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ORIGINAL PAPER

Microwave-assisted solvent-free synthesis and luminescence properties of 2-substituted-4,5-di(2-furyl)-1*H*-imidazoles

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A solvent-free microwave-assisted method for the synthesis of 2-substituted-4,5-di(2-furyl)-1*H*-imidazoles was developed. Imidazoles with moderate to good yields were produced by condensation of furil with aldehydes over acidic alumina impregnated with ammonium acetate, and they were characterized by FT-IR, HRMS, ^{1}H NMR and ^{13}C NMR spectroscopy. Crystal structure of 2,4,5-tri-2-furyl-1*H*-imidazole (*I*) in the orthorhombic space group *Pbca* was reported, which showed more coplanarity than the reported crystal structure of *I* in the monoclinic space group *Cc*. Moreover, their luminescent properties were investigated. It was found that the organic small molecule compounds synthesized possess higher fluorescence quantum efficiency (up to 0.508) in a 0.1 M H_2SO_4 aqueous solution dissolved in 0.5 mL of CH_3OH; along with higher stability; also the emission of some compounds synthesized in the solution was sensitive to the polarity of the solvents.

Keywords: crystal structure, furil, luminescence property, microwave-assisted, 2-substituted-4,5-di(2-furyl)-1*H*-imidazole

Introduction

Imidazole derivatives play an important role in biochemistry (Bräse et al., 2002; Nicolaou et al., 2002; Chen et al., 2005; Costantino & Barlocco, 2006; Joshi & Viswanathan, 2006) as materials including luminescent (Zhao et al., 2006; Fang et al., 2007) and proton conductive materials (Schuster et al., 2004; Benhabbour et al., 2005), medicinal chemicals (Nefzi et al., 1997; Frazén, 2000; Horton et al., 2003; Fantini et al., 2010; Soh & Lam, 2010) and in the determination of heavy metal ions (Han et al., 2011; Kang et al., 2011; Li et al., 2012) as they possess better pharmacological and luminescent properties. Recently, compounds with furan-rings have been reported for the determination of trace amounts of Cu^{2+} with a limit of detection (3σ) of 6.5×10^{-11} mol L^{-1} (Kang et al., 2011), which has prompted us to explore the synthesis and luminescence property of imidazoles bearing furan rings.

Many methods for the synthesis of highly substituted imidazoles have been reported so far (Schubert & Stodolka, 1963; Stoeck & Schunack, 1974; Lipshutz, & Morey, 1983; Tsuji et al., 1983; Consonni et al., 1991; Evans & Lundy, 1992; Claiborne et al., 1998). Some of them involve fussy treatment, long reaction times and relatively low yields. Nevertheless, two research groups have recently reported one-pot condensation of benzil, aldehyde, amine and ammonium acetate on alumina, or silica solid support under microwave irradiation (Usyatinsky & Khmelnitsky, 2000; Balalaie & Arabanian, 2000). The method provides many profound advantages over the conventional methods in chemical transformations such as enhanced reaction rates and yields, significant energy and organic solvents savings.

In the present work, a synthetic strategy providing not only advantaged preparation of 2-substituted-4,5-di(2-furyl)-1*H*-imidazoles from furil and aldehydes according to the reported procedure (Usyatinsky & Khmelnitsky, 2000) (Table 1) but also reducing

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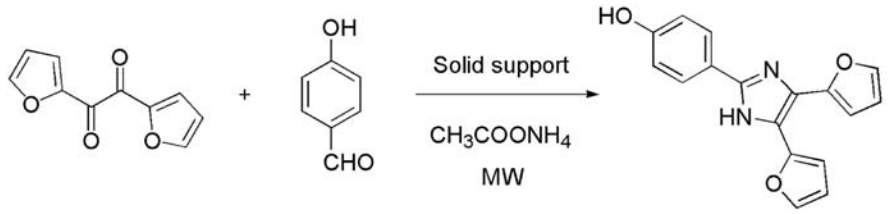
Table 1. Effects of different solid supports on the yield of 4-(4,5-di(furan-2-yl)-1*H*-imidazol-2-yl)phenol



Solid support	Yield/%
Acidic alumina (Al_2O_3) (pH 4.3 ± 0.5)	68
Neutral alumina Al_2O_3	31
Acidic SiO_2	24
Strong acidic resin (activated by HCl)	41

environmental pollution was designed. Although the microwave-assisted method has been successfully applied for the synthesis of 2-substituted-4,5-diphenyl-1*H*-imidazoles, it has seldom been used for the synthesis of 2-substituted-4,5-di(2-furyl)-1*H*-imidazoles. Because compounds containing furan rings have inherent disadvantages, such as easy ring-opening in some reaction media, etc. Thus, it is necessary to explore the stability of furan rings under microwave irradiation.

Furthermore, luminescent materials of imidazole derivatives have emerged as attractive blue-emitting materials (Fang et al., 2007). Our reported crystal structure of 2,4,5-tri(furan-2-yl)-1*H*-imidazole showed that two furan rings (4- and 5-substituted) of the organic fluorescent molecule are not coplanar with the imidazole ring (Wang et al., 2009). It is reported in literature (Gao et al., 1999; Chen et al., 2003; Zhao et al., 2006; Fang et al., 2007) that the non-coplanarity could prevent intermolecular electrostatic interactions between fluorescent molecules. Additionally, imidazole moieties are electron rich and electron donating due to the lone-pair electrons in the sp^3 nitrogen atoms. Thus, an electron donating group contributes to the charge transfer of a molecule. As a result, imidazole derivatives possess better fluorescent and thermal stability properties. Therefore, luminescent and thermal stability properties of the synthesized imidazole derivatives bearing furan rings have been investigated here. Also, the fluorescence quantum yields in a 0.1 M H_2SO_4 aqueous solution dissolved in 0.5 mL of CH_3OH were determined. The effect of the different solutions on the fluorescence spectra of compounds 2,4,5-tri(furan-2-yl)-1*H*-imidazole (*I*), 4,5-di(furan-2-yl)-2-phenyl-1*H*-imidazolen (*II*) and 4,5-di(furan-2-yl)-2-styryl-1*H*-imidazole (*XIII*) were studied. Besides, the fluorescence emission of compounds *I* and *II* was compared with that of 4,5-di(furan-2-yl)-1-(4-methylbenzyl)-2-phenyl-1*H*-imidazole (Chen et al., 2013), suggesting that the 2-position substituted group of imidazole plays a key role in the fluorescence emission shift in the same solution.

