

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy



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

Synthesis and luminescent properties and theoretical investigation on electronic structure of nitrile-based 2-pyridone molecules

Liuqing Chen^{a,b}, Xuguang Liu^{a,c,*}, Bingshe Xu^{a,b}, Chunyan Sun^{a,c}, Peng Tao^{a,b}

^a Key Laboratory of Interface Science and Engineering in Advanced Materials, Taiyuan University of Technology, Ministry of Education, Taiyuan 030024, China

^b The College of Materials Science and Engineering, Taiyuan University of Technology, Taiyuan 030024, China

^c The College of Chemistry and Chemical Engineering, Taiyuan University of Technology, Taiyuan 030024, China

ARTICLE INFO

Article history: Received 8 February 2011 Received in revised form 22 May 2011 Accepted 25 May 2011

Keywords: Pyridine Synthesis Electronic structure OLED

1. Introduction

Organic fluorescent heterocyclic chromophores have a wide range of applications in, for example, traditional textile coloration, molecular probes [1], organic light-emitting diodes (OLED) [2], photovoltaic cells [3], and mass coloration of polymers [4]. 2-Pyridone is such an organic N-heterocyclic compound, its derivatives are also the key intermediates in the synthesis of the corresponding pyridine, quinoline, quinolizidine and indolizidine alkaloids [5]. Milrinone and their analogues which have 2-pyridone moiety are used as cardiotonic agents for the treatment of heart failure [6]. Owing to their luminescent and immense biological properties, substituted 2-pyridone derivatives are catching much interest in the development of simple and convenient methodologies for the synthesis from easily available starting materials [7]. Many synthesis methods of 2-pyrone have been reported to date [8], e.g. oxidation of a N-substituted pyridinium salt [9], and Knovenagel-type reactions [10] such as cyclocondensation of ketene dithioacetals with compounds containing active methylene group like cyanoacetamide. Most of earlier reported methods for the synthesis of 2-pyridones involving the condensation of 1,3binucleophiles with cyanoacetamide need strong bases like sodium hydride, sodium hydroxide or alkoxides [11]. Mathews et al. used ammonium acetate/acetic acid medium to synthesize 2-pyridones [12]. One of the most important methods for the synthesis of

ABSTRACT

3-Cyano-4,6-dimethyl-2-pyridone and 3-cyano-4-methyl-6-phenyl-2-pyridone were synthesized effectively by the reaction of readily available 1,3-diketone and malononitrile directly and in good yield. Upon photoexcitation, 3-cyano-4-methyl-6-phenyl-2-pyridone in ethanol shows strong blue emission. The ground- and excited-state geometries, charge distributions, and excitation energies of 2-pyridone derivatives were evaluated by ab initio calculations. Organic light-emitting diodes (OLED) made using 3-cyano-4-methyl-6-phenyl-2-pyridone as dopant showed blue light emission with a maximum electroluminescence (EL) emission at around 456 nm.

© 2011 Elsevier B.V. All rights reserved.

2-pyridones involves Guareschi–Thorpe condensation of cyanoacetoamide and 1,3-diketone compounds with basic catalysts, and scope of such reactions was well established [13]. Despite the large number of existing synthesis methods, new procedures for 2-pyridones are continuously being developed [14].

2. Experimental

2.1. Characterization methods

¹H NMR (300 MHz) spectra were obtained using a Brucker spectrometer. Chemical shift δ was calibrated against TMS as an internal standard. FT-IR data were collected on a Brucker spectrometer. Differential scanning calorimetry (DSC) was carried out using a PerkinElmer thermogravimeter under a dry nitrogen gas flow at a heating rate of 10 °C/min. Crystal data were obtained with graphine monochromated Cu K α radiation ($\lambda = 0.71073$ Å) on a Smart chargecoupled device (CCD) X-ray diffractometer. The structure was solved by direct method with SHELXL 97 program and refined with full-matrix least-squares methods. The absorption and fluorescence spectra were recorded using a Lambda Bio 40 UV-vis spectrophotometer and an LS-50B fluorescence spectrophotometer, respectively. Elemental analyses were carried out with a VarioIII analyzer. Oxidation potential (E_0^{ox}) and reduction potential (E_{0}^{red}) were measured directly by cyclic voltammetry (Autolab/PG STAT302). To understand the ground- and excited-state electronic properties of chromophore 1 and 2, density functional theory (DFT) as well as time-dependent DFT (TD-DFT) calculations were performed with the B3LYP functional and 6-31g** basis set, using

^{*} Corresponding author. Tel.: +86 351 6014138; fax: +86 351 6010311. *E-mail address:* liuxuguang@tyut.edu.cn (X. Liu).

