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Chemical Physics Letters 408 (2005) 169–173

CHEMICAL PHYSICS LETTERS

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Carbazole–pyrene-based organic emitters for electroluminescent device

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Received 12 January 2005; in final form 19 March 2005
Available online 28 April 2005

Abstract

Carbazole–pyrene-based compounds were synthesized and fully characterized. Their photoluminescence properties were studied. Fluorescence quantum yield was improved dramatically by inserting pyrene as electron-acceptor. Blending 9-(3-(2-(1-(2-(3-(9H-carbazol-9-yl)-9-*p*-tolyl-9H-carbazol-6-yl)ethynyl)pyren-6-yl)ethynyl)-9-*p*-tolyl-9H-carbazol-6-yl)-9H-carbazole (**16**) with poly(*N*-vinylcarbazole) (PVK), simplified electroluminescent (EL) device with green emission was fabricated. Maximum luminance reached 1000 cd/m^2.

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1. Introduction

Organic electroluminescence has attracted considerable attention since the first report of EL device based on multilayered organic molecules [1]. Trends of organic EL devices have been focused both on optimizations of EL structure and on developing new optoelectronic materials [2,3]. Different types of EL structures have been, thereby, proposed to improve the quantum efficiency, conversion efficiency, lifetime, and emission colors [4–6]. Although very bright and efficient EL devices have been achieved by using multilayer device structure, from a manufacturing point of view, devices that have fewer layers are much desirable because they simplify the fabrication process. Meanwhile, organic compounds with fascinating molecular structures have been designed and synthesized to meet different requirements [7,8]. One was the ethynylated acenes, which exhibited excellent optical properties [9–11]. The other was the multifunctional fluorophore, which was recently synthesized and fabricated for simplified device architecture [12–16]. For instance, stilbenoid molecules with pyrene as an acceptor and phenothizine building block as donor could be doped in a polymer blend for a single layer device [13]. Another simplified device structure was composed of dye-dispersed poly(*N*-vinylcarbazole) (PVK) as an emitter layer, which was doped with both hole-transport material and electron-transport material [5,6]. There still existed demand for searching more efficient material in the simplified architecture. In this Letter, carbazole–pyrene-based small molecules were synthesized and fully characterized. For **15** and **16**, carbazole was selected as the donor due to sufficient high triplet energy and the hole-transport property. For instance, carbazole derivatives used as donors were able to emit red [17–19], green [8], and even blue in some cases [20]. On the other hand, pyrene was chosen as acceptor due to its good performance in solution [11] and its electron-acceptor nature [12,21]. PVK was

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doi:10.1016/j.cplett.2005.04.019

chosen as the matrix due to its hole transport property and violet–blue emission [22].

