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Microwave-assisted solvent-free catalyzed synthesis and luminescence properties of 1,2,4,5-tetrasubstituted imidazoles bearing a 4-aminophenyl substituent

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Abstract A solvent-free microwave-assisted four-component synthesis of 1,2,4,5-tetrasubstituted imidazoles bearing a 4-aminophenyl substituent was studied by condensation of *p*-phenylenediamine, aryl diketone, benzaldehyde derivatives and ammonium acetate in the presence of solid support silica gel and catalyst Keggin-$H_3[PW_{12}O_{40}]$. The effects of four components molar ratio along with catalyst loading, irradiation time on the yields were investigated. Also, the structures of synthesized compounds were characterized by FT-IR, HRMS, ^{1}H NMR and ^{13}C NMR spectroscopy. Furthermore, their ultraviolet–visible maximum absorption, liquid fluorescence emission maximum and quantum yields were, respectively, measured in 0.05 M H_2SO_4 aqueous solution and in dichloromethane. Simultaneously, solid fluorescence spectra were determined in the powder state. The relationships between the optical behavior and the polarity of the solvents for some compounds were assessed. The results showed that the fluorescence quantum efficiency was increased by introducing amino phenyl in comparison with benzyl on 1-position of trisubstitued imidazoles. The compounds synthesized were sensitive to the polarity of the solvents.

Keywords Tetrasubstituted imidazole · Microwave radiation · $H_3[PW_{12}O_{40}]$ · Solid support SiO_2 · Solvent free · Luminescence property

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Introduction

Tetrasubstituted imidazole compounds have been widely studied in chemistry, biology and materials science, such as plasma reactors (Heung and Urban 1999), corrosion inhibitors (Liu et al. 2014), anticancer drugs (Wagner et al. 2003), anti-inflammatory agents (Na et al. 2007) and modulators of Pgp-mediated multidrug resistance (Smith et al. 2009). Besides, their attractive emitting properties and the high conjugation degree aromatic nature have received great attention in the last few years. Masaru Kimura et al. studied the functional imidazole derivatives on chemiluminescent reactions (Kimura et al. 2007); Jiří Kulhánek and Filip Bureš researched imidazole as a parent π-conjugated backbone in charge-transfer chromophores (Kulhánek and Bureš 2012); Tian M. et al. focused on the structure–effect relationship of multi-aryl imidazoles with their fluorescence properties (Tian et al. 2014), etc. Therefore, the synthesis and property of substituted imidazoles had become an important part of modern organic synthesis, and attracted more and more chemists, biologists and materials scientists.

Generally, 1,2,4,5-tetrasubstituted midazoles were synthetically obtained by the multicomponent reactions (MCRs) of 1,2-diketone, α-hydroxy/acetoxy/silyloxyketone or 1,2-ketomonoxime, aldehyde, amine and ammonium acetate carried out by microwave irradiation in the presence of silica gel/zeolite HY(Balalaie and Arabanian 2000), silica gel–$NaHSO_3$ (Balalaie et al. 2003; Karimi et al. 2006), etc., along with traditional heating in a suitable solvent using different catalysts (Chhanda and Pradip 2012; Heravi et al. 2007a, b; Jaberi and Barekat 2010; Javid et al. 2011; Kidwai and Mothsra 2006; Mohammadi et al. 2012; Murthy et al. 2010; Siddiqui et al. 2005; Subhasis et al. 2009; Nasr-Esfahani et al. 2015), such as

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$KHSO_4$/DB18C6, Keggin-type heteropolyacid, NaH_2PO_4, poly(AMPS-co-AA), molecular iodine, DABCO, $NiCl_2$/$AlCl_3$, L-proline and nanorod vanadatesulfuric acid (Nasr-Esfahani et al. 2015). The clean, high-yielding, time-saving (reaction time had been shortened to 5–120 min) and environmentally friendly heteropolyacid (HPA) approaches by traditional heating (Javid et al. 2011; Heravi et al. 2007b) attracted us into evaluating the catalysis of HPA under microwave-assisted solvent-free condition. Microwave-assisted solvent-free reaction (Bhoi et al. 2016; Zhang et al. 2016) could decrease the use of organic solvent and expensive catalysts, shorten reaction time and facilitate the separation of products (Baghbanzadeh et al. 2011). It was reported that microwave irradiation as a dielectric heating is a process in which the organic compounds consume electromagnetic energy, which can accelerate the reaction rate several times, ten times or even tens of thousands of times compared with conventional heating (Jin et al. 1999).

