

Origin of the blue emission from poly(1-phenyl-2-alkynes) and poly(phenylacetylenes)

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ABSTRACT

We have studied the electronic structure, absorption, and photoluminescence of poly(1-phenyl-2-alkynes) $-\text{[(C}_6\text{H}_5\text{)C=C(C}_m\text{H}_{2m+1})]_n-$ ($m = 1, 2$), poly(phenylacetylene) $-\text{[HC=C(C}_6\text{H}_5)]_n-$ and its derivatives $-\text{[HC=C(C}_6\text{H}_4\text{-}p\text{-R)]}_n-$ with various non-liquid crystal ring substituents. For poly(1-phenyl-2-alkynes), the PL efficiency is very sensitive to the molecular structure of the alkyl pendant and can be enhanced up to 50 times as the alkyl side-chain increases in length. But for poly(phenylacetylenes), their luminescent efficiency can be improved several times only as the tail becomes bulky. Regardless of the types of the pendants, the emission color of the polymers is pinned at ~ 450 nm (2.7 eV). The band structure of the polymers, which has been calculated using extended Hückel tight-binding method, is essentially an ensemble of the backbone (extended states) and the pendants (localized states), and the processes of optical absorption and blue emission are confined in the directly attached aromatic ring. The interaction between the phenyl chromophore and its nearest neighbors is of vital importance in improving the emission efficiency. Although the band gap of the backbone can be enlarged by the pendant, its $\pi\text{-}\pi^*$ interband transition is insignificant for the blue emission.

Keywords: substituted polyacetylene, poly(1-phenyl-2-alkynes), poly(phenylacetylenes), photoluminescence, density of states, electronic structure, localized states, extended states.

1. INTRODUCTION

The extensive research of polyacetylene (PA) in the last 30 years has contributed greatly to the understanding of the physics of conjugated polymers. PAs, however, are generally regarded as unsuitable candidates for electronic and optoelectronic applications because of its disappointing photoluminescence (PL) behavior.¹⁻⁴ Substitution of the hydrogen atoms of PA with other atoms or groups can perturb the electronic structure of the macromolecules. These substituted polyacetylenes have substantially different optical properties from those of PAs, and indeed a variety of PAs with two substituents [or disubstituted PAs; $-\text{(RC=CR')}_n-$] have been found to be highly luminescent. Emission of intense blue or green light has been observed in a number of disubstituted PAs including poly(diphenylacetylene) derivatives $-\text{[(C}_6\text{H}_5\text{)C=C(C}_6\text{H}_4\text{-}p\text{-R)]}_n-$ {R = OC₆H₅, *n*-C₃F₇, *n*- and *t*-C₄H₉, C₁₀H₁₆ (adamantyl), Si(CH₃)₃, Si[CH(CH₃)₂]₃, and Si(C₆H₅)₃}, poly(1-phenyl-2-alkynes) $-\text{[(C}_6\text{H}_5\text{)C=C(C}_m\text{H}_{2m+1})]_n-$ ($m = 1, 2, 6$), poly(1-chloro-2-arylacetylene) with the aryl groups being phenyl and naphthyl, and poly(1-methyl-2-naphthylacetylene).⁵⁻¹³ The PL behavior of monosubstituted PAs $-\text{(HC=CR)}_n-$ has also been investigated, but (normally) only weak luminescence has been observed in such polymers, examples of which include poly(phenylacetylene) and its derivatives $-\text{[HC=C(C}_6\text{H}_4\text{-R)]}_n-$ with ring substituents of CF₃, Si(CH₃)₃, Si(CH₃)₂C₆H₅, *i*-C₃H₇, and *n*-C₄H₉ at ortho and para positions, and poly(propargyl) derivatives $-\text{[HC=C(CH}_2\text{-R)]}_n-$ with R = diphenylamino and indolyl.^{7, 9, 10, 14} Monosubstituted PAs are thus often referred to as nonluminescent polymers and are generally regarded as unpromising candidates for light emitting materials.

In order to explain why disubstituted polyacetylenes are highly luminescent while monosubstituted polyacetylenes are poorly luminescent, the enlarged band gap of the backbone is widely adopted to explain the intense blue or green emission from some disubstituted polyacetylenes, while the generation of non-emissive solitons in the degenerate backbones of those monosubstituted polyacetylenes is exploited to account for their weak emission.¹⁻¹⁴ Although such interpretations can explain some results qualitatively, they lack of self-consistency because not all disubstituted polyacetylenes are highly luminescent. On the other hand, as a prediction of these interpretations, bulky side-chains should be able to tune the emission color of substituted polyacetylenes no matter they are classified as disubstituted polyacetylenes or monosubstituted ones. The emission energies of poly(1-phenyl-2-alkynes) $-\text{[(C}_6\text{H}_5\text{)C=C(C}_m\text{H}_{2m+1})]_n-$ ($m=1, 2, 6$) and poly(phenylacetylene) $-\text{[HC=C(C}_6\text{H}_5)]_n-$, however, are all pinned at ~ 2.7 eV regardless of the types of alkyl side-chains. Moreover, the pinned emission energy does not change as a result of the change in the excitation energy.^{3, 6-8} Finally, the interpretations contradict to the recent experimental observations. For instance, we have synthesized a group of highly luminescent monosubstituted

