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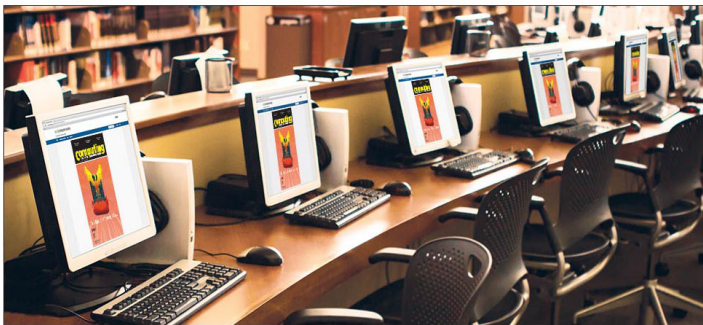
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Strong photoluminescence from monosubstituted polyacetylenes containing biphenyl chromophores

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Monosubstituted polyacetylenes are generally regarded as unlikely candidates for photoluminescent materials. We have, however, observed intense deep-blue emission in a series of photoexcited poly(1-alkynes) (PAs) containing biphenyl pendants ($-\{HC=C[(CH_2)_m-OCO-biphenyl-OC_7H_{15}]\}_n-$ where $m = 2, 3, 4,$ and 9). The photoluminescence (PL) is readily observable by naked eyes under normal room illumination conditions, whose integrated intensity is threefold higher than that of poly(1-phenyl-1-butyne), a well-known highly luminescent disubstituted polyacetylene. A red PL band has also been detected in the PAs. Using the extended-Hückel-tight-binding method, we have calculated the density of states of the PAs, and it is found that the functional pendants have dramatically modified the band states of polyacetylene. The strong PL of the PAs is satisfactorily explained by the engineered electronic structures. © 1999 American Institute of Physics. [S0003-6951(99)03552-4]

Since the discovery of electroluminescence in poly(*p*-phenylenevinylene),¹ light emission from conjugated polymers and its potential applications in optoelectronics have spurred dynamic research activity in macromolecules with extended π electrons.²⁻⁵ Polyacetylene, a prototypical conjugated polymer, has been the subject of extensive research for several decades.⁶ The polymer, however, exhibits practically no photoluminescence (PL) in the visible spectral region.⁷⁻⁹ One advantage of using conjugated polymers in optoelectronic application is that their optical properties and device performance can be manipulated through molecular engineering endeavor.¹⁰ It is envisioned that the optical properties of polyacetylene can be tuned by substitution of its hydrogen atoms with other atoms or functional groups. Indeed, a variety of polyacetylenes with two substituents (i.e., disubstituted polyacetylenes) have been found to be highly luminescent. Emission of intense blue or green light has been observed from a number of disubstituted polyacetylenes.¹¹⁻¹⁹ The PL behavior of monosubstituted polyacetylenes has also been investigated, but so far only weak luminescence has been observed, examples of which include poly(phenylacetylenes) and poly(propargyls).^{13,15,16,20} Monosubstituted polyacetylenes are thus often referred to as nonluminescent polymers and are generally regarded as unpromising candidates for light emitting materials.

The purpose of this work is to demonstrate that monosubstituted polyacetylenes can be highly luminescent in the visible region if a hydrogen atom in the repeat unit of polyacetylene is substituted with a proper functional group.

A group of mesogenic pendants, $(CH_2)_mOCO-biphenyl-OC_7H_{15}$ ($m = 2, 3, 4, 9$), are designed to replace the hydrogen atoms in the molecular structure of polyacetylene.

