Origin of the blue emissions of polyacetylenes bearing carbazole side groups

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Abstract

The optical properties and electronic structures of one mono-substituted polyacetylene and two di-substituted polyacetylenes have been investigated. Each of the substituted polyacetylenes bears a carbazole unit in the side chain. In spite of the differences in their molecular structures, the dilute solutions (~1 x 10^{-6} M) of these substituted polyacetylenes exhibit the same absorptions and the same deep-blue emissions (~360 nm). Interestingly, the absorption and emission spectra of these substituted polyacetylenes are similar to those of the small molecule carbazole. As the concentration of the substituted polyacetylenes increases to about 1 x 10^{-3} M, we have detected intense blue emissions at about 475 nm. Using Hückel tight binding programs, we have calculated the electronic structures of the carbazole-containing polyacetylenes. Our results indicate that the absorption, the deep-blue emission (~360 nm) and the intense blue emission (~475 nm) originate from the carbazole chromophores in the side chain.

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1. Introduction

In the last decade, light-emitting conjugated polymers have attracted intense interest due to their potential applications in optoelectronics. Pristine polyacetylene [-(CH = CH)_n-], which is the simplest \( \pi \) conjugated polymer, can give off weak photoluminescence in the infrared spectral region [1]. In order to achieve strong visible emissions, the hydrogen atoms in the backbone of the polymer are replaced with specific functional...
as a result, Yoshino et al. and Tada et al. detected blue and green emissions from some di-substituted polyacetylenes [2,3]; they proposed that the side-chain-induced distortion in the backbone of the polyacetylene is responsible for the blue/green emissions of the di-substituted polyacetylenes. Years ago, we observed intense deep-blue emissions from a class of mono-substituted polyacetylenes with biphenyl side-chains, and our results have demonstrated that the biphenyl pendants are responsible for the deep-blue emissions of those mono-substituted polyacetylenes [4–7]. Recently, Stagnaro et al. [8] observed blue emission from polyacetylenes bearing biphenyl mesogens to the backbone via short methylene spacers; they suggested that both the polymer backbone and the biphenyl chromophore in the side group play a role in the blue emission. Due to the complexity in the photo-physics of conjugated polymers [9], it is clear that the origin of the blue emissions is still open to question for the polyacetylenes with side chains.

Our previous work on the light emission properties of biphenyl-containing mono-substituted polyacetylenes reveals that the biphenyl unit in the side chain is responsible for the blue emissions of those substituted polyacetylenes [4–7,10–12]. If it is correct, the emission will change if the biphenyl unit in the side chain is replaced by the other kind of chromophore. Being a typical small molecule, carbazole is a fundamental chromophore that gives off emission at ~340 nm in dilute solutions [13–16]. In contrast to their fully investigated chemical properties, the electronic structures and light emission properties of polyacetylenes bearing carbazole pending groups have almost remained intact in spite of a brief report on the emission of a carbazole-containing polyacetylene derivative [17]. Therefore, carbazole is a promising candidate for our purpose. In this paper, we report our results on the optical absorption and photoluminescence spectra of three carbazole-containing polyacetylenes both in dilute and in concentrated solutions. Based on the calculated electronic structures for the carbazole-containing polyacetylenes, we have discussed the origin of their emissions. Our results indicate that the deep-blue emission (~360 nm) in dilute solutions and the intense blue emission (~475 nm) in concentrated solutions originate from the carbazole chromophore in the side chain of the polymers.

2. Experimental details

The molecular structures of the three carbazole-substituted polyacetylenes are shown in Fig. 1. The mono-substituted polyacetylene is denoted as PACz-1 while the two di-substituted polyacetylenes are denoted as PACz-2 and PACz-3 for \( m = 3 \) and 9, respectively. In order to check the effect of di-substitution on the optical properties of the polyacetylenes with carbazole pending groups, we incorporated Cl groups in PACz-2 and PACz-3. The carbazole chromophores are attached to the backbone of the polymers via methylene spacers (–CH\(_2\)–); the spacer lengths for PACz-1, PACz-2 and PACz-3 are 3, 3 and 9, respectively, in the methylene unit. The details on the synthesis and purification of the polymers were reported elsewhere [17]. For the optical measurements, both dilute solutions (~10\(^{-6}\) M) and concentrated ones (~10\(^{-3}\) M) were prepared by dissolving a specific polymer in spectroscopic grade chloroform (CHCl\(_3\)). The molar concentration of a solution was calculated on the basis of the molecular mass of the repeat unit. Small molecule carbazole was purchased from the Third Chemical Corporation of Shanghai, and its dilution solutions (~10\(^{-7}\) M) were prepared in spectroscopic grade ethanol (C\(_2\)H\(_5\)OH) and cyclohexane (C\(_6\)H\(_{12}\)). A 1-mm-thick quartz cell was used to contain the

