Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 117 (2014) 614–621

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

Synthesis, spectroscopic and DFT studies of novel fluorescent dyes: 3-Aminoimidazo[1,2-a]pyridines possessing 4-pyrone moieties

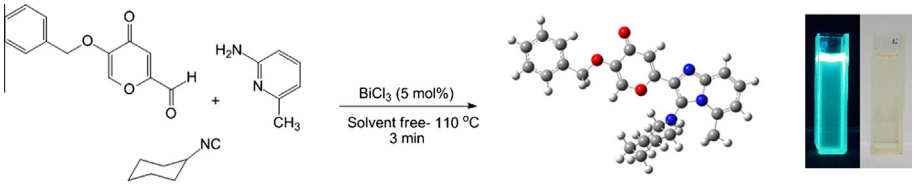
Aziz Shahrisa *, Kazem Dindar Safa, Somayeh Esmati

Department of Organic and Biochemistry, Faculty of Chemistry, University of Tabriz, Tabriz 5166614766, Iran

HIGHLIGHTS

- New bis-heterocyclic compounds were synthesized using GBB multicomponent reaction.
- UV–Vis absorption and fluorescence emission spectra, TGA and CV of compounds were studied.
- Two of these novel compounds showed high fluorescence emissions.
- Optimized molecular geometries and orbital distributions were calculated using DFT.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 8 April 2013
Received in revised form 4 August 2013
Accepted 7 September 2013
Available online 19 September 2013

Keywords:
Multicomponent reactions
4-Pyrone derivatives
UV–Vis spectra
Fluorescence
Density functional theory (DFT)

ABSTRACT

A series of novel imidazo[1,2-a]pyridines possessing 4-pyrone ring were synthesized by three-component condensation of 4-pyrone carbaldehydes, 2-aminopyridines and isocyanides. Bismuth (III) chloride was used as a catalyst in these reactions and desired products were synthesized in good yields at a very short period of time under solvent free conditions. UV–Vis absorption and fluorescence emission spectra of these compounds were investigated. It shown that two of these compounds (**10f** and **10g**) exhibit intense fluorescence in dichloromethane. Optimized ground-state molecular geometries and orbital distributions of these two fluorescent dyes were obtained using density functional theory (DFT). Thermogravimetric analysis and electrochemical properties of these compounds were also studied.

Introduction

Design and synthesis of novel organic fluorescent compounds is one of interesting and active areas in the organic chemistry. Fluorescent dyes have wide applications in the biological labels, photovoltaic cells, light emitting diodes (LEDs), optical sensors, materials for collecting solar energy, fluorescent films for greenhouses, fluorescent colorants and etc [1–15]. In the last decade synthesis of various organic compounds via multicomponent reactions (MCRs) have attracted a great interest, because most of these reactions are simple, one-pot, fast and high yielding [16–21]. Therefore synthesis of fluorescent compounds via MCRs is so favorable and there are some reports on the use of MCRs for the synthesis of fluorescent dyes [22,23].

One of isocyanide based multicomponent reaction (IMCR) is Groebke–Blackburn–Bienaymé multicomponent reaction (GBB MCR) [24–26] in which three-component condensation of aldehyde, isocyanide and 2-aminoazine enables synthesis of imidazo[1,2-a]azines. Compounds containing imidazo[1,2-a]azine ring system have been shown to possess a broad range of useful pharmacological and biological properties [27–29]. Moreover in the recent years fluorescence properties of these compounds have also been investigated [30].

On the other hand, pyran-containing fluorescent dyes are an important class of organic light emitting diodes (OLEDs) and also have been used in dye lasers, sensors, dye-sensitized solar cells (DSSCs), fluorescent probes, logic gates and optical chemosensors

* Corresponding author. Tel.: +98 411 339 3118; fax: +98 411 334 0191.
E-mail address: ashahrisa@yahoo.com (A. Shahrisa).

1386-1425/$ - see front matter © 2013 Published by Elsevier B.V.
http://dx.doi.org/10.1016/j.saa.2013.09.056

[31–39]. Most of these compounds are dicyanomethylene pyran derivatives and the fluorescence properties of 4*H*-pyran-4-ones are rarely investigated.

Because of the wide applicability of these types of compounds, the synthesis and studies of their chemical and photophysical properties is an interesting research field. Therefore, as a part of our ongoing interest in the multicomponent reactions and synthesis of novel derivatives of 4-pyrones [40–43], in this investigation we used GBB MCR for the synthesis of novel 3-aminoimidazo[1,2-a]pyridines possessing 4-pyrones by three-component reaction of aldehydes, isocyanides and 2-aminopyridines catalyzed by $BiCl_3$ under solvent free conditions and then UV–Vis absorption spectra, fluorescence emission spectra, DFT structure optimization, thermogravimetric analysis and electrochemical properties of these compounds were also studied.