^{1386-1425/\$ -} see front matter © 2011 Elsevier B.V. All rights reserved. doi:10.1016/j.saa.2011.05.092

Gaussian(R) 03 program. Ground state and excited state were calculated for HOMO(LUMO) and absorption spectra, respectively. For compound **1**, 30 states have been calculated, while 10 states for **2**. The organic EL devices were fabricated on a glass substrate coated with ITO (30Ω /square) in a vacuum of 2×10^{-4} Pa, and the ITO surface was ultrasonicated in a detergent solution followed by deionzed water rinse and dip into acetone. The evaporating rates were kept at 0.1–0.2 nm/s for organic layers, 0.1 nm/s for LiF and 1 nm/s for Al in the same vacuum run.

2.2. Reagents and solvents

All reagents and solvents were commercially available and used without further purification.

2.3. Preparation of compounds

2.3.1. Preparation of 3-cyano-4,6-dimethyl-2-pyridone (1)

Hexamethyldisilazane 1.84g (0.012 mol) was added to acetic acid (14 ml) and acetylacetone 1.20 g (0.012 mol) at an appropriate rate to maintain the internal temperature at 70 °C. The HMDS and acetic acid mixture was added to a solution of acetylacetone 1.20 g (0.012 mol) and malononitrile 3.17 g (0.048 mol) in acetic acid (14 ml). After 3 h, the mixture was cooled to ambient temperature and washed four times with water. And the residue was isolated by crystallization in CH₃CN. Yield 85%. Compound 1 was characterized by ¹H NMR and ¹³C NMR, IR spectroscopy and elemental analysis. Assignment of NMR spectra was possible using ¹H–¹³C COSY. ¹H NMR (300 MHz, DMSO-d₆), δ (ppm): 12.30(s,1H, -NH), 6.15(s, 1H, -CH), 2.50 (s, 3H, 6-CH₃), 2.21(d, 3H, 3-CH₃). ¹³C NMR (75 MHz, DMSO- d_6), δ (ppm): 162.5(C^1), 161.9(C^3), 152.7(C^5), 117.6(C⁶), 108.9(C⁴), 100.6(C²), 22.1(C⁸), 20.4(C⁷). Anal. calcd. for C₈H₈N₂O (%): C, 64.85; H, 5.44; N, 18.91. Found: C, 64.86; H, 5.41; N, 18.91. Infrared spectra of 1: FTIR (KBr, cm⁻¹): 2894, 3017, 2210, 1677, 1472, 1376, 1335, 1212, 1130, 925, 829, 775, 720, 624, 542, 474.

2.3.2. 3-Cyano-4-methyl-6-phenyl-2-pyridone (2)

Hexamethyldisilazane 0.92 g (0.006 mol) was added to acetic acid (7 ml) and benzoylacetone 0.97 g (0.006 mol) at an appropriate rate to maintain the internal temperature at 70 °C. The HMDS and acetic acid mixture was added to a solution of benzoylacetone 0.97g (0.006 mol) and malononitrile 1.58g (0.024 mol) in acetic acid (7 ml). After 3 h, the mixture was cooled to ambient temperature and washed four times with water. And the residue was subjected to crystallization in CH₃CN. Yield 75.7%. Compound 2 was characterized by ¹H NMR and ¹³C NMR, IR spectroscopy and elemental analysis. Assignment of NMR spectra was possible using ¹H–¹³C COSY. ¹H NMR (300 MHz, DMSO-d₆), δ (ppm): 12.55(s, 1H, -NH), 7.78-7.54(m, 5H, H-Ph), 6.74(s, CH), 2.42(s, 3H. $-CH_3$). ¹³C NMR (75 MHz, DMSO-d₆), δ (ppm): 162.9(C¹¹). 161.8(C⁹), 152.0(C⁷), 133.7(C⁶), 132.6(C³), 130.5(C¹, C⁵), 129.0 (C², C⁴), 117.5 (C¹²), 108.6 (C⁸), 102.3 (C¹⁰), 22.4 (C¹³). Anal. calcd. for C₁₃H₁₀N₂O (%): C, 74.27; H, 4.79; N, 13.33. Found: C, 73.59; H, 4.83; N, 13.20. Infrared spectra of 2: FTIR (KBr, cm⁻¹): 2969, 2929, 2275, 1634, 1392, 1320, 1215, 992, 940, 888, 711, 574.

