Photophysical Properties of Lyotropic Liquid Crystalline Polybenzazoles and Evidence of Aggregate Formation for Polybenzazoles in Methanesulfonic Acid

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ABSTRACT: The photophysical properties of the lyotropic liquid crystalline polybenzazoles [poly(*p*-phenylene benzobis(oxazole)) (PBO), poly(2,5-benzoxazole) (ABPBO), and their random copolymer PBO−ABPBO] and their model compounds in solutions with methanesulfonic acid (MSA) were investigated in detail using UV absorption and emission spectroscopy. It was found that the absorption wavelength and emission wavelength can be well modulated by the composition of PBO in the copolymer from the lowest value for pure ABPBO to the highest for PBO. The photoluminescence spectra at various concentrations were also studied in detail. Both excitation spectra and emission spectra show significant changes in shape and position of the peaks. With the increase of the concentration, the intensity of emission is depressed, and the highly structured emission spectra gradually change to featureless, red-shifted, and broad spectra. The peak position in excitation spectra also shows a slight red shift. Another dramatic change in excitation spectra with concentration is a second broad peak that shows up in the intermediate concentration range. The change in emission spectra can be attributed to the existence of the interchain aggregates, which can be excited from the ground state to the excited-state directly. This explanation is further supported from the evidence in a poor solvent, selective excitation, and time-resolved photoluminescence spectroscopy.

Introduction

Conjugated polymers attracted considerable attention from the scientific community due to their semiconducting and luminescent properties.[1,2] Compared with traditional inorganic light-emitting diodes (LEDs), conjugated polymer-based LEDs have various advantages such as color controllability, bendability, easy fabrication, and low price/cost. Meanwhile, a great deal of effort has been devoted to understanding the underlying physics of luminescence processes of conjugated polymers.

However, there are two major, challenging problems[3] in developing conjugated polymers for LEDs: (1) achieving high fluorescence quantum efficiencies and (2) obtaining spectrally pure blue luminescent polymers. Many researchers have performed studies to discover the origin of low fluorescence quantum efficiencies[4−10] in a solid-state film of conjugated polymer and attempted to obtain spectrally pure blue luminescent polymers.[3,11] It is generally accepted that emission in these polymers arises from interchain excitons. It is found that luminescence quantum efficiency is greatly suppressed, and a featureless, red-shifted emission spectrum occurs upon turning from dilute solutions or solid solutions to solid films.

Aromatic heterocylic polymers of the polybenzazole family have been studied since the early 1980s.[12−15] Here we present some photoluminescence properties of the lyotropic liquid crystalline polybenzazole family. The polymers studied here are poly(*p*-phenylene benzobis(oxazole)) (PBO), poly(2,5-benzoxazole) (ABPBO), and their copolymer PBO−ABPBO with different PBO compositions, shown in Figure 1. As illustrated in Figure 1, the π-conjugated and rigid structures of these polymers bring about many outstanding photoluminescence properties[16] as well as mechanical properties and thermal stability. The benzoxazole group in these polymers has a strong chromophoric effect on the fluorescence of conjugated systems because it enhances the emission quantum yield via a decrease in the nonradiative decay rate constant. So et al.[17] studied the photophysical and photochemical properties of some benzoxazole and benzothiazole compounds in detail.

Jenekhe and his colleagues investigated excimers and exciplexes of such polymers with the donor molecules such as tris(*p*-tolyl)amine (TTA)[3] and PMMA.[18] It was found that the fluorescence of PBO/TTA thin films has a much higher quantum yield of bright blue luminescence. This kind of complex was applied in layered photoreceptors.[19,20]

The rod−coil copolymers consisting of these electroactive and photoactive segments were synthesized.[21−24] The luminescence quantum yield varied with copolymer composition, reaching over 6- and 7-fold enhancements compared to the “bulk” pure conjugated polymers with the formation of nanocomposites.[24]

The intermolecular distances of such π-conjugated polymers are about 3.3−3.6 Å with cofacial chain packing in the solid state,[22] which are similar to the typical distance of 3−4 Å for forming excimers in small molecules. The time-resolved photoluminescence (PL) decay dynamics of dilute solutions of such polymers also exhibited a single-exponential decay while multiexponential decay dynamics for thin films.[10] On the basis of the evidence described above and the concentration dependence of the photoluminescence quantum yield,

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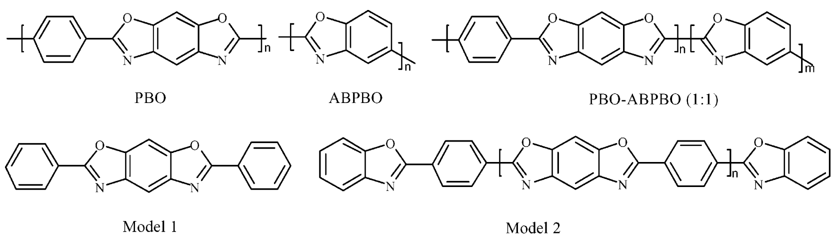

Figure 1. Chemical structures of polybenzazoles and two model compounds.

Jenekhe et al.[10] proposed that the rather low PL quantum yield of thin films of these polymers was caused by excimer formation. An excimer[25] is an intermolecular entity that is only stable in the excited state.

In contrast, the formation of aggregates in solid films and solutions has featured more prominently in recent literature.[4−8,26] The entity of aggregate means that both the ground- and excited-state wave functions are delocalized over several polymer chains. Aggregates have been proposed to happen in ladder poly(*p*-phenylene) (LPPP)[7] based on PL and photocurrent measurements. Some results of continuous wave (CW), time-resolved, and spatially resolved spectroscopic studies of emission and absorption in poly(*p*-pyridylvinylene) (PpyV) also suggest the formation of aggregated regions.[5] There is lack of studies of the related properties of polybenzazoles. In this paper, we present the first systematic studies on the photophysical properties of PBO, ABPBO, and the new random copolymer PBO−ABPBO as illustrated in Figure 1 and show evidence of aggregate formation for polybenzazoles in methanesulfonic acid (MSA). The authors believe that these results will lead to advance the usage of such conjugated polymers as photoelectoactive materials and add to the understanding several interesting phenomena in solutions and solid-state films.