Consequently, it is very necessary to study new, green synthetic processes to construct fused tetraimidazole derivatives in higher yields and short reaction time. Moreover, the used nitrogen sources in the above reactions were ammonia, aniline, aliphatic amine, etc. However, *p*-phenylenediamine has been rarely used, except by Chhanda Mukhopadhyay et al. who reported the synthesis starting from *p*-substituted aniline using $KHSO_4$/DB18C6 as catalyst by traditional heating for 4–8 h (Chhanda and Pradip 2012). Herein, one-pot four-component condensation of *p*-phenylenediamine, aryl diketone, benzaldehyde derivatives and ammonium acetate catalyzed and dispersed by $H_3[PW_{12}O_{40}]$ and a mixture of silica gel under microwave irradiation and solvent-free conditions was explored (Scheme 1).

Furthermore, substituted imidazole exhibited favorable luminescence (Nagarapu et al. 2007; Buttke et al. 1997). It was reported that the emission spectra were redshifted when substituted benzyls were introduced into 1-position of 2,4,5-trisubstituted imidazoles containing furan rings or benzene rings (Chen et al. 2013). However, the fluorescence quantum yields (Φ_u) of these compounds were lower in 0.05 M H_2SO_4 aqueous solution, probably because methylene on 1-benzyl resulted in bad coplanarity of tetrasubstituted imidazoles. To enhance the photoluminescence properties of 1,2,4,5-tetrasubstituted imidazoles in continuation of our search, a series of new tetrasubstituted imidazoles without benzyl but an 4-amino phenyl as an auxochrome group on 1-position and different 4-, 5-substituted groups were prepared, and their photoluminescence properties in solid state and in the different solvents were studied. The results of these studies are reported herein.

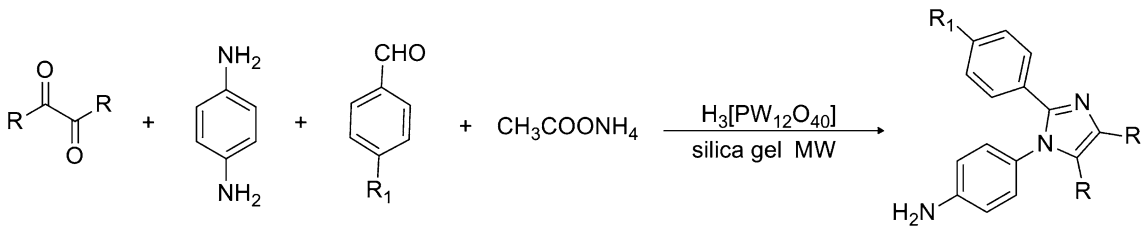
Experimental

All reagents obtained from commercial companies (Tianjin Fuyu Chemical Reagent Company, China; Aladdin-reagent Co.) were of analytical grade and used without further purification. Aryl diketones were synthesized by referring to the reported literature (Gao et al. 1998). All reported yields were isolated yields. A MCL-3-type microwave reactor in Sichuan University, with a thermometer for microwave application, was used in all experiments. All melting points were determined with an XT-4 melting point apparatus and were uncorrected. High resolution mass spectrometry (HRMS) was collected on an Agilen-t1290-micrOTOF Q II spectrometer. ^1H and ^{13}C NMR spectra were measured using a Bruker AVANCE-500 NMR spectrometer with TMS as an internal standard. FT-IR spectra were obtained with KBr pellets using a Shimadzu IRAffinity-1 instrument in the range between 500 and 3500 cm^{-1}. Fluorescence spectra were recorded with a FLS920 spectrofluorimeter. The absorption spectra were recorded on a GBC Cintra 10e UV–Vis spectrometer within the wavelength range from 200 to 800 nm. Fluorescence strengths in solid state were determined at the corresponding excitation wavelength by a Horiba Fluoromax-4 spectrofluorometer.

