ELSEVIER

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy



journal homepage: www.elsevier.com/locate/saa

A blue-emitting organic compound 9-hydroxyl-3-hydroxyethyl-2-methyl-4H-pyrido[1,2-a]pyrimidin-4-one: Synthesis, crystal structure and luminescent properties

Huaihong Zhang^{a,b}, Yu Sun^a, Xiaodan Chen^a, Chao Li^a, Baiwang Sun^{a,*}

^a College of Chemistry and Chemical Engineering, Southeast University, Nanjing 211189, China

^b Department of Chemistry and Biology, Yancheng Institute of Technology, Yancheng 224003, China

ARTICLE INFO

Article history: Received 24 November 2009 Received in revised form 21 February 2010 Accepted 26 February 2010

Keywords: Crystal structure X-ray diffraction Hydrogen bond Blue-emitting

ABSTRACT

A blue-emitting organic compound, 9-hydroxyl-3-hydroxylethyl-2-methyl-4H-pyrido[1,2-a]pyrimidin-4-one (I), was synthesized by the reaction of 2-amino-3-hydroxylpridine with 2-acetylbutyrolactone. The crystal of the title compound in larger size was reported for the first time through the slow evaporation method. The whole molecule in the crystal is non-planar, but the two conjugated rings are almost coplanar (with an average dihedral angle of only about 1.621°). The hydroxyl group is in *trans* position to the pyrido[1,2-a]pyrimidin heterocyclic moiety. The molecules are linked by the N-H···O, O-H···O and C-H···O hydrogen bonds into two-dimensional sheets. Additionally, the π - π interactions (average distance 3.3680 Å) interconnect the sheets stabilizing the crystal structure. At room temperature, the compound exhibits an intense blue emission at 432 nm upon 323 nm excitation in the solid state. The simple EL device with the configuration of ITO/I+PMMA/Ag was fabricated, where the compound (I) was used as a main emitting material. The EL device fabricated had a maximum brightness of 289 cd m⁻². The thermal stability of the compound was also investigated by thermogravimetric analysis (TGA).

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

An ongoing interest over the past two decades has been expressed in developing all-organic light-emitting devices as alternatives to inorganic based systems. Organic small molecules [1–3] and light-emitting polymers [4,5] have potential advantages not only in lower synthetic costs, but most importantly, organic lightemitting device (OLED) materials have been shown to be amenable to large scale-up, high efficiencies, simple and inexpensive fabrication routes to achieve the device [6–8]. Because blue-emitting materials should have a large enough energy gap and many blueemitting materials reported actually emitted blue-green light in their devices, which was induced by their wide emission ranges, bright and stable blue-emitting materials with high color purity are limited. Several efficient UV molecular host materials integrated with suitable blue-emitting dopants have been developed [9]. Recently, many researchers have tried to come up with ultimate, nondoped hosts by utilizing the derivatives of bistriphenylenyl [10] and diarylfluorene/spirobifluorene [11]. The heterocyclic molecules have received much attention for their strong electronwithdrawing capabilities, comparatively better chemical, thermal and photochemical stabilities and excellent fluorescence properties [12–15]. A number of 8-hydroxyquinoline derivatives have been synthesized for the purpose of color tuning and better device performance. In all cases the emission of 8-hydroxyquinoline derivatives has been attributed to the π – π * transitions in 8hydroxyquinoline ligand. The highest occupied molecular orbital (HOMO) is mostly located on phenoxide ring while lowest unoccupied molecular orbital (LUMO) on pyridyl ring [16].

At present report, we describe the synthesis, molecular structure and luminescent property of the 9-hydroxyl-3-hydroxyethyl-2-methyl-4H-pyrido[1,2-a]pyrimidin-4-one. The thermal stability of the title compound was also evaluated.

2. Experimental procedure

2.1. Physical measurements

Elemental analyses (C, H and N) were carried out on a Perkin-Elmer 240C analytical instrument. IR spectra were recorded on a Nicolet 170SX FT-IR spectrophotometer with KBr pellets in the 4000–400 cm⁻¹ region. Fluorescent spectra were measured on an Edinburgh Instruments analyzer model FL920. The TGA was carried out on a Shimadzu thermogravimetric analyzer in dry nitrogen atmosphere and heating rate of 10 °C/min using the TA-50 WS1 program.