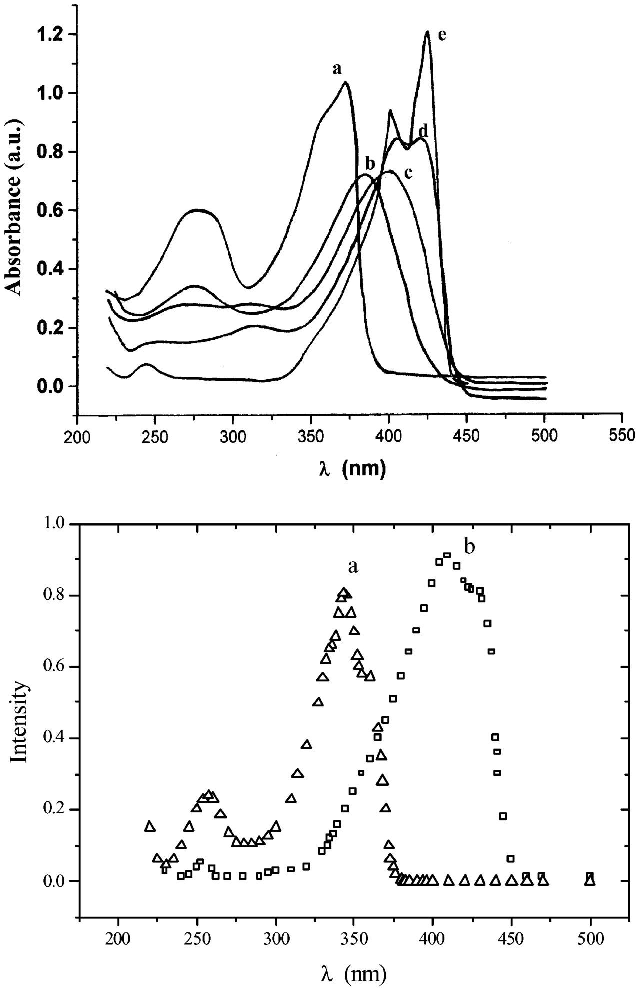

Figure 2. (top) UV spectra of ABPBO (a), PBO (e), and PBO−ABPBO (b, 1:3; c, 1:1; d, 3:1) in MSA ($C = 0.000\ 44$ g dL^{-1}). (bottom) UV spectra of the model compounds (a, model 1; b, model 2).

Experimental Section

Materials. The polybenzazole samples were prepared in our own laboratory according to the previous reports.[27−29] The weight-average molecular weights of PBO and ABPBO are 14 000 and 46 000 g mol^{-1}, respectively, which were estimated by Mark−Houwink equations.[12] PBO−ABPBO samples were synthesized by random copolymerization illustrated elsewhere,[30] and they have an intrinsic viscosity of 6.7 dL g^{-1} in pure methanesulfonic acid (MSA) at 25 °C. MSA was obtained from Aldrich-Sigma Chemical Co. The PBO model compound 2,6-diphenylbenzo[1,2-*d*:5,4-*d*′]bis(oxazole) (model 1 for short) and the PBO−ABPBO model compound (model 2 for short) were also synthesized in our laboratory according to the literature.[13,17,31] Polymer solutions were prepared in MSA in the glovebox. Eight PBO solutions were used in the PL measurements with their concentrations varied from 0.00044 to 0.12 g dL^{-1}, which corresponds to 3.14×10^{-7} and 8.57×10^{-5} M given the molecular weight of 14 000 g mol^{-1}. For some other polymer solutions, they were prepared with three concentrations 0.000 44, 0.0048, and 0.12 g dL^{-1} in order to see the consistency. The polymer films used in this study were prepared using the method proposed by Jenekhe,[32,33] i.e., the solution casting from the polybenzazoles in AlCl$_3$/nitromethane solution with a polymer concentration of about 3 wt %. The thin films were dried at 80 °C in a vacuum oven for 12 h after complete decomplexation in deionized water for at least 3 days.

Measurements. Absorption spectra were recorded on a Shimadzu UV-365 UV−vis spectrophotometer, and photoluminescence spectra were recorded on a Hitachi 850 fluorescence spectrophotometer at room temperature. The picosecond laser experiments utilized a Spectra Physics M3800 CW Nd:YAG laser equipped with a Spectra Physics M3500 ultrashort pulse dye laser (Rhodamine 6G) and a Spectra Physics M3295 cavity dumper operated at 800 kHz. The dye laser was operated at 600 nm. The fluorescence lifetime measurements were carried out on a time-correlated single-photon-counting spectrofluorimeter (EG&G). The photons were detected by a Hamamatsu S3059-00 microchannel plate photomultiplier. This part was done in the Institute of Chemistry, Academia Sinica, Beijing.

Results and Discussion

UV Absorption Spectra of Polybenzazoles and Their Model Compounds in MSA. The polymers discussed in this paper are PBO, ABPBO, and their copolymers with different compositions (PBO:ABPBO = 1:3, 1:1, and 3:1). The model compounds are described in Figure 1 as model 1 and model 2. The concentrations of the polymers and model compounds in MSA are all 0.000 44 g dL^{-1}. Figure 2 shows the absorption spectra of the polymer solutions and model compound solutions.

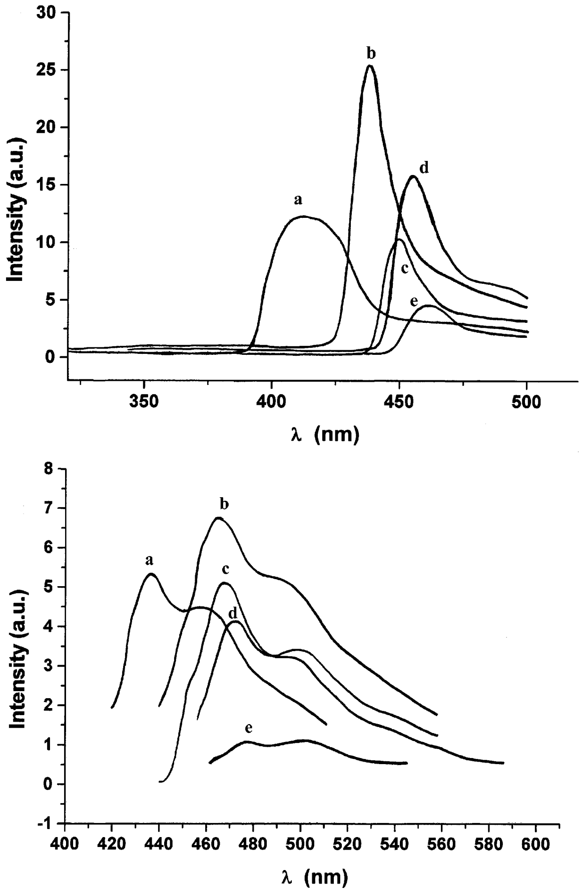

Figure 3. Photoluminescence excitation spectra (top) and emission spectra (bottom) of ABPBO (a), PBO−ABPBO (b, 1:3; c, 1:1; d, 3:1), and PBO (e) in MSA ($C = C_1 = 0.12$ g dL^{-1}).

