Vol 15 No 10, October 2006
1009-1963/2006/15(10)/2347-05

Chinese Physics

© 2006 Chin. Phys. Soc.
and IOP Publishing Ltd

The effect of intermolecular interactions on photoluminescence of a porphyrin side-chain polymer*

Wang Hui(王 惠)[a)†], Zhang Wei(张 伟)[a)], Yu Han-Cheng(余汉城)[b)], Huang Jin-Wang(黄锦汪)[a)b)], Lin Wei-Zhu(林位株)[a)], and Ji Liang-Nian(计亮年)[a)b)]

[a)] *State Key Laboratory of Optoelectronic Materials and Technologies of Zhongshan University, Guangzhou* 510275, *China*

[b)] *Institute of Chemistry and Chemical Engineering of Zhongshan University, Guangzhou* 510275, *China*

(Received 1 October 2005; revised manuscript received 1 June 2006)

Photoluminescence properties and exciton decay dynamics in a porphyrin side-chain polymer, poly[porphyrin acrylate- acrylonitrile (abbreviated p[(por)A-AN]), have been investigated by femtosecond time-resolved photoluminescence spectroscopy. All the luminescences of p[(por)A-AN] films are due to the emissive decay of the photoexcited singlet excitons in the porphyrins. The luminescence efficiencies and lifetimes are increased for samples from pure films to dilute blend films. However, they are increased as the intrachain concentration of the porphyrin sidechain groups is decreased. The intrachain rotation motions of porphyrin sidechain groups result in the initial ultrafast luminescence decays, which are much faster than those due to the interchain interactions. All the samples show no significant red-shift and broadening of the transient luminescence spectra. The interchain and intrachain nonradiative exciton relaxation processes may play an important role in the luminescence dynamics in the p[(por)A-AN] films. The possible origin of different intrachain and interchain dynamic behaviours in p[(por)A-AN] films is discussed.

Keywords: porphyrin side-chain polymer, transient luminescence, exciton dynamics

PACC: 4270J, 3350D

1. Introduction

Luminescent conjugated polymers have been extensively studied due to their use as active materials in cheap and efficient light-emitting diodes (LED).[1,2] However, despite the fact that much exciting progress has been made, a lot of work is still needed to develop new polymers (or modified version of existing ones) that can emit red, green and blue light. One concern is that the emission spectra from polymer films are relatively broad, which causes the emitting colours to be impure.[3,4] This is in part due to the presence of a distribution of segments with distinct conjugation lengths, which is characterized in most conjugated polymers. As a result, the exciton dynamics is strongly affected by the energy migration to lower-energy sites within the inhomogeneously broadened density of states.[5,6]

Doping of the emission layers in LEDs with luminescent dyes can control the colour of emission as well as improve device efficiency.[7] Porphyrins have potential applications in LED because of their pure red-light emission and optimized efficiency over all other fluorescent materials. However, there have been few reports about their use in LEDs. This is due to their poor processing and their propensity to $\pi - \pi$ stack, which causes the material non-luminescent in the solid state.[8] These problems can be overcome by incorporating porphyrin chromophores as the sidechain groups or a core of a dendrimer to control the porphyrin-porphyrin interactions in solid states.[9,10] Recently, weak pure-red electroluminescence has been observed in porphyrin sidechain-PPV film.[9] However, the nature of the luminescence dynamics in these materials is not clear now. In the present paper, we report an investigation on the photoluminescence properties and the exciton dynamics in a porphyrin sidechain polymer, poly(porphyrin acrylate-acrylonitrile)(abbreviated p[(por)A-AN]). Our research is motivated by a desire to understand the photophysics of the porphyrin sidechain polymer and use this knowledge to improve porphyrin-based LED devices. The study is focused on the effect of interchain and intrachain interactions of porphyrins on the lu-

*Project supported by the National Natural Science Foundation of China (Grant Nos 60478013, 20571089 and 10274107), the Natural Science Foundation of Guangdong Province, China (Grant No 05101819), and the Doctoral Program Foundation of Institute of Higher Education of China(Grant No 20040558031).

†E-mail: stswh@mail.sysu.edu.cn

minescence efficiency and the relaxation dynamics of photoexcited excitons in p[(por)A-AN] films.