^{*} Corresponding author. Tel.: +86 25 52090614. *E-mail address:* chmsunbw@seu.edu.cn (B. Sun).

^{1386-1425/\$ –} see front matter $\ensuremath{\mathbb{C}}$ 2010 Elsevier B.V. All rights reserved. doi:10.1016/j.saa.2010.02.036



Scheme 1.

2.2. Materials

The starting materials were purchased commercially and used without further purification.

2.3. Synthesis and crystal growth

The synthesis route of the title compound was expressed in Scheme 1. A suspension of 2-amino-3-hydroxypyridine (4.4 g, 0.04 mol), 2-acetylbutyrolactone (6.5 g, 0.05 mol), *p*toluenesulfonic acid monohydrate (0.23 g, 1.2 mmol) in 50 ml chlorobenzene was heated to reflux for 20 h. The reaction solution was allowed to cool slowly to room temperature. The light yellow solid was collected by filtration and dried in vacuum. Yield: 0.51 g, 84%. ¹H NMR (DMSO-*d*₆, ppm): 10.46 (1H, phenolic), 8.63–8.71 (2H, aromatic), 7.20–7.36 (1H, aromatic), 4.72 (1H, –CH₂OH), 2.19(2H, –*CH*₂), 2.89(3H, –*CH*₃), 3.52 (2H, –*CH*₂OH). Element analysis Calcd. (%) for C₁₁H₁₂N₂O₃: C 60.02, H 5.47, N 12.73; Found: C 60.01, H 5.49, N 12.81. IR (KBr, cm⁻¹); 3530 (–OH stretching); 3055 (C–H stretching, aromatic); 2984 (C–H stretching of methyl); 1735 (C=O stretching); 1605 (C=N stretching); 1510, 1472 (C=C stretching, aromatic); 1278 (O–H deformation). MS (*m*/*e*): 219.1[M⁺].

The solution growth technique is widely employed to grow single crystals of organic compounds. In order to select the suitable solvent for crystal growth, the solubility of title organic compound, in different solvents such as methanol, ethanol, 2-propanol, acetonitrile, chlorobenzene and ethyl acetate was measured. The solubility of title compound in different solvents was assessed as a function of temperature in the range 25–60 °C. The saturated solution was allowed to reach the equilibrium in about 24 h at a chosen temperature, and then the solubility was gravimetrically analyzed. The same process was repeated for different temperatures, and the solubility curve was obtained. The typical solubility curves of the title organic compound in 2-propanol, acetonitrile and chlorobenzene are shown in Fig. 1. The title compound exhibits good solubility and a positive solubility–temperature gradient in 2-



Fig. 1. Solubility of (I) in different solvents.

propanol. The title compound crystals were grown from saturated 2-propanol solution at 30 °C by slow evaporation technique.

2.4. Single crystal X-ray diffraction

Suitable crystal of title compound was selected and subjected to single crystal X-ray structure solution studies. Intensity data were collected at 293(2)K on a Siemens SMART-CCD diffractometer with graphite monochromatic MoK_a radiation (λ = 0.7107 Å). Data reductions and absorption corrections were performed with the SAINT and SADABS software packages, respectively. The structures were solved by direct methods using SHELXS-97 and were refined by full-matrix least-squares methods using SHELXL-97 [17]. Anisotropic displacement parameters were refined for all nonhydrogen atoms except for the disordered atoms. The hydrogen atoms except for those of water molecules were generated geometrically and refined using a riding model. The crystallographic data and structure refinement of (I) are stacked in Table 1.

2.5. Fabrication of organic electroluminescent (EL) devices (OLEDs)

The simple EL device with the structure of ITO/I + PMMA/Ag was fabricated under clean-room conditions in a nitrogen atmosphere inside a glove box ($[O_2]$, $[H_2O] < 1$ ppm) by using indium tin oxide (ITO)-coated glass substrates (sheet resistance = $30 \Omega/sq$) that were first cleaned with detergents and deionized water, dried in an oven at 120 °C for 4 h and then treated in an UV-ozone reactor. The electroluminescent layer consisted of I as the main component, mixed with 25% (w/w) poly(methyl methacrylate) (PMMA) to improve film formation and stability [18]. The layer was spin-coated at

Table 1

Crystal data and structure refinement for (I).