3. Results and discussion

3.1. General considerations

The reaction of malonitrile with 1,3-diketones to afford 2pyridones is well known [15], and very mild reaction conditions are also known. But in past reports, pyridone and methoxypyridine are formed in the presence of Et_3N and MeOH. We present here a facile way to prepare novel nitrile-based 2-pyridones (Scheme 1)



Scheme 1. Reaction of 1,3-diketone with malononitrile.

that are potential candidate for application in organic electronics under mild reaction conditions. Nitrile-based 2-pyridone molecules 3-cyano-4,6-dimethyl-2-pyridine (1) and 3-cyano-4-methyl-6-phenyl-2-pyridone (2) were synthesized in moderate to good yields (75–90%) by a one-step condensation of acetylacetone or benzoylacetone with malononitrile in refluxing acetic acid in the presence of weak base hexamethyldisilazane (Scheme 1). The IR absorptions of the C=O stretching bands were observed at around 1656 and 1634 cm⁻¹ for 1 and 2, respectively. These red-shifted values relative to free carbonyl stretching frequency may reflect the effect of the hydrogen bond. The NMR signal of the NH protons at a low field of δ = 12.30 and 12.55 ppm, observable for 1 and 2, also indicates the presence of hydrogen bonds. Some structural characteristics of 1 and 2 were compared in Table 1.

3.2. X-ray structures

Their structures were also confirmed by single-crystal X-ray analysis (Fig. 1 for **1** and Fig. 2 for **2**). In the crystal structure of **1** and **2**, two molecules are arranged in close proximity to each other, so that intermolecular hydrogen bonds of the N–H…O type are formed between the pyridines, which seem to be typical of 2-pyridones. A summary of the refinement details and the resulting factors is given in Table 2. The N–H…O hydrogen bond distances are 1.886(9) Å and 1.851(15) Å for **1** and **2**, respectively, and the corresponding N–H…O angles are approximately 173.1(12)° and 174.8°, respectively (see Table 1).

3.3. Spectroscopy

The UV–vis spectrum of the chromophore **1** recorded in ethanol shows strong absorption bands at around 327 nm and between 200 and 300 nm at the concentration of 1×10^{-5} mol/L. Absorption band of **1** between 200 and 300 nm is assigned to pyridine ring π – π^* electron transition, while 327 nm is assigned to carbonyl n– π^* electron transition. With excitation of 291 nm, **1** shows blue fluorescence with emission maximum at 375 nm and a high quantum yield of 70.9% (using quinine sulphate as standard [15]) while the Stokes shift amounts to 7698 cm⁻¹ (Stokes shift = $1/\lambda_{ex} - 1/\lambda_{em}$). Furthermore, the fluorescence–excitation spectrum (measured at 375 nm emission wavelength) agrees well with the corresponding absorption profile. On the other hand, chromophore **2** absorbs at 250 nm and 357 nm at the concentration of 1×10^{-5} mol/L, as shown

Table 1	
Some structural characteristics of 1 and 2 .	

		Compound 1	Compound 2
N—H·…O	Bond distance	1.886(9)Å	1.851(15)Å
	Bond angles	173.1(12)°	174.8°
IR _(C=O)		1656 cm ⁻¹	1634 cm ⁻¹
¹ H NMR _(NH)		12.30 ppm	12.55 ppm
Boiling point		290°C	313°C



Fig. 1. X-ray crystal structure and the overall packing diagram of 1 (ORTEP, thermal ellipsoids set at the 50% probability level). Selected bond lengths [Å]: O(1)–C(1) 1.2495(15), N(1)–C(5) 1.3619(16), N(1)–C(1) 1.3779(15), N(1)–H(1) 0.995(16), N(2)–C(6) 1.1497(15), C(4)–C(5) 1.3691(17), C(2)–C(3) 1.3865(18), C(3)–C(7) 1.5003(16).