It is evident that the absorption peak of the polymer shifts to long wavelength with the increase of PBO composition in the copolymers, from 373 nm for the pure ABPBO solution to 425 nm for the pure PBO solution. The intermediate peak positions for PBO−ABPBO (1:3, 1:1, and 3:1) are 383, 397, and 423 nm, respectively. This result is expected because it is known that the coplanarity of PBO rigid chain in the dilute solutions is better than that of ABPBO. ABPBO adopts two conformations,[15] i.e., trans and cis at low concentrations. Moreover, the cis conformation can induce the coillike array in ABPBO solution, and then the coplanarity of the polymer chain is deteriorated. In Figure 1, it can be found that the conjugate length of model 2 is larger than that of model 1; the corresponding absorption peak position also red shifts from 343 nm for model 1 to 410 nm for model 2. The absorption peak positions of model 1 and PBO in MSA are consistent with the earlier values reported by So et al.[17] (343 and 429 nm, respectively) and Jenekhe et al.[34] (348 and 417 nm, respectively).

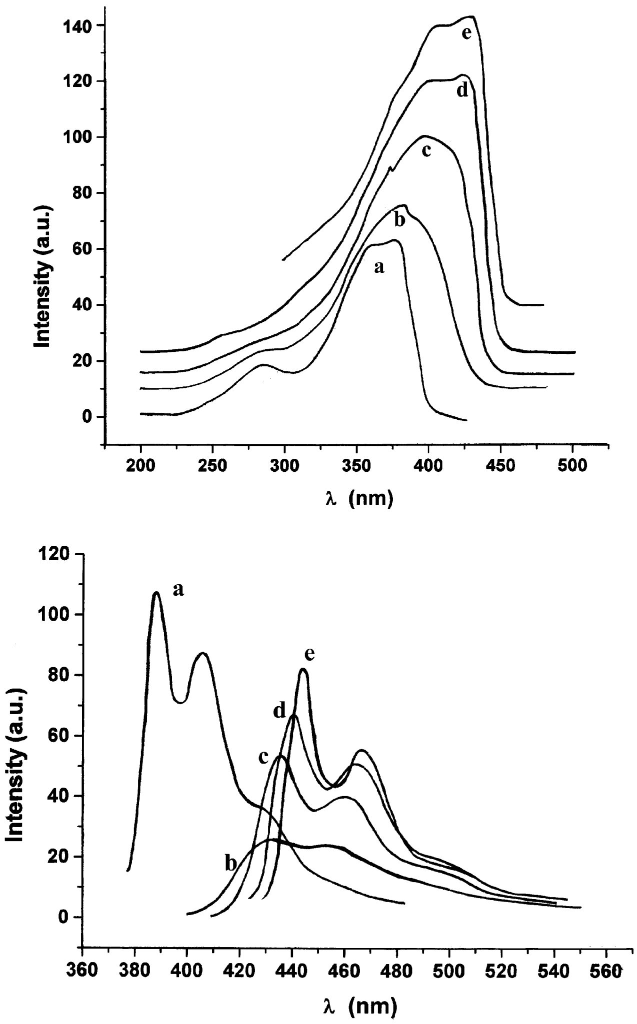

Figure 4. Photoluminescence excitation spectra (top) and emission spectra (bottom) of ABPBO (a), PBO−ABPBO (b, 1:3; c, 1:1; d, 3:1), and PBO (e) in MSA ($C = C_2 = 0.000\ 44$ g dL^{-1}).

Photoluminescence Spectra of Polybenzazoles in MSA. The photoluminescence spectra of polybenzazoles in MSA with two different concentrations ($C_1 = 0.12$ g dL^{-1}, $C_2 = 0.000\ 44$ g dL^{-1}) were presented here. All the emission spectra in this paper were obtained after the polymer solutions were excited at the peak positions in the corresponding excitation spectra. When there are two excitation peaks, the samples were excited at either peak wavelengths, and the resulting emission spectra were identical in the shape with a difference in the intensity of the peak. The excitation spectra and emission spectra at different compositions display striking difference in both shape and wavelength of the peak. The difference in the concentration in photoluminescence spectra will be discussed in detail later. Figure 3 and Figure 4 show the excitation spectra and emission spectra at two compositions, and the peak positions are listed in Table 1. Similar to absorption spectra, the excitation spectra and emission spectra also show the red shift of the peak with the increase of PBO fraction in PBO−ABPBO copolymer. The wavelength of the emission light could be controlled by changing the composition of copolymer. The difference in the intensity of the peaks for the different polymers can also be observed. It is due to the difference in polymer chain length and, therefore, the mole concentration. The critical concentration for self-quenching is different for different polymers, and consequently one can observe that the polymer showing the stronger emission peak at the concentration C_1 may have a weaker emission peak than that of other polymers at the concentration C_2, for example, PBO. However, it is ubiquitous that the emission efficiency is depressed when the concentration is increased. It should be noted that the emission curve for ABPBO at the concentration of 0.000 44 g dL^{-1} is quite far away from the other polymers at the same concentration while the difference is not that large for the concentration of 0.12 g dL^{-1}. As mentioned in the

Table 1. Excitation and Emission Bands of Polymers and Model Compounds in MSA at Different Concentrations

sample	C (g dL^{-1})	Ex^{a} (nm)	I_x^{b} (au)	Em$_1$^{c} (nm)	I_1 (au)	Em$_2$ (nm)	I_2 (au)	Em$_3$ (nm)	I_3 (au)
ABPBO	0.00044	376	63	388	107	406	87		
	0.0048	315	33			406	52		
		388	36						
	0.12	410	12			437	6	460	5
PBO−ABPBO (1:3)	0.00044	382	65	432	25	452	23		
	0.0048	322	49			454	15		
		420	76						
	0.12	438	26			468	7	~500	
PBO−ABPBO (1:1)	0.00044	399	85	438	53	461	39		
	0.0048	334	62			462	26		
		435	70						
	0.12	450	10			467	5	~500	
PBO−ABPBO (3:1)	0.00044	424	100	440	67	466	50		
	0.0048	330	77			464	38		
		440	76						
	0.12	455	16			471	4	~500	
model 1	0.00044	347	114	376	119	393	175	~415	
	0.0048	304	78			393	159	~415	
		373	103						
	0.12	393	116			396	91	415	85
model 2	0.00044	391	95	440	59	462	51		
	0.0048	324	79			461	41		
		439	77						
	0.12	451	16			470	7	~500	
PBO	0.00044	430	102	442	72	466	55		
	0.0008	390	82	444	52	466	47		
		417	80						
		437	83						
	0.0048	443	62			467	34		
		341	62						
	0.011	446	67			468	23		
		325	41						
	0.02	448	55			469	31		
	0.0277	450	44			468	25		
	0.06	452	27			471	14		
	0.12	461	5			476	1	500	1

[a] Excitation wavelength. [b] Intensity. [c] Emission wavelength.

last paragraph, ABPBO can assume the cis conformation when the concentration is low enough and PBO is a rigid-rod polymer at all concentrations. So the larger difference at the lower concentration may suggest that the PBO segments can efficiently give hindrance to the cis conformation of the ABPBO chain.