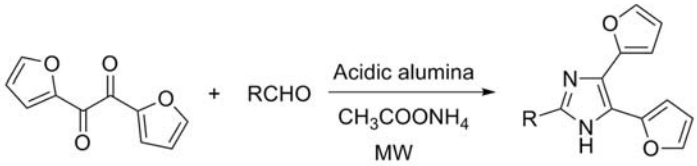
Experimental

A MCL-3-type microwave reactor (Sichuan University, China) with a thermometer for microwave application was used in all experiments. All reagents obtained from commercial companies (Tianjin Fuyu Reagent, China; Aladdin-reagent, China) were of analytical reagent (AR) quality and were used without further purification. Furoin and furil were synthesized according to the Li method (Li et al., 2006) and the Gao method (Gao et al., 1998), respectively. Furfural was distilled under reduced pressure before its use. Thin layer chromatography was carried out on silica gel (GF-254) TLC plates. All melting points were determined on a XT-4 melting point apparatus (China) without correction. IR spectra were collected with an Nicolet 5PC FT–IR spectrometer (USA). ^{1}H and ^{13}C NMR spectra were measured using an Varian Mercury-300 NMR spectrometer (USA) or a Bruker AVANCE-500 NMR spectrometer (Germany) with TMS as an internal standard. MS was collected on an Agilent HP1100/6890 LC/MS spectrometer. Elemental analyses were done using a FlashEA1112 elemental analyzer (Italy). TGA was measured on a Shimadzu DTG-60H simultaneous DTA-TG apparatus (Japan) at the heating rate of 5 °C min^{-1} under nitrogen atmosphere. The absorption spectra were recorded on an Australian GBC Cintra 10e UV-VIS Spectrophotometer within the wavelength range from 200 nm to 800 nm. Fluorescence spectra were recorded on a Shimadzu RF-5301 spectrofluorimeter (Japan). Fluorescence quantum yields (Φ_F) were determined against quinine sulfate in 0.1 M H_2SO_4 (Φ_F = 0.55) as the standard. Characterization data and spectral data of prepared compounds are in Table 2 and Table 3, respectively.

General procedure for the synthesis of 2-substituted-4,5-di(2-furyl)-1H-imidazoles

A mixture of acidic alumina (1.02 g, 10 mmol),

Table 2. Structures and yields of the synthesized compounds



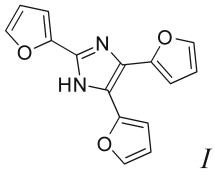
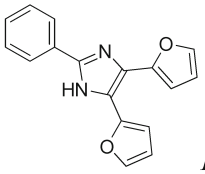
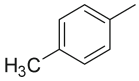
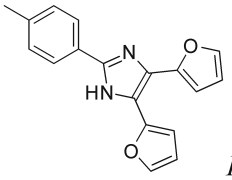
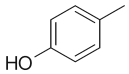
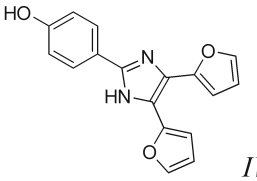
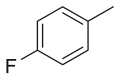
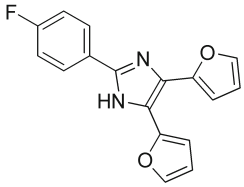
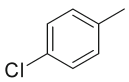
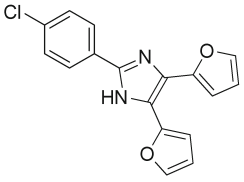
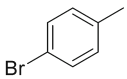
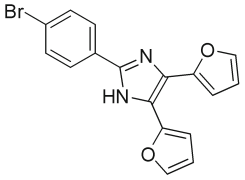
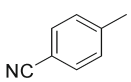
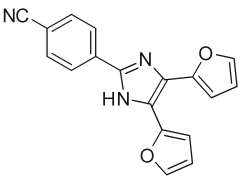
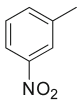
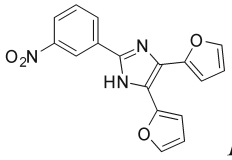
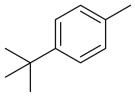
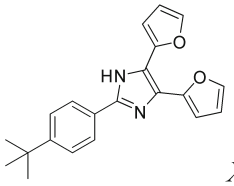
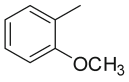
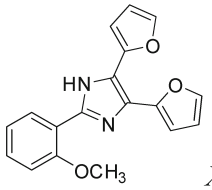
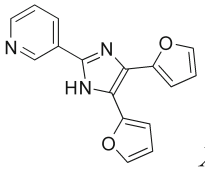
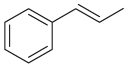
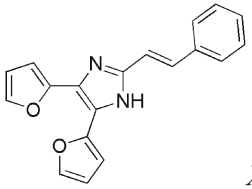
Entry	R	Compound	Yield[a]/%	M.p./℃	Φ_F
1		 *I*	63	206–209[b]	0.250
2		 *II*	65	207–209[b]	0.376
3		 *III*	62	217–219[b]	0.366
4		 *IV*	68	254–256	0.311
5		 *V*	65	168–170	0.350
6		 *VI*	71	216–218[b]	0.310
7		 *VII*	79	224–226	0.220
8		 *VIII*	86	186–187	0.213

Table 2. (continued)

Entry	R	Compound	Yield[a] /%	M.p./ ℃	Φ_F
9		 *IX*	87	197–198	0.003[c]
10		 *X*	78	189–191	0.325
11		 *XI*	82	132–134	0.357
12		 *XII*	47	244–246[b]	0.008[c]
13		 *XIII*	49	209–211[b]	0.508

a) Yield refers to recrystallized product after column chromatography; *b*) according to Li et al. (2012); *c*) fluorescence quenching.

furil (0.19 g, 1 mmol), ammonium acetate (0.38 g, 5mmol) and the appropriate aldehydes (1.2 mmol) was fully ground in a mortar. The reactive mixture was transferred to a 50 mL dry two-neck round bottomed flask containing a thermometer and a condenser, and heated with microwave irradiation for 10 min (the reaction temperature was 130 ℃ when the reaction was over.). The procedure was repeated twice. The reaction was monitored by TLC. The residue was directly purified by column chromatography on Chemapol (200–300 mesh) silica gel (eluent, petroleum ether–EtOAc, 3 : 1 vol.) to provide 2-substituted-4,5-di(2-furyl)-1*H*-imidazoles.

Crystal structure determination for compound I

The structures were solved by a direct method (Sheldrick, 1997a) and refined by full-matrix least squares based on F^2 using the SHELXTL 5.1 software package (Sheldrick, 1997b). All non-hydrogen atoms were refined anisotropically. Unless otherwise noted, hydrogen atoms were in idealized positions and were allowed to ride. The details on crystallographic collection and refinement data are given in Table 4. CCDC–990908 (*I*), contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/ deposit [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk.

Results and discussion

Synthesis of 2-substituted-4,5-di(2-furyl)-1H-imidazoles

It is reported that silica-gel and alumina play an outstanding role in microwave assisted organic chemical synthesis (Loupy et al., 1998; Varma, 1999). In our previous work, the application of silica-gel and alumina in microwave synthesis was extended. Some 2-substituted-4,5-di(2-furyl)-1*H*-imidazoles were synthesized starting from 1,2-di(furan-2-yl)-2-oxoethyl

