Electrically tunable photoluminescence of liquid crystalline polyacetylene solutions

Yuan Ming Huang [a], Jacky Wing Yip Lam [b], Kevin Ka Leung Cheuk [b], Weikun Ge [a], Ben Zhong Tang [b],*

[a] *Department of Physics, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong*
[b] *Department of Chemistry, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong*
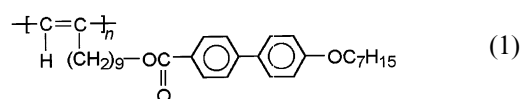
Abstract

Light emission from tetrahydrofuran solutions of a liquid crystalline polyacetylene, poly(11-{[(4′-heptoxy-4-biphenylyl)carbonyl]oxy}-1-undecyne), is investigated in the electrical field. The field exerts little effect on the photoluminescence of the polymer solution with a low concentration (1.03×10^{-4} M). The photoluminescence of a concentrated solution (113×10^{-4} M) is, however, noticeably quenched under an electrical field with a field strength of $> 3 \times 10^{5}$ V m^{-1}. When the field strength is increased to $\geqslant 3.67 \times 10^{5}$ V m^{-1}, the bimodal emission spectrum of the solution changes to a monomodal one. Thus, both the emission intensity and spectral profile of the photoluminescence of the concentrated solution can be tuned by the electrical field, which is probably caused by the aggregate dissociation and mesogen realignment induced by the external stimulus. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Photoluminescence; Electric field; Polyacetylene

1. Introduction

Electrical field is one of the most convenient tools of manipulation and is an indispensable part of modern devices of high technology. The alignment of mesogenic molecules by electrical field, for example, forms the basis of liquid crystal optical display systems [1–3]. Light emitting materials have high potential for a wide variety of technological applications [4–9], and it is of considerable interest to control the optical property by electrical means. We have recently developed a group of new substituted polyacetylenes that are both liquid crystalline and light emitting [10–18]. In this report, we demonstrate that the spectral profile and emission intensity of the photoluminescence of one of such polyacetylenes, poly(11-{[(4′-heptoxy-4-biphenylyl)carbonyl]oxy}-1-undecyne) (1) can be modulated by externally applied electrical field.

$$\begin{array}{c} +\text{C}=\text{C}+_n \\ | \quad\; | \\ \text{H} \;\; (\text{CH}_2)_9-\text{OC}-\!\!\bigcirc\!\!-\!\!\bigcirc\!\!-\text{OC}_7\text{H}_{15} \\ \;\;\;\;\;\;\;\;\;\;\;\; \| \\ \;\;\;\;\;\;\;\;\;\;\;\; \text{O} \end{array} \qquad (1)$$

2. Experimental details

The synthetic experimental details and full characterization data of **1** have been reported elsewhere [14,16]. Two polymer solutions with distinctly different concentrations (1.03×10^{-4} and 113×10^{-4} M) were prepared by dissolving accurately weighed amounts of the polymer in spectroscopic grade tetrahydrofuran. The molar concentration was calculated on the basis of the molecular mass of the repeat unit of **1**. The solution was placed in a 1-mm quartz cell sandwiched with a pair of ITO electrodes, to which dc fields of different strengths were applied. A 325-nm line from an Omnichrome helium–cadmium laser was used as the excitation source. The photoluminescence spectra of the polymer solutions were measured on a Spex-500M

* Corresponding author. Tel.: +852-2358-7246; fax: +852-2358-7375.
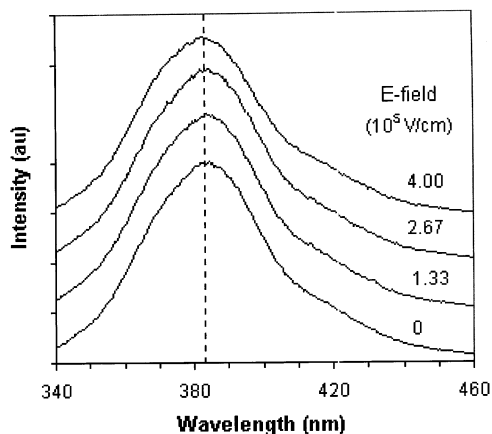
E-mail address: tangbenz@ust.hk (B.Z. Tang).

Fig. 1. Normalized emission spectra of a THF solution of **1** in the electrical fields. Concentration: 1.03×10^{-4} M; excitation wavelength: 325 nm; excitation power: ~ 1 mW.
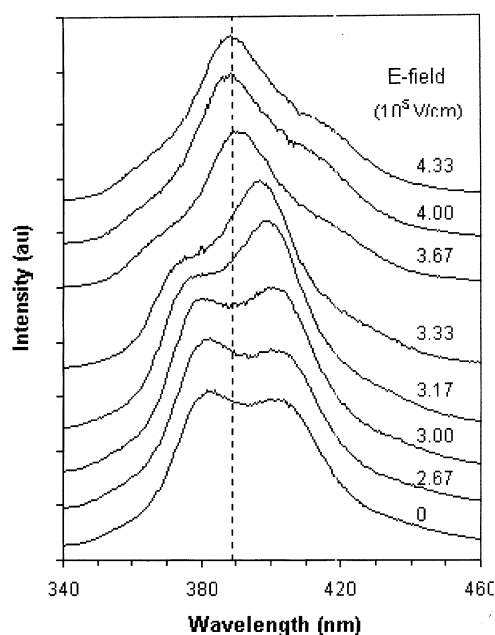

Fig. 2. Normalized emission spectra of a THF solution of **1** in the electrical fields. Concentration: 113×10^{-4} M; excitation wavelength: 325 nm; excitation power: ~ 1 mW.

spectrofluorometer at room temperature in the quartz cell.