Photoluminescence Spectra of Polybenzazoles in MSA at Various Concentrations. The photoluminescence spectra of ABPBO and PBO in MSA at various concentrations are shown in Figures 5 and 6. Since the spectra are quite similar to each other, we just put PBO as the typical polymer to investigate in detail eight concentrations from 0.000 44 to 0.12 g dL^{-1} (shown in Figure 6). For simplicity, the other spectra are only for three different concentrations, i.e., 0.00044, 0.0048, and 0.12 g dL^{-1}. The peak positions and intensity of peaks are listed in Table 1.

In the figures and tables listed above, it can be seen that there are similarities in the excitation spectra and emission spectra for various polymers and small molecular model compounds in MSA. First, the intensity of emission peak (or the photoluminescence quantum efficiency) decreases with increasing concentration. Second, the line shape of excitation spectra changes dramatically with the concentration, which was not reported for PBZT/MSA solutions.[10] At the intermediate concentration of 0.0048 g dL^{-1}, there are two peaks. One is a broad peak at the lower wavelength range and another one at the higher wavelength range, which red shifts slightly when the concentration increases. The third change occurs in emission spectra. From very dilute solution to semidilute solution, the emission spectra change from well-resolved spectra to broad, featureless, and red-shifted spectra. With increasing the concentration, it can be observed that the peak at the lower wavelength range diminishes to disappear at the intermediate concentration, while the peak at the higher wavelength range shows up gradually with an increase in relative intensity.

Now we investigate in detail the change in photoluminescence spectra of the typical polymer, PBO in MSA, at eight concentrations, i.e., 0.00044, 0.0008, 0.0048, 0.011, 0.02, 0.0277, 0.06, and 0.12 g dL^{-1}. The excitation and emission spectra are shown in Figure 6. The related peak positions and intensity are tabulated in Table 1.

From the excitation and emission curves shown in Figure 6 and detailed data in Table 1, one can find that the gradual change with the concentration clearly. At the lowest concentration of 0.000 44 g dL^{-1}, a broad and strong peak can be observed. A lower concentration was tested, but no further difference from the reported lowest concentration is seen. This broad and strong peak in fact contains two components. One component is at the longer wavelength, and it red shifts with the concentration from 430 to 461 nm. Another component is at the shorter wavelength; it separates from the broad peak when the concentration increases and blue shifts from 390 nm at the concentration of 0.0008 g dL^{-1} to 280 nm at 0.0277 g dL^{-1}. Finally, this excitation peak disappears due to the self-quenching effect.

Similar to earlier reports on PBZT and other conjugated polymers in solutions, emission spectra of PBO in MSA show a dramatic change with concentration. The peaks appearing in the emission spectra can be

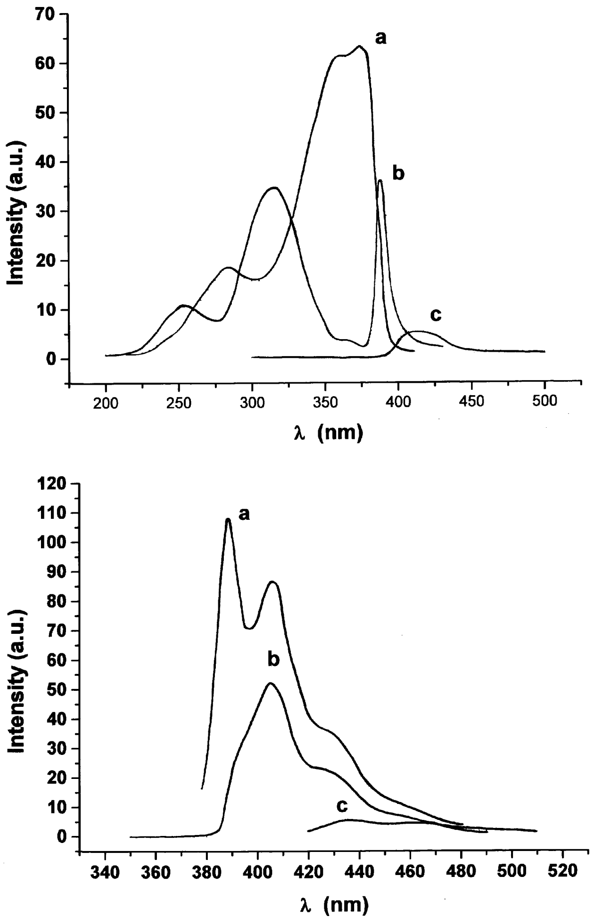

Figure 5. Photoluminescence excitation spectra (top) and emission spectra (bottom) of ABPBO in MSA (a, 0.000 44 g dL^{-1}; b, 0.0048 g dL^{-1}; c, 0.12 g dL^{-1}).

Table 2. Intensity Ratios of the Two Kinds of Peaks in Emission Spectra of PBO/MSA at Different Concentrations

	a	b	c	d	e	f	g	h
I_1/I_2	1.31	1.10	0.68	0.51	/	/	/	/
I_2/I_3	3.13	3.07	2.90	2.82	2.60	2.56	2.11	0.97

divided into three groups, as shown in Table 1 as Em_1, Em_2, and Em_3. The first group is around the wavelength of 440 nm, the second is around 470 nm, and the third is around 500 nm. To make a clear comparison, we put the ratios of the intensity of the first peak and the second peak for the lowest four concentrations and the ratios of the intensity of the second peak and the third peak for the highest four concentrations in Table 2. At some concentrations, the peak is just a shoulder on the emission curves; the intensity is the magnitude of the shoulder. It is evident that the emission curve containing the first two groups of peaks at the lowest concentration shows a well-resolved vibronic structure. When the concentration increases to 0.0008 g dL^{-1}, the broad peak begins to show the tendency to split in the excitation spectrum; the corresponding emission curve is still similar to that of 0.000 44 g dL^{-1}, but the ratio of the first peak intensity and the second peak intensity decreases from 1.31 to 1.10, as shown in Table 2.