Synthesis and characterization

General synthesis approach for aryl diketones

Aryl diketones were synthesized according to the reported literature (Gao et al. 1998). A mixture of $CuSO_4 \bullet 5H_2O$



Scheme 1 Synthesis of 1, 2, 4, 5-tetrasubstituted imidazoles bearing a 4-aminophenyl substituent

15.80 g (0.0633 mol), pyridine 21.54 g (0.272 mol), and H_2O 10.26 dm^3 (0.520 mol) were taken in a three-necked bottle with a thermometer and a spherical condenser, and was fully stirred in a water bath. 2-hydroxy-1,2-diaryl-ethanone (0.0302 mol) was added to the three-necked bottle when the blue solution became colorless, and then stirred at 98–100 °C for 1.5 h. The reaction slurry was poured into cold water for crystallization, then filtered and washed with plenty of water. Sequentially, the filter cake was recrystallized in ethanol. The desired aryl diketones were obtained in 84–93% yield.

General synthesis approach for tetrasubstituted imidazoles with different substituted groups

A mixture of *p*-phenylenediamine (1 mmol), aryl diketone (2 mmol), benzaldehyde derivatives (2 mmol), ammonium acetate (8 mmol), silica gel (1 g) and $H_3[PW_{12}O_{40}]$ (0.7%) was fully ground in a mortar, then transferred to a 50 mL dried round-bottomed flask and heated with microwave irradiation for 15 min (the reaction temperature was 130 °C). The reaction progress was monitored by TLC on Silufol-254 plates. When the microwave-assisted reaction was over, the residue was cooled to room temperature and purified by column chromatography on Chemapol (200–300 mesh) silica gel (petroleum ether/ethyl acetate = 3/1) and then recrystallized in ethanol to give the desired products.

Determination of fluorescence quantum yield

The fluorescent quantum yields were measured against quinine sulfate ($\Phi_u = 0.55$ in 0.05 M sulfuric acid, 200 nm $\leq \lambda \leq$ 400 nm) as a standard (Gill 1969; Fletcher 1969) and was calculated according to the literature (Ci and Jia 1986).