Table 3. Characterization data of synthesized compounds

Compound	Characterizing data
I	Yield: 63 % (0.14 g) M.p.: 206–209 °C ^{1}H NMR (500 MHz, $CDCl_3$), δ: 10.48 (s, 1H, imidazole NH), 7.43 (s, 2H, furyl H5), 7.37 (s, 1H, furyl H5), 6.93 (d, J = 3.3 Hz, 3H, furyl H3), 6.46 (dd, J = 3.0 Hz, J = 1.7 Hz, 2H, furyl H4), 6.41 (dd, J = 3.1 Hz, J = 1.6 Hz, 1H, furyl H3 ^{13}C NMR (125 MHz, $CDCl_3$), δ: 146.9, 145.0, 143.0 (furyl C2), 141.6 (imidazole C2), 139.2 (imidazole C4, C5), 112.2 (furyl C5), 111.8 (furyl C5), 108.6 (furyl C4), 107.8 (furyl C3) MS, m/z: 267.9 (Calc. 267.26) $[M + H]^+$ w_i(found)/%: C, 67.53; H, 3.71; N, 10.45 w_i(calc.)/% for $C_{15}H_{10}N_2O_3$: C, 67.67; H, 3.79; N, 10.52
II	Yield: 65 % (0.18 g) M.p.: 207–209 °C ^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.92 (t, J = 1.9 Hz, 1H, phenyl H2), 7.89 (t, J = 1.9 Hz, 1H, phenyl H6), 7.51–7.37 (m, 5H, furyl H4, H5, phenyl H3), 6.98 (d, J = 3.3 Hz, 2H, phenyl H4, H5), 6.52 (dd, J = 3.4 Hz, 1.8 Hz, 2H, furyl H3). NH proton signal of imidazole was not observed ^{13}C NMR (75 MHz, $CDCl_3$), δ: 146.4 (imidazole C2), 129.4(furyl C2, phenyl C1, imidazole C4, C5), 129.2 (furyl C5), 129.0 (phenyl C4), 125.7 (phenyl C2, C3, C5, C6), 111.8 (furyl C4), 107.0 (furyl C3) MS, m/z: 277.9 (Calc. 277.30) $[M + H]^+$ w_i(found)/%: C, 73.78; H, 4.29; N, 9.97 w_i (calc.)/% for $C_{17}H_{12}N_2O_2$: C, 73.90; H, 4.38; N, 10.14
III	Yield: 62 % (0.18 g) M.p.: 217–219 °C ^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.83 (d, J = 8.1 Hz, 2H, phenyl H2, H6), 7.50 (d, J = 1.2 Hz, 2H, furyl H5), 7.23 (s, 2H, furyl H3), 7.01 (d, J = 3.2 Hz, 2H, phenyl H3, H5), 6.53 (dd, J = 3.3 Hz, 1.8 Hz, 2H, furyl H4), 2.38 (s, 3H, CH_3). NH proton signal of imidazole was not observed ^{13}C NMR (75 MHz, $CDCl_3$), δ: 146.5 (imidazole C2), 139.4 (imidazole C4, C5, furyl C2), 129.7 (furyl C5), 126.6 (phenyl C1, C4), 125.5 (phenyl C2, C3, C5, C6), 112.0 (furyl C4), 107.6 (furyl C3), 21.5 (CH_3) MS, m/z: 291.2 (Calc. 291.32) $[M + H]^+$ w_i (found)/%: C, 74.52; H, 4.76; N, 9.85 w_i (calc.)/% for $C_{18}H_{14}N_2O_2$: C, 74.47; H, 4.86; N, 9.65
IV	Yield: 68 % (0.20 g) M.p.: 254–256 °C IR (KBr), $\tilde{\nu}$ /cm^{-1}: 3444 (phenyl—OH), 3409, 3123 (imidazole—NH), 1612, 1532, 1470, 1452, 1386 (C═C, C═N), 1284 (C—N), 1203, 1026 (C—O—C), 993, 887, 841, 729, 592 ^{1}H NMR (300 MHz, DMSO), δ: 12.57 (s, 1H, imidazole—NH), 9.75 (s, 1H, phenyl—OH), 7.94–7.91 (m, 1H, phenyl H6), 7.90–7.88 (m, 1H, phenyl H2), 7.81 (dd, J = 1.8 Hz, 0.7 Hz, 1H, furyl H5), 7.70 (dd, J = 1.8 Hz, 0.8 Hz, 1H, furyl H5), 6.92 (dd, J = 3.4 HZ, 0.7 Hz, 1H, furyl H3), 6.88–6.85 (m, 1H, furyl H3), 6.85–6.82 (m, 1H, furyl H4), 6.71 (dd, J = 3.3 Hz, 0.8 Hz, 1H, furyl H4), 6.65 (dd, J = 3.4 Hz, 1.8 Hz, 1H, phenyl H5), 6.57 (dd, J = 3.3 Hz, 1.8 Hz, 1H, phenyl H3) ^{13}C NMR (75 MHz, DMSO), δ: 158.1 (imidazole C2), 149.5 (phenyl C4), 146.8 (furyl C2), 127.2 (furyl C5), 120.9 (imidazole C4, C5), 118.6 (phenyl C1), 115.4 (phenyl C2, C6), 111.8 (phenyl C5), 111.3 (phenyl C3), 108.0 (furyl C4), 106.6 (furyl C3) MS, m/z: 293.9 (Calc. 293.30) $[M + H]^+$ w_i (found)/%: C, 70.13; H, 4.32; N, 9.62 w_i (calc.)/% for $C_{17}H_{12}N_2O_3$: C, 69.86; H, 4.14; N, 9.58
V	Yield: 65 % (0.19 g) M.p.: 168–170 °C IR (KBr), $\tilde{\nu}$ /cm^{-1}: 3125 (imidazole—NH), 3068, 3026 (═C—H), 1611, 1492, 1442, 1419, 1365(C═C, C═N), 1232 (C—N), 1201, 1014(C—O—C), 976, 885, 841, 736, 592 ^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.90–7.84 (m, 2H, furyl H5), 7.48 (dd, J = 1.8 Hz, 0.7 Hz, 2H, phenyl H2, H6), 7.09 (t, J = 8.7 Hz, 2H, furyl H3), 6.96 (dd, J = 3.4 Hz, 0.6 Hz, 2H, phenyl H3, H5), 6.51 (dd, J = 3.4 Hz, 1.8 Hz, 2H, furyl H4). NH proton signal of imidazole was not observed ^{13}C NMR (75MHz, $CDCl_3$), δ: 164.7 (imidazole C2), 162.7 (phenyl C4), 147.3 (furyl C2), 145.9 (imidazole C4, C5), 141.9 (furyl C5), 127.9 (phenyl C1), 125.9 (phenyl C2, C6), 116.4 (phenyl C5), 116.2 (phenyl C3), 112.1 (furyl C4), 108.1 (furyl C3) MS, m/z: 295.8 (Calc. 295.29) $[M + H]^+$ w_i (found)/%: C, 69.21; H, 4.02; N, 9.46 w_i (calc.)/% for $C_{17}H_{11}FN_2O_2$: C, 69.38; H, 3.77; N, 9.52

Table 3. (continued)