Empirical formula	$C_{11}H_{12}N_2O_3$
Formula weight	220.23
Temperature	298(2)K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, $P2_1/n$
Unit cell dimensions	$a = 11.1111(11)$ Å, $\alpha = 90.00^{\circ}$,
	$b = 6.8032(7)$ Å, $\beta = 96.0720(10)^{\circ}$,
	$c = 13.3625(15)$ Å, $\gamma = 90.00^{\circ}$
Volume	1004.42(18)Å ³
Z, calculated density	4, 1.456 Mg/m ³
Absorption coefficient	$0.108 \mathrm{mm^{-1}}$
F(000)	464
Crystal size	$0.4mm \times 0.3mm \times 0.27mm$
Theta range for data collection	2.27–25.01°
Limiting indices	<i>−</i> 8 <i><h<</i> 13, <i>−</i> 8 <i><k<</i> 7, <i>−</i> 15 <i><l<</i> 15
Reflections collected/unique	4710/1724[<i>R</i> (int)=0.0436]
Completeness to theta	25.01, 97.8%
Max. and min. transmission	0.9715 and 0.9582
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	1724/0/145
Goodness-of-fit on F_2^{\wedge}	1.047
Final R indices [I > 2sigma(I)]	R1 = 0.0934, wR2 = 0.2612
R indices (all data)	R1 = 0.1224, wR2 = 0.2870
Largest diff. peak and hole	0.720 and -0.353e Å ⁻³



Fig. 2. A view of (I) molecule showing displacement ellipsoids at the 50% probability level and H atoms as a sphere of arbitrary radii.

5000 rpm from DMSO solution on the ITO-coated glass substrates and volatilizing the solvent in a vacuum oven yielding a final thickness of about 250 nm. Prior to spin-coating the solutions were dried with molecular sieves and filtered. Ag, as the top electrode, was applied by vacuum evaporation through a mask at an evaporation rate of $5 \text{ Å} \text{ s}^{-1}$ to yield a final thickness of 100 nm. The emission area of the devices was 15 mm^2 as determined by the overlap area of the anode and the cathode. The EL spectra were measured using a PR650 spectra colorimeter. The current–density–voltage and brightness-voltage curves of the devices were measured using a Keithley 2400 source meter and a calibrated silicon photodiode. All the experiments and measurements were carried out at room temperature under ambient conditions.

3. Results and discussion

3.1. Infrared spectra

The FT-IR analysis of (I) was carried out to investigate the presence of functional group and their vibrational modes, which is summarized in Table 2. The importance of hydrogen bonding in the packing of (I) molecules in the crystal lattice is greatly evident by the broadened envelope due to phenolic stretch around 3530 cm^{-1} . The aromatic C–H stretching shows a signal at 3055 cm^{-1} . The bands at 2916 and 2525 cm^{-1} are due to the O–H stretching of the hydroxyethyl group involved in intramolecular hydrogen bonding. The presence of C=O stretching is indicated by the peak at 1735 cm^{-1} . The C=C stretching vibrations of the aromatic ring skeleton are observed by the two bands at 1510 and 1472 cm⁻¹. The intense peak at C–N stretch is observed at 1402 cm⁻¹. From this spectroscopic investigation, the grown crystal was deciphered qualitatively to be the title compound.

fable 2		
T-IR spectral data of	(\mathbf{I})	١.