2. Experiment

The p[(por)A-AN] was synthesized by the reaction of porphyrin acrylate and acrylonitrile in the presence of initiator, and the polymer obtained was characterized by UV-visible, IR spectrography and nuclear magnetic resonance. Porphyrin is attached covalently to the polymer chain. The polymer monomer also contained a cyano-substitution side-chain, which can increase electron affinity and has been used in poly(phenylene vinylene) (abbreviated PPV) based electroluminescence polymers.[11] The inset in Fig.1 shows the molecular structure of p[(por)A-AN]. Pure film samples were prepared by spin-coating from N, N-dimethylformamide(DMF) solution of p[(por)A-AN]. The blend films of dilute p[(por)A-AN] in polystyrene host were prepared by spin coating from DMF solutions of p[(por)A-AN] and polystyrene, with the thickness of the resulting thin films being about 2μm.

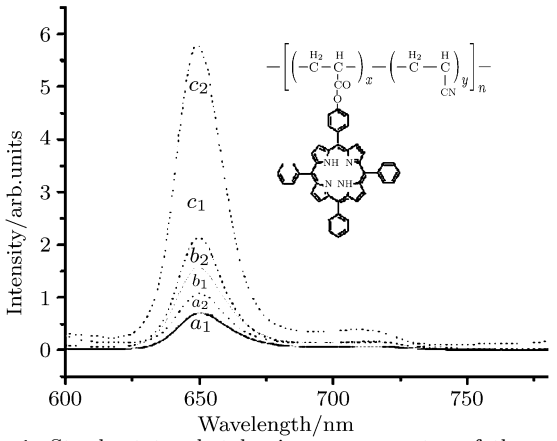


Fig.1. Steady-state photoluminescence spectra of the pure p[(por)A-AN] film(a), 60%(b) and 10%(c) blend films of p[(por)A-AN] in polystyrene, respectively. The solid lines (a_1, b_1, c_1) and the dotted lines (a_2, b_2, c_2) are of 8% and 15%, respectively, porphyrin sidechain content compared with the cyano-substitute side-chain content along the polymer backbone. Inset is the molecular structure of the p[(por)A-AN].

The transient luminescence measurements were performed by employing a mode-locked Ti-sapphire laser, which generated 100fs pulse with a wavelength of 800nm and a repetition rate of 82 MHz. The laser pulses were frequency-doubled in a barium metaborate (BBO) crystal to produce light pulse with a wavelength of 400nm and average power of 6 mW. They were used to excite the sample films. The luminescence was collected by a set of lenses and recorded in a synchroscan streak camera.

3. Results and discussion

The steady-state absorption spectra of pure and dilute p[(por)A-AN] films are almost identical. The spectra consist of a very narrow absorption band around 413nm (B bands) and a set of weaker long wavelength absorption bands (Q bands) around 510, 550, 590, and 648nm, which are typical for porphyrin-based systems.[11,12] The steady-state photoluminescence spectra of various p[(por)A-AN] films are shown in Fig.1. All the samples show the spectral features typical of porphyrins, namely the Q(0,0) and Q(0,1) porphyrin transitions at about 650 and 720nm,respectively.[13] The luminescence yield is dramatically increased for samples from pure films (a) to the dilute blend films (c). The luminescence efficiency of 10% p[(por)A-AN] blend films (c) is increased by more than one order of magnitude as compared with that of the pure films (a). A similar result has been observed in MEH-PPV film.[14] It is interesting to note that the luminescence yield is clearly decreased with the decrease of the porphyrin content attached to the polymer backbone. There is an approximately twofold decrease of photoluminescence efficiency as the porphyrin content is decreased from about 15% to 8% in comparison with the content of cyano-substitution sidechains (from 85% to 92%). The results are illustrated by the curves a_1, b_1, c_1 and a_2, b_2, c_2 in Fig.1.

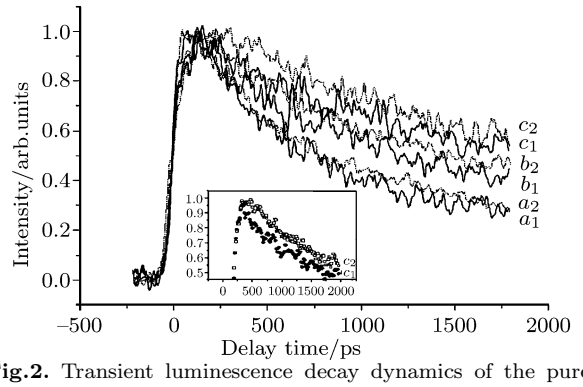


Fig.2. Transient luminescence decay dynamics of the pure film(a), 60%(b) and 10%(c) blend films of p[(por)A-AN] in polystyrene at 650nm. The solid lines (a_1, b_1, c_1) and the dotted line (a_2, b_2, c_2) are of 8% and 15% porphyrin content, respectively. Inset is the comparison of the initial luminescence decay between 15% (open dots) and 8% (solid dots) porphyrin content for 10% p[(por)A-AN] blend film.