Experiments

General

Melting points were determined with a MEL-TEMP model 1202D and are uncorrected. FT-IR spectra were recorded on a Bruker Tensor 27 spectrometer as KBr disks. The ^{1}H NMR spectra were recorded with a Bruker Spectrospin Avance 400 spectrometer with $CDCl_3$ as solvent and TMS as internal standard. ^{13}C NMR spectra were determined on the same instrument at 100 MHz. All chemical shifts were reported as δ (ppm) and coupling constants (*J*) are given in Hz. UV–Vis spectra were recorded on analytikjena SPECORD 250 spectrometer. Fluorescence spectra were obtained on a Jasco FP-750 spectrofluorometer. The fluorescence quantum yields (Φ_f) were determined in CH_2Cl_2 dilute solutions by using quinine sulfate (Φ_s = 0.546 in 0.05 M H_2SO_4) as standard. Calculations are done by Eq. (1), where Φ_f is the fluorescence quantum yield of the sample, Φ_s the fluorescence quantum yield of the standard, *F* and F_S are the areas under the fluorescence emission curves of the samples and the standard, respectively. *A* and A_S are the relative absorbance of the samples and standard at the excitation wavelength, respectively. η and η_s are the refractive indices of solvents for the sample and standard, respectively [44]:

$$\Phi_f = \Phi_s(F/F_s)(A_s/A)(\eta/\eta_s)^2 \quad (1)$$

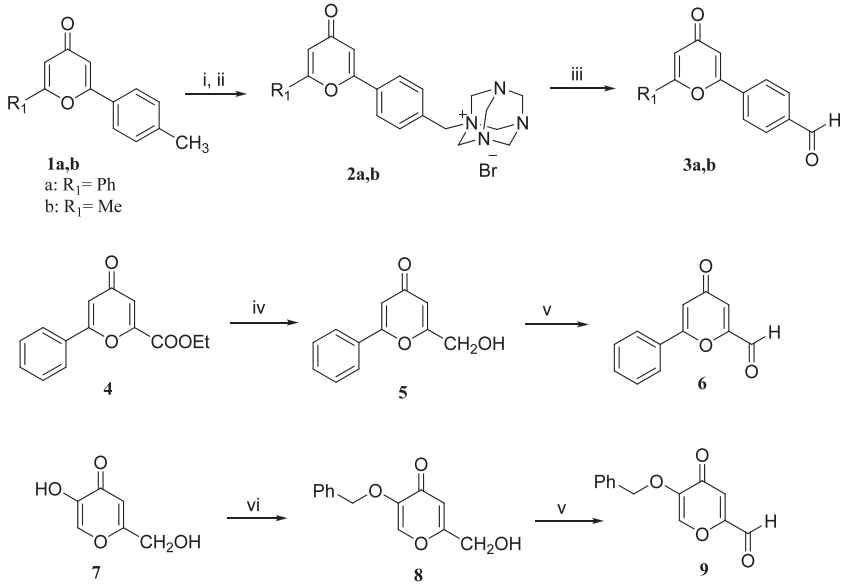
Thermogravimetric analysis (TGA) was conducted under nitrogen at a heating rate of 10 °C min^{-1} with a TGA/SDTA851 (Mettler Toledo) from 50 °C to 600 °C under 20 ml min^{-1} of argon flow. Electrochemical experiments were performed using Autolab PGSTAT 30 electrochemical analyzer system and GPES 4.9 software package (Eco Chemie, The Netherlands). The utilized three-electrode cell was composed of a glassy carbon electrode with 2 mm diameter as the working electrode, a platinum wire as auxiliary electrode, and SCE (saturated calomel electrode) as reference electrode (0.01 M $AgNO_3$) in CH_2Cl_2 solution (10^{-3} mol L^{-1}) in the presence of $TBAPF_6$ (tetrabutylammonium hexafluorophosphate) (0.10 mol L^{-1}) as supporting electrolyte. Mass spectra (MS) were measured by a Shimadzo (70 eV) spectrometer and elementary analyses (C,H,N) were performed on a Vario EL III analyzer. Thin-layer chromatography was done with prepared glass-backed plates (20 × 20 cm^2, 500 μ) using silica gel (Merk Kieselgel 60 HF_{254}, Art. 7739). The chemical reagents used in synthesis were purchased from Merck and Sigma–Aldrich CO. Synthetic details and characterizations of compounds **3a**, **6** and **9** are given in Supplementary material.

General procedure for the synthesis of 3-aminoimidazo[1,2-a]pyridines *10a–g*

To a mixture of 4-pyrone carbaldehyde (0.5 mmol), 2-aminopyridine or 2-amino-6-methyl pyridine (0.5 mmol) and isocyanide (0.5 mmol) was added $BiCl_3$ (5 mol%) and the reaction mixture was stirred on a preheated oil bath at 110 °C. After completion of the reaction (monitored by TLC), the crude residue was either treated with ethyl acetate/n-hexane (1:3) to afford the product as a precipitate, or was subjected to silica gel preparative layer chromatography (ethyl acetate: n-hexane; 1:3).

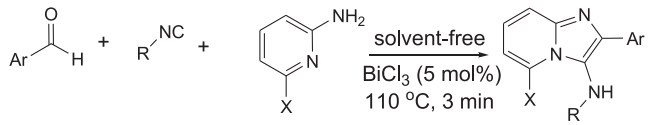
2-[4-(3-(Cyclohexylamino)imidazo[1,2-a]pyridin-2-yl)phenyl]-6-phenyl-4H-pyran-4-one (*10a*)

Yellow solid. Yield: 97%. M.p: 180–182 °C. FT-IR (KBr): 3249 (N—H), 3072 (aromatic C—H), 2924 (aliphatic C—H), 1646 (pyrone C=O). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.19–1.90 (m, 10H); 3.04 (m, 1H); 3.17 (bs, 1H); 6.82–6.87 (m, 2H); 6.90 (d, *J* = 2 Hz, 1H); 7.18–7.22 (m, 1H); 7.55–7.59 (m, 4H); 7.88–7.94 (m, 2H); 7.97 (d, *J* = 8.4 Hz, 2H); 8.13 (d, *J* = 6.8, 1H); 8.31 (d, *J* = 8.4 Hz, 2H). ^{13}C