When the strong peak in the excitation spectrum splits to two separate peaks at the intermediate concentrations in Figure 6 (shown as the curve c in excitation spectra), the line shape of the emission spectra begins to change. The first peak diminishes to a shoulder, and the second peak becomes dominant in the emission curve. It can be observed that the ratio of the second peak intensity and the third peak intensity decreases with the further increase in concentration in Table 2. The broad, featureless peak appears at around 500 nm. In fact, it shows up as a broad tail in the dilute solutions and only become a separate peak with a comparable intensity when the concentration is relatively high. Compared with the literature report on the emission curve for PBO solid thin film, the third peak becomes dominant from the concentrated solution to solid thin film.[3] This red-shifted, featureless emission of the concentrated solution and of the solid thin film originates from associated states like excimers or aggregates.

It should be noted that each group of peak red shifts weakly before it diminishes with increasing concentration. It is also worthwhile to discuss about the Stokes shift, i.e., the difference in wavelengths of absorption peak and emission peak. For convenience, we use excitation spectra to substitute absorption spectra. The Stokes shift reflects the structural relaxation.[35] In the aromatic polymers utilized in LED, geometric structural relaxation is closely related to ring distortion.[35] In our polymers, the Stokes shift may have two origins.[35] One is the emission occurs from the same segments when they assume a more coplanar conformation if the time allows. Another origin is that emission occurs from ring rotation on the different segments without being hindered.

From Figure 6 and Table 1, one can observe that the Stokes shift is rather small in the most dilute PBO/MSA solution. It is only 12.2 nm (corresponding to 0.08 eV), and the emission curve is a highly structured sharp curve which is the emission of the singlet excited state $^1A^*$ of the "single chain" or the isolated chromophore. With the increase in concentration, the first peak at 440 nm in emission spectra vanishes, and the second peak at 470 nm shows up gradually and becomes dominant in emission spectra. Meanwhile, the excitation peaks red shift slightly, so the Stokes shift increases to 20.4 nm (0.12 eV) at the concentration of 0.02 g dL^{-1}. For solid thin films of PBO, the second peak disappears, and there is only the third peak at around 500 nm in emission spectrum. The Stokes shift becomes 129 nm (0.71 eV). The increase in the Stokes shift with the concentration also indicates the aggregation of PBO chains. Here, the aggregation is a rather broad term including the physical aggregate and excimer proposed by Jenekhe[10] for solid PBZT films. So there is one question: is aggregate or excimer formed in semidilute solutions?

Generally speaking, it is not easy to distinguish excimer from physical aggregate in emission spectrum. Though physical dimer and aggregate have associated characteristic absorption peaks, those peaks are liable to be hidden under the inhomogeneously broadened absorption spectrum of conjugated polymers. Both physical aggregate and excimer have typical broad structureless and red-shifted emission spectrum. Excimer is formed by interaction of an excited chromophore $^1A^*$ with an unexcited choromophore ^1A through this path: $^1A^* + {}^1A \Leftrightarrow {}^1(AA)^*$.[24] Such an excited-state complex can only exist after the absorption while aggregates can be formed before the absorption. Aggregates are formed by two or more neighboring chains when they are in the

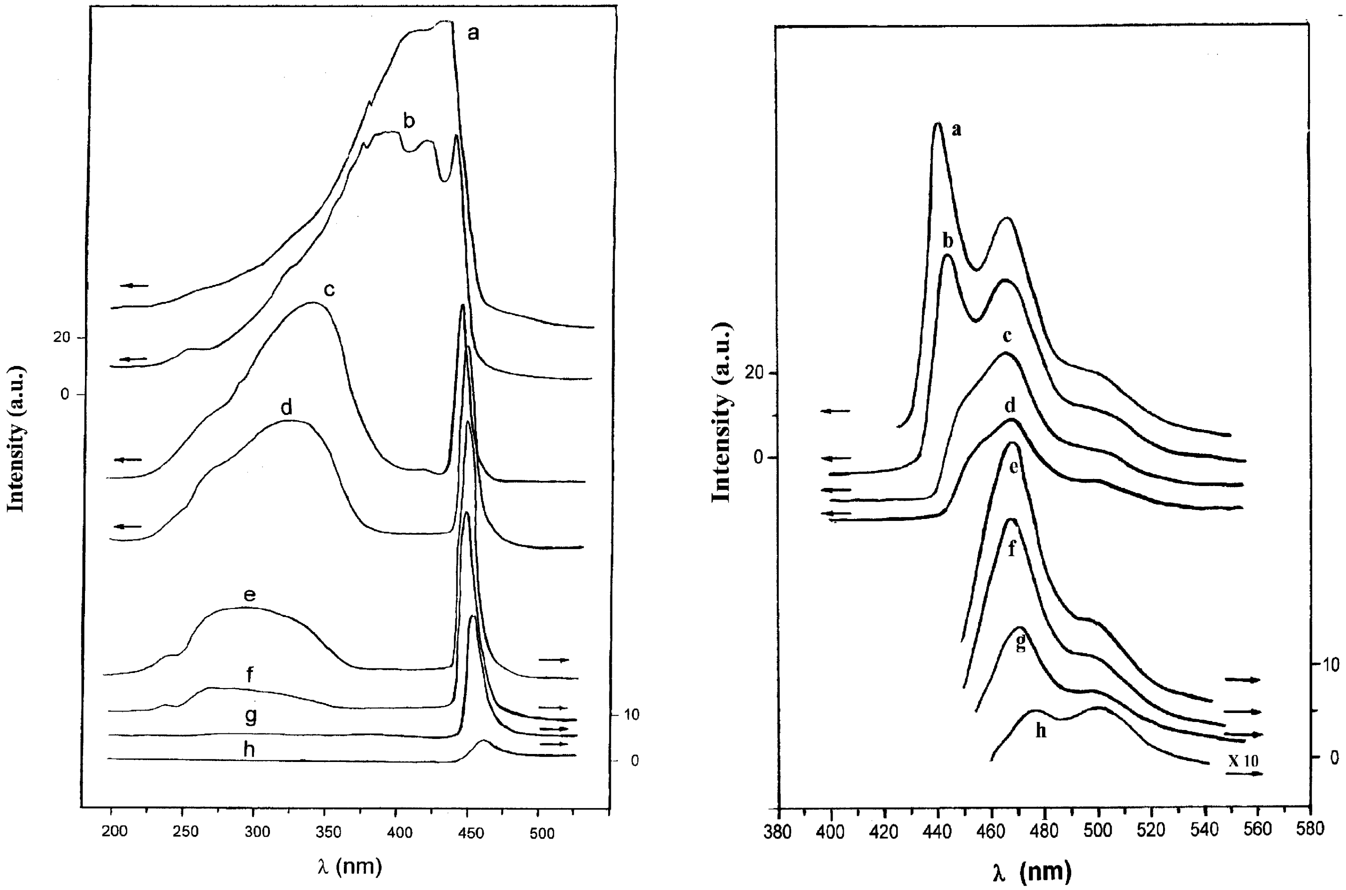

Figure 6. Photoluminescence excitation spectra (left) and emission spectra (right) of PBO in MSA (a, b, c–h: 0.000 44, 0.0008, 0.0048, 0.011, 0.02, 0.0277, 0.06, and 0.12 g dL^{-1}).