polyacetylenes with liquid crystalline pendants.¹⁵⁻²² They can emit intense and electrically tunable deep-blue PL.¹⁸⁻²² The electronic structures are of crucial importance in the interpretation of their optical properties because they are closely related. A semi-quantitative calculation is proven to be very helpful in giving a physically reasonable interpretation because conjugated polymers can be considered as organic semiconductors, and the concepts of energy band theory can be used to characterize their electronic states and optical properties.^{23, 24} The calculated electronic structures for our highly luminescent monosubstituted PAs indicate that, instead of the distorted backbone, the side-chains with biphenyl chromophores are the origin of their deep-blue emissions.²⁰

In this paper, we studied the origin of the blue emissions from non-liquid crystalline substituted polyacetylenes. Disubstituted polyacetylenes poly(1-phenyl-2-alkyns) $-\{(\text{C}_6\text{H}_5)\text{C}=\text{C}(\text{C}_m\text{H}_{2m+1})\}_n-$ ($m = 1, 2$) and monosubstituted polyacetylene and its derivatives $-\{\text{HC}=\text{C}(\text{C}_6\text{H}_4-p\text{-R})\}_n-$ are used as typical examples to serve our purpose. Regardless of the types of the side-chains or the bulky tails, all of these polymers emit blue lights with their emission energy pinned at 2.7 eV. In Section 2, the experimental details are described. In Section 3, we have probed the roles of the alkyl pendant and the phenyl pendant in the blue emissions of poly(1-phenyl-2-alkyns). In Section 4, we have investigated the effect of the phenyl ring-substituent on the blue emissions of poly(phenylacetylenes). Theoretical calculations are outlined and compared to experimental results obtained by optical absorption and PL, and our study leads to the establishment of the origin of their blue emissions. A conclusion is given in Section 5.

2. EXPERIMENTAL DETAILS

In Section 3, Monosubstituted poly(phenylacetylene) (PPA), disubstituted poly(1-phenyl-2-propyl) (PPP) and poly(1-phenyl-2-butyne) (PPB) were used in our experiment. Their molecular structures are shown in Fig. 1. The first replacement, an aromatic ring, is directly attached to the polymer backbone while the second replacement is an alkyl such as CH_3 and C_2H_5 . The sample synthesis and characterization were reported elsewhere.²⁵ In Section 4, poly(phenylacetylene) and its derivatives were used in the study. The molecular structures of poly(phenylacetylenes) with various ring-substituents are shown in Table 1. Polymers 3-7 have more bulky and branched tails than 1 and 2.

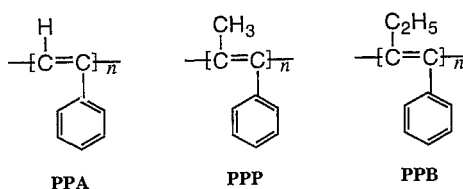


Figure 1 Molecular structures of poly(phenylacetylene) (PPA), poly(1-phenyl-2-propyl) (PPP) and poly(1-phenyl-2-butyne) (PPB).

The solutions for the PL measurements were prepared by dissolving the polymers in spectroscopic grade chloroform (CHCl_3). The concentrations (mM) of the solutions PPA, PPP and PPB were about 1.16, 0.125, and 0.064, respectively. The concentrations of solutions of 1-7 were about 10^{-3} mM. The molar concentrations of the polymer solutions were calculated on the basis of the molecular masses of their repeat units. Solutions were kept in a 1-mm-thick quartz cell. The absorption spectra of the polymer solutions were recorded on a Shimadzu UV-Vis spectrophotometer (UV-2401PC). The 325-nm line from an Omnichrome helium-cadmium laser was used as the excitation source. The PL spectra were measured at room temperature in the quartz cell on a Spex-500M spectrofluorometer. To compare their luminescent efficiency, we took PL data under similar measurement conditions. All the absorption and PL spectra were reproducible.

Table 1 Molecular structures of poly(phenylacetylene) and its derivatives. E_g : band gap of the backbone.

