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Electroluminescent properties of naphthalimide derivative thin film devices

Shougen Yin[a,b], Xingyuan Liu[c], Chenxi Li[a,b], Wenqiang Huang[a,b,*], Wenlian Li[c], Binglin He[a,b]

[a]*The State Key Laboratory of Adsorption Separation and Functional Polymer Materials, Nankai University, Tianjin 300071, People's Republic of China*
[b]*Institute of Polymer Chemistry, Nankai University, Tianjin 300071, People's Republic of China*
[c]*Changchun Institute of Physics, Chinese Academy of Sciences, Changchun 130021, People's Republic of China*

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Abstract

N-alkyl or arenyl-4-acetylamide-1,8-naphthalimides (NA) were synthesized by reaction of 4-acetylamide-1,8-naphthalic acid with organic amines. Optical properties were studied in the UV-visible region. By using Joule evaporation thin films of the NA, the double layer of EL devices (ITO/PVK/NA/Al) were fabricated. Yellow and green EL emission at around 569.0–504.2 nm was observed. It was found that the emission wavelength of the devices using naphthalimides with bulkier *N*-alkyl groups shifted to red while the emission wavelength of those devices using naphthalimides with *N*-arenyl substituted groups shifted to blue. This is identified with the results calculated by the MINDO/3 model. Moreover, experimental results revealed that the Joule heat by non-radiative decay has a significant affect on the device life, and the life of the device using naphthalimide compounds with high melting points is longer than that of the device fabricated using those with low melting points.

Keywords: Naphthalimide; Organic thin film electroluminescence; Photoluminescence; MINDO/3

1. Introduction

Over the past 10 years, a considerable number of studies have been made on organic electroluminescenct (EL) devices, and superior EL characteristics have been successfully demonstrated by many research groups [1–5]. Up to now there is still a big problem in the stability and lifetime of the organic thin electroluminescent devices. Recently, good stability data have been reported which demonstrate a long-term durability of the organic EL diode [5,6]. However, the degradation mechanism of the device due to the operation is not fully understand. Although the mechanism of degradation of the organic EL devices is not clearly understood, the possible phenomena of degradation in the non-emissive area and voltage rise in the constant-current model are increased [7].

In this paper, *N*-alkyl or arenyl-4-acetylamide-1,8-naphthalimides (NA) were synthesized and the double layer EL devices (ITO/PVK/NA/Al) were fabricated with NA thin films. The properties of EL spectra on the structure of naphthalimide derivatives were investigated, moreover, the degradation of the devices caused by the crystallization of the organic thin films were also studied.

2. Experiment details

IR spectra were recorded on a Nicolet 5DX FTIR spectrometer, ^{1}H-NMR measurements were carried out with a Varian Unity Plus-400 spectrometer, fluorescence spectra were obtained with an Hitachi-4000 and the luminance–voltage characteristics were measured with a luminance meter ST-86LA. Naphthalimide derivatives were prepared with the modified literature procedure [8] and according to a previously reported synthetic method [9], the chemical and physical constants of NA are illustrated in Table 1. PVK was obtained from Aldrich, the indium–tin–oxide (ITO)-coated glass was purchased from DaBo (China). It has a sheet resistance of approximately 30 Ω/(□). Experimental results indicated that the cleanliness of the ITO was found to be an important factor governing the performance of the

* Corresponding author.

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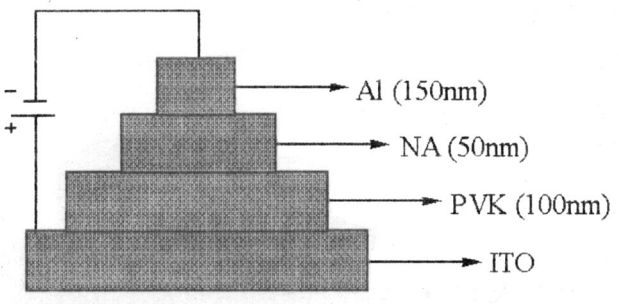


Fig. 1. Configuration of EL device.

organic EL devices. Firstly, the glass was sonicated in a detergent solution followed by a deionized water rinse, dipped into isopropanol, then boiled in toluene and ethanol solution. After degreasing, the substrate was allowed to dry naturally.

The organic EL device structure of NA and PVK are shown in Fig. 1. All of the NA derivative thin films were deposited by standard thermal vapor deposition techniques at a chamber pressure of about 6.67×10^{-3} Pa, PVK films were directly spin-coated on a glass substrate and dried naturally. Metallization was accomplished by heat evaporation of the aluminum granules to give the upper electrode.