The synthetic procedures and characterization data of the poly(1-alkynes) (PAs) were reported elsewhere.²¹⁻²⁴ The molecular structures of the PAs, denoted as **7**(*m*), are given in Fig. 1. The aromatic rings in the PAs are well separated from the polymer backbone by the alkyl spacers. Solutions for absorption and emission measurements were prepared by dissolving **7** in spectroscopic grade tetrahydrofuran. The concentrations of the solutions were $\sim 10^{-5}$ M. The absorption spectra of the polymer solutions were recorded on a Milton Roy Spectronic 3000 array spectrometer, and their PL spectra were measured in a 1-mm-thick quartz cell on a Spex-500M spectrofluorometer. The 325 nm line from a helium-cadmium laser (Omnichrome) was used as the excitation source, and the excitation powers were $\sim 1-2.3$ mW.

Figure 2 shows the absorption and emission spectra of **7**(2-9). The absorption maximums of the polymers are located at 295 nm (4.20 eV), while the corresponding deep-blue emission peaks center at ~ 385 nm (3.22 eV). The Stokes shift is up to ~ 1 eV. As the spacer length increases,

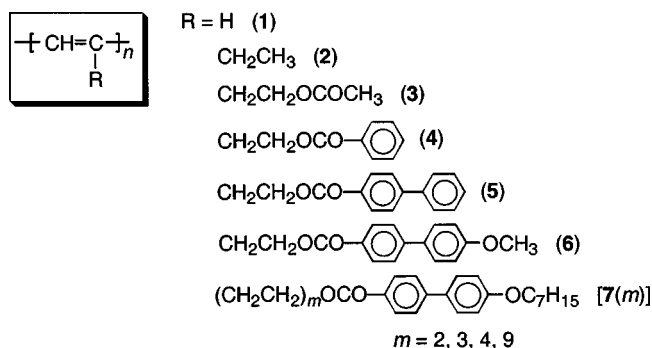


FIG. 1. Molecular structures of polyacetylenes. Polymers **1-6** and **7**(2) are used in the theoretical calculations, while **7**(2-9) are employed in the experimental measurements.

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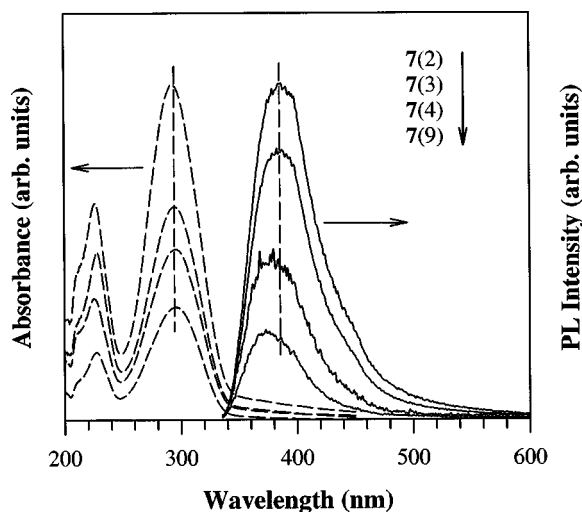


FIG. 2. Absorption (dash lines) and emission (solid lines) spectra of tetrahydrofuran solutions of **7**(2–9); concentration: $\sim 10^{-5}$ M, excitation wavelength: 325 nm, excitation power: ~ 1 mW. (The intensities are not normalized but are arbitrarily adjusted for the sake of clear illustration.)

the absorption profile of **7** does not change much, but its PL peak experiences a slight blueshift. Each of the four PAs is highly luminescent, and indeed the deep-blue emission is so strong that it can be clearly observed by naked eyes under normal laboratory lighting. Poly(1-phenyl-1-butyne) was taken as a reference for comparison. The PL of the disubstituted polyacetylene has been well studied,^{11–19} which emits strong blue light of ~ 450 nm when excited at 325 nm. Under the similar measurement conditions, the integrated PL intensity of poly(1-phenyl-1-butyne) is less than one third of that of **7**(9). The 1-alkyne monomers absorb and emit at the similar spectral region ($\lambda_{ab} \sim 295$ nm, $\lambda_{em} \sim 365$ nm), suggesting that the biphenyl chromophores are responsible for the strong deep-blue PL of the PAs. However, when we attached the similar biphenyl chromophores to a poly(phenylacetylene) backbone,^{25,26} the polymers emit extremely weak PL signals.^{24,26} Thus, the PL properties of polyacetylenes depend not only on the chromophore pendants but also on the backbone structures.