$-\{\text{HC}=\text{C}(\text{C}_6\text{H}_4-p\text{-R})\}_n-$	R	E_g (eV)
	H (1)	1.4
	$(\text{CH}_2)_4\text{CH}_3$ (2)	2.2
	$\text{CONH}(\text{CHCH}_3)\text{CO}_2\text{CH}_3$ (3)	2.4
	$\text{CONH}(\text{CHC}(\text{CH}_3)_2)\text{CO}_2\text{CH}_3$ (4)	1.4
	$\text{CONH}(\text{CHCH}_2\text{CH}(\text{CH}_3)_2)\text{CO}_2\text{CH}_3$ (5)	1.4
	CO_2 -glucose (6)	1.2
	CO_2 -galactose (7)	1.2

The calculations were performed with the extended Hückel tight binding method,^{26, 27, 28} which can give a good semi-qualitative description of the band structures of conjugated polymers. As a check on the accuracy of our calculations, the band structure of *trans*-PA was computed. Our computed band gap for *trans*-PA of an infinite conjugation length is ~ 1.2 eV, which agrees very well with experimental result.⁴ *Cis* backbone conformation was used in the calculations, molecular structure optimisation was implemented by minimizing its steric energy. Standard Slater parameters for hydrogen, carbon and oxygen atoms were selected from Ref. 28 and kept fixed in our computations.

3. THE ROLE OF ALKYL AND PHENYL PENDANTS IN THE BLUE EMISSIONS OF DISUBSTITUTED POLYACETYLENES

3.1 DENSITIES OF STATES OF DISUBSTITUTED POLYACETYLENES

The densities of states (DOSs) for PPA, PPP and PPB are shown in Fig. 2. The DOS of a *cis*-PA with infinite conjugation length is shown for comparison, its π - π^* transition yields an infrared PL because of its narrow band gap.⁴ When comparing the DOSs of PA, PPA, PPP, and PPB, one can see that the alkyl pendant can effectively engineer the electronic structures of the polymers. The modifications in DOSs include: (1) alkyl pendants can enlarge the band gap of the conjugated backbone to ~ 2 eV; (2) characteristic electronic states of the phenyl pendant are introduced into the widened π and π^* bands of the backbone; (3) the electronic states introduced by the phenyl pendant are sensitive to the molecular structures of the alkyl side-chains, and shift gradually towards the band edge of the backbone; and (4) the DOS of the conjugated backbone is comparably low in intensity and is hidden in the states generated by the phenyl. The change in the electronic states is responsible for the optical properties of these polymers. In Table 2, we list the band gaps of the backbones, the energy differences between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) of the phenyl pendants (Δ_1), and the energy differences between the π - π^* of the backbone (Δ_2).

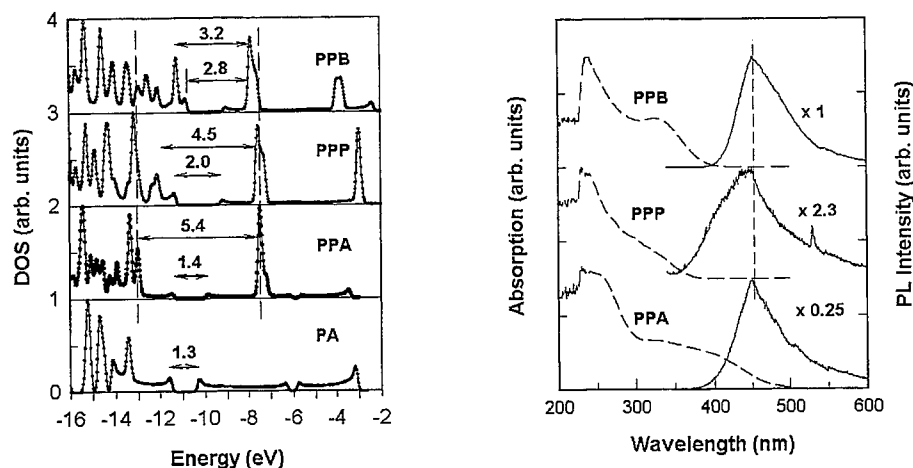


Figure 2 Electronic structures of PPA, PPP and PPB (left panel).

Figure 3 Normalized absorption (dashed line) and photoluminescence (solid line) spectra of PPA, PPP and PPB (right panel). Excitation wavelength: 325 nm; solvent: chloroform; concentration (mM)/power (mW): 1.61/14(PPA), 0.125/14(PPP), 0.064/1.78(PPB).