Fig. 2. X-ray crystal structure and the overall packing diagram of **2** (ORTEP, thermal ellipsoids set at the 50% probability level). Selected bond lengths [Å]: O(1)–C(11) 1.2450(13), N(1)–C(7) 1.3678(15), N(1)–C(11) 1.3806(14), N(1)–H(1A) 0.921(9), C(1)–C(2) 1.3835(16), C(6)–C(7) 1.4800(16), C(7)–C(8) 1.3686(16), C(12)–N(2) 1.1492(14).



Fig. 3. Electronic absorption together with the calculated oscillator strength (a) and fluorescence (b) spectra of **1** (λ_{ex} = 291 nm, λ_{em} = 378 nm); electronic absorption together with the calculated oscillator strength (c) and fluorescence (d) spectra of **2** (λ_{ex} = 391 nm, λ_{em} = 430 nm) in EtOH solution.



Fig. 4. Molecular orbitals of 1 and 2 that are involved in the S_0-S_1 and S_0-S_2 transitions.

Table 2Crystallographic data of **1** and **2**.

	1	2
Empirical formula	$C_8H_8N_2O$	C ₁₃ H ₁₀ N ₂ O
fw	148.16	210.23
Cryst syst	Triclinic	Monoclinic
Space group	P-1	P2[1]/n
a, Å	3.9049(8)	12.8513(3)
<i>b</i> , Å	7.3288(15)	7.0586(14)
<i>c</i> , Å	12.694(3)	13.042(6)
$\alpha, \gamma, \beta, (^{\circ})$	77.09(3), 89.16(3),	$\alpha = \gamma = 90.00$,
	89.40(3)	120.31(2)
<i>V</i> , Å ³	354.06(12)	1021.3(6)
Ζ	2	4
F(000)	156	440
D (calcd.), mg cm ⁻³	1.390	1.367
λ, Å	0.71073	0.71073
Temperature, K	143(2)	113(2)
2θ range (°)	1.65-25.01	3.41-25.02
Final R indices	<i>R</i> 1 = 0.0324,	R1 = 0.0351,
$[I > 2\sigma(I)]$	wR2 = 0.0903	wR2 = 0.0960
R indices (all data)	<i>R</i> 1 = 0.0413,	R1 = 0.0410,
	wR2 = 0.0942	wR2 = 0.0998
Goodness-of-fit on F^2	1.003	1.062

in Fig. 3. Upon UV excitation at 391 nm, chromophore **2** shows an intensive blue fluorescence with emission peak maximum at 430 nm and a high quantum yield of 88.3% (using quinine sulphate as standard). Compared with chromophore **1**, chromophore **2** shows a shifted emission of about 52 nm to longer wavelengths. Optical properties of **1** and **2** were list in Table 3. Such a behavior indicates that the incorporation of benzene segment to pyridone frame changed the optical properties of chromophore **2** and increased the effective conjugation length.

3.4. Computational studies

For **1**, the vertical TD-DFT calculation predicts the S_0-S_1 excitation to be carbonyl $n-\pi^*$ transition (*f*=0.19) at 306 nm

Table 3

	Materials	Units	1	2
Optical properties	Abs (EtOH) ^a $E_{\rm m}$ (EtOH) ^b $E_{\rm m}$ (SF) ^c $\varphi_{\rm f}^{\rm d}$	λ _{max} (nm) %	223 375 395 70.9	357 430 547 88.3

^a Absorption in EtOH.

^b Emission in EtOH.

^c Emission in solid film.

^d Fluorescence quantum efficiency, relative to quinine sulphate in H_2SO_4 ($\varphi_f = 55\%$).