ground state, and such aggregates are excited to $^{1}(AA)^*$ after absorption in another path: $^{1}A + {}^{1}A \Leftrightarrow {}^{1}(AA) \Leftrightarrow {}^{1}(AA)^*$ (for simplicity, here we only show an association of two units). The radiative decay of an excimer or aggregate follows the same pathway, and both are detrimental to the luminescence efficiency of the polymer.[5] Both excimer and aggregate share some basic requirements for their formation. For an excimer, the excited chromophore needs a short enough distance to another unexcited chromophore to overlap their orbitals. But if the interaction is too strong, aggregates can be formed before the choromophores are excited. So it has been suggested that the formation of aggregates needs a smaller interaction distance between neighboring chains in the ground state.[36] The evidence of the formation of aggregates of PBO chains in MSA will be discussed in the next section.

Evidence of Aggregate Formation of PBO Chains in MSA. In this section, we will show some experimental evidence for supporting the formation of aggregate in PBO's MSA solutions using a poor solvent, selective excitation, and time-resolved photoluminescence spectroscopy.

Polymer condensed structure and crystalline structure can be determined by X-ray diffraction. As for the aggregate structure, it is closely related to solvent environment. It is well-known that the polymer chain can assume a more extended conformation in good solvents while a more coiled conformation in a poor solvent. When the conjugated polymer is in the solid state, the backbone of the polymer chain is most likely a planar conformation due to the interchain interaction, i.e., a geometrical conformation with a least inter-ring distortion angle. The more planar the polymer chain is, the easier it is for the π electron to delocalize on the polymer chain and the lower the band gap between HOMO and LUMO (or between π and π^*), which consequently causes the red shift in absorption and emission spectra.[37] Some researchers used different solvents to analyze the photoluminescence spectra and found that polymers are more liable to form aggregates in poor solvents.[8,38,39]

Methanol was selected as the nonsolvent of PBO to disturb the protonation and dissolution of PBO in MSA by adding 1, 2, 5, and 10 mL methanol into 10 mL of PBO/MSA solution with a concentration of 0.000 44 g dL^{-1}. During the adding of methanol into the PBO/MSA solution, heat was produced. The PL spectra of PBO in a mixed solvent MSA/methanol are shown in Figure 7. To understand the effect of methanol in the PBO/MSA solution, the emission curve of the PBO in mixed solvent with a maximum content of methanol is shown separately in Figure 7.

The effect of methanol as a nonsolvent on the PL spectra is significant without discussing the quenching effect and other disturbances from methanol from Figure 7. Compared with the PBO/MSA solution at 0.000 44 g dL^{-1} (Figure 6 and Table 1), addition of 1 mL of methanol does not bring much difference and 2 mL of methanol reduces the relative intensity of the first peak. With the addition of more methanol into the original PBO/MSA solution, the initially extended protonated PBO chains are forced to coil by the nonsolvent. The aggregation of the molecular chains of PBO is more

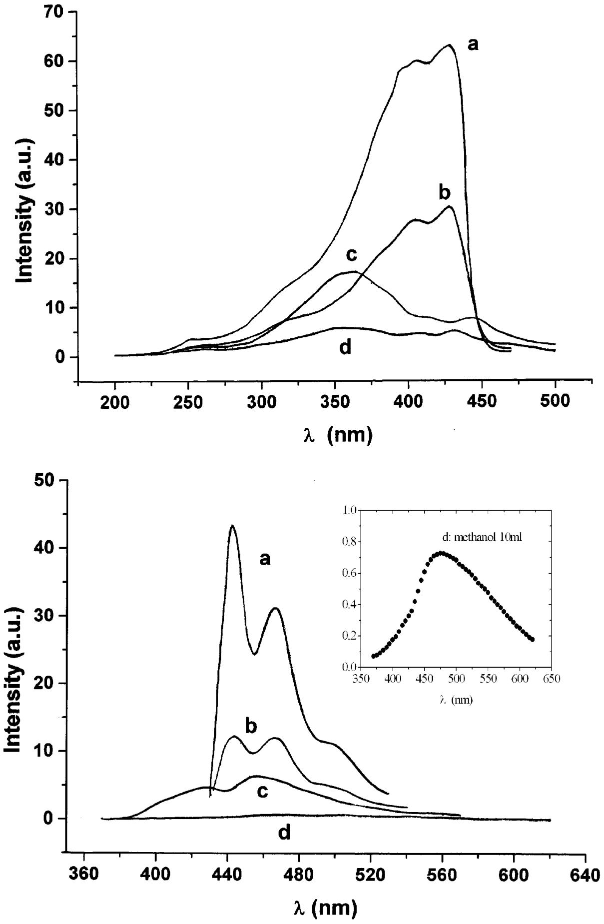

Figure 7. Photoluminescence excitation spectra (top) and emission spectra (bottom) of PBO/(MSA + methanol) (a, b, c, d: 1, 2, 5, 10 mL of methanol + 10 mL of PBO/MSA solution at $C = 0.000\ 44$ g dL^{-1}). Inset: photoluminescence emission spectrum of PBO in 10 mL of MSA and 10 mL of methanol.

significant in Figure 7, in which the emission peak shifts from 442 nm for the original PBO/MSA solution to 478 nm and the emission peak is a characteristic broad featureless peak. The changes in Figure 7 are similar to those changes with the increase of concentration. When the "solution" of PBO in mixed solvents stays for a long period, PBO chains will precipitate and the macroscopic aggregates can be visually observed.

A simple calculation can be used to describe the density of PBO chains in MSA. The concentration unit used in this paper is weight of PBO per volume of the solution. Since the repeating unit's molecular weight of PBO is 234 g mol^{-1} and the weight-average molecular weight of PBO was measured as 14 000 g mol^{-1} as described in the Experimental Section, the average number of repeating units for PBO chain is 60. Given the persistent length of the PBO repeating unit, which is 12.08 Å,[40] the corresponding length of a PBO chain is about 70 nm. The average distance between the centers of two neighboring PBO chains can be calculated as 30 nm for the highest concentration (0.12 g dL^{-1}) using the information on concentration and molecular weight, whereas the lowest concentration (0.000 44 g dL^{-1}) gives a distance of 180 nm. This method was also used in illustrating the poly(pyridine-2,5-diyl) solutions with different concentrations.[41] Apparently, the PBO chains tend to interact sterically and aggregate together after collision in the PBO/MSA solution with a concentration of 0.12 g dL^{-1} since the length of PBO chain is 70 nm and the average distance between the centers of two neighboring PBO chain is about 30 nm, while in dilute solution (0.000 44 g dL^{-1}), PBO chains exist as single protonated molecules isolated by MSA. The possibility of collision between two rigid rod molecules still exists, but it is rather lower than the case in the higher concentration solutions.