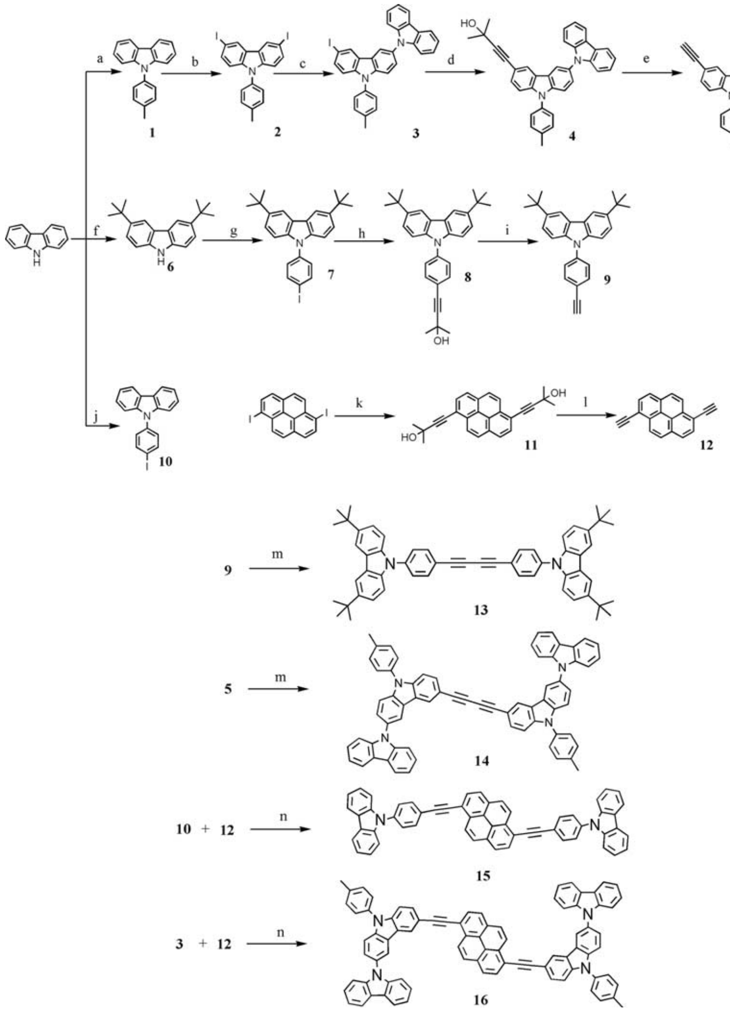
2. Experimental

2.1. Synthesis

Preparation routes to **13**, **14**, **15** and **16** were depicted in Scheme 1. Triple bond was used as a bridge to link the pyrene and carbazole unit. Symmetrical and asymmetrical structures were designed for comparison of luminescence properties. Sonogashira coupling reaction was used to construct ethynyl bridged conjugated structures. Compounds **1** [23], **2** [24], **6** [25], **7** [26], **8** [27], **9** [27], **10** [26] and **12** [11] were prepared by reference methods, respectively.

2.2. Instrument

Solvents used were of spectrograde and purified by distillation before use. The fluorescence spectra were recorded on a *Shimadzu* RF-5301pc. The absorption spectra were obtained on a *Shimadzu* UV-2450 spectrophotometer. The quantum yields were calculated based on 9,10-diphenyl-anthracene (DPA) ($\Phi_f = 0.95$ in cyclohexane) [28]. Chloroform solution was degassed with N_2 for 40 min. Cyclic voltammetry experiments were performed with a BAS 100 B/W electrochemical analyzer. All measurements were carried out at room temperature with a conventional three-electrode configuration consisting of a platinum working electrode, an auxiliary platinum electrode, and a non-aqueous Ag/Ag^+ reference electrode. The solvent in this experiment was DMF and the supporting electrolyte was



Scheme 1. Synthesis of **13**, **14**, **15** and **16**: (a) K_2CO_3, Cu, 18-crow-6, 1-iodo-4-methylbenzene, DMF, N_2, 170 °C, 12 h; (b) KI, KIO_3, acetic acid, refluxed, 70 min; (c) K_2CO_3, Cu,18-crown-6, carbazole, DMF, N_2, 170 °C, 12 h; (d) 3-methyl-1-butyn-3-ol, CuI, $Pd(PPh_3)_2Cl_2$, NEt_3, 100 °C, 24 h, N_2; (e) KOH, isopropyl alcohol, refluxed, 3 h, N_2; (f) 2-chloro-2-methylpropane, $AlCl_3$; (g) K_2CO_3, Cu,18-crown-6, 1,4-diiodobenzene, DMF, 170 °C, N_2, 12 h; (h) 3-methyl-1-butyn-3-ol, CuI, $Pd(PPh_3)_2Cl_2$, NEt_3, 100 °C, 24 h, N_2; (i) KOH, isopropyl alcohol, refluxed, 3 h, N_2; (j) K_2CO_3, Cu,18-crown-6, 1,4-diiodobenzene, DMF, 170 °C, N_2, 12 h; (k) 3-methyl-1-butyn-3-ol, CuI, $Pd(PPh_3)_2Cl_2$, NEt_3, 100 °C, 12 h, N_2; (l) KOH, isopropyl alcohol, refluxed, 3 h, N_2; (m) CuI, $Pd(PPh_3)_2Cl_2$, NEt_3, 100 °C, 12 h, N_2; (n) CuI, $Pd(PPh_3)_2Cl_2$, NEt_3/benzene: 3/5 (v/v), 100 °C, 12 h, N_2.

tetra-*n*-butylammonium perchlorate (TBAP). ^{1}H and ^{13}C NMR spectra were obtained on a Bruker AVANCE DMX 500 spectrometer. ^{13}C NMR spectra were obtained with a broad band proton decoupling mode. Spectra were run in $CDCl_3$, $(CD_3)_2SO$ or C_6D_6, and internally referred to tetramethylsilane. EI (70 ev) was applied to obtain mass spectra on HP 5989B (Hewlett–Packard). MALDI-TOF-MS data were obtained from IonSpec 4.7 T FTMS.