Compound	Characterizing data
VI	Yield: 71 % (0.22 g) M.p.: 216–218 °C ^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.90–7.87 (m, 1H, phenyl H6), 7.87–7.84 (m, 1H, phenyl H2), 7.51 (d, J = 1.7 Hz, 2H, furyl H5), 7.46–7.39 (m, 2H, furyl H3), 7.01 (d, J = 3.2 Hz, 2H, phenyl H3, H5), 6.54 (dd, J = 3.4, 1.8 Hz, 2H, furyl H4). NH proton signal of imidazole was not observed ^{13}C NMR (75 MHz, DMSO), δ: 145.2(imidazole C2), 141.7 (furyl C2), 135.3 (imidazole C4, C5), 129.5 (furyl C5), 127.3 (phenyl C1, C4), 127.7 (phenyl C3, C5), 126.9 (phenyl C2, C6), 112.0 (furyl C4), 108.0 (furyl C3) MS, m/z: 312.8 (Calc. 311.74) $[M + 2]^+$, 311.8 (Calc. 311.74) $[M + H]^+$ w_i (found)/%: C, 65.46; H, 3.65; N, 8.73 w_i (calc.)/% for $C_{17}H_{11}ClN_2O_2$: C, 65.71; H, 3.57; N, 9.02
VII	Yield: 79 % (0.28 g) M.p.: 224–226 °C IR (KBr), $\tilde{\nu}$ /cm^{-1}: 3114(imidazole—NH), 3052, 3013 (=C—H), 1602, 1550, 1481, 1430, 1373 (C=C, C=N), 1260 (C—N), 1201, 1071 (C—O—C), 830, 732, 590 ^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.82–7.77 (m, 2H, furyl H5), 7.61–7.56 (m, 2H, phenyl H2, H6), 7.51 (dd, J = 1.8 Hz, 0.7 Hz, 2H, phenyl H3, H5), 7.00 (d, J = 3.3 Hz, 2H, furyl H3), 6.54 (dd, J = 3.4 Hz, 1.8 Hz, 2H, furyl H4). NH proton signal of imidazole was not observed ^{13}C NMR (75 MHz, DMSO), δ: 145.4 (imidazole C2), 142.0 (furyl C2), 132.5 (furyl C5), 128.5(imidazole C4, C5, phenyl C1), 127.3 (phenyl C2, C3, C5, C6), 123.8 (phenyl C4), 112.2 (furyl C4), 108.2 (furyl C3) MS, m/z: 357.3(Calc.345.00) $[M + 2 + H]^+$, 355.1 (Calc. 354.00) $[M + H]^+$ w_i (found)/%: C, 57.24; H, 2.98; N, 7.49 w_i (calc.)/% for $C_{17}H_{11}BrN_2O_2$: C, 57.49; H, 3.12; N, 7.89
VIII	Yield: 86 % (0.23 g) M.p.: 186–187 °C IR (KBr), $\tilde{\nu}$ /cm^{-1}: 3404, 3116 (imidazole—NH), 3063, 3003 (=C—H), 2227 (C≡N), 1689, 1609, 1559, 1525, 1489, 1437, 1372 (C=C, C=N), 1283 (C—N), 1203, 1012(C—O—C), 885, 846, 732, 595 ^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.02 (t, J = 1.7 Hz, 1H, furyl H5), 7.99 (d, J = 1.5 Hz, 1H, furyl H5), 7.73–7.70 (m, 1H, phenyl H6), 7.70–7.67 (m, 1H, phenyl H2), 7.55–7.49 (m, 2H, phenyl H3, H5), 7.04–7.00 (m, 2H, furyl H3), 6.55 (dd, J = 3.4 Hz, 1.8 Hz, 2H, furyl H4). NH proton signal of imidazole was not observed ^{13}C NMR (75 MHz, DMSO), δ: 146.5 (imidazole C2), 144.0 (furyl C2), 142.0 (phenyl C1), 133.1 (imidazole C4, C5, —C≡N), 132.7 (furyl C2), 125.6 (phenyl C3, C5), 118.7 (phenyl C4), 112.4 (phenyl C2, C6), 112.3 (furyl C4), 108.5 (furyl C3) MS, m/z: 302.9 (Calc. 302.31) $[M + H]^+$ w_i (found)/%: C, 71.53; H, 3.94; N, 13.67 w_i (calc.)/%for $C_{18}H_{11}N_3O_2$: C, 71.75; H, 3.68; N, 13.95
IX	Yield: 87 % (0.28 g) M.p.: 197–198 °C IR (KBr), $\tilde{\nu}$ /cm^{-1}: 3152 (imidazole—NH), 3095, 3032 (=C—H), 1600, 1520, 1469, 1345 (C=C, C=N), 1232 (C—N), 1202, 1069 (C—O—C), 915, 871, 812, 739, 715, 591 ^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.72 (t, J = 1.9 Hz, 1H, phenyl H5), 8.36 (ddd, J = 7.8 Hz, 1.6 Hz, 1.1 Hz, 1H, phenyl H3), 8.23 (ddd, J = 8.2 Hz, 2.2 Hz, 1.0 Hz, 1H, phenyl H6), 7.64 (t, J = 8.0 Hz, 1H, phenyl H2), 7.53 (dd, J = 1.8 Hz, 0.7 Hz, 2H, furyl H5), 7.05 (d, J = 3.0 Hz, 2H, furyl H3), 6.56 (dd, J = 3.4, 1.8 Hz, 2H, furyl H4). NH proton signal of imidazole was not observed ^{13}C NMR (75 MHz, DMSO), δ: 148.8 (imidazole C2), 143.6 (furyl C2), 142.0 (phenyl C4), 131.6 (furyl C5), 130.9 (imidazole C4, C5, phenyl C1), 130.2 (phenyl C2, C6), 123.7 (phenyl C5), 120.1 (phenyl C3), 112.08 (furyl C4), 108.5 (furyl C3) MS, m/z: 322.9(Calc. 321.29) $[M + H]^+$ w_i (found)/%: C, 63.25; H, 3.52; N, 12.98 w_i (calc.)/% for $C_{17}H_{11}N_3O_4$: C, 63.55; H, 3.45; N, 13.08

carboxylates (Li et al, 2012). Herein, chemical reactions were accelerated which might be caused by microwaves decreasing the activation energy of the reactions (Langa et al., 1997). Furthermore, some corresponding tetra-imidazoles containing furan rings were synthesized from 2-substituted-4,5-di(2-furyl)-1*H*-imidazoles. Luminescence properties of the synthesized tetra-imidazoles were studied (Chen et al., 2013). As a continuation of our work, in order to explore the possibility of 2-substituted-4,5-di(2-furyl)-1*H*-imidazoles synthesis from furil and aldehydes under microwave irradiation, optimization of solid supports, inorganic oxide and acid resins, was attempted. Effects of different solid supports on the yield of 4-(4,5-di(furan-2-yl)-1*H*-imidazol-2-yl)phenol were investigated by employing 4-hydroxybenzaldehyde and

Table 3. (continued)