(4.06 eV), as shown with the stick spectrum in Fig. 3(a). Both the transition energy and intensity are in very good agreement with the longest wavelength absorption (327 nm), for which the 281–366 nm energy-integrated absorption also yields an oscillator strength of f=0.19. The S₀–S₂ excitation is predicted to be a π – π * transition at 223 nm, with an oscillator strength of f=0.023. For **2**, the S₀–S₁ excitation to be an intense n– π * transition (f=0.36) at 341 nm (3.65 eV), as shown with the stick spectrum in Fig. 3(c). Both the transition energy and intensity are in very good agreement with the longest wavelength absorption (357 nm), for which the 284–414 nm energy-integrated absorption yields an oscillator strength of f=0.48. The S₀–S₂ excitation is predicted to be a π – π * transition at 247 nm, with an oscillator strength of f=0.20. This is in excellent agreement with the second UV absorption band observed at 250 nm with intensity similar to the S₀–S₁ band.

According to the TD-DFT calculation, the S_0-S_1 electronic excitation of **1** is dominated by the HOMO–LUMO contribution (80%). As Fig. 4 shows, this corresponds partially to a n-electron flow from the carbonyl O atom toward the pyridine ring, where electron density spreads toward the methyl group. The S_0-S_2 transition is mainly dominated by the one-electron excitation from HOMO-2 to the LUMO (52%). On the other hand, the S_0-S_1 electronic excitation of **2** is dominated by the HOMO–LUMO contribution (82%). As Fig. 4 shows, this corresponds partially to a n-electron flow from the carbonyl O atom toward the benzene and pyridine ring, where electron density spreads toward the methyl group. The S_0-S_2 transition is mainly dominated by the one-electron excitation from HOMO-3 to the LUMO (72%). This transition moves π -electron density from the C–O bonding π orbital into the benzene ring and carbonitrile.

3.5. Form-filming ability

Forming homogeneous and stable amorphous film by thermal evaporation is a basic requirement for the application in OLEDs as electronic material. Fig. 5 shows two dimensional AFM micrographs taken for 2 films (about 500 Å thickness) deposited on quartz substrates by thermal evaporation in vacuum chamber at 5×10^{-4} Pa. The root-mean-square roughness of **2** obtained by conducting section analyses was about 1.877 nm. Such quantitative values indicate that **2** formed a more uniform and flatter molecular film, which is required for OLED materials.

3.6. Energy gap

The emission color of the organic materials is a function of HOMO–LUMO energy gap (E_g) of luminescent molecule. The features of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of **2** are presented



Fig. 5. Two-dimensional AFM images for the 4.0 $\mu m \times 4.0 \ \mu m$ 2 thin films.



Fig. 6. PL of **2** powder and EL spectra (device structure: ITO/NPB (50 nm)/CBP: **2** (6%) (20 nm)/Bphen (20 nm)/LiF (1 nm)/Al (100 nm)).

in Fig. 4. The HOMO density is mostly located on the pyridine site. Accordingly, the LUMO density can be found at the pyridine and benzene rings. The empirical values of $E_{\rm HOMO}$ or $E_{\rm LUMO}$ can be obtained by cyclic voltammetry, which is one of the simplest and most practical methods to give much information needed to reveal the electronic structures of materials. The values of $E_{\rm o}^{\rm ox}$, $E_{\rm o}^{\rm red}$ are 1.38 V and -1.24 V, respectively. Therefore, $E_{\rm HOMO}$ is -6.12 eV, and $E_{\rm LUMO}$ is -3.50 eV in terms of Eq. (1) [16] below the vacuum energy level. $E_{\rm g}$ is calculated to be 2.62 eV as $E_{\rm g} = E_{\rm LUMO} - E_{\rm HOMO}$.

$$E_{\text{HOMO}}\left(or E_{\text{LUMO}}\right) = -4.74 - eE_{0}^{\text{ox}}\left(or E_{0}^{\text{red}}\right) \tag{1}$$

The calculated values of E_{HOMO} , E_{LUMO} and E_{g} are -6.12 eV, -3.50 eV and 2.62 eV, respectively.

3.7. EL property

In this study, an EL device was fabricated using NPB as holetransporting layers, and BPhen as electron-transporting layers, CBP: **2** (6%) as an emitting layer, ITO as anode, and LiF/Al as cathode to form a structure of ITO/NPB(50 nm)/CBP: **2** (6%) (20 nm)/Bphen (20 nm)/LiF (1 nm)/Al (100 nm). PL of powder and EL spectra of device of **2** were measured. PL and EL spectra can be seen in Fig. 6. PL emission maximum is located at 546 nm and maximum value of EL emission is 456 nm, EL spectrum has a very big blue shift of 90 nm. The CIE coordinates for the device based on **2** are X = 0.2071, Y = 0.2061.