3. Results and discussion

Fig. 1 shows the luminescence spectra of the solution of **1** with a low concentration (1.03×10^{-4} M). Upon photoexcitation at 325 nm, the polymer solution emits a deep blue light. Little change is observed in the emission spectrum when an electrical field of 1.33×10^5 V m^{-1} is applied to the polymer solution. The spectrum remains unchanged even when the field strength is
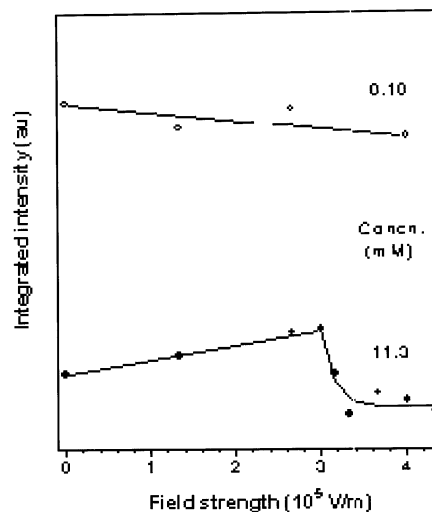

Fig. 3. Effect of field strength on the integrated intensity of photoluminescence of THF solutions of **1**.

increased to as high as 4×10^5 V m^{-1}. Clearly the electrical field has no any effect on the spectral profile of the dilute polymer solution.

While the dilute solution exhibits only one emission peak at ~ 383 nm, the polymer solution with a high concentration (113×10^{-4} M) shows an additional peak at ~ 404 nm (Fig. 2). When an electrical field is applied to the concentrated solution, the emission spectrum gradually blue shifts. The spectral shift undergoes a large change at a field strength of 3.67×10^5 V m^{-1}, where the two peaks merge into one at ~ 389 nm. The new peak still blue shifts with the further increase in the field strength but the extend of the shift is marginally small.

The integrated intensity of the emission from the dilute solution monotonically decreases as the field strength increases (Fig. 3). The emission from the concentrated solution is weaker and shows a complex pattern with the change in the field strength. The intensity increases in the low field strength region ($< 3 \times 10^5$ V m^{-1}), rapidly drops in the medium region (3–3.33×10^5 V m^{-1}), and slightly decreases in the high region ($> 3.67 \times 10^5$ V m^{-1}). It is noteworthy that the rapid drop in the integrated intensity coincides with the rapid growth of the lower-energy emission peak shown in Fig. 2.

In dilute solutions, luminescent chromophores are separated far apart by the solvent molecules and experience little intermolecular interaction; light emitted from such isolated species is usually called "monomer" emission [19]. As the concentration increases, the chromophores are brought in contact and the intermolecular interaction intensifies [20]. The chromophores may cluster or aggregate in a quasi-parallel fashion and the luminescence from such aggregated species are often referred to as "dimer" emission [19,21].

An externally applied electrical field may not alter the intermolecular interaction of the isolated chromophores, accounting for the nil effect of the field on the spectral profile of the emission from the dilute solution. The electrical field may partially separate the charges of the excitons and reduce the chances for the photogenerated electrons and holes to recombine, hence weakening the monomer emission.

The concentrated solution exhibits one emission peak at ~ 383 and another at ~ 404 nm; the former is clearly associated with the monomer emission, while the latter may be related to the dimer emission because it is not observed in the emission spectra of the dilute solution. The aggregates (dimers) may partially quench the emission from the isolated chromophores (monomers) [19], and the integrated intensity of the emission from the concentrated solution is thus lower than that from the dilute solution.

When an electrical field is applied to the concentrated solution, polarization of the chromophores takes place. It is known that the induced dipole moment μ is proportional to the field strength E, i.e., $\mu = \alpha E$, where α is the polarizability of a mesogenic pendant or a conjugated segment in a polymer chain. In the low fields, the dimers may partially separate. The field-induced aggregate dissociation should weaken the quenching effect; in other words, the emission intensity becomes stronger as the dimer separation progresses. When the field strength is increased to 3×10^5 V m^{-1}, the strong field may render the chromophores partially charged. The repulsion and attraction of the charged species may now well separate the dimers to a larger extend, thus blue shifting the emission spectrum. The charged species may effectively neutralize the charges of the excitons and hence considerably reduce the intensity of the light emission. When the field strength reaches 3.67×10^5 V m^{-1}, the aggregate dissociation and the chromophore reorientation processes may approach completion, creating an equilibrium state in which the chromophores partially overlap in the three-dimensional space with their long axes aligning along the direction of the applied field, as schematically illustrated below. Further increase in the field strength may not alter the intermolecular interaction to a great extend, accounting for the small change in the spectral profile and emission intensity in the high fields.
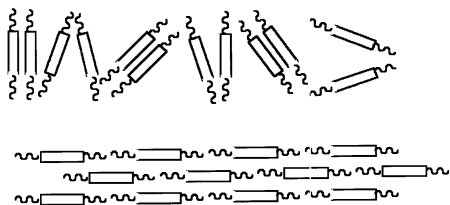
In a control experiment, we applied ac fields (50 Hz) of different strengths to the polymer solution but ob-