More insight into the reason for the changes in luminescence efficiencies for p[(por)A-AN] films is provided by the measurement of the decay dynamics of

the photoluminescence. Figure 2 shows the transient luminescence decays of p[(por)A-AN] films at the main emission peak of 650nm.

All the samples exhibit the nonexponential decay, which can be well fitted by a triple exponential function convolved with the instrument response function. The values of the time constants τ_1, τ_2 and τ_3 are summarized in Table 1.

Table 1. Summary of the time constants of luminescence decay in p[(por)A-AN] films at the main emission peak of 650 nm.

	8% porphyrin content*			15% porphyrin content		
	τ_1 /ps	τ_2/ps	τ_3/ns	τ_1/ps	τ_2/ps	τ_3/ns
pure film	28.22	439.77	2.28	38.55	453.83	3.10
60%blend film	23.18	729.4	4.5	33.21	808.41	4.39
10%blend film	24.46	1088.07	4.97	35.33	1434.24	5.56

*porphyrin content is compared with the cyano-substitutions side chains attached to the polymer backbone.

The transient luminescence decays in p[(por)A-AN] films are significantly slower for samples from the pure films to the dilute blend films as shown in Fig.2 and Table 1. It is evident that interchain $\pi - \pi$ stack of porphyrin sidechain groups enhances the interchain interactions of pophyrins, which provide an efficient pathway for the nonemissive relaxation of the photoexcited singlet excitons in porphyrins, and the average decay time τ_2 increases from about 447 ps to 1.26 ns for the pure films and the 10% dilute blend films. However, with the decrease of the porphyrin content along the chain, the initial luminescence decay becomes faster. The average decay time τ_1 decreases from 35 to 25 ps as the porphyrin content goes from 15% to 8%. The inset in Fig.2 shows the comparison of the initial luminescence decays for the 10% dilute p[(por)A-AN] blend film with 15% and 8% porphyrin contents, which suggests that the initial ultrafast decays of the luminescence are due to the intrachain nonemissive relaxations of the photoexcited singlet excitons in porphyrins.

The migration of excitation to lower energy region and the formation of excimers or dimmer can result in the ultrafast decay of luminescence in electroluminescent polymers such as PPV.[6] At the same time, the red-shift and the broadening of the transient luminescence spectra in these polymers occurs.[6,7,15] However, in our experiment, all the samples exhibit no pronounced red-shift and broadening of the transient luminescence spectra, which are almost identical to the steady-state luminescence spectra as shown in Fig.1. Figure 3 shows the transient luminescence spectra of the pure p[(por)A-AN] film with 15% porphyrin content.

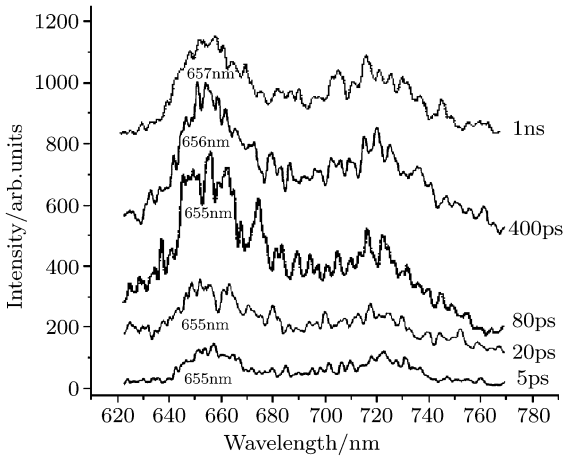


Fig.3. The transient luminescence spectra of the pure p[(por)A-AN] film with 15% porphyrin content for different decay time.