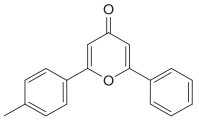
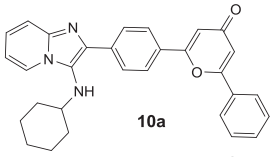
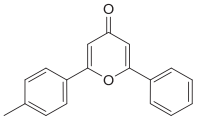
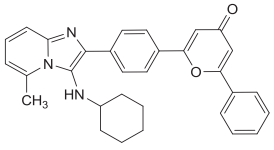
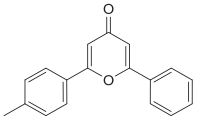
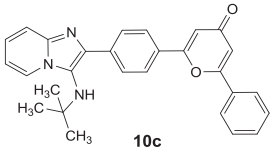
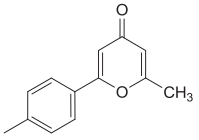
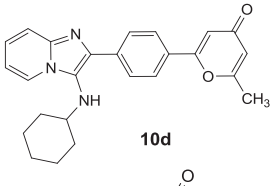
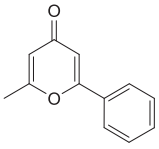
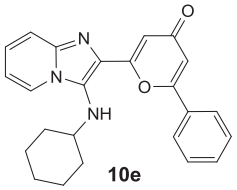
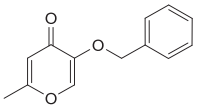
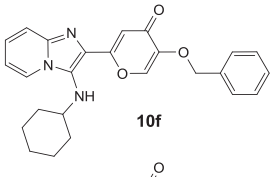
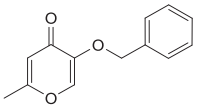
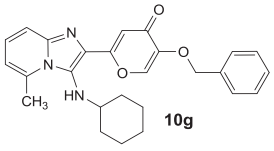


Scheme 1. Synthesis of 4-pyrone carbaldehydes. Reagents and conditions: (i) NBS, BPO, CCl_4, reflux, 48 h; (ii) HMTA, $CHCl_3$, reflux, 30 min; (iii) EtOH/H_2O (3:2), reflux, 24 h; (iv) $NaBH_4$ (4eq), MeOH, reflux, 3 h; (v) Active MnO_2 (8eq), CH_2Cl_2, rt., 3 days; and (vi) $PhCH_2Br$ (1eq), NaOH (1eq), MeOH/H_2O: 10/1, 60 °C, 4 h.

Table 1
Synthesis of 3-aminoimidazo[1,2-a]pyridines possessing 4-pyrones.



10a-g

Entry	Ar	R	X	Product	Yield (%)
1		Cyclohexyl	H	 **10a**	97
2		Cyclohexyl	CH_3	 **10b**	96
3		t-Butyl	H	 **10c**	94
4		Cyclohexyl	H	 **10d**	95
5		Cyclohexyl	H	 **10e**	75
6		Cyclohexyl	H	 **10f**	72
7		Cyclohexyl	CH_3	 **10g**	74

NMR (100 MHz, $CDCl_3$): δ 24.9; 25.7; 34.3; 57.1; 111.1; 111.5; 111.9; 117.7; 122.7; 124.4; 125.8; 126.0; 126.1; 127.4; 129.2; 129.8; 131.4; 131.6; 135.4; 137.9; 141.9; 163.3; 180.3. MS (m/z,%): 461 (M^+, 12), 385 (90), 303 (100), 275 (53), 250 (77), 157 (58), 102 (38), 78 (89). Anal. Calcd. For $C_{30}H_{27}N_3O_2$: C, 78.07; H, 5.90; N, 9.10; Found: C, 77.84; H, 5.92; N, 8.98%.

*2-(4-(3-(Cyclohexylamino)-5-methylimidazo[1,2-a]pyridin-2-yl)phenyl)-6-phenyl-4H-pyran-4-one (**10b**)*

Yellow solid. Yield: 96%. M.p: 184–186 °C. FT-IR (KBr): 3245 (N—H), 3068 (aromatic C—H), 2926 (aliphatic C—H), 1644 (pyrone C=O). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.09–1.73 (m, 10H); 2.83 (m, 1H); 2.97 (s, 3H); 3.16 (bs, 1H); 6.48 (d, *J* = 6.4 Hz, 1H); 6.84 (d, *J* = 2 Hz, 1H); 6.90 (d, *J* = 2 Hz, 1H); 7.04–7.08 (m, 1H); 7.45 (d, *J* = 9.2 Hz, 1H); 7.57–7.59 (m, 3H); 7.91–7.96 (m, 4H); 8.22 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.1; 24.9; 25.7; 33.3; 59.2; 111.1; 111.5; 113.9; 116.1; 124.7; 125.9; 126.0; 127.2; 128.2; 129.2; 129.8; 131.4; 131.6; 136.2; 137.7; 138.5; 143.6; 163.3; 180.3. MS (m/z, %): 475 (M^+, 3), 392 (9), 368 (11), 278 (31), 250 (68), 92 (74), 55 (100). Anal. Calcd. For $C_{31}H_{29}N_3O_2$: C, 78.29; H, 6.15; N, 8.84; Found: C, 77.97; H, 6.17; N, 8.76%.