![Fig. 1. The molecular structures of a mono-substituted carbazole-containing polyacetylene (PACz-1) and two di-substituted polyacetylenes PACz-2 (for \( m = 3 \)) and PACz-3 (for \( m = 9 \)).](image-url)
as-prepared solution for optical absorption and emission measurements. The white light from a xenon lamp passed through a monochromator (Spex-1640) and subsequently focused onto the quartz cell with a focus lens. The 300-nm line from a xenon lamp was used as the excitation line for the deep-blue fluorescence measurement, while the 325-nm line from a helium–cadmium laser was used as the excitation line for the blue emission measurement. All emission spectra were measured at room temperature in the quartz cell on a Spex-500M spectrofluorometer, and all spectra were reproducible. BICON-CEDiT, an extended Hückel band structure and oscillator strength calculation package, was developed by Prof. Gion Calzaferri at University of Berne, Switzerland. It is a set of FORTRAN programs that allow extended-Hückel tight-binding calculations for 1D–3D compounds to get their band structures and density of states. Using the extended Hückel tight-binding program, we calculated the electronic structures for the three substituted polyacetylenes in order to give a qualitative description on the optical properties of the conjugated polymers. In order to obtain the optimal molecular structure for the electronic structure calculation, we performed a geometry optimisation of an oligomer at AM1 level and extracted the geometry of the central unit cell. The AM1 program was implemented in the MOPAC package (Quantum Chemistry Program Exchange, Indiana University, USA). The standard Slater parameters for C, H and N atoms were adopted from Ref. [20].

3. Results and discussions

Fig. 2 shows the absorption spectra of the mono-substituted PACz-1, di-substituted PACz-2 and PACz-3. The absorption spectra of these three substituted polyacetylenes are identical to each other, whether they are classified as mono-substituted polyacetylenes or di-substituted polyacetylenes. The length of the spacer has no obvious effect on the absorption, either. In each absorption spectrum, there are five peaks which are located at 358 nm (3.5 eV), 335 nm (3.7 eV), 298 nm (4.2 eV), 265 nm (4.7 eV), 240 nm (5.2 eV), which indicates the optical gap of each substituted polyacetylene is at least two times larger than the band gap of the pristine polyacetylene (~1.4 eV). We measured the absorptions for the monomers of the three polymers and the small molecule carbazole; we found that both the carbazole-containing monomers and the small molecule carbazole exhibit similar absorptions when compared to those of the three substituted polyacetylenes. According to Ref. [13], the first absorption peak of carbazole is close to 330 nm; while the first absorption peak of the substituted polyacetylenes is close to 358 nm. Thus, a significant red shift is observed when the carbazole chromophore is linked to the polyacetylene backbone.

In addition to the identical absorptions, the three carbazole-containing polyacetylenes show the same emission and electronic structures; therefore, in the following sections we represent the fluorescence and electronic structures for the mono-substituted polyacetylene PACz-1 only. Under the excitation of the 300-nm line from the xenon lamp, deep-blue emission has been recorded for the dilute PACz-1 solution. The emission
spectrum of a dilute PACz-1 solution (~1 μM) is shown by curve (a) in Fig. 3. The fluorescence spectrum has two peaks located at 350 and 365 nm, respectively. The first emission peak of the polymers (~350 nm) appears at a wavelength smaller than that of their respective absorption band (358 nm). As mentioned in Section 2, the excitation line for the polymer emissions was 300 nm, it can excite the two absorption bands at 335 and 358 nm; this results the mirror-like emission peaks at 350 and 365 nm, respectively. In Ref. [9], the mirror-like relation between the absorption and emission spectra has been documented for some organic chromophores. After having checked the monomer of PACz-1 and other carbazole-containing small molecules, we surprisingly found that all of the carbazole-containing molecules have quite similar deep-blue emission [13–17]. Curves (b) and (c) show the fluorescence spectra of the small molecule carbazole in the solvents ethanol (~0.1 μM) and cyclohexane (~0.1 μM), respectively. The fluorescence spectra of carbazole in Fig. 3 are not exactly conformed to those illustrated in Ref. [13]. Indeed, according to Fig. 3, these spectra seem red-shifted. This may be due to the differences in the solution concentrations because higher concentrations were used in our experiment. When the solution concentration of carbazole increases, our additional experiments have shown that its emission spectrum red-shifts progressively. These experimental data indicate that the origin of the fluorescence of our polymer PACz-1 is primarily derived from the carbazole chromophore in the pendant. According to Fig. 3, there is an obvious red shift of the fluorescence spectra of the polymers compared to that of carbazole. Thus the polymer backbone seems to affect the emissive properties of carbazole.