2.3. Preparation and characterization of LED device

Indium-tin oxide (ITO) coated glass with a sheet resistance below 30 Ω/□ was used as a substrate for LEDs. The PVK layer doped with **16** was spin coated from a chloroform solution onto the indium-tin-oxide (ITO) glass substrates. Evaporation of the small organic layers and the aluminum electrode were done at a vacuum of 2×10^{-4} Pa. The emitting area of the EL devices was 4 mm^2. The EL spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer. Luminance was measured with Photo research 650 spectrascan colorimeter. Current–voltage measurements were carried out using a Hewlett–Packard 4140B semiconductor parameter analyzer. All the measurements were performed under ambient atmosphere at room temperature.

3. Result and discussion

3.1. Photoluminescence studies

Absorption and emission spectra of the synthesized compounds are given in Supporting Information. Their optical properties are summarized in Table 1. By using 9,10-diphenyl-anthracene (DPA) as a reference, fluorescence quantum yields (Φ_f) of compounds **13–16** were obtained. Compound **13** shows a moderately high fluorescence quantum yield with $\Phi_f = 0.61$, whereas lower quantum yield of **14** was found. This result may arise from the twisted structure of **14** relative to **13**. When inserting pyrene acceptor, both Φ_f of **15** and **16** are improved significantly. Both **15** and **16** show extremely high fluorescence quantum yield of nearly 100%. In order to examine the potential application of these new synthesized compounds, **16** was selected as the candidate for EL device fabrication due to its higher solubility and easier fabrication than those of **15**. Therefore, electrochemistry and electroluminescence studies of **16** were carried out.

Table 1
Optical properties of **13**, **14**, **15** and **16** (25 °C, $CHCl_3$)[a]

Compounds	$\lambda_{abs(max)}$ (nm)	λ_{ex} (nm)	λ_{em} (nm)	Φ_f
13	358	350	422	0.61
14	373	350	433	0.02
15	412	350	448	1.18
16	422	350	460	1.03

[a] Quantum yields were calculated based on DPA.

3.2. Electrochemistry studies

The cyclic voltammograms (CVs) of **16** is shown in Fig. 1. A small amount of ferrocene was added as an internal standard. During the process of anodic scan, the peak at +0.70 V was observed against the reference electrode, **16** exhibited oxidation reaction at +1.10 V. This can be attributed to the electron-donating nature of carbazole segment. Moreover, the oxidation is irreversible. HOMO and LUMO energy levels of **16** (−5.86 and −2.90 eV) were calculated from cyclic voltammetry by −4.5 eVox/red [29,30], while −4.5 eVox/red is referred to normal hydrogen electrode (NHE). The reduction peak at 2.0 V was observed and it was reversible. This implied that improvement of electron-transport property of **16** was achieved by inserting pyrene acceptor.

3.3. Electroluminescence studies

Since **16** is difficult to be evaporated onto the ITO substrate, a single-layer electroluminescence device was fabricated by doping **16** into PVK. We use PVK as the host because its emission band is almost overlapped with the absorption band of **16** (please see Fig. 5 in Supporting information), so an effective energy transfer may occur in this host–guest system. As shown in Fig. 2, **16** can exhibit its own luminescence well, and green light emission at 500 nm was observed. The current–voltage–luminance (*I–V–L*) characteristics were given in Supporting information. The single-layer device (ITO/PVK:**16** (10:1, w/w)/Al) showed turn-on voltage at 8 V, the maximum luminance of 60 cd/m^2 at 17 V, and the luminous efficiency of 0.023 lm/W at 20 V.