*2-[4-(3-(tert-Butylamino)imidazo[1,2-a]pyridin-2-yl)phenyl]-6-phenyl-4H-pyran-4-one (**10c**)*

Yellow solid. Yield: 94%. M.p: 217–219 °C. FT-IR (KBr): 3238 (N—H), 3071 (aromatic C—H), 2925 (aliphatic C—H), 1642 (pyrone

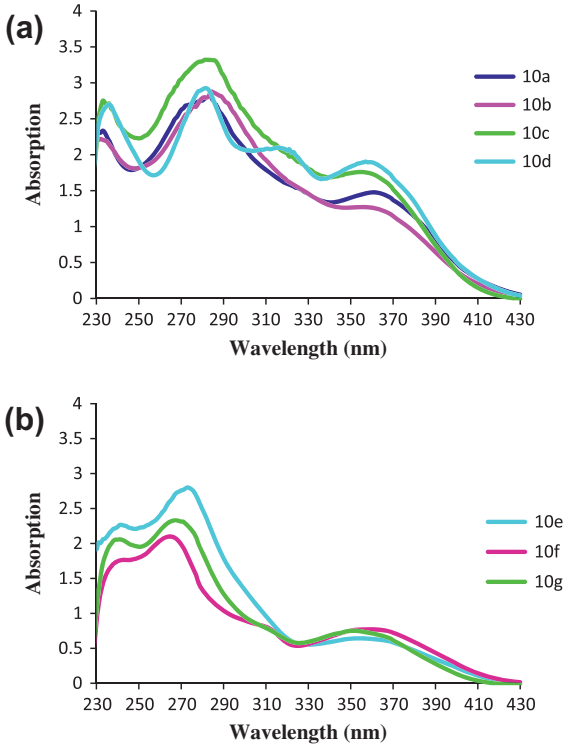


Fig. 1. (a) UV–Vis absorption spectra of **10a–d** and (b) **10e–g** (10^{-5} M) in CH_2Cl_2 at room temperature.

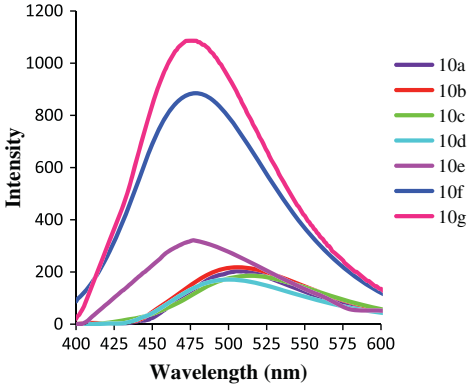


Fig. 2. The emission spectra of compounds **10a–g** (10^{-5} M) in CH_2Cl_2 at room temperature.

Table 2
Photophysical properties of compounds **10a–g**.

Compound	λ_{abs} (nm)	λ_{em} (nm)	$\Delta\nu_{st}$ (nm)	Φ_f[a]
10a	283, 359	508	149	0.028
10b	284, 356	506	150	0.032
10c	282, 355	515	160	0.024
10d	282, 357	500	143	0.019
10e	273, 353	475	122	0.082
10f	265, 357	478	121	0.209
10g	267, 352	476	124	0.231

[a] Measured in CH_2Cl_2 solution using quinine sulfate ($\Phi_s = 0.546$) as a standard at room temperature.

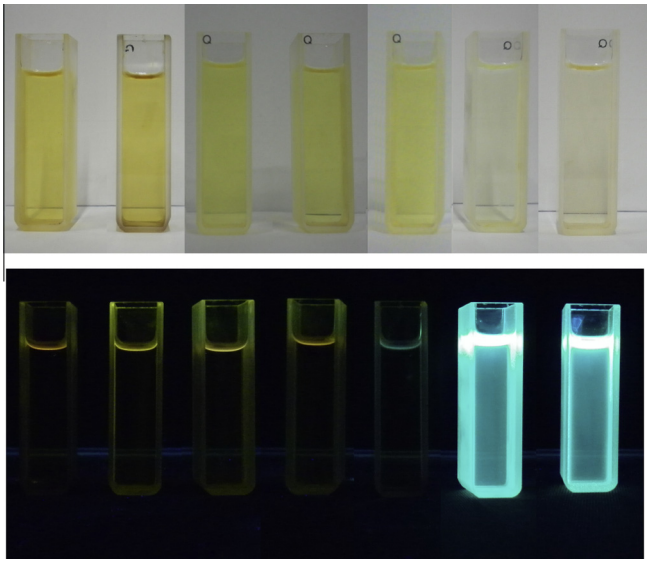


Fig. 3. Photographs of dyes **10a–g** (left to right) in daylight and long UV (365 nm).

C=O). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.09 (s, 9H); 3.13 (bs, 1H); 6.78–6.82 (m, 2H); 6.86 (s, 1H); 7.14–7.18 (m, 1H); 7.54–7.56 (m, 4H); 7.87–7.93 (m, 4H); 8.18–8.22 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 29.4; 55.6; 110.0; 110.4; 110.6; 116.5; 122.4; 123.2; 123.5; 124.7; 124.9; 127.5; 128.1; 128.8; 130.3; 130.5; 137.1; 137.6; 141.3; 162.2; 162.3; 179.2. MS (m/z, %): 435 (M^+, 28), 379 (100), 351 (80), 102 (16), 78 (92). Anal. Calcd. For $C_{28}H_{25}N_3O_2$: C, 77.22; H, 5.79; N, 9.65; Found: C, 77.14; H, 5.81; N, 9.59%.