3. Results and discussion

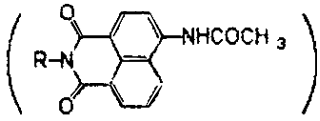
3.1. Optical characterization

From Table 2 we know that the organic EL device (ITO/PVK/NA/Al) fabricated with naphthalimide derivatives emitted yellow-green light at about 569.0–504.2 nm. The devices turn on at a voltage of 5 V, and luminance of 140–340 cd/m^2 is achieved at 20 V and can be clearly seen in day light. In order to clarify the dependence of EL on the chain length of *N*-substituted group, the luminescence of devices constructed by compounds 1–8 was detected. Table 2 shows the relationship between the carbon number of the *N*-alkyl group and the luminance. As Doi [10] reported, the luminance increased linearly with increasing the carbon length of the *N*-alkyl group. This may imply that the longer length of the alkyl-substituted group not only reduces the ratio of the non-radiative process due to preventing migration of excitons to traps but also reduces the electron aggregation, thereby improving luminescent efficiency [11].

From Table 2 we also know that the devices emitted longer wavelength light (red-shift) as the carbon number of the *N*-alkyl group was increased, i.e. $\lambda_{El(N-CH2CH3)} = 543.8 < \lambda_{EL(N-C8H17)} = 569.0$. The most likely explanation to the phenomenon is that an increase in the carbon chain

Table 1

The chemical and physical constants of NA



Compound	*R*	Recrystallized Solid	Yield (%)	Color	Melting point (°C)
1	Methyl	AcOH	85.0	Pale Yellow	280–281
2	Ethyl	AcOH	86.6	Pale Yellow	276–278
3	*n*-Propyl	AcOH	81.3	Pale Yellow	250–251
4	iso-butyl	AcOH	87.7	White	235–237
5	sec-butyl	AcOH	78.2	White	274–275
6	*n*-Butyl	AcOH	73.5	White	278–279
7	*n*-Pentyl	AcOH	83.2	White	212–213
8	*n*-Octyl	Ethanol	69.8	White	187–189
9	Allyl	Ethanol	86.5	White	264–265
10	Phenyl	Ethanol	81.9	Pale Yellow	235–237
11	Benzyl	Ethanol	80.3	White	277–278

Table 2

The emission wavelength of devices (ITO/PVK/NA/Al) and the energy band gap values of NA compounds calculated by the MINDO/3 model

Compound	Device	λ_{PL} (nm)	λ_{EL} (nm)	Luminance (cd/m^2) (20 V)	HOMO (eV)	LUMO (eV)	ΔE_g (eV)
1	1	506.4	550.0	140	–5.208	–1.796	3.412
2	2	470.6	543.8	160	–5.643	–2.113	3.530
3	3	489.6	536.2	190	–5.546	–2.106	3.440
4	4	482.4	535.0	220	–5.504	–2.068	3.436
5	5	485.8	536.2	225	–5.506	–2.076	3.43
6	6	492.6	533.8	230	–5.480	–2.055	3.425
7	7	500.8	559.8	265	–5.480	–2.062	3.418
8	8	502.4	569.0	340	–5.474	–2.061	3.413
9	9	494.6	570.0	150	–5.529	–2.068	3.461
10	10	476.3	504.2	145	–5.574	–2.070	3.504
11	11	489.5	523.0	155	–5.523	–2.063	3.460

HOMO, highest occupied molecular orbital; LUMO, lowest unoccupied molecular orbital.

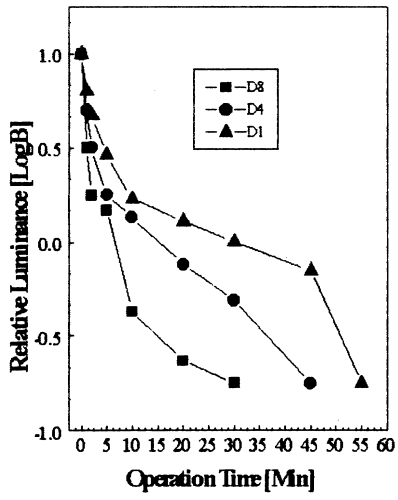


Fig. 2. Luminance decay of the device 1,4,8, at 15v continuous dc-driving.