Compound	Characterizing data
X	Yield: 78 % (0.26 g) M.p.: 189–191 °C IR (KBr), $\tilde{\nu}$ /cm^{-1}: 3122 (imidazole—NH), 3068, 3020 (=C—H), 2962, 2860 (—CH_3), 1602, 1528, 1491, 1426, 1364 (C=C, C=N), 1268 (C—N), 1201, 1080 (C—O—C), 971, 886, 839, 732, 593 ^{1}H NMR (300 MHz,$CDCl_3$), δ: 7.89–7.85 (m, 1H, phenyl H6), 7.85–7.83 (m, 1H, phenyl H2), 7.49 (dd, J = 1.8 Hz, 0.7 Hz, 2H, furyl H5), 7.47 (d, J = 2.0 Hz, 1H, furyl H3), 7.45–7.43 (m, 1H, furyl H2), 7.00 (d, J = 3.3 Hz, 2H, phenyl H3, H5), 6.52 (dd, J = 3.4 Hz, 1.8 Hz, 2H, furyl H4), 1.34 (s, 9H, 3 × CH_3). NH proton signal of imidazole was not observed ^{13}C NMR (75MHz, $CDCl_3$), δ: 152.6 (imidazole C2), 146.4 (furyl C2, phenyl C4), 126.6 (imidazole C4, C5, phenyl C1), 126.0 (furyl C5), 125.4 (phenyl C2, C3, C5, C6), 112.0 (furyl C4), 107.7 (furyl C3), 34.9 (—$C(CH_3)_3$), 31.4 (3 × CH_3) MS, m/z: 333.2 (Calc. 333.40) $[M + H]^+$ w_i (found)/%: C, 75.81; H, 6.20; N, 8.59 w_i (calc.)/% for $C_{21}H_{20}N_2O_2$: C, 75.88; H, 6.06; N, 8.43
XI	Yield: 82 % (0.25 g) M.p.: 132–134 °C IR (KBr), $\tilde{\nu}$ /cm^{-1}: 3431, 3116 (imidazole—NH), 3073, 3042 (=C—H), 2973, 2842 (CH_3), 1586, 1542, 1483, 1438, 1394 (C=C, C=N), 1262(C—N), 1203, 1020(C—O—C), 886, 736, 594 ^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.58 (d, J = 1.6 Hz, 1H, phenyl H5), 7.52 (d, J = 1.1 Hz, 2H, furyl H5), 7.43–7.32 (m, 1H, phenyl H4), 7.18–6.98 (m, 4H, furyl H3, phenyl H3,H5), 6.54 (dd, J = 3.3 Hz, 1.8 Hz, 2H, furyl H4), 4.09 (s, 3H, —O—CH_3). NH proton signal of imidazole was not observed. ^{13}C NMR (75 MHz, DMSO), δ: 156.3 (furyl C2, phenyl C6), 144.6 (imidazole C2), 141.7 (imidazole C4, C5), 130.4 (furyl C5), 129.3 (phenyl C2, C4), 122.0 (phenyl C3), 117.9 (phenyl C1), 112.1 (phenyl C5), 111.6 (furyl C4), 107.7 (furyl C3), 56.3 (—O—CH_3) MS, m/z: 307.9 (Calc. 307.32) $[M + H]^+$ w_i (found)/%: C, 70.42; H, 4.85; N, 8.89 w_i (calc.)/% for $C_{18}H_{14}N_2O_3$: C, 70.58; H, 4.61; N, 9.15
XII	Yield: 47 % (0.13 g) M.p.: 244–246 °C ^{1}H NMR (300 MHz, DMSO), δ: 9.27 (s, 1H, pyridine H2), 8.61 (dd, J = 5.0 Hz, 1.5 Hz, 1H, pyridine H6), 8.49–8.40 (m, 1H, pyridine H4), 7.80 (d, J = 1.2 Hz, 2H, furyl H5), 7.55 (dd, J = 8.0 Hz, 4.8 Hz, 1H, pyridine H5), 6.89 (d, J = 2.9 Hz, 2H, furyl H3), 6.64 (dd, J = 3.4 Hz, 1.8 Hz, 2H, furyl H4). NH proton signal of imidazole was not observed ^{13}C NMR (75MHz, DMSO), δ: 148.9 (pyridine C2), 146.3 (pyridine C6), 143.5 (furyl C2, imidazole C2, 142.4 (furyl C5), 133.3 (pyridine C4), 125.8 (imidazole C4, C5, pyridine C3), 123.9 (pyridine C5), 111.7 (furyl C4), 108.0 (furyl C3) MS, m/z: 278.8 (Calc. 278.29) $[M + H]^+$ w_i (found)/%: C, 69.19; H, 4.05; N, 14.93 w_i (calc.)/% for $C_{16}H_{11}N_3O_2$: C,69.31; H, 4.00; N, 15.15
XIII	Yied: 49 % (0.15 g) M.p.: 209–211 °C ^{1}H NMR (500 MHz, DMSO), δ: 12.75 (s, 1H , imidazole—NH), 7.78 (d, J = 48.9 Hz, 2H, furyl H5), 7.59 (d, J = 7.5 Hz, 2H, phenyl H2, H6), 7.52 (d, J = 16.5 Hz, 1H, phenyl H4), 7.41 (t, J = 7.6 Hz, 2H, furyl H3), 7.32 (t, J = 7.3 Hz, 1H, furyl H4), 7.06 (d, J = 16.5 Hz, 1H, furyl H4), 6.97 (s, 1H, phenyl H5), 6.66 (dd, J = 44.5 Hz, 31.3 Hz, 3H, phenyl H3, —CH=CH—) ^{13}C NMR (125 MHz, DMSO), δ: 146.7 (furyl C2), 137.1 (imidazole C4, C5, imidazole C2, phenyl C6), 129.8 (furyl C5), 127.5 (phenyl—CH=), 117.4 (phenyl C3, C5), 113.4 (phenyl C2, C6), 112.9 (phenyl C4), 112.3 (=CH—imidazole), 108.9 (furyl C4), 107.6 (furyl C3) MS, m/z: 303.0 (Calc. 303.34) $[M + H]^+$ w_i (found)/%: C, 75.82; H, 4.81; N, 9.45 w_i (calc.)/% for $C_{19}H_{14}N_2O_2$: C, 75.58; H, 4.67; N, 9.27

furil under uniform mixing of solid supports under microwave irradiation conditions for 10 min and in the absence of any organic solvent. The experiment results are summarized in Table 1.

The results indicate that the yield of 4-(4,5-di(furan-2-yl)-1*H*-imidazol-2-yl)phenol was higher when an identical loading of acidic alumina was used as the supported medium. The reason might be that acidic alumina provides more appropriate acidity to catalyze the reaction than acidic SiO_2. Nonetheless, acidity of a strong acidic resin is too strong. Therefore, acidic alumina was applied as the solid support to synthesize imidazole derivatives with furan rings.

The conventional method for synthesizing imida-

Table 4. Crystal data and structure refinement for compound *I*

Data	*I*
Formula	$C_{15}H_{10}N_2O_3$
Molecular mass	266.25
Temperature/K	293(2)
Crystal system	Orthorhombic
Space group	*Fdd*2
a/Å	14.854(3)
b/Å	32.981(7)
c/Å	10.523(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	5154.8(18)
Z	16
D_{calcd}/(mg m^{-3})	1.372
F(000)	2208
θ range for data collection/°	3.01–27.47
Limiting indices	$-19 \le h \le 18$ $-42 \le k \le 42$ $-13 \le l \le 13$
Data/restraints/parameters	2933/99/223
Goodness-of-fit on F^2	1.101
Final R indices [I ¿ 2σ(I)]	R1^a = 0.0406 wR^b = 0.0960
R indices (all data)	R1^a = 0.0566 wR^b = 0.1024
Largest diff. peak and hole/(e A^{-3})	0.191 and –0.133

a) R1 = $\sum ||F_o|-|F_c|| / \sum |F_o|$; *b*) wR = $\left[\sum \left[w(F_o^2 - F_c^2)^2\right] / \sum \left[w(F_o^2)^2\right]\right]^{1/2}$.

zole derivatives includes 1,2-diketone and appropriate aldehydes reflux in the presence of ammonium acetate and glacial acetic acid (Wang et al., 2003; Parveen et al., 2007; Wang et al., 2011). In fact, these reactions commonly require higher temperature (over 118 ℃) and the reaction time of 5–6 hours, whereas similar or higher yields and cleaner reaction profiles can be obtained using microwave heating for 10 minutes on solid support acidic alumina under solvent-free conditions (Table 2).