The optical properties of organic polymers are closely related to their electronic structures. Using the extended Hückel tight-binding method [18–20], we have calculated the electronic structures for the side-chain polymer PACz-1. Fig. 4 shows the band structure (left panel) and the total electronic density of states (right panel) for PACz-1. Similar to a mono-substituted polycetylene in our previous work [21], the energy levels in Fig. 4 can be divided into two independent sets. The sharp peaks in Fig. 4(b) correspond to the horizontal energy levels in Fig. 4(a), while the smooth bands in Fig. 4(b) correspond to the curved energy levels in Fig. 4(a). From a viewpoint of energy, the band gap of the polymer is only ~1.6 eV, it is far below its 3.5 eV optical band gap as obtained from Fig. 2. Such a small band gap (1.6 eV) can hardly give off any deep-blue emission. In order to give a clear picture, we have calculated the densities of states for pristine trans-polyacetylene, the carbazole-containing side group and the polymer PACz-1, respectively. Our results show that the sharp peaks are contributed by the pendants while the smooth and wide bands are contributed by the conjugated backbone of the polymer. These features on the electronic structures of side-chain polymer PACz-1 can be understood in this way: for pendant-group polymers, the interaction between pendants is negligible when compared to the strong interaction between the carbons in the backbone; therefore, the electronic states characteristic of the pendant are localized states (sharp peaks) while those of the conjugated backbone are extended states (wide bands). For the same reason, the two sets of density of states are independent of each other.

![Fig. 3. Photoluminescence spectra for (a) a dilute PACz-1 solution in chloroform (~1 μM); (b) carbazole molecule in ethanol (~0.1 μM); and (c) carbazole molecule in cyclohexane (~0.1 μM). Excitation wavelength: 300 nm.](image-url)
From Fig. 4 we can see that the bandgap of the polymer PACz-1 is actually the bandgap of the backbone. In spite of the small bandgap of the distorted backbone, the large band gap of the pendant is responsible for the deep-blue emission. Therefore, our experimental results and calculated electronic structures support that the deep-blue emission comes from the carbazole chromophore in the pendant.

As shown in Fig. 3, the emission of the carbazole-containing polymer PACz-1 is red-shifted about 20 nm when compared to the emission of the small molecule carbazole. This is due to the difference in concentration because intermolecular interaction between two adjacent carbazole molecules starts to work as the solution becomes concentrated. Although no red-shifted emission has been reported for carbazole-containing small molecules, intermolecular interaction is easily formed for the carbazole-containing polyacetylene derivatives, so blue emission is readily achievable for concentrated solutions. Fig. 5 illustrates the typical blue emission of a moderately concentrated PACz-1 solution. A strong and broad emission band appears in the blue spectral region with its peak located at about 475 nm while the two characteristic peaks of the carbazole molecule are still discernible at 370 and 400 nm, respectively. The red shift emission is well documented for organic semiconductors when the solution becomes concentrated. For example, we
demonstrated the large-scale red shift in the emission of a biphenyl-containing mono-substituted polyacetylene by changing the concentration of the solutions [12]. By changing the concentration of the PACz-1 solution, we can modify the dimer emission intensity and colour; the increased intermolecular interactions between carbazole units linked to different polymer chains are supposed to be responsible for the red-shifted emissions. For PACz-1, its blue emission at 475 nm is about ten times stronger than the deep-blue emission at 360 nm.

4. Conclusion

In summary, we have studied the optical absorptions, photoluminescent properties and electronic structures of three substituted polyacetylenes, each of the polymers bears carbazole chromophores in its side chains. Our results have shown that the deep-blue emission primarily originates from the monomer emission of the carbazolyl chromophores in the side-chains of the polymer while the blue emission comes from the dimer emission of the carbazole chromophores. The dimer emission at 475 nm is about one order stronger than the monomer emission at 360 nm. Furthermore, we have documented the effect of polymer backbone on the emissive properties of the carbazolyl chromophores in the pendants.

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