Assignments
Phenolic O–H stretching
Aliphatic O–H stretching
Aromatic C–H stretching
Aliphatic C–H stretching
C=O stretching
C=N stretching
Aromatic C=C stretching
C–N–C stretching
Aromatic C-H out of plane bending
C–N wagging

Table 3

Selected torsion angles	[°]	for	(I)
-------------------------	-----	-----	----	---

O(3)-C(9)-C(10)-C(2)	-173.1(3)
C(3)-C(2)-C(10)-C(9)	-93.2(5)
C(1)-C(2)-C(10)-C(9)	86.3(5)

Table 4 Selected bond lengths (Å) in (I).	
N(1) C(2)	1

N(1)-C(8)	1.374(6)
N(1)-C(4)	1.383(6)
N(1)-C(1)	1.440(5)
N(2)-C(4)	1.330(6)
N(2)-C(3)	1.352(5)
O(1)-C(1)	1.246(5)
O(2)-C(5)	1.338(5)

3.2. Crystal structure of the title compound

The asymmetric unit of the crystal is illustrated in Fig. 2, the two conjugated rings are almost co-planar with an dihedral angle of only about 1.621(130)°. The values of torsion angles around the bonds C10-C9 and C10-C2, where free rotation can occur, determine the molecule's shape (Table 3). Fig. 2 shows the hydroxyethyl group is out of the pyrido[1,2-a]pyrimidine plane, where the hydroxyl group is in *trans* position to the pyrido[1,2alpyrimidine heterocyclic moiety. The C-N bond lengths of the pyrido[1,2-a]pyrimidine heterocyclic moiety are in the range of 1.330(6)-1.440(5)Å. The N(2)-C(4) bonds are shorter than the remaining four C-N bonds within pyrido[1,2-a]pyrimidine heterocyclic moiety (Table 4). This can be ascribed to the double N(2)-C(4) bond. The O(1)-C(1) bond with a distance of 1.246(5)Å is shorter than the O(2)-C(5) bond (1.338(5)Å) and O(3)-C(9) bond (1.422(6) Å) (Table 4), which is due to the double O(1)–C(1) bond (Fig. 3).

There are significant intermolecular hydrogen bond interactions in the solid state of title compound (I) involving the O-H···O (O2-O1=2.599(4)Å, O3-O2=3.025(5)Å) and O-H···N



Fig. 3. A view of the 1D chain in the compound along *b*-axis. All do not take part in H-bond H atoms are omitted for clarity.



Fig. 4. A view of the 2D chain in the compound along b-axis. All do not take part in H-bond H atoms are omitted for clarity.

(O3-N2=3.085(6)Å), which makes the whole compound forming one-dimensional chains. Two neighbouring chains interact via the weak C-H···O hydrogen bonds (C7-O3 distance 3.286(6)Å, (CHO=156.329(282)°) connecting the C7H7 moiety of one molecule to the O3 of the neighbouring one into two-dimension sheets (Fig. 4). Furthermore, the 2D sheets are extended into a 3D supramolecular framework via the face-to-face stacking interactions between conjugated rings of pyrido[1,2-a]pyrimidine heterocyclic moiety (Fig. 5). All hydrogen bond parameters are listed in Table 5.

3.3. Optical property of the compound

3.3.1. UV-vis absorption and fluorescence emission spectrum

The luminescent properties including absorption and fluorescent characteristics of (I) in ethanol solution $(2 \times 10^{-5} \text{ mol/L})$ have been studied. The solution of compound exhibits an absorp-



Fig. 5. View of the crystal packing of (I). Dashed lines represent the N-H···O, O-H···O and C-H···O hydrogen bonding that stabilize the 3D structure.

tion maximum at 338 nm (Fig. 6). The absorption bands in the 250–380 nm range can be assigned to intramolecule $(\pi - \pi^*)$ transitions. Upon irradiation by UV-light at room temperature, the compound solution shows a deep blue emission with a peak at 403 nm. In the solid state, the compound shows broad emission bands at 432 nm, which is red-shifted from the solution emission

Table 5

Hydrogen bonds for (I) [Å and $^{\circ}$].

D−H···A	d(D-H)	$d(H \cdot \cdot \cdot A)$	$d(D \cdots A)$	<dha< th=""></dha<>
$\begin{array}{c} 02 - H2 \cdots 01^{a} \\ 03 - H3 \cdots N2^{b} \\ 03 - H3 \cdots 02^{b} \end{array}$	0.820 0.820 0.820	1.820 2.376 2.434	2.599 3.085 3.026	158.15 145.07 129.87

$$x + 1/2, -y + 1/2, z + 1/2$$

^b x - 1/2, y + 1/2, z - 1/2.