*2-(4-(3-(Cyclohexylamino)imidazo[1,2-a]pyridin-2-yl)phenyl)-6-methyl-4H-pyran-4-one (**10d**)*

Yellow solid. Yield: 95%. M.p: 156–158 °C. FT-IR (KBr): 3251 (N—H), 3072 (aromatic C—H), 2928 (aliphatic C—H), 1659 (pyrone C=O). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.17–1.87 (m, 10H); 2.41 (s, 3H); 3.00 (m, 1H); 3.16 (bs, 1H); 6.19 (s, 1H); 6.77 (d, J = 2 Hz, 1H); 6.82 (t, J = 8 Hz, 1H); 7.18 (t, J = 8 Hz, 1H); 7.57 (d, J = 8 Hz, 1H); 7.85 (d, J = 8 Hz, 2H); 8.11 (d, J = 8 Hz, 1H); 8.24 (d, J = 8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.9; 24.9; 25.7; 34.3; 57.0; 110.4; 111.9; 114.3; 117.6; 122.7; 124.4; 125.8; 125.9; 127.3; 129.6; 135.3; 137.7; 141.9; 163.5; 165.4; 180.3. MS (m/z, %): 399 (M^+, 32), 316 (87), 289 (95), 92 (22), 78 (100). Anal. Calcd. For $C_{25}H_{25}N_3O_2$: C, 75.16; H, 6.31; N, 10.52; Found: C, 75.03; H, 6.35; N, 10.45%.

*2-[3-(Cyclohexylamino)imidazo[1,2-a]pyridin-2-yl]-6-phenyl-4H-pyran-4-one (**10e**)*

Pale yellow solid. Yield: 75%. M.p: 146 °C (decom.). FT-IR (KBr): 3382 (N—H), 3108 (aromatic C—H), 2926 (aliphatic C—H), 1647 (pyrone C=O). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.11–186 (m, 10H); 3.03 (m, 1H); 3.86 (d, J = 8 Hz, 1H); 6.78 (d, J = 2 Hz, 1H); 6.86 (t, J = 8 Hz, 1H); 7.17 (d, J = 2 Hz, 1H); 7.22 (t, J = 8 Hz, 1H); 7.56–7.58 (m, 4H); 7.82–7.88 (m, 2H); 8.06 (d, J = 8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.8; 25.5; 33.9; 56.9; 111.8; 112.6; 118.3; 123.2; 125.4; 126.1; 127.0; 129.2; 129.5; 131.4; 131.9; 142.1; 161.2; 163.2; 179.7. MS (m/z, %): 385 (M^+, 75), 303 (100), 275 (55), 157 (82), 105 (28), 78 (86). Anal. Calcd. For $C_{24}H_{23}N_3O_2$: C, 74.78; H, 6.01; N, 10.90; Found: C, 74.62; H, 6.06; N, 10.82%.

*5-(Benzyloxy)-2-[3-(cyclohexylamino)imidazo[1,2-a]pyridin-2-yl]-4H-pyran-4-one (**10f**)*

Pale yellow solid. Yield: 72%. M.p: 188–190 °C. FT-IR (KBr): 3311 (N—H), 3081 (aromatic C—H), 3036 (aromatic C—H), 2925

(aliphatic C—H), 2852 (C—H), 1634 (pyrone C=O). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.20–1.88 (m, 10H); 2.92 (m, 1H); 3.54 (d, *J* = 8 Hz, 1H); 5.15 (s, 2H); 6.82 (t, *J* = 6.8, 1H); 7.16–7.20 (m, 2H); 7.33–7.44 (m, 5H); 7.51 (d, *J* = 9.2 Hz, 1H); 7.60 (s, 1H); 7.99 (d, *J* = 6.8, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.9; 24.5; 33.2; 55.9; 70.9; 110.6; 111.5; 117.2; 122.0; 124.3; 126.9; 127.3; 127.6; 128.5; 134.8; 139.7; 140.9; 146.1; 159.2; 173.5. MS (m/z, %): 415 (M^+, 100), 332 (33), 242 (35), 91 (84). Anal. Calcd. For $C_{25}H_{25}N_3O_3$: C, 72.27; H, 6.06; N, 10.11; Found: C, 72.08; H, 6.14; N, 9.95%.

*5-(Benzyloxy)-2-(3-(cyclohexylamino)-5-methylimidazo[1,2-a]pyridin-2-yl)-4H-pyran-4-one (**10g**)*

Pale yellow solid. Yield: 74%. M.p: 190-192 °C, FT-IR (KBr): 3307 (N—H), 3080 (aromatic C—H), 2926 (aliphatic C—H), 2853 (C—H), 1631 (pyrone C=O). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.08–1.85 (m, 10H); 2.77 (m, 1H); 2.92 (s, 3H); 3.32 (d, *J* = 8 Hz, 1H); 5.18 (s, 2H); 6.48 (d, *J* = 6.8 Hz, 1H); 7.07 (dd, *J* = 6.8 Hz, *J* = 9.2 Hz, 1H); 7.19 (s, 1H); 7.33–7.42 (m, 4H); 7.45 (d, *J* = 7.2 Hz, 2H); 7.62 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.6, 25.3; 25.7; 33.2; 60.3; 72.1; 112.6; 114.4; 116.5; 125.7; 128.0; 128.4; 128.7; 129.7; 130.9; 135.9; 136.8; 141.0; 143.8; 147.2; 160.4; 174.6. MS (m/z,%): 429 (M^+, 59), 346 (70), 319 (26), 256 (57), 91 (100). Anal. Calcd. For $C_{26}H_{27}N_3O_3$: C, 72.71; H, 6.34; N, 9.78; Found: C, 72.48; H, 6.28; N, 9.73%.