served no changes in the photoluminescence. This shows the overwhelming importance of the directionality over the strength of the field and supports the proposed mechanism involving the *directional* aggregate dissociation and chromophore alignment induced by the dc field.

In summary, in this study, we succeeded in tuning the wavelength (color) and intensity (brightness) of the light emitted from a solution of a liquid crystalline polyacetylene by electrical field. Of particular interest is the quenching of the light emission by the external field. We are currently working on the optimization of the field quenching process, with the aim of developing an optical switching system, whose emission can be sharply, completely, and repeatedly quenched by the application of an electrical field of low voltage.

Acknowledgements

References

[1] V.G. Chigrinov, Liquid Crystal Devices: Physics and Applications, Artech House, Boston, 1999.
[2] R. Shashidhar, R.U. Efron (Eds.), Liquid Crystal Materials, Devices, and Displays, SPIE–the International Society for Optical Engineering, Bellingham, WA, 1995.
[3] L.M. Blinov, Electro-Optical and Magneto-Optical Properties of Liquid Crystals, Wiley, New York, 1983.
[4] X.-C. Li, S.C. Moratti, in: D.L. Wise, G.E. Wnek, D.J. Trantolo, T.M. Cooper, J.D. Gresser (Eds.), Photonic Polymer Systems, Marcel Dekker, New York, 1998, pp. 335–371 Chapter 10.
[5] J.H. Burroughes, D.D.C. Bradley, A.R. Brown, R.N. Marks, K. Mackay, R.H. Friend, P.L. Burns, A.B. Holnes, Nature 347 (1990) 539.
[6] S.C. Chang, Y. Yang, Appl. Phys. Lett. 75 (1999) 2713.
[7] Y. Cao, I.D. Parker, G. Yu, G.C. Zhang, A.J. Heeger, Nature 397 (1999) 414.
[8] S.H. Chen, D. Katsis, A.W. Schmid, J.C. Mastrangelo, T. Tsutsui, T.N. Blanton, Nature 397 (1999) 506.
[9] X. Zhang, S.A. Jenekhe, Macromolecules 33 (2000) 2069.
[10] B.Z. Tang, X. Kong, X. Wan, H. Peng, W.Y. Lam, X. Feng, H.S. Kwok, Macromolecules 31 (1998) 2419.
[11] X. Kong, B.Z. Tang, Chem. Mater. 10 (1998) 3352.
[12] X. Kong, J.W.Y. Lam, B.Z. Tang, Macromolecules 32 (1999) 1722.
[13] B.Z. Tang, H.Z. Chen, R.S. Xu, J.W.Y. Lam, K.K.L. Cheuk, H.N.C. Wong, M. Wang, Chem. Mater. 12 (2000) 213.
[14] J.W.Y. Lam, X. Kong, Y.P. Dong, K.K.L. Cheuk, K. Xu, B.Z. Tang, Macromolecules 33 (2000) 5027.
[15] B.Z. Tang, J.W.Y. Lam, X. Kong, P.P.S. Lee, X. Wan, H.S. Kwok, Y.M. Huang, W. Ge, H.Z. Chen, R.S. Xu, M. Wang, in: I. Khoo (Ed.), Liquid Crystals III, SPIE–the International Society for Optical Engineering, Bellingham, WA, 1999, pp. 62–71.

[16] Y.M. Huang, W. Ge, J.W.Y. Lam, B.Z. Tang, Appl. Phys. Lett. 75 (1999) 4094.

[17] Y.M. Huang, J.W.Y. Lam, K.K.L. Cheuk, W. Ge, B.Z. Tang, Macromolecules 32 (1999) 5976.

[18] C.W. Lee, K.S. Wong, J.W.Y. Lam, B.Z. Tang, Chem. Phys. Lett. 307 (1999) 67.

[19] J.F. Rabek, Mechanisms of Photophysical Processes and Photochemical Reactions in Polymers: Theory and Applications, Wiley, New York, 1987.

[20] J.M.G. Cowie, Polymers Chemistry and Physics of Modern Materials, second ed., Blackie Academic and Professional, London, 1991, 362–398 (Chapter 16).

[21] M. Aguiar, B. Hu, F.E. Karasz, I.L. Akcelrud, Macromol. Chem. Phys. 199 (1998) 1255.