concentration. The emission strength of **2** in toluene, THF, and CHCl$_3$ is 715.6, 508.6, and 152.9, respectively. The main peak of the emission from the solution of **2** in toluene, THF, and CHCl$_3$ is at 417.6, 423.4, and 429.0 nm excited at 380.0, 389.6, and 380.0 nm, respectively. The fluorescence spectrum from solution of **2** in THF (or in CHCl$_3$) shows overlapping of the emission at 423.4 nm (or at 429.0 nm) with another emission band at about 440 nm (or 455 nm). The fluorescence from solution of **2** in toluene is different from that in THF or CHCl$_3$; there is a main emission peak at 417.6 nm and a subpeak at 436.8 nm. The results indicate that the solution of **2** in the three solvents exhibits not only the excimer-like emission but also the emission from the single molecules. The apparent Stokes shift is also different with the different solvents. The above results may suggest that the interaction between the polymer molecules, the degree to form excimer-like emission, the coupling to vibrational states, and the relaxation from excited states through nonradiative processes are different with the different solvents.

The Relationship Between the Emission Properties and the Concentration

Our results in Figures 4 and 5 show the dependence of fluorescence on the concentration of **2** in CHCl$_3$ (0.0025–0.1 mg/mL). The strength of the
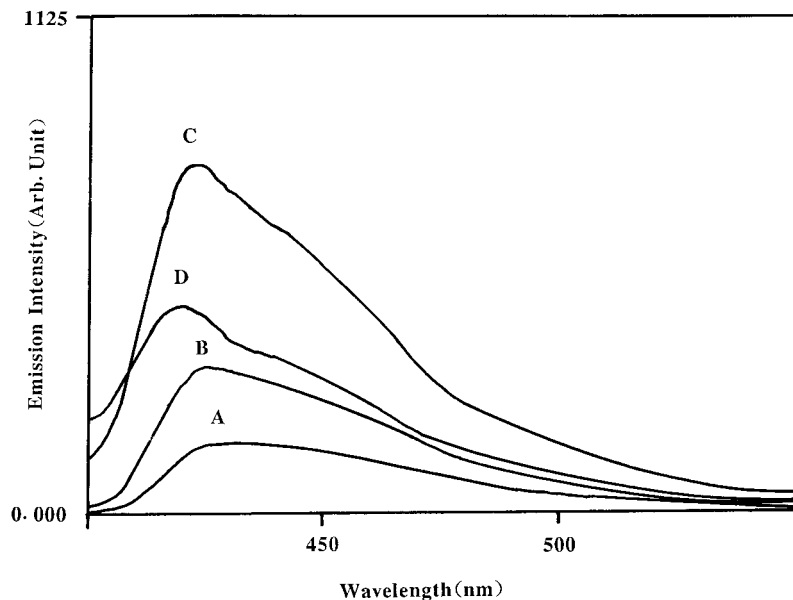
Figure 4 Fluorescence spectra of polymer **2** in $CHCl_3$ [(A) 0.1, (B) 0.05, (C) 0.025, and (D) 0.0025 mg/mL] at room temperature. Slit (ex/em): 5/5 nm.

emission from the solution of **2** in $CHCl_3$ is increased with the increase of the concentration (0.0025–0.025 mg/mL) and then decreased with the increase of the concentration (0.025–0.1 mg/mL). This is attributed to the concentration quenching effect and the difference of the average distance and the interactions between the single polymer molecules with various concentrations. In the lower concentration, the distance is larger, and the interactions are weaker between molecules. Thus, the fluorescence intensity is dependent mainly on the single polymer molecular
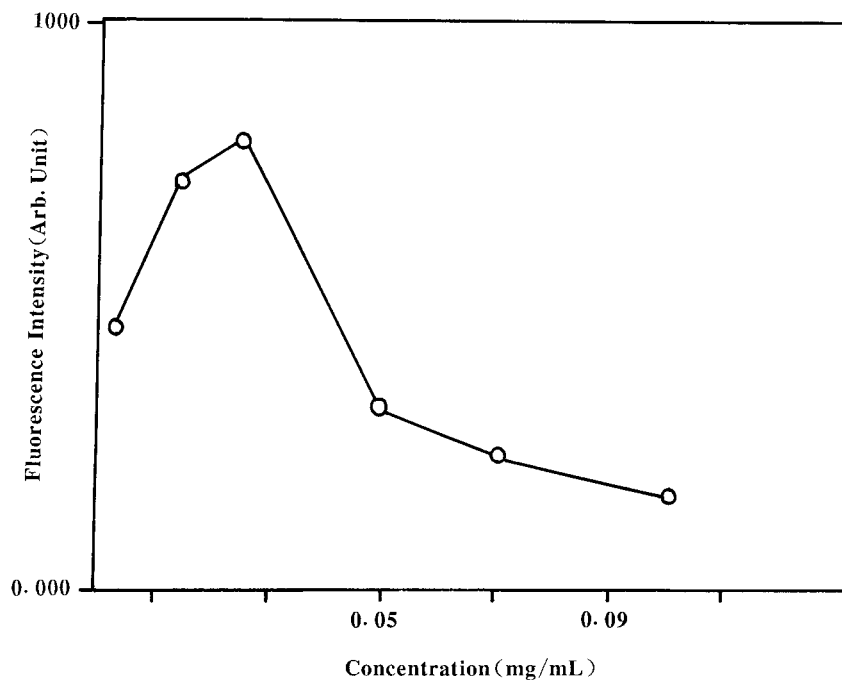