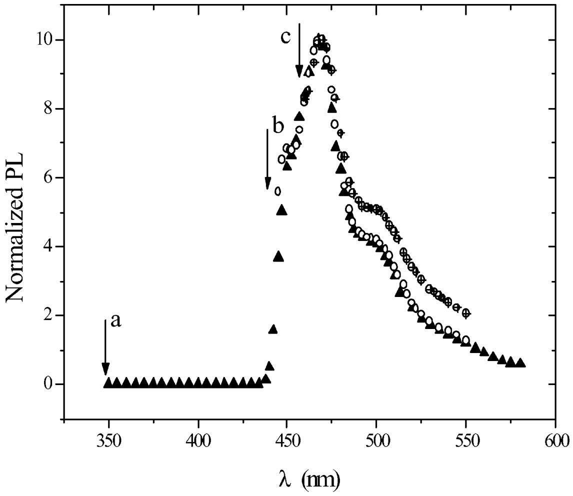

Figure 8. Photoluminescence emission spectra of PBO/MSA ($C = 0.0048$ g dL^{-1}) excited at (a, 350 nm; b, 440 nm; c, 450 nm) shown as arrows. The spectra have been normalized to the same magnitude near 470 nm.

In PL excitation spectra shown in Figures 5 and 6, it can be observed that the excitation spectrum for the highest concentration, 0.12 g dL^{-1}, is dramatically different from that for the lowest concentration. The excitation peak for the concentration of 0.12 g dL^{-1} in Figures 5 and 6 appears where the absorption in Figure 2 for the concentration of 0.000 44 g dL^{-1} is essentially zero. This was suggested to be the strong evidence of the formation of aggregates.[5] When the PBO/MSA with the concentration of 0.0048 g dL^{-1} was excited using the peak wavelengths in its excitation spectrum (about 350 and 444 nm) and a nonpeak wavelength of 450 nm, the emission spectra in these three cases have little difference in line shape and peak position (the emission wavelength is about 470 nm), except a slight red shift and a change in intensity with the increase in excitation wavelength. To make a clear comparison, three emission curves have been put together with a normalized intensity at the wavelength of 470 nm, as shown in Figure 8. The corresponding excitation wavelengths are shown in Figure 8 as arrows with labels a−c. The overlapped three emission curves can be observed, especially for the two curves using 350 and 444 nm as excitation wavelength. The shoulder intensity at around 500 nm in the emission curve excited at 450 nm is higher than that in other two spectra, which also indicates the effect of the aggregation of PBO molecular chains.

This selective-excitation analysis[5,7,8] is very helpful in verifying the existence of aggregates. A significant emission spectrum can be obtained even at the low-energy excitation (450 nm), and the gap between the emission peak and the excitation wavelength is only 20 nm. When the excitation wavelength was further increased to 465 nm, where the intensity is very weak in excitation spectrum, a similar emission spectrum still can be achieved. The disappearance of the Stokes shift rules out the possibility of the formation of eximer,

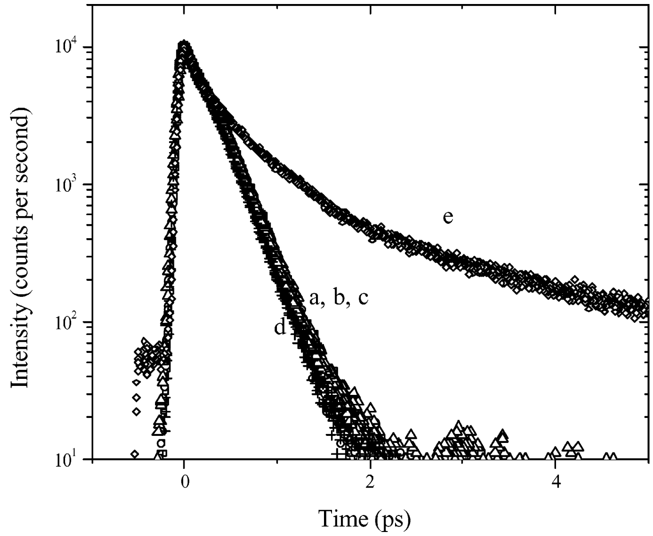

Figure 9. Time-resolved PL decay dynamics of PBO/MSA solution (C = 0.000 44 g dL^{-1}), excited at 400 nm and measured at 442 nm (a, open circles), 466 nm (b, open squares), and 495 nm (c, open triangles), respectively, indicating a single exponential that was fitted with a lifetime of ~0.3 ns. (d, crosses) Time-resolved PL decay dynamics of PBO/MSA solution (C = 0.0048 g dL^{-1}), indicating a single exponential that was fitted with a lifetime of ~0.3 ns. (e, open diamonds) Time-resolved PL decay dynamics of PBO film excited at 400 nm and measured at 554 nm, indicating a biexponential data, which were fitted with lifetimes of ~80 and 560 ps.

which does not exist in the ground state and cannot be excited directly. The PL spectra shown in the Supporting Information for other polymers and model compounds in MSA at 0.0048 g dL^{-1} are similar to the result of PBO/MSA solution.

The results for time-resolved luminescence measurements on PBO in MSA solution and PBO solid thin film are discussed in the next paragraph (shown in Figure 9). The PBO/MSA solution at 0.0048 g dL^{-1} was excited at 300 nm, and the decay of the PL was collected at 467 nm. The PBO/MSA solution at 0.000 44 g dL^{-1} was excited at 400 nm, and the decay of the PL was collected at three different wavelengths (three groups of peaks described above, 442, 466, and 500 nm). The PBO solid thin film was excited at 400 nm, and the decay of the PL was measured at 554 nm.

The time-resolved PL decay dynamics of PBO/MSA solution at the concentrations of 0.000 44 and 0.0048 g dL^{-1} all showed a single-exponential decay with a lifetime of ~0.3 ns, while that for PBO thin film exhibited to be nonexponential, which can be best described by a biexponential with lifetimes of ~80 and ~560 ps. The experimental results presented here are consistent with the earlier findings on PBZT,[10] PBO,[3] and benzoxazole model compounds.[17] There is a very slight difference in the lifetime for the single-exponential decay in PBO/MSA solution at 0.000 44 g dL^{-1} at different emission wavelengths. With the increase in the emission wavelength, there is a weak increase in the lifetime from ~0.23 ns at 442 nm to ~0.25 ns at 466 nm, further to ~0.30 ns at 495 nm. This phenomenon is consistent with other results[4] but much weaker because the measured PBO/MSA solution has a rather lower concentration. A PL decay dynamics with the same lifetime (0.25 ns) can be found in Figure 9 for the concentration of 0.0048 g dL^{-1} excited at a lower wavelength, 300 nm as the first excitation peak shown in Figure 6. This means the origin of the extra peak in excitation spectra at intermediate concentrations is the same as that of the peak around 440 nm.