The luminescence decays at 640, 650 and 670nm are illustrated in Fig.4. The absence of the transient red-shift and broadening of the luminescence spectra

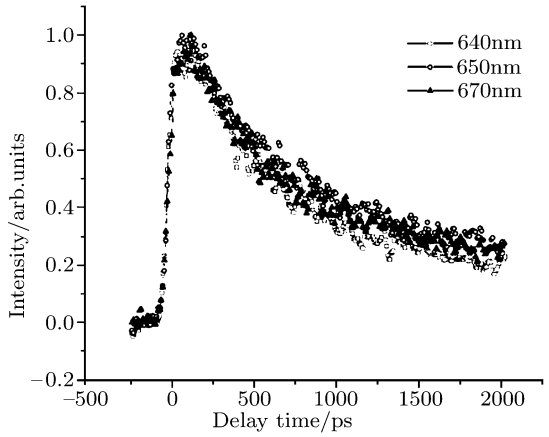


Fig.4. The transient luminescence decays of the pure p[(por)A-AN] film with 15% porphyrin content at 640, 650 and 670 nm.

suggests that all the photoluminescence from p[(por)A-AN] films are due to the radiative relaxation

of the photo-excited singlet excitons formed in porphyrin chromophores. Therefore, the interchain interactions may result in the formation of the nonemissive interchain pieces, and the formation of spatial indirect excitons is localized on adjacent pophyrin chromophores, which competes with the radiative decay of the photoexcited singlet excitons in porphyrins.

The porphyrins attached to the polymer backbone can easily adopt a syndiotactic arrangement, i.e. the symmetrical substitution of porphyrins on both sides of the main chain.[9,15] These may have a tendency to crystallize, giving cofacial chain packing of the porphyrin chromophores and favouring the formation of the interchain indirect excitons. On the other hand, the porphyrin rings, as the highly flexible macromolecules, can rotate about all the single bonds in the side chains, and the rotation usually lasts tens of picoseconds before other nonradiative relaxation dynamics occurs.[16,17] However, as the porphyrin content becomes relatively higher (about 15%), the intrachain porphyrin–porphyrin distance becomes shorter, resulting in the limitation of the rotation of porphyrins. Therefore, in this case, the photo-induced nonradiative relaxation of excitons in P[(por)A-S] films is mainly dominated by the interchain $\pi - \pi$ interactions of porphyrins, and this relaxation process should be more rapid in the pure P[(por)A-S] film than in the dilute blend film. As the porphyrin concentration is lower (about 8%), more porphyrin side-chain groups is allowed to rotate freely, which can result in more rapid initial nonradiative relaxation of excitons and luminescence decay, as shown in Fig.2. Similar result has been reported in other electroluminescence organic materials.[18] Furthermore, this rotation towards the intrachain co-facial $\pi - \pi$ stack of porphyrins[19] may facilitate the formation of the intrachain indirect excitons, which is confirmed by the faster luminescence decay ($\tau_2 \sim 700$ ps) at 8% porphyrin content than that (~ 950 ps) at 15% porphyrin content, as estimated from Table 1. This is also consistent with the requirement that the charges forming the indirect excitons should be sufficiently close to have large binding energy. If confined on separate conjugation segments of the main chain, the charges would be tens of angstroms apart, whereas adjacent chains are only spaced by a few angstroms.[14] In addition, the electron transition between the porphyrin side-chain groups and the cyano-substitution side-chain groups with excellent electron affinity also may have some contribution to the initial ultrafast dynamics in p[(por)A-AN films. Similar result has been observed in poly(cyano- phenylene vinylene)(abbreviated CN-PPV).[20]

Our experimental results show that the intrachain rotations of porphyrins would compete with the interchain interactions of the porphyrins in the nonemissive relaxation processes of the photo-induced excitons in p[(por)A-AN] films. The more obvious changes in the transient luminescence dynamics from pure film to dilute blend film, compared with the change of the porphyrin concentration from 15% to 8%, as shown in Fig.2, indicate that the luminescence dynamics of p[(por)A-AN] films are dominated mainly by the interchain interaction of the pophyrins. This can explain the much slower luminescence decay in 10% dilute blend film ($\sim$1.09ns, $\sim$1.43ns) at the porphyrin content of 15%, compared with the pure film ($\sim$439ps, $\sim$453ps) at the porphyrin content of 8%. Similar results have been observed in several electroluminescent polymers.[15,20]

Anyway, the interchain and intrachain nonradiative exciton relaxation can result in the ultrafast luminescence decay in the p[(por)A-S] films. Former studies have shown that the natural luminescence lifetime of the free base porphyrin monomer is about 12.4ns.[21] However, the emission lifetime τ_3 of the photo-excited singlet excitons in p[(por)A-AN] films become shorter because of the interchain and intrachain interactions of the porphyrins. The average luminescence lifetime of p[(por)A-AN] films is about 3.92 ns.