Results and discussion

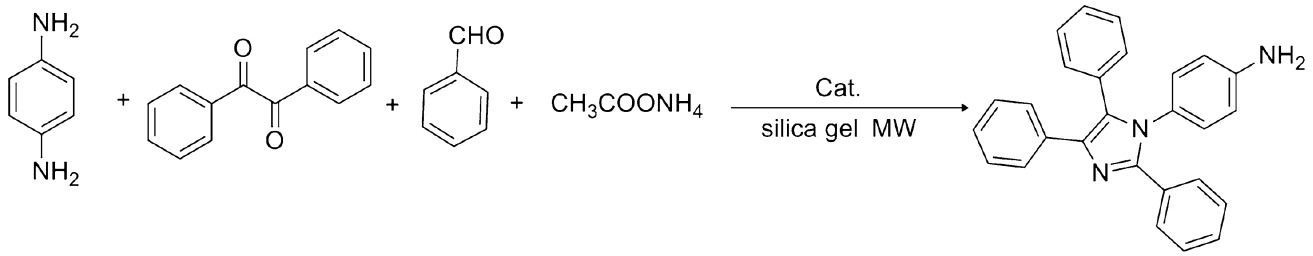
Synthesis of the compounds

In our previous work, some 2-substituted-4,5-di(2-furyl)-1*H*-imidazoles were synthesized using Al_2O_3 as solid supports starting from 1,2-di(furan-2-yl)-2-oxoethyl carboxylates (Li et al. 2012) or furil (Zhang et al. 2015) under microwave irradiation and solvent-free conditions. Herein, the reactions were accelerated which might be because of the action of microwave to decrease the activation energy of the reaction. Furthermore, some corresponding tetrasubstituted imidazoles containing furan rings were synthesized via condensation of 2-substituted-4,5-di(2-furyl)-1*H*-imidazoles and benzyl chloride in the presence of alkali. The method for synthesizing 1,2,4,5-tetrasubstituted imidazoles required not only a long reaction time (12–24 h), but also a base as an acid-binding agent and plenty of solvent (Chen et al. 2013). Besides, the fluorescence quantum yields of the compounds reported were lower. In the present work, the corresponding aryl diketones (benzil, furil and 1,2-bis-(4-chlorophenyl)-2-hydroxy-ethanone) were synthesized, respectively, in 84, 91 and 93% yields. 1,2,4,5-Tetrasubstituted imidazoles bearing a 4-aminophenyl substituent were synthesized using silica gel as solid support and $H_3[PW_{12}O_{40}]$ as a catalyst through the condensation of aryl diketones, *p*-phenylenediamine, benzaldehyde and ammonium acetate under microwave irradiation and solvent-free condition.

It was reported that HPA was an effective catalyst to synthesize 1,2,4,5-tetrasubstituted imidazole derivatives starting from benzil, aniline or benzyl amine or methyl amine in ethanol (Javid et al. 2011; Heravi et al. 2007b). At the beginning of our investigation, to obtain imidazole derivative with good luminescence property, *bis*(1,2,4,5-tetrasubstituted imidazole) connected by a benzene ring was designed and synthesized, changing conventional heating into microwave irradiation. Unfortunately, the target product was not obtained starting from benzil, *p*-phenylenediamine and benzaldehyde using SiO_2 or $H_3[PW_{12}O_{40}]$ as a solid support or a catalyst. The obtained product was confirmed to be 4-(2,4,5-triphenyl-1*H*-imidazol-1-yl)aniline by detection with HRMS and NMR. The possible reason was that the 2,4,5-triphenyl-1*H*-imidazol-1-yl group resulted in the poor nucleophilicity of the amino group on the benzene ring, along with the steric hindrance of 4-(2,4,5-triphenyl-1*H*-imidazol-1-yl)aniline. Sequentially, the synthesis of 1,2,4,5-tetrasubstituted imidazole was attempted in ethanol using $H_3[PW_{12}O_{40}]$ as a catalyst, starting from benzil and aniline or *p*-phenylenediamine referring to the literatures (Javid et al. 2011; Heravi et al. 2007b). As a result, 1,2,4,5-tetraphenyl-1*H*-imidazole was obtained with a 82.8% yield in 15 min. Nonetheless, the yields of obtained 4-(2,4,5-triphenyl-1*H*-imidazol-1-yl) aniline (**2a**) only was 39.8% for 30 min and 50.3% for 6 h (repeated twice), respectivly. To obtain a higher yield, $H_3[PW_{12}O_{40}]$ as a catalyst and silica gel as a solid support were explored under microwave irradiation. Herein, the effects of catalyst loading, microwave irradiation time and the molar ratio of the reactant on the yield of the synthesizing 4-(2,4,5-triphenyl-1*H*-imidazol-1-yl)aniline (**2a**) were explored by employing benzil, *p*-phenylenediamine, benzaldehyde and ammonium acetate (Table 1).

As shown in Table 1, we successfully synthesized the desired product **2a** in 23.5–78.3% using *p*-phenylenediamine (A), benzil (B), benzaldehyde (C) and ammonium acetate (D) in the presence of $H_3[PW_{12}O_{40}]$ as a catalyst (Table 1, entries 3–12) and in catalyst-free condition