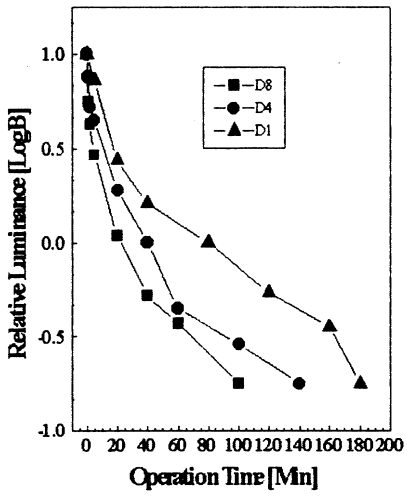


Fig. 3. Luminance decay of the device 1,4,8 at pulse driving [dr = 0.5].

length of the *N*-alkyl group strengthens the ability of the electron-donor, and decreases the $\pi-\pi^*$ band gap of the *N*-alkyl substituted NA derivatives; thus a red-shift in the emission spectrum results. Moreover, *N*-phenyl or benzyl substituted NA derivatives lead to smaller conjugation while *N*-allyl substituted NA molecular values lead to higher conjugation. Those experimental results are in agreement with the $\pi-\pi^*$ band gap values of NA molecules calculated by the MINDO/3 model. However, the reason why the blue shift in λ_{EL} occurred when the alkyl groups changed from R = Me to R = Et on the NA molecule is not clear.

3.2. Lifetest results

Figs. 2 and 3 show the degradation properties of devices 1, 4 and 8 constructed by compounds 1, 4 and 8, respectively. Under a constant voltage driving (Fig. 2) or a pulse driving ($d_r = 0.5$) (Fig. 3) at an ambient temperature, it was found that the luminance of all three devices decreased very quickly at the initial step of the degradation then gradually slowed down. The phenomenon indicated that the cathode (Al) was presumably destroyed by the harmful gases such as the moisture or oxygen in the atmosphere. This affected the life of EL devices [12]. Also from both of the Figs. 2 and 3, the device lives are as follows: device 1 > device 4 > device 8. The results mean that the lives of the devices fabricated from the high melting point compounds are longer than that of the devices obtained from the compounds of low melting point. The degradation rates of the EL devices are much slower by using pulse driving than that of the same device by using continuous d_e-driving. It revealed that the crystallization of the organic layers caused by Joule heat has a significant effect on the device life [13].

4. Conclusion

The properties of the organic thin film EL devices (ITO/PVK/NA/Al) constructed by the naphthalimide derivatives were investigated. It was found that the emission wavelength was observed at a range of 569.0–504.2 nm, and the luminance increased as the carbon chain length of the *N*-alkyl substituted groups became longer. The emission wavelength of the devices composing of naphthalimides with bulkier *N*-alkyl groups shifted to red, while those composing of *N*-arenyl substituted groups shifted to blue. This is consistent with the results calculated by the MINDO/3 model. Experimental results also showed that the crystallization of organic materials is an important factor affecting the EL device life.

References

[1] C.W. Tang, S.A. Van Slyke, Appl. Phys. Lett. 51 (1987) 913.
[2] C.W. Tang, S.A. Van Slyke, C.H. Chen, J. Appl. Phys. 65 (1989) 3610.
[3] J.H. Burroughes, D.D.C. Bradley, Nature 347 (1990) 539.
[4] H. Tokailin, M. Matsuura, Proc. SPIE 1910 (1993) 38.
[5] C.W. Tang, SID Int. Symp. Dig. Tech. Papers, SID, San Diego, CA, 1996, p. 181.
[6] Y. Hamada, T. Sano, K. Shibata, K. Kuroki, Jpn. J. Appl. Phys. 34 (1995) L824.
[7] C. Adachi, T. Tsutsui, S. Saito, Appl. Phys. Lett. 56 (1990) 799.
[8] L.A. Jones, C.T. Joyner, H. Kim, R.A. Kyff, Can. J. Chem. 48 (1970) 3132.
[9] M. Okazaki, T. Tanaka, S. Taniguchi, Yuki Gosei Kagaku Kyokai Shi 14 (1956) 344.
[10] S. Doi, M. Kuwabara, T. Noguchi, T. Ohnishi, Synth. Met. 55–57 (1993) 4147.
[11] C.M. Heller, I.H. Campbell, B.K. Laurich, D.L. Smith, Phy. Rev. B 54 (8) (1996) 5516.
[12] M. Kawaharada, M. Ooishi, T. Saito, E. Hasegawa, Int. Conf. Electroluminescence of Molecular Materials and Related Phenomena, Fukuoka, Japan, May 21–24 1997, p. 15.
[13] Y. Sato, S. Ichinosawa, H. Kanai, Inorganic and Organic Electroluminescence/EL 96, Berlin, Wissenschaft und Technik Verlag, Berlin, 1996, p. 255.