Due to the bond distortion induced by the alkyl and phenyl pendants, the band gap of the backbone becomes enlarged. This is well acknowledged that the alkyl side-chains can increase the band gap of substituted polyacetylenes.⁵⁻¹⁴ We, however, find that a limit of ~ 2.0 eV is quickly reached as the alkyl pendant increases in length. The widened band gap of the backbone can, at most, give off red emission. Therefore the π - π^* transition in the backbone is impossible to be the origin for the blue emissions for the disubstituted polyacetylenes.¹⁴

In the *E-k* diagram, the phenyl related energy levels are nearly horizontal, which suggests the electronic states of the phenyl pendant be localized. The electronic structure of pendant-group polymer is essentially that of an ensemble of molecular

subunits because the overlap of pendant groups is so small,^{20, 24} and the electronic properties of pendant-group polymers are determined by localized electronic states characteristic of the pendants. By inspection Fig. 2, one can see clearly that the electronic states generated by the phenyl pendant can be tailored efficiently by the alkyl side-chains. The localized states of the phenyl can be modulated by its polymeric environment, such as the molecular and geometrical structure of the alkyl substituent and the backbone. As shown in Table 2, the large-scale change in the numerical values of Δ_1 and Δ_2 reflects the effect of the alkyl side-chain on the electronic states of the polymers. The effective engineering of the electronic states possibly stems from the strong electron coupling between the phenyl pendant attached to backbone and its polymeric environment.

Table 2 Band gaps (E_g) of the backbones, the energy differences between the LUMO and the HOMO of the phenyl (Δ_1), and the energy differences between the π - π^* band of the backbone (Δ_2), energy "gap" obtained from absorption (E_{Abs}), and PL peak energy (E_{PL}) for PPA, PPP and PPB.

	in our work (eV)					data in literature (eV)		
	E_g	Δ_1	Δ_2	E_{Abs}	E_{PL}	$E_g(\text{exp})$	PL	Ref
PPA	1.4	5.4	3.1	2.8	2.75	3.0~3.42	~2.5	7, 8, 11, 30
PPP	2.0	4.5	3.8	3.6	2.75	3.2~3.35	~2.7	8, 11
PPB	1.8	3.3	2.2	3.3	2.75	3.2~3.35	2.7	8, 11

3.2. UV ABSORPTION AND PHOTOLUMINESCENCE OF DISUBSTITUTED POLYACETYLENES

Fig. 3 shows the normalized absorption and PL spectra of PPA, PPP and PPB. The absorption from 230 to 300 nm is associated with the phenyl side-chain, the absorption maximum at ~230 nm (5.4 eV) is phenyl-related. PPA starts its absorption at ~500 nm, PPP at ~350 nm, and PPB at ~400 nm. Interestingly, PPB exhibits an eminent absorption peak at ~325 nm. From the photon energy of maximum slope of optical absorption, which is commonly used to determine the energy gap for a conjugated polymer,²⁹ the energy "gaps" are estimated to be about 2.8, 3.6, and 3.3 eV for PPA, PPP and PPB, respectively. We list these "gap" values in Table 2 for comparison. The three polymers exhibit quite different absorption behaviours in the range of 300-500 nm. It is safe to conclude that such differences are the results of the interaction of the phenyl chromophore and its polymeric environment. Surprisingly, the PL peaks of PPA, PPP and PPB locate at the same position of ~450 nm (2.75 eV). In literature, the PL energies of PPA, PPP and PPB have also pinned at ~2.7 eV despite the excitation energies vary in a wide range from 3.2 to 3.8 eV.^{7, 8, 11, 30} Even for poly(1-phenyl-2-acetylenes) with excessively long alkyl pendants, such as poly(1-phenyl-2-hexyne), the PL energy is also reported to pin at the same value.¹⁰ Regardless of the different absorption behaviour and different excitation energy, the emission energy is still pinned at 2.7 eV, which suggests the blue emission of poly(1-phenyl-2-alkynes) is phenyl inherent.

Although the alkyl side chain cannot shift the emission colour of the polymers, it can increase their emission efficiency. When measured under similar measurement conditions, PPB emits strong blue emission while PPA and PPP exhibit only faint blue light. The ratio of integrated intensity per unit concentration per unit excitation power is about 1:2:50 for PPA:PPP:PPB. Compared to the PL efficiency of PPA, PPP doubles only, but PPB is about 50 times higher. Our data agree well with the published results.¹¹ In principle, PL efficiency is determined primarily by the product of carrier generation rate and recombination rate,³¹ while the high densities created by the phenyl pendant in the HOMO and LUMO contribute to high absorption rate and recombination rate, too. On the other hand, it has also reported that the bulky alkyl side-chain in PPB can lower its non-radiative process, which helps PPB to gain a high recombination rate for intense emission.³⁰ Therefore, the high DOS product for PPB is a key factor for its strong absorption at 2.8 eV and its intense PL emission.