4. Conclusion

In summary, we have investigated the luminescence properties and the exciton decay dynamics in a porphyrin sidechain polymer, p[(por)A-AN]. The luminescence efficiency and the decay time are increased for samples from pure films to dilute blend films. However, they are decreased with the decrease of porphyrin content along the polymer backbone. All the sample films exhibit no significant transient redshift and broadening of the luminescence spectra, indicating that the luminescences are due to the radiative decay of the photo-excited singlet excitons in porphyrins. The interchain interaction of porphyrins competes with the intrachain rotations of porphyrins after photo-excitation in the p[(por)A-AN] films. Our results suggest that the essential difference between the effects of the interchain–intrachain and porphyrin–

porphyrin packs should be the transient nonemissive exciton decay. The more significant changes of the luminescence decay for samples from pure film to dilute blend film, as compared with the change of the intrachain porphyrin concentration (from 15% to 8%), indicate that the luminescence dynamics of p[(por)A-AN] films are mainly dominated by the interchain interaction of the pophyrins. To this end, theoretical work and further investigation are required to understand the origin of the luminescence in p[(por)A-AN] films. Our study may be helpful to the molecular engineering strategy in the design of new electroluminescent polymers.

References

[1] Friend R H, Gymer R W, Holmes A B, Burroughes J H, Marks R N, Taliani C, Bradley D D C, Dos Santos D A, Bredas J L, Logdlund M and Salaneck W R 1999 *Nature* **397** 121

[2] Cleave V, Yahioglu G, Barny P Le, Friend R H and Tessler N 1999 *Adv. Mater.* **11** 285

[3] O'Brien D F, Gieblev C, Fletcher R B, Cadby A J, Palilis L C, Lidzey D G, Lane P A and Bradley DDC 2001 *Synth. Mat.* **116** 379

[4] Kwong R C, Sibley S, Dubovoy T, Baldo M, Forrest S R and Thompson M E 1999 *Chem. Mater.* **11** 3709

[5] Beljonne D, Pourtois G, Silva C, Hennebicq E, Herz L M, Friend R H, Scholes G D, Setagesh S, Mullen K and Bredas J L 2002 *Proc. Natl. Acad. Sci.* **99** 10982

[6] Kersting R, Lemmer U, Mahrt R F, Leo K, Kurz H, Bassler H and Gobel E O 1993 *Phys. Rev. Lett.* **70** 3820

[7] Bassler H, Brandl V, Deussen M, Gobel E O, Kersting R, Kurz H, Lemmer U, Mahrt R F and Ochse A 1995 *Pure Appl. Chem.* **67** 377

[8] Frampton Michael J, Magennis Steven W, G.Pillow Jonathan N, Burn Paul L and Samuel Ifor D W 2003 *J. Mater. Chem.* **13** 235

[9] Lo S C and Burn P L 1999 *Synth. Mat.* **102** 1089

[10] Greenham N C, Moratti S C, Bradley D D C, Friend R H and Holmes A B 1993 *Nature* **365** 628

[11] Venugopal R S, Maiya N K M, Philip Reji and Ravindra K G 2000 *Opt. Comm.* **182** 255

[12] Yu H Z, Baskin J S, Steiger B, Wan C Z, Anson F C and Zewail A H 1998 *Chem. Phys. Lett.* **293** 1

[13] Schweitzer G, DeBelder G, Latterini L, Rowan A E, Miller R J and DeSchryver F C 1999 *Chem. Phys. Lett.* **307** 261

[14] Yan M, Rothberg L J, Kwock E W and Miller T M 1995 *Phys. Rev. Lett.* **75** 1992

[15] Samuel I D W, Rumbles G and Collison C J 1995 *Phys. Rev.* B **52** R11573

[16] Wang H, Huang Y P, Liu Z G, Zhao F L, Lin W Z, Wang J and Liang Z O 2003 *Appl. Phys. Lett.* **82** 3394

[17] Fiebig Torsten, Wan C Z, Kelley Shana O, Barton J K and Zewail AH 1999 *Proc. Natl. Acad. Sci.* **96** 1187

[18] Yu G, Yin S, Liu Y Q, Chen J S, Xu X J, Sun X B, Ma D G, Zhang X W, Peng Q, Shuai Z G, Tang B D, Zhu D B, Fang W H and Luo Y 2005 *J. Am. Chem. Soc.* **127** 6335

[19] Comwell E M, Perlstein J and Shaik S 1996 *Phys. Rev.* B **54** R2308

[20] Xu B and Holdcrott S 1993 *Macromolecules* **26** 4457

[21] Gradyushko A T, Seuchenko A N, Solouyv K N and Tsuirko M D 1970 *Photochemistry and photobiology* **11** 387