Results and discussion

Synthesis

Recently we reported the synthesis of some 3-aminoimidazo[1,2-a]pyridines via $BiCl_3$ catalyzed GBB MCR [45]. As a part of our ongoing interest in the MCRs and synthesis of novel derivatives of 4-pyrones, we describe the synthesis of 3-aminoimidazo[1,2-a]pyridines possessing 4-pyrones by three-component reaction of 4-pyrone carbaldehydes, isocyanides and 2-aminopyridines catalyzed by $BiCl_3$ (5 mol%) under solvent free conditions. Therefore four 4-pyrone carbaldehydes were prepared and used in these investigations. The syntheses of 4-pyrone carbaldehydes **3a** and **3b** have been reported in our recent works [46]. As shown in Scheme 1 bromination of 4-pyrones **1** and **2** with *N*-bromosuccinimide (NBS) produced the corresponding bromopyrones which then reacted with hexamethylenetetramine (HMTA) in dry chloroform to afford hexaminium salts **2a**,**b**. Treatment of **2a**,**b** with

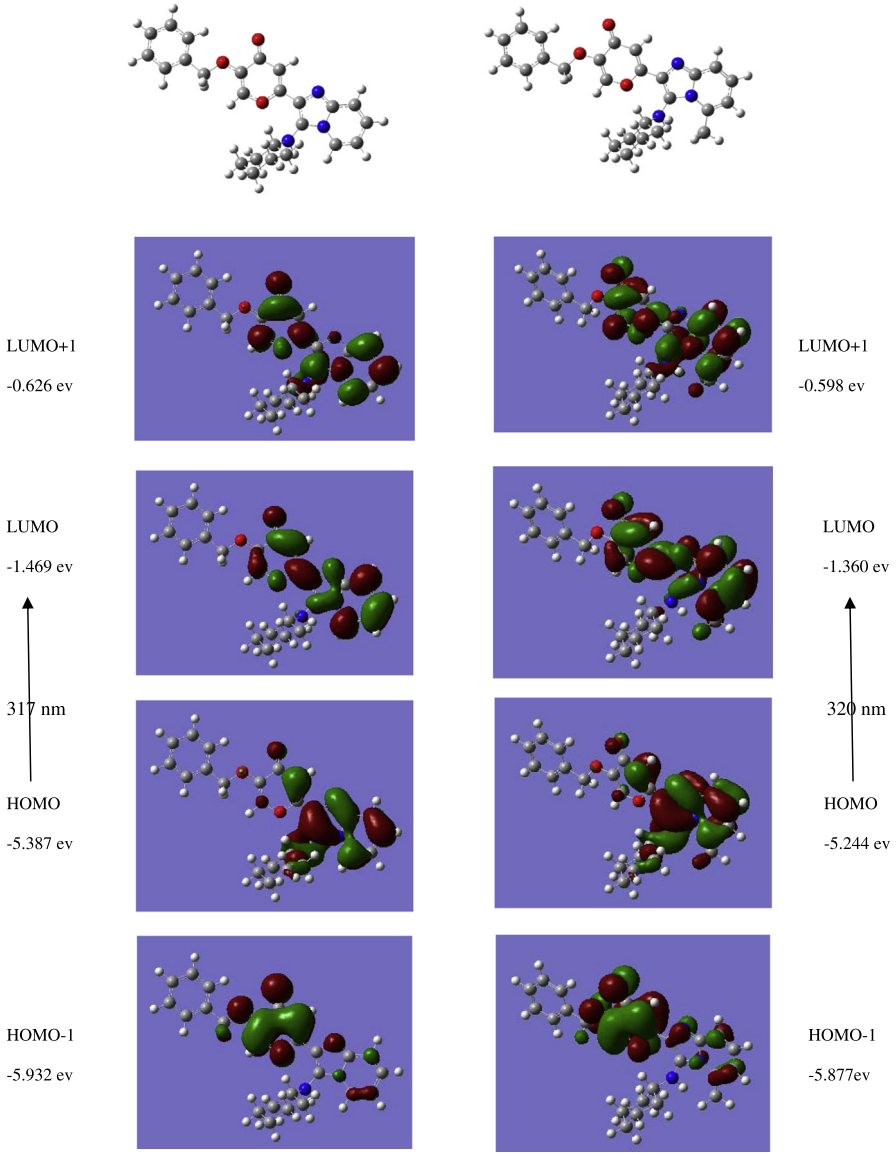


Fig. 4. Optimized ground-state geometry and calculated spatial distributions of the HOMO, LUMO levels of compounds **6** (left) and **7** (right) with B3LYP/6-31G*.

EtOH:H_2O (3:2) under reflux afforded the corresponding 4-pyrone carbaldehydes **3a**,**b**. Aldehyde **6** was synthesized from the corresponding ethoxycarbonyl derivative **4** according to the reported procedure [47]. Ester group was reduced to the corresponding alcohol with $NaBH_4$ and then oxidized to the aldehyde group using active MnO_2 to produce 4-pyrone carbaldehyde **6**. Aldehyde **9** was obtained from commercially available Kojic acid **7** by benzylation of phenolic OH [48], followed by oxidation of the hydroxymethyl group with active MnO_2. These 4-pyrone carbaldehydes were used in GBB MCRs and the corresponding derivatives **10a**–**g** were synthesized in good to high yields in a very short period of time (Table 1).