3.3. EFFECT OF THE PHENYL ROTATION ON THE ELECTRONIC STRUCTURES OF POLY(1-PHENYL-2-BUTYLNE)

Bulky alkyl side-chain will inevitably cause the phenyl to rotate. In order to understand the origin of the blue emission, we now probe the effect of the phenyl rotation on the electronic structures of the polymers. An azimuthal angle, ϕ , is defined to be zero when the phenyl locates in its equilibrium plane. As phenyl rotates out of its equilibrium plane along the axis of the pendant, we keep the geometry of the backbone and the alkyl pendant untouched. PPB is used here as a representative. Fig. 4 illustrates the DOS evolution of PPB with the rotation of the phenyl ring. For small angle rotation, i.e., $0 \leq \phi \leq 5^\circ$, the localized states of the phenyl remains intact. For medium angle rotation, i.e., $5 \leq \phi \leq 15^\circ$, the localized states in HOMO shift

toward the π band edge of the backbone while its localized states in LUMO still keeps unchanged. For large angle rotation, i.e., $\phi \geq 15^\circ$, phenyl's localized states in HOMO continue to shift, but the localized states in LUMO begin to move to higher energy. As the phenyl rotates, its localized states move into the band-gap of the backbone, looking like "gap states" but physically they are not. Although the localized energy levels of the phenyl pendant are independent of the extended energy levels of the backbone, the polymeric environment in the neighbourhood of the phenyl is changed. That is, the electron coupling between the phenyl and its neighbour atoms also change. That is why the electronic structure of the polymer changes as the phenyl rotates. On the other hand, we can check it with experiment because it is well known that gap states are the main energy loss mechanism of fast charged particles in polymers and may quench, partially or completely, the blue PL. For a highly luminescent substituted polyacetylene, its deep-blue PL undergoes progressive 1.2-eV-redshift when its solution gets concentrated and finally becomes squeezed powder. Instead of complete quenching, its luminescent intensity remains at a reasonable level. In concentrated solutions or in squeezed powder, the macromolecules are so close that they are entangled with each other. The most straightforward change in the configuration of the molecules is the rotation of the phenyl chromophore. If the blue PL originates from the transition between the localized states in the phenyl pendant, then its emission colour will undergo red shift when the phenyl rotates. That is just what we have observed.

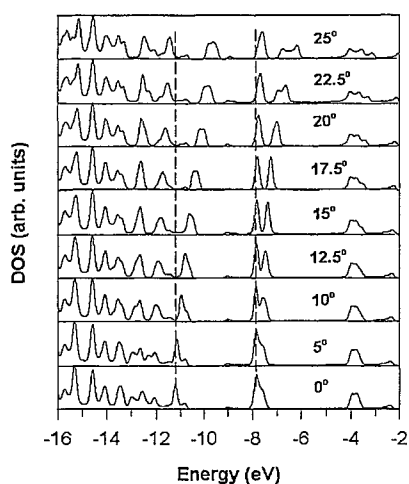


Figure 4 DOS evolution with the rotation of the phenyl in PPB.

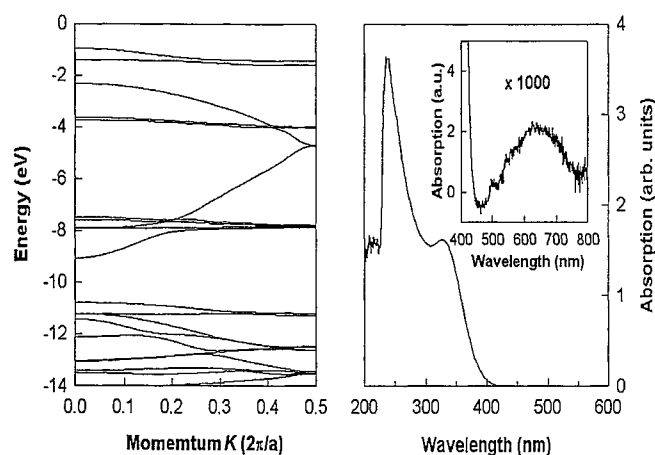


Figure 5 Band structure (left) and red absorption of PPB (right).

The colour of emission can also be tuned by attaching a bulky molecule to the ortho position of the phenyl chromophore. For example, poly(*o*-iso-propylphenyl)acetylene gives off red emission by attaching an *i*-C₃H₇ molecule at the ortho position of the phenyl chromophore.¹⁰ This bulky molecule at ortho position can induce phenyl rotation more easily than at para position. We will discuss that topic in Section 4.