Fig. 6. UV-vis absorption of (**I**) in ethanol at room temperature. Insert: The emission spectra of the compound in the solid state (red line) and in ethanol (blue line) with excitation at 323 nm and 283 nm at room temperature. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of the article.)



Fig. 7. Fluorescence spectra of (I) in ethanol solution with different concentrations.

spectra. As revealed by the crystal packing diagram of (I), the aromatic π - π interactions of the pyrido[1,2-a]pymidine moieties in the solid state should be responsible for the observed low-energy solid-state emissions.

3.3.2. Effects of concentration on photoluminescence

The fluorescence spectra of (I) in ethanol solution at different concentrations were measured and shown in Fig. 7. It can be seen that the concentration of (I) in low concentration 1.0×10^{-5} mol/L, the maximal fluorescence emission is at 403 nm, which exhibits only one emission band and its spectrum as 'a' shown. On progressive increase in concentration of compound, the fluorescence intensity of compound decreases obviously, which is ascribed to quench efficiently.

3.3.3. Effects of solvent on photoluminescence

The investigation on the interaction between the compound molecules and the solvents was helpful to understand the optical property of the compound and apply it to small molecule organic light-emitting diodes (SMOLEDs). The interaction between them in diluted solutions is examined by fluorescence spectrophotometry. The emission spectra of (I) in different solvents with the same concentration $(2.0 \times 10^{-5} \text{ mol/L})$, including ethanol, DMF and DMSO and the results are shown in Fig. 8. It can be seen from Fig. 8 that the compound exhibited a very similar PL emission behavior in DMSO and ethanol and the dominant signal is observed



Fig. 8. The emission spectra of (I) in different solvents.



Fig. 9. EL at different values of voltages for the device.

around 400 nm. However, the PL emission behavior of (I) in DMF is significantly different from that in DMSO or ethanol. In DMF, the fluorescence spectrum of (I) shows emission maxima around 435 nm and displays a quite change as a function of the solvent polarity. Meanwhile, the emission intensity of (I) is varying with the surrounding medium. The greatest emission intensity in ethanol is observed, while there is least emission intensity in DMSO. This may be attributed to charge transfer between compound and solvent in excited states. Further research toward a better understanding of this action is currently in progress.

3.3.4. Electroluminescence characteristics

To study the electroluminescence characteristics, a regulated voltage supply with current limitation was connected to the ITO (positive) and silver (negative) electrodes and the voltage was raised until electroluminescent appeared. The color emitted by the fabricated device was blue with an EL peak at 453 nm (Fig. 9), which indicates clearly that the emission at 453 nm is from the title compound used as light-emitting material in OLEDs fabrication. Though EL and PL spectra exhibited similar emitting patterns, the EL maximum peak position shifted about 21 nm with respect to its PL peak at 432 nm in solid state. The results also showed that some interaction occurs at the interface between the title organic compound (I) and the PMMA in the EL device structure. The electroluminescence (EL) intensity of the device increased with increase in voltage from 8 V to 14 V as shown in Fig. 9.

The representative luminance–voltage curve and the current intensity–voltage curve of device containing the synthesized title



Fig. 10. Current-voltage curve and luminance-voltage curve of the EL device.



Fig. 11. TGA/DTA curve of (I) crystal.

organic compound are shown in Fig. 10. The turn-on voltage of the device was 9 V, where turn-on voltage was taken as the voltage required in achieving the luminance of 1 cd m⁻². Current intensity and the luminance increased with the increase of bias voltage. The blue light emitted from the EL device had a maximum brightness of 289 cd m⁻² at 16 V.

3.4. Thermal properties of the compound crystal

Fig. 11 shows the thermal properties of (I) crystal carried out by TGA and DTA. The DTA curve of (I) shows an endothermic peak at 151.4 °C, which can be attributed to the melting point of the sample. The (I) melting point of 151 °C is confirmed by direct observation using MONOTECH melting apparatus. There is a gradual weight loss from 151 to 170 °C due to evaporation. The steep weight loss around 190 °C is due to the boiling of the melt. The boiling of the melt is confirmed by direct observation. The final residue weight left was about 4% after heating beyond 210 °C.