UV–Vis absorption and fluorescence emission spectra

The UV–Vis absorption spectra of all seven 3-aminoimidazo[1,2-a]pyridines possessing 4-pyrones were measured in CH_2Cl_2 solutions with a concentration of about 1.0×10^{-5} mol L^{-1} (Fig. 1). According to the structure pattern of these compounds we could investigate them at two groups. At compounds **10a**–**d** the 4-pyrone ring is connected to imidazo[1,2-a]pyridine via a *para*-phenylene group and at compounds **10e**–**g**, 4-pyrone is directly connected to imidazo[1,2-a]pyridine. Each group of these compounds exhibit similar UV–Vis absorption spectra. Compounds **10a**–**d** display intense absorption bands at about 283 nm that should be attributed to $\pi \rightarrow \pi^*$ type transitions and weak broad bands centered at about 356 nm which are attributed to $n \rightarrow \pi^*$ type transitions. The maximum UV–Vis absorptions of the compounds **10e**–**g** are located in the range of 265–273 nm, ascribed to the $\pi \rightarrow \pi^*$ type transition of the conjugated molecular backbone and broad bands in the 352–357 nm attributed to $n \rightarrow \pi^*$ type transitions. These similar absorption spectra are owing to their similar molecular structures. The maximum absorption peaks of compounds **10a**–**d** are relatively red-shifted in comparison with the absorption of compounds **10e**–**g** that can be attributed to more delocalized and extended π-conjugated systems in these compounds.

Furthermore, the fluorescence spectra of these compounds were investigated at room temperature in CH_2Cl_2 solutions. As shown in Fig. 2, fluorescence emission spectra of compounds **10a**–**g** with the excitation wavelength at 370 nm, exhibiting a blue to green fluorescence emission with the maximum emission peaks varying from 500 to 515 nm for compounds **10a**–**d** and 475–478 nm for compounds **10e**–**g**. The maximum emission band of compounds **10e**–**d** are blue shifted compared to compounds **10e**–**g**. Compounds **10f** and **10g** with 5-benzyloxy-4*H*-pyran-4-one moiety at imidazo[1,2-a]pyridine showed strong cyan emission compared with the other compounds.

The photophysical properties including absorption and emission maxima (λ_{abs} and λ_{em}), Stokes' shift ($\Delta\nu_{st}$) and fluorescence quantum yields (Φ_f) of the compounds **10a**–**g** were summarized in Table 2. Interestingly, compounds **10f** and **10g** showed high fluorescence quantum yields (Φ_f = 0.209 and 0.231) and relatively large Stokes shifts (about 120 nm) were observed for these two compounds. Photographs of dyes in daylight and under laboratory UV lamp (365 nm) are presented in Fig. 3.

Theoretical calculations

The geometrical structures and electronic configurations of the new dyes were examined using density functional theory (DFT) calculations with B3LYP functional and 6-31G* basis set on the compounds **10f** and **10g** with Gaussian03 program package [49]. The orbital distributions of HOMO-1, HOMO, LUMO and LUMO+1 for these two fluorescent dyes are shown in Fig. 4. It is obvious that both of the HOMO and LUMO of them localize at the 4-pyrone and imidazo[1,2-a]pyridine rings. The theoretical estimation of the HOMO–LUMO gaps for **10f** and **10g** are 3.918 eV (317 nm) and 3.884 eV (320 nm) respectively that are in good agreement with the measured UV–Vis bands (357 and 352 nm).

Thermal properties

Thermal stabilities of the organic dyes play an important role in the performance and lifetime of OLEDs during operation. The thermal properties of compounds **10a**–**g** were investigated by thermogravimetric analysis (TGA). As shown at the thermogravimetric curves in Fig. 5, these compounds demonstrated relatively high thermal stability. Compounds **10a**–**d** which decomposed at about 360–400 °C are more stable than compounds **10e**–**g**. Compound **10e** showed the least decomposition temperature (T_d) at 150 °C and compounds **10f** and **10g** with similar structures showed relatively similar TGA curves with T_d at about 300 °C.

Electrochemical properties

The electrochemical properties of compounds **10a**–**g** are explored by the cyclic voltammetry in the CH_2Cl_2 solutions in the presence of tetrabutylammonium hexafluorophosphate (0.10 mol L^{-1}) as the supporting electrolyte. Cyclic voltammogram of $\sim 10^{-3}$ M solutions of these compounds are shown in Fig. 6. Interestingly, similar voltammograms were obtained for the each group of compounds. It demonstrates that compounds with similar structures are oxidized at almost the same potential. Compound **10a**–**d** exhibited two oxidation peaks at about 0.5 and 1.2 V and two reduction peaks at about 0.2 and 1.0 V. The cyclic voltammogram of compound **10e** exhibited one cathodic peak at 1.2 V, without any anodic peak at reverse scan, indicating that the cathodic peak is an irreversible electron transfer processes. According to the molecular structure, compounds **10f** and **10g** showed similar

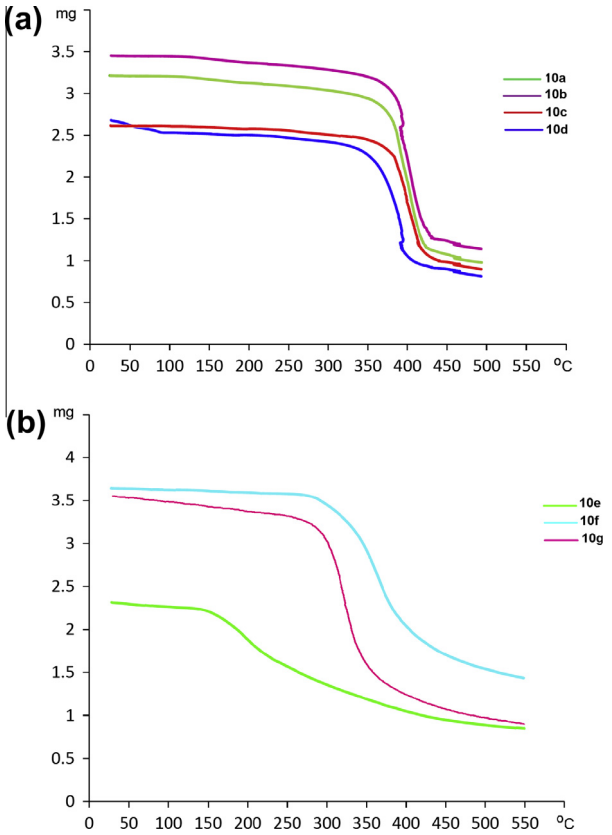


Fig. 5. Thermogravimetric analysis graph for (a) compound **10a**–**d** and (b) compound **10e**–**g**.