3.4. THE ROLE OF THE PHENYL PENDANT IN THE BLUE EMISSIONS OF DISUBSTITUTED POLYACETYLENES

Our results suggest that the detected 2.7 eV emissions are phenyl inherent. We now need to clarify the nature of electronic states of the phenyl pendant—are they extended or localized? There is no doubt that the energy band picture of extended states can be applied to many polymers such as PA and the backbone of our polymers. Duke *et al* has described the nature of localization in these systems.^{32, 33, 24} For pendant-group polymer, its electronic structure is an ensemble of the backbone (extended states) and the pendants (localized states) due to the weak inter-pendant bonding. Because of the localization, the electronic and optical properties of pendant-group polymers are determined by localized electronic states characteristic of the pendants.²⁴ Fig. 5 shows the band structure of PPB (left panel). The localized states of the phenyl pendant are represented by the horizontal lines, and the extended states of the backbone are presented by curves. The interaction between the phenyl and its environment makes these "horizontal" lines not perfectly horizontal. The optical absorptions shown in Fig. 3 for the three pendant-group polymers are clearly related to those of the isolated pendant groups.²⁴

If our interpretation is correct, excited carriers should be also created in the backbone. Fig. 5 depicts the red absorption of PPB (right panel). In addition to its strong absorption in the UV region, a very weak absorption appears at about 620 nm (2.0 eV). For a same solution of PPB and in a same scan, the absorption of the backbone at its peak is about one thousandth of its phenyl chromophore at 325 nm. Moreover, infrared PL at ~740 nm has been detected in a class of highly luminescent substituted polyacetylenes.²⁰ These results indicate that the blue PL originates from the phenyl pendant while the infrared PL from the distorted backbone.

As stated above, the localized states and hence the PL emission can be tailored by the polymeric environment of the phenyl chromophores. Because of the electron coupling in the polymer, the localized states can be engineered by changing the polymeric environment of the phenyl chromophore. For example, faint orange (2.0 eV),¹⁰ intense green (2.4 eV),¹⁰ and intense deep-blue (3.1 eV)^{18, 20} emissions have been obtained by changing the molecular structures of the other substituent in the neighbour of the phenyl pendant. Figs. 2 and 3 also show clearly that the characteristic low-lying excited states in these polymers are those of pendants, more or less disturbed by polymeric environment to which the side groups are chemically linked. Upon photoexcitation, majority of the carriers is generated in the localized states of the phenyl chromophore, and energy transfer takes place subsequently.³⁴ It is expected that the excited states migrate via energy transfer among various sites until it finds a trap. The pinned PL energy implies that the carrier recombination occurs in the phenyl chromophores and most probably via traps.³⁴

4. ORIGIN OF THE BLUE EMISSIONS FROM POLY(PHENYLACETYLENE) WITH DIFFERENT RING SUBSTITUENTS

4.1. ABSORPTION AND PHOTOLUMINESCENCE

Fig. 6 shows the normalized absorption and PL spectra of 1, 3-7. Many polymers composed of an aliphatic backbone and aromatic side groups absorb in the near UV region, for example, aromatic vinyl polymers. The absorption of our polymers in the range 250-300 nm is associated with the phenyl in the pendant. 1 and 3 start their absorption at ~500 nm, 4 and 5 at ~450 nm, while 6 and 7 at ~520 nm. Additional absorption bands appear at ~450 nm for 6 and 7. The differences in the absorptions are produced by the bulky tails. The characteristic low-lying excited states (> 300 nm) in these polymers are those of the tails, more or less disturbed by polymeric environment to which the side groups are chemically linked.²⁴

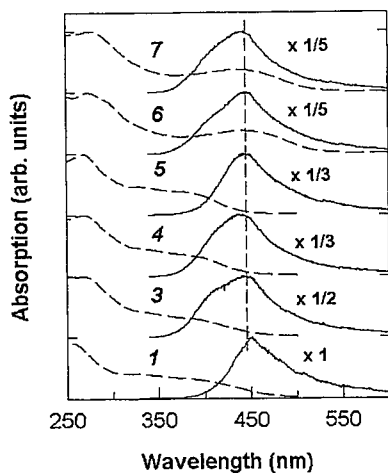


Figure 6 Normalized absorption and PL spectra of 1 and 3-7.

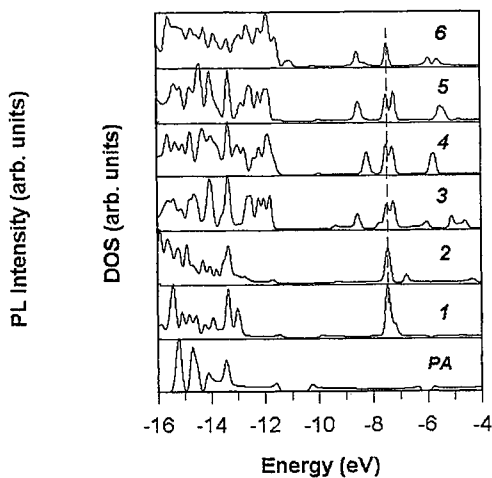


Figure 7. Density of states of cis-PA and 1-6.