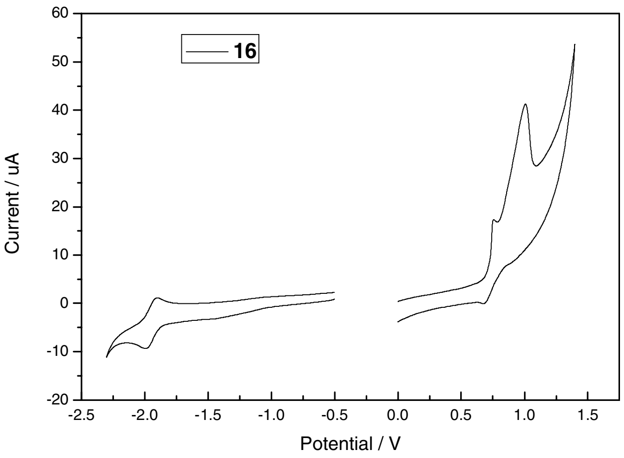


Fig. 1. Cyclic voltammograms (CVs) of **16**.

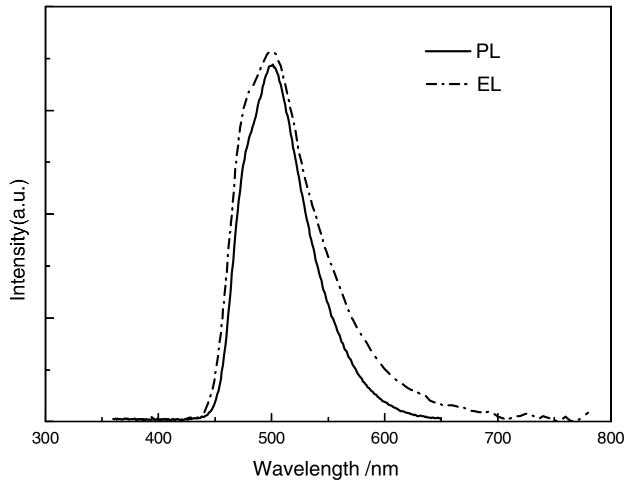


Fig. 2. The EL spectrum of **16** (ITO/PVK:**16** (10:1, w/w)/Al), and photoluminescence (PL) spectrum in solid state of **16**.

It is known that in PVK holes are dominant and electrons are minor, leading to the unbalance of electrons and holes. Therefore, the EL performances of the single-layer device are not satisfying. To improve the device performance, an additional electron-transporting layer (1,3,5-tris-(phenyl-2-benzimidazole)-benzene (TPBI), whose structure was shown in Supporting information) was deposited by vacuum thermal evaporation under 3×10^{-4} Pa. (ITO/PVK: **16** (10:1 w/w) (60 nm)/TPBI (30 nm)/Al (100 nm)). The *I–V–L* characteristics are shown in Fig. 3. Device performance was improved without variety at the emission wavelength [31]. Physical performance appeared to be improved: turn-on voltage 11 V, maximum luminance reached 1000 cd/m^2, external quantum efficiency was found to 0.85% at 15.5 V, and luminous efficiency was 1.1 lm/W at 15.5 V. Analysis of HOMO and LUMO energy levels of layers for this device was shown in Fig. 4. HOMO energy level of **16** (5.86 eV) lies between those of ITO (4.70 eV) or PVK (5.80 eV) [32] and that of TPBI (6.20 eV) [33], while the LUMO energy level of **16** (2.90 eV) lies under those of TPBI (2.70 eV) or PVK (2.31 eV). There is a barrier of 0.4 eV for holes to migrate from PVK to TPBI layer. Thus, under the present configuration (ITO/PVK:**16** (10:1 w/w) (60 nm)/TPBI (30 nm)/Al (100 nm)), TPBI acts as a electron-transporter and a hole blocker and charge recombination is confined to PVK layer. On the other hand, an efficiency energy transfer [3,33] was approached from the host PVK (404 nm) [34] to the guest **16** due to the wide range overlap (Fig. 5). Such an energy transfer is consistent with the relative energy levels due to the suitable HOMO and LUMO energy levels [35] of **16**.