4. Conclusion

The 9-hydroxyl-3-hydroxyethyl-2-methyl-4H-pyrido[1,2a]pyrimidin-4-one was synthesized and its single crystals structure was confirmed by X-ray diffraction analysis. X-ray investigations show that the aromatic rings of (I), which adopt a *trans* configuration about the hydroxyethyl group are nearly co-planar. A significant intermolecular interaction is noted, involving O-H···O, O-H···N, C-H···O and π - π stacking, such that a three-dimensional feature is formed. At room temperature, the organic material exhibits a deep blue emission at 432 nm upon 323 nm excitation in solid state. The compound (I) was employed as an emitting component in fabricating OLEDs that had emission peak at 453 nm with a maximum brightness of 289 cd m^{-2} . The compound (I) is stable up to $190 \,^{\circ}$ C. The performance of the fabricated device was not very good at brightness but it is supposed to improve by some optimizations in the device parameters, which will be our further investigation.

Supplementary material

The crystallographic data have been deposited at the Cambridge Crystallographic Data Center (CCDC 740893). Copies of this information may be obtained free of charge from: CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgements

The present work was supported by the National Natural Science Foundation of China (No. 20671019). The authors thank the Order Material Central of Southeast University for supporting this work.

References

- [1] L.S. Huang, C.H. Chen, Mater. Sci. Eng. R 39 (2002) 143-222.
- [2] C.T. Chen, Chem. Mater. 16 (2004) 4389-4400.
- [3] Y. Wei, C.T. Chen, J. Am. Chem. Soc. 129 (2007) 7478–7479.
 [4] J.H. Burroughes, D.D.C. Bradley, A.R. Brown, R.N. Marks, K. Mackay, R.H. Friend,
- P.L. Burns, A.B. Holmes, Nature 347 (1990) 539–541.
- [5] R. Pudzich, T. Fuhrmann-Lieker, J. Salbeck, Adv. Polym. Sci. 199 (2006) 83– 142.
- [6] U. Mitschke, P. Bauerle, J. Mater. Chem. 10 (2000) 1471-1507.
- [7] L. Akcelrud, Prog. Polym. Sci. 28 (2003) 875–962.
- [8] A. Misra, P. Kumar, M.N. Kamalasanan, S. Chandra, Semiconductor Sci. Technol. 21 (2006) R35–R47.
- [9] J.R. Gong, L.J. Wan, S.B. Lei, C.L. Bai, X.H. Zhang, S.T. Lee, J. Phys. Chem. B 109 (2005) 1675–1682.
- [10] H.T. Shih, C.H. Lin, H.H. Shih, C.H. Cheng, Adv. Mater. 14 (2002) 1409–1412.
- [11] S. Tao, Z. Peng, X. Zhang, P. Wang, C.S. Lee, S.T. Lee, Adv. Funct. Mater. 15 (2005) 1716–1721.
- [12] G.S. He, J. Swiatkiewicz, Y. Jiang, P.N. Prasad, B.A. Reinhardt, L.S. Tan, R. Kannan, J. Phys. Chem. A 104 (2000) 4805–4810.
- [13] R. Kannan, G.S. He, L. Yuan, F. Xu, P.N. Prasad, A.G. Dombroskie, B.A. Reinhardt, J.W. Baur, R.A. Vaia, L.S. Tan, Chem. Mater. 13 (2001) 1896–1904.
- [14] K.D. Belfield, A.R. Morales, B.S. Kang, J.M. Hales, D.J. Hagan, E.W.V. Stryland, V.M. Chapela, J. Percino, Chem. Mater. 16 (2004) 4634–4641.
- [15] P. Shao, B. Huang, L. Chen, Z. Liu, J. Qin, H. Gong, S. Ding, Q. Wang, J. Mater. Chem. (2005) 4502–4506.
- [16] A. Curioni, W. Andreoni, IBM J. Res. Dev. 45 (2001) 101–114.
- [17] G.M. Sheldrick, Acta Crystallogr. Sect. A: Found. Crystallogr. 64(2008)112-122.
- [18] H. Rudmann, M.F. Rubner, J. Appl. Phys. 90 (2001) 4338–4345.