Comparing the new approach to 2-substituted-4,5-di(2-furyl)-1*H*-imidazoles synthesis by the conventional method and by our new reported method (Li et al., 2012), microwave-assisted solvent-free assembled process represents a much more convergent route by utilizing a common intermediate and introducing solid support acidic alumina. Herein, the nucleophilic addition of aldehydes and furil and the self-cycloaddition reaction with ammonium acetate was readily carried out and 2-substituted-4,5-di(2-furyl)-1*H*-imidazoles were obtained in moderate and preferable yields. However, the compounds synthesized using our reported method (Li et al., 2012) were also prepared by this method. A possible reason is that solid support acidic alumina prevents ammonia from forming the ammonium ion without nucleophilic reactivity and acts as the catalyst and dispersant in the reaction. As shown in Table 2, the yields of products with stronger electron-withdrawing substituted groups (—CN, —NO_2) (entries 8 and 9) on the aromatic ring are higher than those of the products with electron-donating substituted groups (—CH_3, —OH, *t*-butyl and styryl) (entries 3, 4, 10 and 13) and with

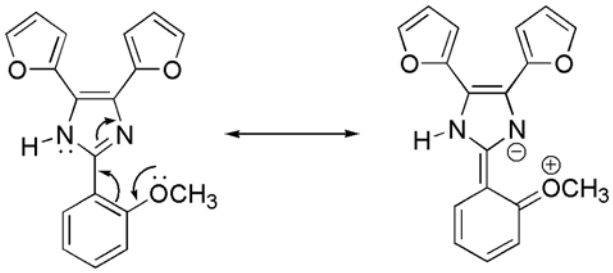


Fig. 1. Resonance structures of product *XI*: *XIa* (left) and *XIb* (right).

weak electron-withdrawing substituted groups (—F, —Cl and —Br) (entries 5, 6 and 7) on the aromatic ring, probably due to the electron-withdrawing substituted groups enhancing the electrophilicity of the aldehyde carbonyl group. However, the yield was also higher when the reaction was preformed with 2-methoxyl benzaldehyde with an electron-donating substituted group and furil as the starting materials. A possible reason is that the target product, *XI* (entry 11), showed better stabilization of the stable resonance structure *XIb* formed in an acidic medium (Jayabharathi et al., 2012a) (Fig. 1). Besides, when solid support acidic alumina was five times recycled to synthesize *XIII*, the yields of the obtained *XIII* were 45.5 %, 47.6 %, 49.3 %, 48.9 % and 47.4 %, respectively, suggesting that acidic alumina can be recycled.

Single crystal determination of product I

Recently, another synthesis method for trisubsti-

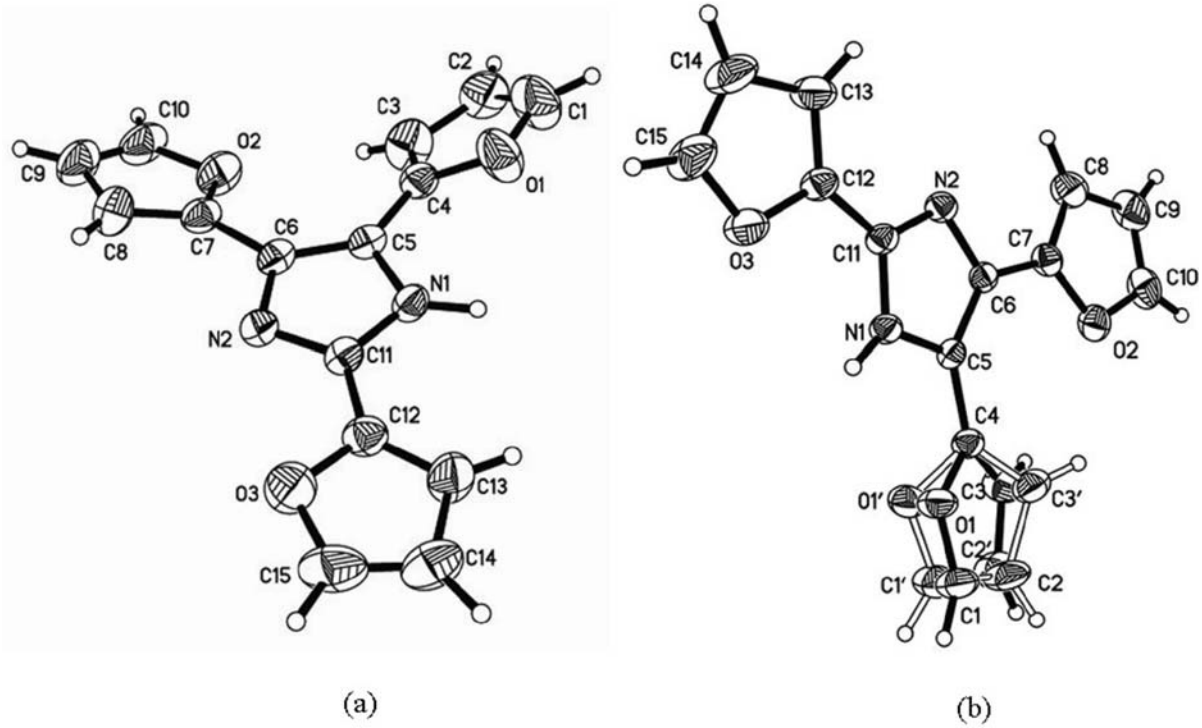


Fig. 2. Molecular structure of compound *I* in the monoclinic space system (Wang et al., 2009) (a); molecular structure of compound *I* in the orthorhombic space system (b); thermal ellipsoids are drawn at the 30 % probability levels.

Table 5. Hydrogen bond geometries and C—H$\cdots\pi$ interaction parameters for *I*

Structure	D—H$\cdots$A	d(D—H)/Å	d(H$\cdots$A)/Å	d(D$\cdots$A)/Å	α(DHA)/°
I	N(1)—H(100)$\cdots$N(2)^a	0.88(2)	2.08(2)	2.946(2)	168.1(18)
	C(3)—H(3A)$\cdots$O(2)	0.93	2.54	3.093(9)	118.8
	C(8)—H(8)$\cdots$Cg(1)^b	0.93	2.7369(4)	3.5834(5)	151.780(12)

a) $x+1/4, -y+1/4, z+1/4$; *b*) $-x, -y+1/2, z-1/2$. Cg(1) represents the centroid of the imidazole ring (N1/C5/C6/N2/C11).

tuted imidazoles containing furan rings has been reported (Li et al., 2012; Wang et al., 2009). In this study, product *I* was recrystallized after the column chromatography to obtain two kinds of single crystals with different polymorphs, one of which, in monoclinic system, was reported in our previous work (Wang et al., 2009). Here, the crystal structure of product *I* in the orthorhombic system is reported. Three furan rings and an imidazole ring in the orthorhombic system are nearly coplanar. The dihedral angles between the three furan rings, C1/C2/C3/C4/O1, C7/C8/C9/C10/O2, C12/C13/C14/C15/O3 and the imidazole ring, N1/C5/C6/N2/C11, are 1.5°, 7.7° and 11.7°, respectively, suggesting that the three furan rings and the imidazole ring of compound *I* are more coplanar than those in the reported single crystal structure (Wang et al., 2009), which is probably the reason for the higher melting point of compound *I*. An S(7) ring motif (Bernstein et al., 1995) is formed due to the intramolecular C3—H3$\cdots$O2 interaction (Fig. 2 and Table 5). In the monoclinic system, the ring atoms in all three furan rings are all oriented clockwise while in the orthorhombic system, the ring atoms in two furan rings are oriented clockwise and those in the third furan ring are oriented anticlockwise (Fig. 2). Similarly to the packing of the molecule in the monoclinic polymorph, neighboring molecules in the orthorhombic system are also nearly vertical to each other with the dihedral angle of 84.0° (98.0° in the monoclinic polymorph) and linked together by intermolecular N—H$\cdots$N hydrogen bonds into 1-D infinite chains (Table 5, Fig. 2a). The 1-D infinite chains are further linked by weak intermolecular C—H$\cdots\pi$ interactions (Table 5, Fig. 2b) to form a 3-D network. The furan ring in the 5-position of the imidazole ring is disordered over two positions with the site occupation factors of 0.448 and 0.552.