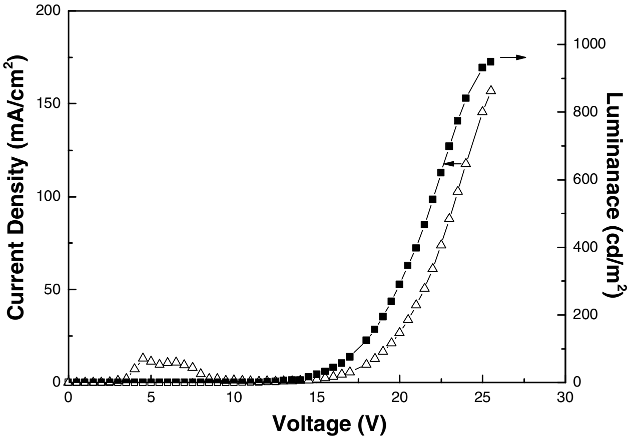


Fig. 3. *I–V–L* characteristics of the device (ITO/PVK:**16** (10:1, w/w)/TPBI/Al).

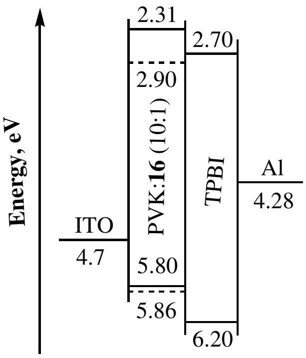


Fig. 4. Relative energy alignments in the device ITO/PVK:**16** (10:1, w/w)/TPBI/Al.

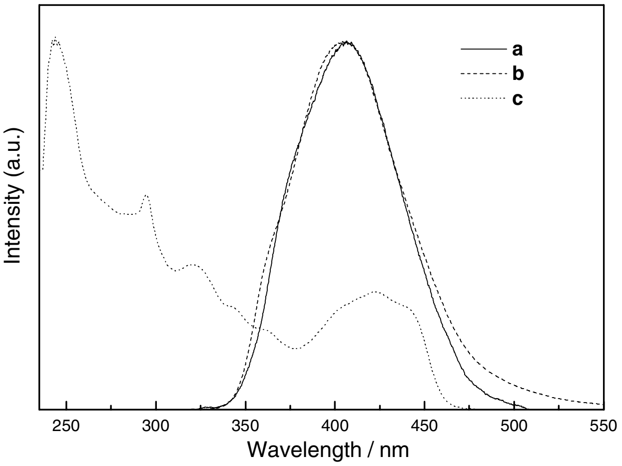


Fig. 5. PL emission spectra of PVK (a), TPBI (b) and absorption spectrum of **16** (c).

4. Conclusions

In this Letter, carbazole–pyrene-based compounds were synthesized and fully characterized. Their photoluminescence properties were studied. Emission efficiency was improved dramatically by inserting pyrene as electron-acceptor. Blending **16** with PVK, EL device with green emission was fabricated. Maximum luminance reached 1000 cd/m^2 and the maximum power efficiency was 1.1 lm/W. Though the performance of device was not good enough, carbazole–pyrene-composed compounds might be used as the active materials in simplified organic EL devices based on this report.

Acknowledgments

Ping Lu thanks National Science Foundation of China (20374045). This work was partially supported by the Major State Basic Research Development Program and the Chinese Academy of Sciences.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cplett.2005.04.019.

References

[1] C.W. Tang, S.A. VanSlyke, Appl. Phys. Lett. 51 (1987) 913.

[2] A. Kraft, A.C. Grimsdale, A.B. Holmes, Angew. Chem., Int. Ed. 37 (1998) 402.

[3] A.C.A. Chen, S.W. Culligan, Y. Geng, S.H. Chen, K.P. Klubek, K.M. Vaeth, C.W. Tang, Adv. Mater. 16 (2004) 783.

[4] F. Nüesch, L. Si-Ahmed, B. Francois, L. Zuppiroli, Adv. Mater. 9 (1997) 222.

[5] J. Kido, M. Kohda, K. Okuyama, K. Nagai, Appl. Phys. Lett. 61 (1992) 761.

[6] J. Kido, H. Shionoya, K. Nagai, Appl. Phys. Lett. 67 (1995) 2281.

[7] M.A. Baldo, D.F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M.E. Thompson, S.R. Forrest, Nature 395 (1998) 151.

[8] K. Brunner, A. van Dijken, H. Börner, J.J.A.M. Bastiaansen, N.M.M. Kiggen, B.M.W. Langeveld, J. Am. Chem. Soc. 126 (2004) 6035.