Optical properties of a polymer are ultimately associated with its electronic structures.²⁷ When a pendant is attached to the backbone of polyacetylene, the electronic structure of the macromolecule will be modified. We thus calculated the density of states (DOS) of a series of monosubstituted polyacetylenes. The DOS calculations were performed using the extended-Hückel-tight-binding method,^{28,29} which can give a good semiquantitative description of band structures of conjugated polymers. Standard Slater parameters for the atoms were selected from Ref. 29, and polymers **1**–**6** and **7**(2) with cis backbone conformation were used in the DOS calculations. The calculated results are depicted in panels 1–7 in Fig. 3. Panel 1 shows the DOS of polyacetylene (**1**): its π – π^* transition yields the infrared PL as reported in literature.^{8,9} When the hydrogen atom in polyacetylene is substituted by an alkyl side chain (**2**), the band gap becomes enlarged, but the enlargement is very limited because it results from the limited distortion of the backbone. With the progressive substitutions with the side chains containing ester (**3**), phenyl (**4**), and biphenyl groups (**5**), the electronic

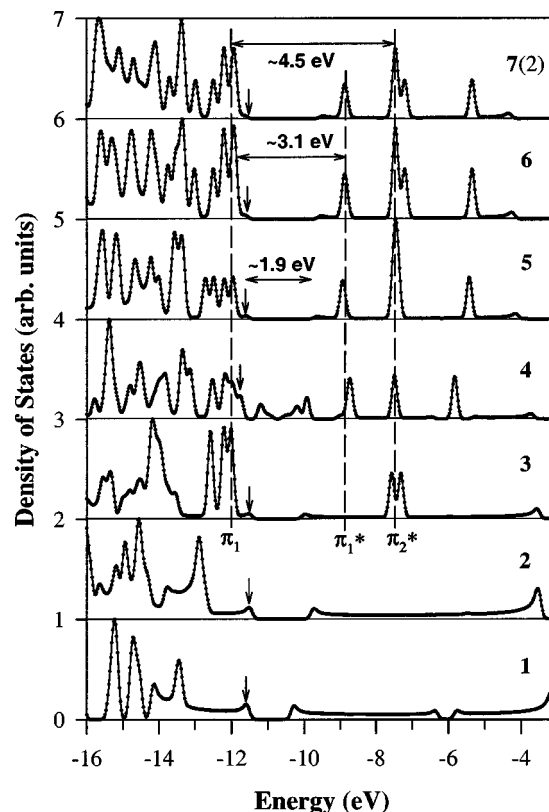


FIG. 3. Evolution of calculated density of states of polyacetylenes **1**–**7**.

structures of the π and π^* bands are modified dramatically. As can be seen in panels 3–7, the ester, phenyl, and biphenyl introduced spikes greatly depress the backbone contributed DOS. For an eye guidance, the oxygen- and biphenyl-introduced spikes are linked with three dashed lines in the π and π^* bands, which are correspondingly denoted as π_1 , π_1^* , and π_2^* . Vertical arrows mark the Fermi levels. It is obvious that the oxygen, phenyl, and biphenyl introduced DOS are many times larger than that contributed by the backbone. As a result, the DOS contributed by the backbone is depressed greatly. Under this situation, the band gap is overwhelmed by a pseudo band gap, as indicated in panel 6 (~ 3.1 eV). By inspection of the DOS shown in Fig. 3, one can identify two separate bands to which the transitions can be assigned. These are the interband transitions between the π_1 – π_1^* and π_1 – π_2^* states. The absorption maxima (~ 4.2 eV) in Fig. 2 can be assigned to the transition of $\pi_1 \rightarrow \pi_2^*$, while the deep-blue emission (~ 3.2 eV) to the $\pi_1 \leftarrow \pi_1^*$ transition, although this may not be the only possible explanation.