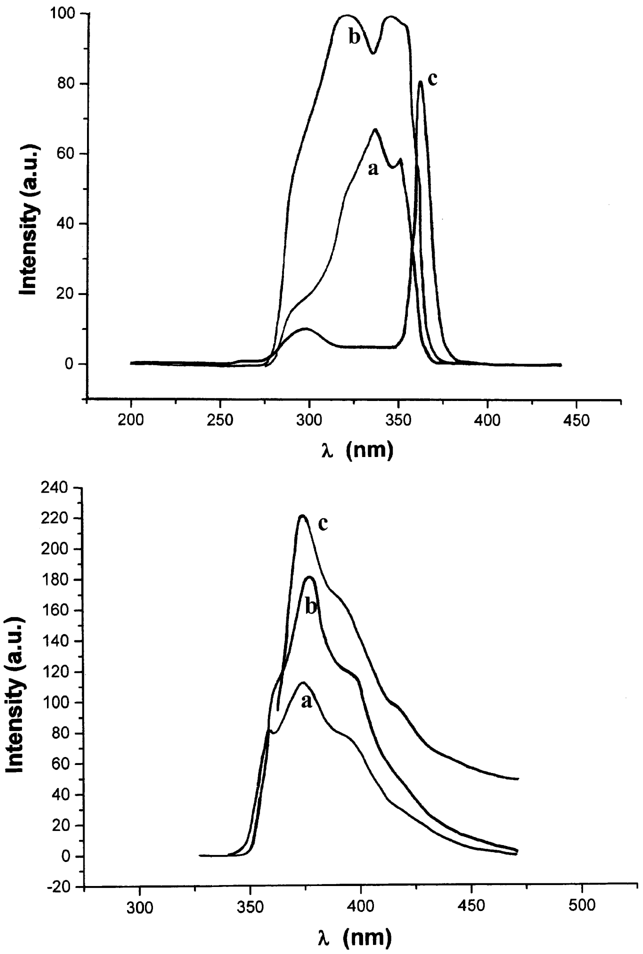

Figure 10. Photoluminescence excitation spectra (top) and emission spectra (bottom) of model 1 in toluene (a, 0.000 21 g dL^{-1}; b, 0.001 25 g dL^{-1}; c, 0.02 g dL^{-1}).

From the time-resolved PL decay dynamics, it is difficult to conclude that excimer exists in polybenzazole solid films or to rule out such a possibility because the multiexponential decay dynamics of PBO thin film may originate from ^{1}A* and other different species such as excimers and aggregates as Jenekhe also suggested.[10]

Photoluminescence Spectra of Model 1 in Toluene. In all the polymers and two model compounds studied here, only model 1 can be dissolved in toluene. Here the PL spectra of model 1 in toluene at different compositions are shown in Figure 10 in order to investigate the effect of solvent, especially the effect of protonation on the formation of the aggregates. Since the solubility of model 1 in toluene is very small, it is hard to achieve the concentration of 0.12 g dL^{-1}. Here the highest concentration is 0.02 g dL^{-1}, then 0.001 25 g dL^{-1}, and 0.000 21 g dL^{-1}.

Comparing the peak positions for model 1/MSA solutions in Table 1 with model 1/toluene solutions in Figure 10, it can be observed that a significant red shift takes place in PL spectra when the solvent changes from toluene to MSA regardless of concentration. This behavior was also reported in UV-absorption spectra.[17] This is consistent with the conclusion that protonation of the model compound by MSA enhances the delocalization of the electron over the heterocycle and aromatic ring.[42]

Similar to the PL spectra in MSA, the intensity of emission spectra of model 1 does not change with concentration in the same way as those of polymers and model 2. When the concentration is below 0.000 125 g dL^{-1}, the self-quenching effect is no longer there, and the intensity of emission is proportional to the concentration of chromophore.

In the excitation spectra of the model 1 in toluene shown in Figure 10a, the same phenomenon happens when the concentration is varied; i.e., the peaks in the excitation spectra split at intermediate concentration. The excitation peak at lower wavelength blue shifts and diminishes when the concentration increases, while the excitation peak at higher wavelength red shifts with the concentration. The change in the emission spectra of model 1 in toluene, shown in Figure 10b, is not as clear as in the emission spectra of polymers and model 2. No new significant emission bands are detected within the concentration range studied in this paper, which is consistent with earlier report.[17] The PL emission spectra of model 1 in nonprotonic solvent toluene and in protonic acid MSA show that the interchain aggregation indeed increases with the ionic strength of the solvent as reported[43] using light scattering and viscometry for rodlike polymer PBO and poly(1,4-phenylene terephthalamide) (PPTA).

The formation of aggregates in polybenzazole solutions in MSA is detrimental to the PL quantum efficiency of the polymers. Currently some studies[3,8,44] have suggested some means to control the degree of aggregation by decreasing the intermolecular interactions such as attaching bulky side groups to the polymer conjugated backbone and modulating the solution from which the thin film is prepared. There are many derivatives of polybenzazoles,[45] most of which are with enhanced lateral interactions for the mechanical purposes. The study on how to control the intermolecular interactions should be vital to the utilization of polybenzazoles in LED.[16]

Conclusion

The photophysical properties of polybenzazoles (PBO, ABPBO, and their random copolymer PBO−ABPBO) and their model compounds in solutions of methanesulfonic acid (MSA) have been studied. The absorption, excitation, and emission wavelength of the copolymers in solutions can be modulated by the composition of PBO in the copolymer between the lowest value for pure ABPBO and the highest one for PBO. The excitation and emission spectra change significantly with the concentration in both shape and position of the peaks. The presence of aggregates for polybenzazoles in MSA in the emission spectra has been demonstrated, and the aggregates are found to be closely dependent on the solvent environment. The protonation by MSA enhances the possibility of interchain aggregation. The explanation is further supported by using the poor solvent, selective excitation, and time-resolved photoluminescence spectroscopy.

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Supporting Information Available: Figures showing photoluminescence excitation spectra of PBO−ABPBO (1:3, 1:1, and 3:1), model 1, and model 2 in MSA; tables of excitation and emission bands of PBO and model 1 in solvents. This material is available free of charge via the Internet at http://pubs.acs.org.

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