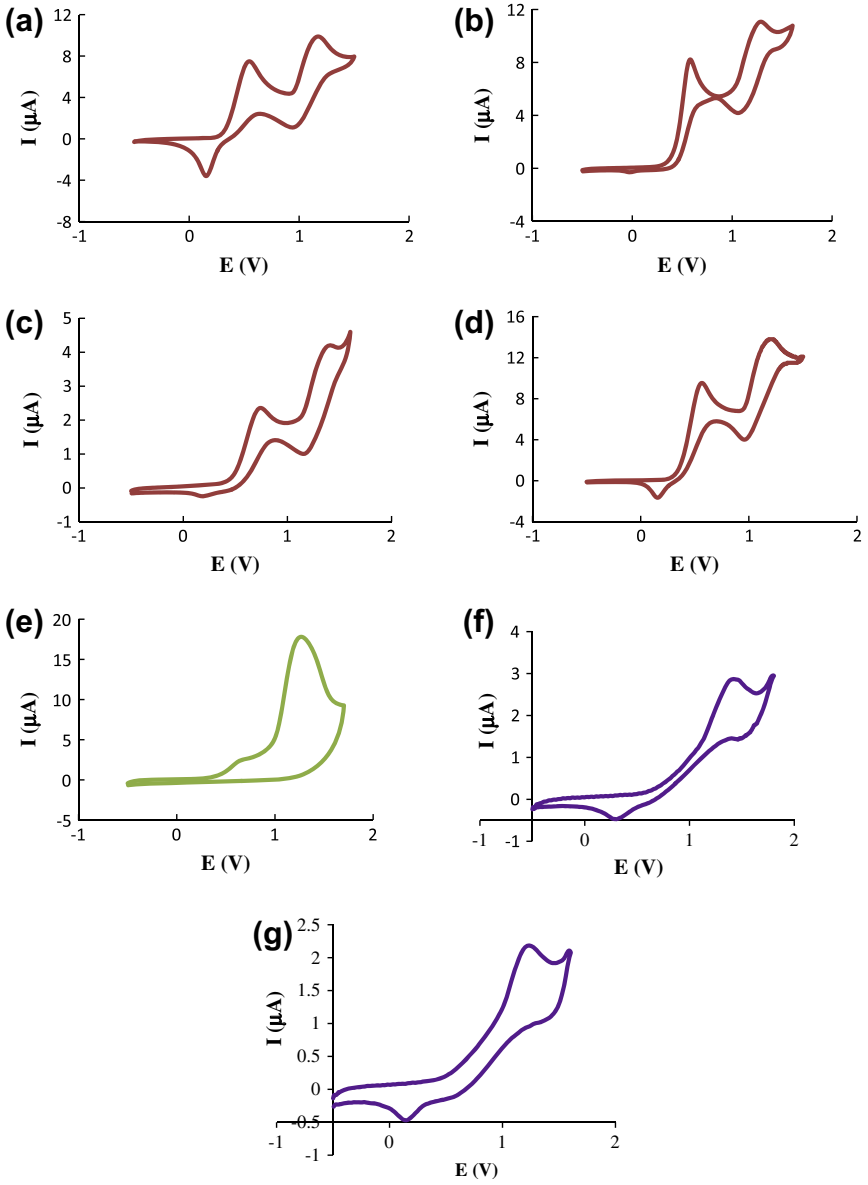


Fig. 6. Cyclic voltammogram of (a) compound **10a**, (b) compound **10b**, (c) compound **10c**, (d) compound **10d**, (e) compound **10e**, (f) compound **10f** and (g) compound **10g** (10^{-3} mol L^{-1}) in 0.1 mol L^{-1} Bu_4NPF_6–CH_2Cl_2, scan rate 50 mV/s.

voltammogram with one oxidation (at 1.42 and 1.24 V respectively) and one reduction peak (at 0.32 and 0.15 V respectively).

Conclusions

In conclusion, a novel series of 3-aminoimidazo[1,2-a]pyridines possessing 4-pyrones were designed and synthesized by three-component condensation of 4-pyrone carbaldehydes, 2-aminopyridines and isocyanides in the presence of bismuth chloride (5 mol%) under solvent free conditions. This method for synthesis of 3-aminoimidazo[1,2-a]pyridines offers several advantages including operational simplicity, short reaction times and high yields of products. The results obtained by the absorption and emission spectra of these compounds indicated that two of them (**10f** and **10g**) are highly fluorescent in CH_2Cl_2 and can be used as blue light emitting materials. The DFT calculations indicated that HOMO and LUMO of these compounds localize at the 4-pyrone and imidazo[1,2-a]pyridine rings and they possess a relatively high HOMO energy levels (−5.39 and −5.24 eV). The electrochemical properties of these compounds were also investigated. Thermogravimetric analysis (TGA) of compounds **10a–g** showed that these compounds have relatively high thermal stability.

Acknowledgments

The authors thank research affairs of the University of Tabriz for financial support. We also would like to thank Dr. Abolghasem Jouyban (Faculty of Pharmacy, Tabriz University of Medicinal Sciences) for his help in providing fluorescence emission spectra.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2013.09.056.

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