[9] S.A. Manhart, A. Adachi, K. Sakamaki, K. Okita, J. Ohshita, T. Ohno, T. Hamaguchi, A. Kunai, J. Kido, J. Organomet. Chem. 592 (1999) 52.

[10] S.A. Odom, S.R. Parkin, J.E. Anthony, Org. Lett. 5 (2003) 4245.

[11] J. Ohshita, K. Yoshimoto, Y. Tada, Y. Harima, A. Kunai, Y. Kunugi, K. Yamashita, J. Organomet. Chem. 678 (2003) 33.

[12] A. Knorr, J. Daub, Angew. Chem., Int. Ed. 34 (1995) 2664.

[13] J. Daub, K. Kelnhofer, T. Gareis, A. Knorr, M. Kollmannsberger, Polym. Prepr. 38 (1997) 339.

[14] A. Knorr, J. Daub, Angew. Chem., Int. Ed. 36 (1997) 2817.

[15] X. Gong, P.K. Ng, W.K. Chan, Adv. Mater. 10 (1998) 1337.

[16] W.L. Jia, X.D. Feng, D.R. Bai, Z.H. Lu, S. Wang, G. Vamvounis, Chem. Mater. 17 (2005) 164.

[17] T. Tsutsui, M.J. Yang, M. Yahiro, K. Nakamura, T. Watanabe, T. Tsuji, Y. Fukuda, T. Wakimoto, S. Miyaguchi, Jpn. Appl. Phys. 38 (1999) 1502.

[18] D.F. O'Brien, M.A. Baldo, M.E. Thompson, S.R. Forrest, Appl. Phys. Lett. 74 (1999) 442.

[19] C. Adachi, M.A. Baldo, S.R. Forrest, S. Lamansky, M.E. Thompson, R.C. Kwong, Appl. Phys. Lett. 78 (2001) 1622.

[20] C. Adachi, R.C. Kwong, P. Djurovich, V. Adamovich, M.A. Baldo, M.E. Thompson, S.R. Forrest, Appl. Phys. Lett. 79 (2001) 2082.

[21] Z. Shen, R. Prochazka, J. Daub, N. Fritz, N. Acar, S. Schneider, Phys. Chem. Chem. Phys. 5 (2003) 3257.

[22] J. Kido, K. Hongawa, K. Okuyama, K. Nagai, Appl. Phys. Lett. 63 (1993) 2627.

[23] S.W. Cha, J. Jin, J. Mater. Chem. 13 (2003) 479.

[24] S.H. Tucker, J. Chem. Soc. (1926) 546.

[25] S. Ito, K. Takami, Y. Tsujii, M. Yamamoto, Macromolecules 23 (1990) 2666.

[26] A. Hameurlaine, W. Dehaen, Tetrahedron Lett. 44 (2003) 957.

[27] S.H. Lee, T. Nakamura, T. Tsutsui, Org. Lett. 3 (2001) 2005.

[28] M. Mardelli, J. Olmsted, J. Photochem. 7 (1977) 277.

[29] F. Wu, W. Tian, Z. Zhang, Y. Ma, G. Li, J. Shen, L. Zhang, B. Zhang, Y. Cao, Thin Solid Films 363 (2000) 214.

[30] F. Wu, W. Tian, J. Sun, J. Shen, X. Pan, Z. Su, Mater. Sci. Eng. B85 (2001) 165.

[31] Please see Supporting information.

[32] M.M. Shi, H.Z. Chen, J.Z. Sun, J. Ye, M. Wang, Chem. Phys. Lett. 381 (2003) 666.

[33] Z. Gao, C.S. Lee, I. Bello, S.T. Lee, R.M. Chen, T.Y. Luh, J. Shi, C.W. Tang, Appl. Phys. Lett. 74 (1999) 865.

[34] Y. Qiu, L. Duan, X. Hu, D. Zhang, M. Zheng, F. Bai, Synthetic Met. 123 (2001) 39.

[35] Y. Hamada, H. Kanno, T. Tsujioka, H. Takahashi, T. Usuki, Appl. Phys. Lett. 75 (1999) 1682.