Studies of thermal stability and photoluminescence properties

In general, thermal stability of organic materials is an important factor influencing their application. Herein, thermal properties of imidazoles (entries 1,

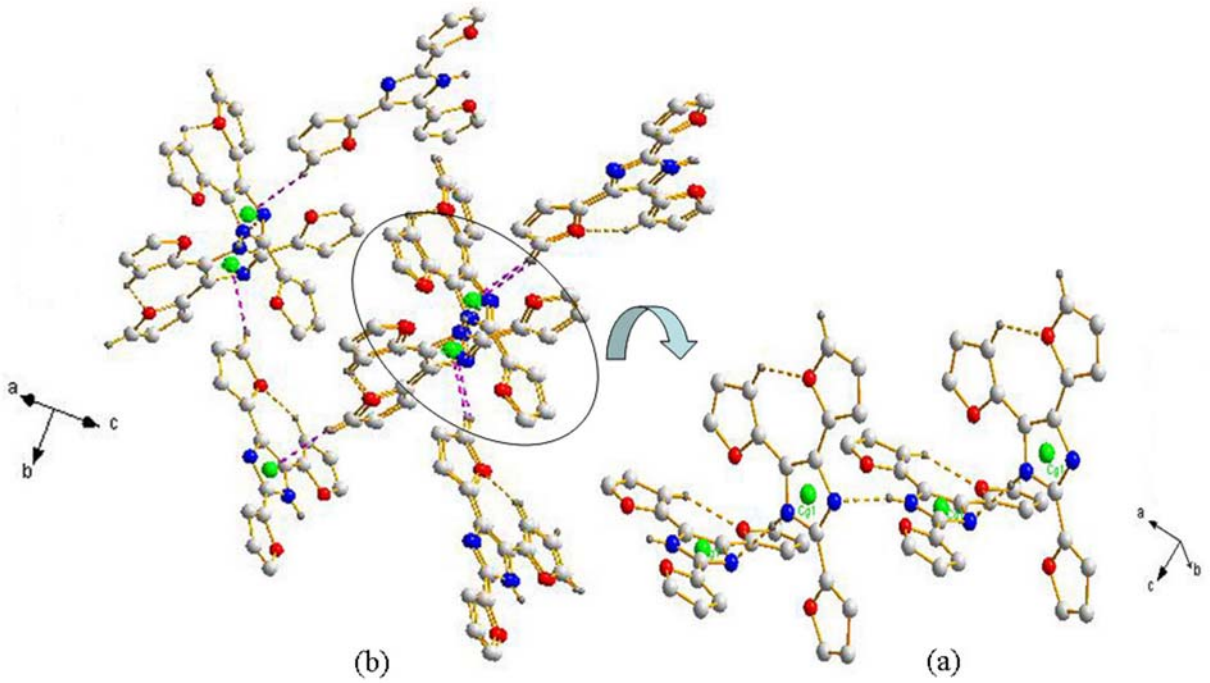


Fig. 3. Packing of molecule *I*: packing of the molecules showing intermolecular N—H· · · · N interactions forming a 1-D chain (a); packing of molecules showing a 3-D network formed by intermolecular N—H· · · · N interactions and C—H· · · · π interactions (b). Color scheme: blue – nitrogen; red – oxygen; light grey – carbon; grey – hydrogen. Green points represent the centroids of the imidazole rings (N1/C5/C6/N2/C11): d(C10· · · · Cg) = 3.5834(5) Å. Hydrogen bonds are indicated by dashed lines. Yellow dashed lines represent N—H· · · · N and C—H· · · · O interactions. Purple dashed lines represent C—H· · · · π interactions.

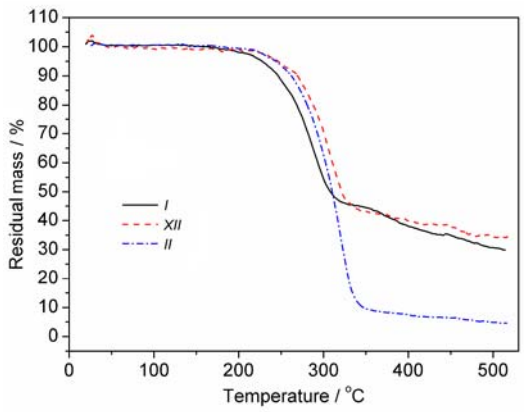


Fig. 4. TGA curves of *I*, *II* and *XII*.

2 and 12) were investigated by the thermogravimetric (TGA) analyses (Fig. 4). The temperatures found are 227 °C (*I*), 243 °C (*II*) and 245 °C (*XII*) when the weight of the compounds decomposed by 5 %, which shows that thermal stability of the synthesized 2-pyridyl and 2-phenyl substituted imidazoles is higher.

In our previous work (Chen et al., 2013), photoluminescence properties of 1,2,4,5-tetrasubstituted imidazoles containing a furan ring were studied. However, the photoluminescence properties of 2,4,5-trisubstituted imidazoles containing a furan ring have only rarely been studied. The value of Φ_F of the synthesized 2-substituted-4,5-di(2-furyl)-1*H*-imidazoles (1.6×10^{-6} mol L^{-1}) in a 0.1 M H_2SO_4 aqueous solution dissolved in 0.5 mL of CH_3OH were measured against quinine sulfate in 0.1 M H_2SO_4 (Φ_F = 0.55) (Table 2). Φ_F were measured against quinine sulfate in 0.1 M H_2SO_4 (Φ_F = 0.55) referring to the reported literature (Fletcher, 1969; Gill, 1969; Molard et al., 2006; Chen et al., 2013).

As shown in Table 2, Φ_F of the synthesized compounds (*I*–*XIII*) were 0.213–0.508 except for those for compounds *IX* (0.003) and *XII* (0.008) fluorescence quenching in a 0.1 M H_2SO_4 aqueous solution dissolved in 0.5 mL of CH_3OH. In fact, Φ_F determined was the Φ_F of imidazoles (*I*–*XIII*) salifying with sulfuric acid. Compared with non-substituted benzene, when benzene was replaced with other electron-donating substituted groups (entries 2, 3, 4, 10 and 11) and electron-withdrawing substituents (entries 5, 6, 7, 8 and 9), the influence on their Φ_F is low except for compound *XIII* (0.508). This can be attributed to styryl with a long conjugated chain which was introduced into the molecule, suggesting that the 2-position substituent groups had a significant influence on the luminescence properties of the synthesized compounds. Moreover, Φ_F of benzene with the hydroxyl (entry 4) and *t*-butyl (entry 10) group slightly decreased probably due to the hydroxyl group being protonized in the acidic solvent and *t*-butyl excessively increasing the vibrational and rotational degrees of the imidazole derivatives. However, when benzene was replaced with low electron-withdrawing halogen (entries

Table 6. Emission wavelengths of I, *II* and *XIII* in solvents with different polarities (λ_{ex} = 320 nm)

Solvent	λ/nm			
	I	*II*	*XIII*	*XIV*
Cyclohexane	379	396	441	394
Toluene	394	401	452	402
THF	388	406	459	409
Methanol	399	410	464	416
Ethanol/water	405	418	472	423

XIV = 4,5-di(furan-2-yl)-1-(4-methylbenzyl)-2-phenyl-1*H*-imidazole from literature (Chen et al., 2013).