Fig. 6 shows that, no matter what types the tails are or how bulky they are, the emission energy of the polymers is always pinned at ~450 nm (2.7 eV). Very bulky tails (6, 7) still fails in enhancing their luminescent efficiency. When measured under similar conditions, the PL intensity of 3-7 is only several times higher than 1. As reported, bulky alkyl pendants in poly(1-phenyl-2-alkynes) can enhance their luminescent efficiency up to 50 times. However, the same alkyl tails or even more bulky ones (2) failed to achieve similar effect for poly(phenylacetylenes). The failure stems from the origin of the blue luminescence, which will be discussed later.

4.2. ELECTRONIC STRUCTURES OF POLY(PHENYLACETYLENES)

The features of absorption and PL of these polymers are related to their electronic structures. Fig. 7 shows the density of states (DOS) of *I-6*. As a comparison, the DOS of *cis-PA* has also illustrated. A pendant, even though a single aromatic ring (*I*), can drastically disturb the electronic states of pristine PA: due to steric effect, the band gap of the conjugated backbone is enlarged up to 1.8 eV for *I*. It is well acknowledged that pendants can distort the backbone and thus can widen the band gap of substituted PAs.¹⁻¹⁰ For *I-3*, the increase in the band-gaps is shown clearly in Fig. 7. We have noted that a limit of ~2.3 eV is quickly reached even for short alkyl tails (*I-3*), and that excessively bulky tails (*4-7*) can cause shrinkage of the band gap. For a comparison, the band gaps (E_g) of the backbones of the polymers are listed in Table 1. Although the band gap can be enlarged, they can, at most, ensure red or infrared emissions. That is, the π - π^* interband transition of the backbone is impossible to be the origin for the observed blue emissions.

After comparing the DOS of *I* to that of pristine polyacetylene, the phenyl pendant can introduce its characteristic states into the widened π and π^* bands of the backbone. Similar characteristic states of other phenyl-containing pendant polymers (*2-7*) are easily discernable in Fig. 7. Other atoms such as oxygen and nitrogen in the tails also generate their characteristic states in the bands of the backbone, and the total DOS of the polymer becomes sensitive to the molecular structures of the tail. Now the information about the nature of electronic states—extended or localized—is important for our data interpretation. Organic polymers are molecular solids with weak intermolecular bonding. Their intramolecular covalent bonding, however, is strong and can be described by one-dimensional energy bands. For linear polymers without side groups, energy band picture of the extended states can be applied. In the top panel of Fig. 8, we illustrate the energy levels of *cis-polyacetylene*. Its clear-cut dispersion curves, which are consistent with those documented in literature, show that the electronic states of pristine polyacetylene are extended states. For pendant-group polymers, the electronic states characteristic of the pendant are localized because the overlap between the pendant groups is very small.¹⁷ Typical band structures of pendant polymers *5* and *6* are depicted in the middle and bottom panels of Fig. 5.8, respectively. The dispersion curves of the pendants are nearly horizontal, that is, $E(k)$ is independent of k . Such independence gives credit to our assignment of the localized states to the pendant. Fig. 8 indicates that the electronic structure of pendant-polymer is essentially an ensemble of the molecular subunits: the backbone and the phenyl-containing pendant.²⁴

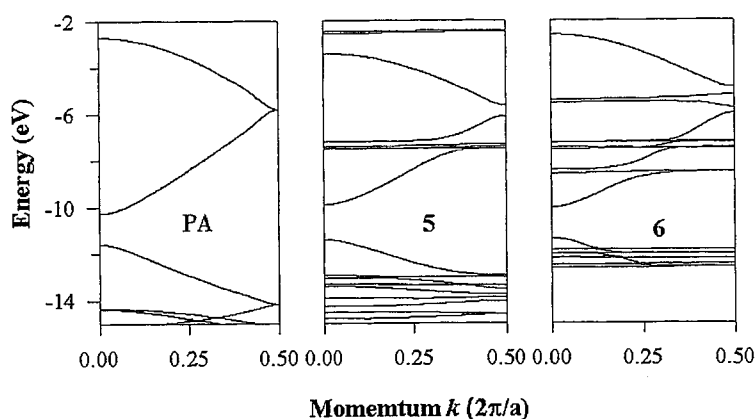


Figure 8 Typical electronic energy levels of *1*, *5*, and *6*.

4.3. LOCALIZED STATES OF PENDANT-GROUP POLYMERS

For pendant-group polymers, Duke *et al*^{22,23} has described the nature of localization, later Baeriswyl²⁴ and Mort and Pfister reviewed it.³⁴ Generally speaking, the nature of the electronic localization is due to disorder in a fashion similar to that proposed by Anderson.³⁵ There are two kinds of disorder: “diagonal disorder” and “off-diagonal disorder”. Diagonal disorder is characterized by a distribution of on-site energies, $\Delta\alpha$. For most organic materials, $\Delta\alpha$ is ~0.5 eV. Similarly, off-diagonal disorder produces a distribution, β , in the transfer integrals. While the specific requirements for Anderson localization depend on dimensionality, localization occurs when $\Delta\alpha \gg \bar{\beta}$, where $\bar{\beta}$ is the average transfer integral.