4. Conclusion

In summary, a convenient and brief synthesis route for polysubstituted pyridine, highly functionalized with 4,6-disubstituted group flanked by one carbonitrile substituent has been proposed. Remarkably, this efficient one-pot procedure provides a new and straightforward entry to the regioselective formation of polysubstituted pyridine. The formation of **1** and **2** is explained by the Knoevenagel condensation reaction of ketone followed by cyclization reaction. Moreover, it is noteworthy that **1** and **2** have promising topology and functionality as useful substrates for conjugate additions, thereby further generating molecular diversity and functionality. Apart from this, the device designed as ITO/NPB(50 nm)/CBP: **2** (6%) (20 nm)/Bphen (20 nm)/LiF (1 nm)/Al (100 nm) emits blue light emission with a maximum EL emission at around 456 nm.

Acknowledgements

The authors acknowledge financial support from Program for Changjiang Scholar and Innovative Research Team in University (IRT0972), National Natural Science Foundation of China (20971094, 20671068, 60976018) and Research Fund for Returned Scholars (2008-31), Natural Science Foundation of Shanxi Province (2010021023-2, 2008011008). The authors thank professor Hao Yuying, College of science of Taiyuan University of Technology, for GAUSSIAN 03 calculations.

References

- G. Rao, S.B. Bambot, S.C.W. Kwong, H. Szmacinsk, J. Sipior, R. Holavanahali, G. Carter, in: J.R. Lakowicz (Ed.), Applications of Fluorescence Sensing to Bioreactors, Plenum Press, New York, 1994, pp. 501–521.
- [2] L.Q. Chen, P. Tao, C.Y. Sun, X.G. Liu, B.S. Xu, Synth. Met. 161 (2011) 1145–1149.
- [3] GYu, J. Gao, J.C. Hummelen, F. Wudl, A.J. Heeger, Science 270 (1995) 1789-1791.
- [4] H. Gold, in: K. Venkataraman (Ed.), In the Chemistry of Synthetic Dyes, Aca
 - demic Press, New York, 1971, pp. 535–679.
 [5] R. Fujita, K. Watanabe, W. Ikeura, Y. Ohtake, H. Hongo, Heterocycles 53 (2000) 2607–2610.
 - [6] E.L. Presti, R. Boggia, A. Feltrin, G. Menozzi, P. Dorigo, L. Mosti, Farmaco 54 (1999) 465–474.
 - [7] T.J. Donohoe, L.P. Fishlock, P.A. Procopiou, Org. Lett. 10 (2008) 285-288.
 - [8] J. Staunton, in: P.G. Sammes (Ed.), Comprehensive Organic Chemistry, vol. 4, Pergamon Press, Oxford, 1979, pp. 629–646.
- [9] H. Mohrle, H. Weber, Tetrahedron 26 (1970) 2953–2958.
- [10] V.P. Litvinov, Russ. Chem. Rev. 68 (1999) 737–763.
- [11] M. Nitta, T. Sakakida, H. Miyabara, H. Yamamoto, S. Naya, Org. Biomol. Chem. 3 (2005) 638-644.
- [12] A. Mathews, E.R. Anabha, K.A. Sasikala, K.C. Lathesh, K.U. Krishnaraj, K.N. Sreedevi, M. Prasanth, K.S. Devaky, C.V. Asokan, Tetrahedron 64 (2008) 1671–1675.
- [13] V.R. Rybakov, A.A. Bush, E.B. Babaev, L.A. Aslanov, Acta Crystallogr. E E60 (2004) 0160-0161.
- [14] L. Ghosez, E. Jnoff, Ph. Bayard, F. Sainte, R. Beaudegnies, Tetrahedron 55 (1999) 3387–3400.
- [15] Y.X. Ci, X. Jia, Chin. J. Anal. Chem. 14 (8) (1986) 616-617.
- [16] Y.S. Yao, J. Xiao, X.S. Wang, Z.B. Deng, B.W. Zhang, Adv. Funct. Mater. 16 (2006) 709.