Figure 5 The dependence of the fluorescence intensity on the concentration of polymer **2** in $CHCl_3$ at room temperature. Slit (ex/em): 5/5 nm.

emission (emitting center), and the strength of the emission will therefore be increased with the increase of concentration, which may correspond to the emitting center ($<$ 0.025 mg/mL). In contrast, in the higher concentration ($>$ 0.025 mg/mL), the smaller the distance the interactions are stronger between molecules, and the polymer exhibits not only the single molecule emission but also the excimer-like emission coupled with the vibration. The relaxation from the excited states through non-radiative processes is enhanced with the increased interactions between the molecules; thus, the intensity of the emission is decreased with the increase of the concentration ($>$ 0.025 mg/mL). The fluorescence spectrum of **2** in CHCl$_3$ shows peaks at longer wavelengths with higher concentration. The apparent Stokes shift is changed with concentration. These are again relevant to the formation of excimer-like emission.

Polymers **1–6** gave brittle films. A luminescent film of good quality was made by mixing 0.5 mg of polymer **6** into 250 mg of polystyrene ($M_w \sim 5 \times 10^5$). The film emits strong light at 449.7 nm excited at 422.0 nm. Further increase of the content of polymer **6** in the film results in the emission at longer wavelength and leads to the decrease of emission intensity.

CONCLUSIONS

Metal containing poly-ynes of this system possess the structure fitted for photoluminescence. Polymers/oligomers **1–6** exhibit strong fluorescence at the excitation of UV-visible light at room temperature. Inserting thiophene-2.5-diyl or 1,4-phenylene into palladium poly-ynes to form polymers increases fluorescence by four- to eighteen-fold. The emission of the palladium poly-ynes is relatively sensitive to the molecular structure, solvents, concentration, and to the nature of the ligands coordinated to palladium atoms.

REFERENCES

1. J. H. Burroughs, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Machay, R. H. Friend, P. L. Burn, and A. B. Holmes, *Nature,* **347,** 539 (1990).
2. P. L. Burn, A. B. Holmes, A. Kraft, D. D. C. Bradley, A. R. Brown, R. H. Friend, and R. W. Gymer, *Nature,* **356,** 47 (1992).
3. T. Yamamoto, T. Maruyama, Z. H. Zhou, T. Ito, T. Fukuda, Y. Yoneda, F. Begum, T. Ikeda, S. Sasaki, H. Takezoe, A. Fukuda, and K. Kubota, *J. Am. Chem. Soc.,* **116,** 4832 (1994).
4. N. C. Greenham, A. R. Brown, D. D. C. Bradley, and R. H. Friend, *Synth. Met.,* **55–57,** 4134 (1993).
5. H. X. Wang and S. Mukamel, *Chem. Phys. Lett.* **192,** 417 (1992).
6. D. D. C. Bradley, *Synth. Met.* **54,** 401 (1993).
7. M. M. Richter, P. F. Fan, F. Klavetter, A. J. Heeger, and A. J. Bard, *Chem. Phys. Lett.* **226,** 115 (1994).
8. S. Heum, H. Bassler, U. Muller, and K. Mullen, *J. Phys. Chem.,* **98,** 7355 (1994).
9. A. P. Davey, S. Elliott, O. O'Connor, and W. Blau, *J. Chem. Soc., Chem. Commun.* 1433 (1995).
10. C. C. Frazier, S. Guba, W. P. Chen, M. P. Cockerham, P. L. Porter, E. A. Chauchard, and C. H. Lee, *Polymer,* **28,** 553 (1987).
11. S. Guba, C. C. Frazier, W. P. Chen, P. L. Porter, K. Kang, and S. E. Finberg, *Proc. SPIE,* **14,** 1105 (1989).
12. P. L. Porter, S. Guba, K. Kang, and C. C. Frazier, *Polymer,* **32,** 1756 (1991).
13. D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, *Purification of Laboratory Chemicals,* 2nd ed. Pergamon Press, New York, 1980.
14. A. S. Hay, *J. Org. Chem.* **25,** 637 (1960).
15. H. A. Tayim, A. Bouldoukian, and F. Awad, *J. Inorg. Nucl. Chem.* **32,** 3799 (1970).
16. L. Malatesta and C. Cariello, *J. Chem. Soc.* 2323 (1958).
17. J. M. Barker, P. R. Huddleston, and M. L. Wood, *Synth. Commun.* **5,** 59 (1975).
18. S. Sonogashira, Y. Tohda, and N. Hggihara, *Tetrahedron Lett.* 4467 (1975).
19. S. Takahashi, M. Kariya, T. Yatake, S. Sonogashira, and N. Hagihara, *Macromol.,* **11,** 1063 (1978).
20. L. J. Bellamy, *The Infra-red Spectra of Complex Molecules,* Wiley, New York, 1954, p. 59.