Transfer integrals for intramolecular interaction are estimated as $\bar{\beta}_{\text{intra}} \leq 0.1$ eV, and for intermolecular interactions $\bar{\beta}_{\text{inter}} \leq 0.01$ eV. Therefore, the charged electronic states of pendant-group polymers consist of electrons (or holes) localized primarily on the pendant group.³⁴

As shown in Fig. 6, the intensity of the localized states is many times higher than that of the extended states. The electronic structures, and hence the absorption and photoemission spectrum, of the pendant-group polymers should be dominated by electrons bound in the molecular orbitals of the pendant group. As a result of photon excitations, majority of photogenerated carriers do not exist in extended energy band states (backbone) but rather are localized in the pendant. Our interpretation has been supported by numerous experimental results. For example, for pendant polymers such as poly(1-phenyl-2-butyne), we have detected a weak absorption at ~620 nm (2.0 eV) in addition to its strong ultraviolet absorption. Moreover, weak infrared emissions at ~740 nm are detected in a number of monosubstituted PAs in addition to their intense blue emissions.²⁰ Transient PL also yields additional evidence. If a luminescence originates from localized states, its luminescence decay should be a simple exponential, i.e., $I = I_0 \exp(-t/\tau)$.³⁶ Indeed, single decay time (~180 ps) has been reported for pendant polymer *I*.³⁰

Fig. 6 also shows that the emission energy of *I-7* does not change with the types of the tails, no matter how bulky they are. The blindness of the emission colour to the molecular structures of the tails strongly supports that the blue emission is phenyl inherent. Although the emission colour is determined by the localized states, the luminescent efficiency can be improved by a few times for the polymers with bulky tails. The limited improvement in the efficiency is possibly due to the limited change in the polymeric environment in the neighbourhood of the phenyl chromophore because the atoms near the phenyl chromophore affect the polymeric environment more effectively. The modulation of the polymeric environment can enhance the luminescent efficiency or even be able to tune its emission colour of a pendant-group polymer. For instance, the PL efficiency of *I* can be enhanced by more than 50 times as a butyl side-chain substitutes the other hydrogen atom in the repeat unit.³⁷ In another case, the emission colour of *I* shifts to ~330 nm as its backbone becomes saturated (polystyrene).³⁸ The eminent change in the emission efficiency and in the emission colour is believed to stem from the wavefunction overlap of the electrons in the aromatic ring and in its neighbour atoms. The nearer a group approaches to the phenyl chromophore, the larger the overlap is. That is one of the reasons why the bulky side-chains can effectively enhance the PL efficiency for poly(1-phenyl-2-acetylenes) but they fail to do so for poly(phenylacetylenes).

5. CONCLUSION

Contrary to the general belief that the blue PL of substituted polyacetylenes originates from the distorted backbones, we have shown that the distorted backbone can emit red PL at most while the blue emissions stem from the phenyl chromophores in the pendants. Our results show that the alkyl side-chain can dramatically improve the PL efficiency but fail to tune the emission color. For poly(phenylacetylenes) with numerous non-liquid crystal tails, all the polymers exhibit weak blue emissions with the PL peak energy pinned at ~450 nm (2.7 eV) in spite of their bulky tails.

Using Hückel tight binding method, we have calculated their electronic structures. The electronic structure of the pendant polymer is essentially an ensemble of the extended states characteristic of backbone and the localized states characteristic of the phenyl-containing pendant. The processes of optical absorption and blue emission are confined in the localized states of the pendant. Our results suggest that the origin of the blue emission is phenyl inherent, resulting from transitions between some localized states of the aromatic ring in the pendant polymer. Most of the observed blue emissions from mono- and di-substituted polymers belongs to this category. The localized states of the phenyl pendant and the optical properties of the substituted polyacetylenes are strongly correlated. We have also shown that the interaction between the phenyl chromophore and its neighbors is of vital importance for improving the emission efficiency and tuning the emission color of pendant polymers. Our calculations are quite successful in explaining the main features of the polymer photoemission spectra, they provide a physical ground for the molecular engineering endeavor in the design of new highly luminescent materials.

By intentionally incorporating chromophous aromatic rings and by carefully engineering their polymeric environment, highly efficient emissions with required emission color can be achieved. It is here that the concept of molecular design proves so extremely powerful because it allows one to choose, at will, the density and the kind of localized states since they are associated with pendant molecules. Hence by using this concept, it has been possible to explore on a molecule level the steps involved in the transfer of carrier generation and recombination. Various polyacetylene derivatives with novel optical properties can be obtained by careful macromolecular design and by delicate electronic states tailor.

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