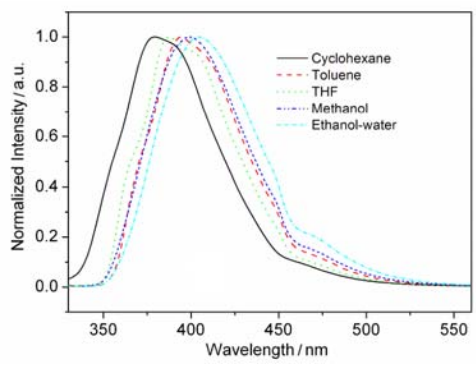


Fig. 5. Normalized emission spectra of *I* in solvents with different polarities (λ_{ex} = 320 nm).

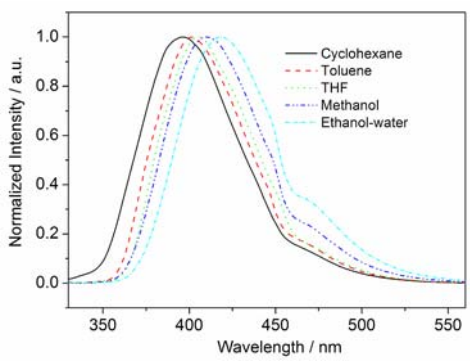


Fig. 6. Normalized emission spectra of *II* in solvents with different polarities (λ_{ex} = 320 nm).

5, 6 and 7), Φ_F of the synthesized compounds gradually decreased with the 2-position of trisubstituted imidazoles bearing 4-fluorophenyl, 4-chlorophenyl and 4-bromophenyl, which can be ascribed to a heavy atom introduced into the molecule and resulting in a great enhancement of the rate of the S_1–T_1 spin-forbidden process with the decrease of Φ_F (Chandra et al., 1978; Chen et al., 1990; Chen & Tong, 2014). Besides, comparing the effect of 2-substituted phenyl, pyridyl and furyl groups on Φ_F, Φ_F value of the benzene ring as a substituent group was the highest (entry 2), followed by that of the furan ring (entry 1), while that of the pyridine ring as a substituent group (entry 12) possesses the lowest Φ_F. A possible reason is the π–π^* transition energy of the benzene ring being much higher than the n–π^* and π–π^* energy of the furan ring. Moreover, the pyridine ring possesses an n-electron of the electronic spin-forbidden transition. Finally, Φ_F values of the synthesized trisubstituded imidazoles were higher than those of our reported corresponding tetrasubstituted imidazoles (Chen et al., 2013) as the 1-position substituent groups made the plane of the trisubstituted imidazole (Zhao et al., 2006; Wang et al., 2009) twist by a smaller angle (Jayabharathi et al., 2012b), which resulted in bad coplanarity of the tetrasubstituted imidazoles.

Fluorescence emission spectra of *I*, *II* and *XIII* (1.6 × 10^{-6} mol L^{-1}) in solvents with different polarities (cyclohexane, toluene, THF, methanol and ethanol–water 1 : 1, vol.) are shown in Figs. 5, 6 and 7, respectively. The corresponding data are summarized in Table 6.

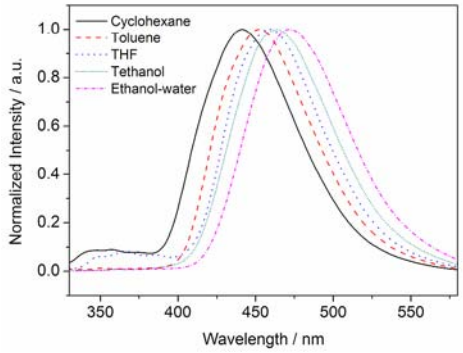


Fig. 7. Normalized emission spectra of *XIII* in solvents with different polarities (λ_{ex} = 320 nm).

Emission bands of compounds *II* and *XIII* were significantly red-shifted with an increase of the solvent polarity. In cyclohexane, the emissions of *II* and *XIII* were at 396 nm (Fig. 6, Table 6) and 441 nm (Fig. 7, Table 6), respectively. However, in ethanol–water (1 : 1, vol.), they were red-shifted to 418 nm (*II*) and 472 nm (*XIII*) (Table 6), respectively. The red-shift of an emission band might be caused by the stronger interaction between the solvent and the excited state molecules (Jayabharathi et al., 2012a). Polar solvents stabilized the excited state of *II* and *XIII* (Mi et al., 2003; Jayabharathi et al., 2012a). There-

fore, the emission spectra of both compounds, *II* and *XIII*, are broad and solvent dependent (Loiseau et al., 2005; Yang et al., 2009). With regard to compound a, its emission was basically red-shifted with an increase of the solvent polarity. However, in a low polar solvent, like toluene and THF, its emission spectra broke the red-shifted rule with the solvent polarity and were observed at 394 nm in toluene and at 388 nm in THF, respectively (Fig. 5, Table 6). This might result from compound a being solvated by the THF solvent according to the principle of similar miscibility and/or an H-bond being formed between compound *I* and THF leading to the decreased stability of the excited state. It is well known that excited state hydrogen bonding of *N*-heterocyclic compounds luminescence depends on the excited singlet state *I* (n, π^*) or (π, π^*). The ability to form hydrogen bonds between compounds in the (π, π^*) excited singlet state and THF is weaker than that of compounds in the (n, π^*) ground state and THF.

However, the emission spectra of trisubstituted imidazoles were red-shifted with the longer conjugated chain in the same kind of solvent (Figs. 5, 6, 7 and Table 6), for instance, in methanol, the emissions of compounds *I*, *II* and *XIII* were at 388 nm, 407 nm and 462 nm, respectively. The emission spectra of *II* and *XIII* were red-shifted by about 19 nm and 74 nm, respectively, when the 2-position substituent of 4,5-di(furan-2-yl)-1*H*-imidazole was a phenyl group or a styryl group compared with those observed for a furan ring. In addition, the emission spectra of 4,5-di(furan-2-yl)-1-(4-methylbenzyl)-2-phenyl-1*H*-imidazole (*XIV*) (Chen et al., 2013) were hardly or slightly red-shifted as compared to that of 4,5-di(furan-2-yl)-2-phenyl-1*H*-imidazole (*II*), which can be explained by no influence of methylbenzyl introduction on the coplanarity of imidazole derivative *II*. Consequently, the structure of 2-position substituent groups and the polarity of the solvents had a significant influence on the luminescence properties of imidazole derivatives.

Conclusions

A solvent-free, convenient, and efficient synthesis of 2-substituted-4,5-di(2-furyl)-1*H*-imidazoles coupled with solid support acidic alumina has been introduced. Thirteen 2-substituted-4,5-di(2-furyl)-1*H*-imidazoles were synthesized by the presented method of solvent-free heterogeneous organic reactions under microwave irradiation. The orthorhombic 2,4,5-tri-2-furyl-1*H*-imidazole (*I*) showed good coplanarity. Fluorescence quantum yields of the synthesized imidazoles with different substituted groups were 0.004–0.508 in the 0.1 M H_2SO_4 aqueous solution against quinine sulfate in 0.1 M H_2SO_4. It is helpful for the systematic investigation of the structure–property relationship and for the design of novel and efficient organic small molecule optoelectronic materials. Also, emissions of imidazole compounds in solutions can be controlled by varying the polarity of the solvents. A 1-substituent group attached to the nitrogen atom had only a small influence on the emission spectra. Therefore, the synthesized solvent dependent fluorescence compounds might have latent applications in the detection of environments, microenvironments and material science fields, especially in biological processes. Besides, a study on the applications of 2,4,5-trisubstituted imidazoles in the metal ion detection is in progress.

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