We have noted that the phenyl group in **4** introduces gap states, which are cleared up by the biphenyl group in **5**. The gap states introduced by the phenyl group in **4** may quench, partially or completely, the deep-blue PL. Although the oxygen- and biphenyl-introduced DOS become dominant in **7**(2), the DOS contributed by the backbone still exists. It seems reasonable that the polymer emits a red or infrared PL band associated with the π – π^* transition (the genuine band gap). Experimentally we have indeed detected red PL bands for all of the **7**(*m*) samples. Figure 4 shows the red PL of **7**(9) when excited by a 325-nm He–Cd laser with a power of 2.3 mW. The peak of the red band locates at ~ 740 nm (1.68

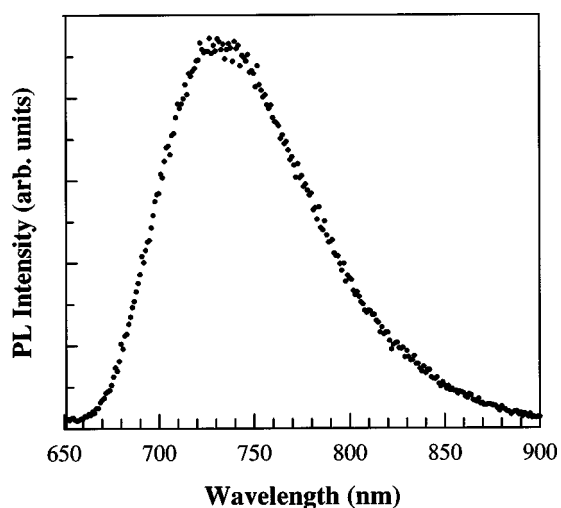


FIG. 4. Photoluminescence spectrum of 7(9) in the red spectral region; excitation wavelength: 325 nm, excitation power: 2.3 mW.

eV). Polyacetylene with a cis content of $>90\%$ has been found to fluoresce at 1.68 eV upon excitation.⁹ The excellent agreement of our experimental observation (red band at 1.68 eV) with the literature data for the cis-rich polyacetylene⁹ supports the cis backbone assumption we made in our DOS calculations.

From the above results, it becomes clear that the DOS introduced by the oxygen and biphenyl in the side chain create a pseudo band gap, which is responsible for the deep-blue PL, while the genuine band gap is associated with the red PL. The DOS introduced by the phenyl, however, efficiently quenches the blue PL, which may explain our experimental observations that all the poly(phenylacetylene) derivatives we checked, no matter how strongly fluorescent the pendant chromophores are, are weak luminescent emitters.^{24,26}

Thus, in contrast to the general belief that monosubstituted polyacetylenes are a group of nonluminescent polymers, we prove in this work that light emission from monosubstituted polyacetylenes can be greatly tuned by molecular engineering. While the polymers with a poly(phenylacetylene) backbone emit faint light, those with a poly(1-alkyne) skeleton are highly luminescent, even when the two groups of polyacetylenes bear the same chromophoric pendants. The DOS calculations provided a satisfactory explanation for the observed structure–property relationship, which may guide future research efforts in the design of molecular structures for light emitting polyacetylenes. Because of the rigid nature of the alternating-double-bond backbone, polyacetylenes can be readily aligned by external forces.^{22,30} Indeed, we have succeeded in manipulating the light emission from the PAs by applying an electrical field²⁶ and have observed polarized luminescence from oriented PAs. The synergistic interplay of the conjugated backbones and the chromophoric pendants may endow the PAs intriguingly unique optoelectronic properties, which can hardly be accessed with conventional non-conjugated vinyl polymer systems with flexible backbones.

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