Table 1 Effect of reaction factors on synthesizing **2a**



A B C D 2a

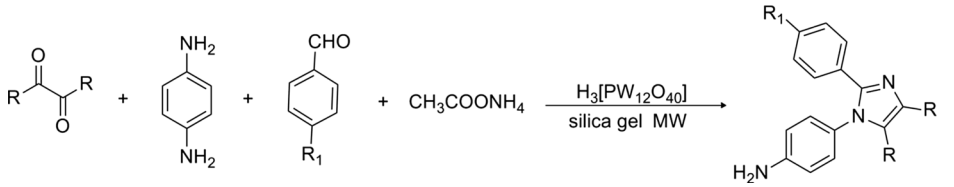
Entry	Substrate A:B:C:D	Catalyst		*T* (°C)	Time (min)	Yield[a] (%)
		Catalyst	Equiv (%)			
1	1:2:2:8	None	–	130	15	56.8
2	1:2:2:8	None	–	130	20	57.3
3	1:2:2:8	$H_3[PW_{12}O_{40}]$	0.7	130	15	78.3
4	1:2:2:8	$H_3[PW_{12}O_{40}]$	0.2	130	15	63.7
5	1:2:2:8	$H_3[PW_{12}O_{40}]$	1.2	130	15	78.1
6	1:2:2:8	$H_3[PW_{12}O_{40}]$	0.7	130	5	23.5
7	1:2:2:8	$H_3[PW_{12}O_{40}]$	0.7	130	10	47.3
8	1:2:2:8	$H_3[PW_{12}O_{40}]$	0.7	130	18	78.3
9	1:2:2:8	$H_3[PW_{12}O_{40}]$	0.7	130	20	78.9
10	1:1:1:4	$H_3[PW_{12}O_{40}]$	0.7	130	15	71.2
11	1:1:1:8	$H_3[PW_{12}O_{40}]$	0.7	130	15	69.6
12	1:1.3:1.3:8	$H_3[PW_{12}O_{40}]$	0.7	130	15	72.2

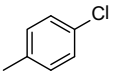
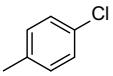
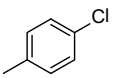
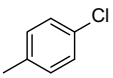
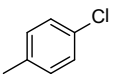
[a] Isolated product yield

(Table 1, entries 1, 2), respectively. Further, the reaction condition was optimized. The influence of catalyst loading on the yield was investigated. The yield of **2a** was increased significantly with increasing catalyst loading from 0 to 0.7% mol of *p*-phenylenediamine or benzil (Table 1, entries 1, 3 and 4). Nevertheless, the yield of **2a** was basically the same when $H_3[PW_{12}O_{40}]$ was loaded to 1.2% (Table 1, entry 5). Also, the effect of microwave irradiation times on the yields of the product was observed. The yield of **2a** was substantially increased under microwave irradiation for 15 min (78.3%) compared with that of shorter irradiation time. However, the yield was not obviously enhanced when the reaction time was further increased to 18 min (78.3%) and 20 min (78.9%) (Table 1, entries 3 and 6–9). Further, the effects of the different molar ratios of A, B, C, D (1:1:1:4, 1:1:1:8 and 1:1.3:1.3:4) on the yield were investigated (Table 1, entries 3 and 10–12), and the target product was, respectively, obtained with 71.2, 69.6 and 72.2% yield. Therefore, from the perspective of economic and environmental considerations, the optimized reaction conditions were identified as follows: The molar ratio of the four components was 1:1:1:4, microwave irradiation 15 min and catalyst load 0.7% mol of aryl diketone.

Subsequently, a series of novel 1,2,4,5-tetrasubstituted imidazoles bearing 4-amino phenyl had been synthesized in 46.4–79.1% yields under the optimized reaction conditions (Table 2). As shown in Table 2, aromatic aldehydes bearing both electron-donating and electron-withdrawing groups readily underwent the reaction and obtained the target products in a moderate to good yield. Better yields were obtained when using *p*-substituted benzaldehyde containing electron-donating groups and without substitutents (Table 2, $–CH_3$, entries 3 and 8; –H, entries 1, 5 and 10) as starting materials than that containing electron-withdrawing groups (Table 2, $–NO_2$, –Cl, –Br, entries 2, 4, 6, 7 and 9). When *R* was furyl, the yield was much lower than that of phenyl and substituted phenyl (Table 2, entries 1–4 and 10–12), because lower conjugation energy and rich π electron feature of the furan ring reduced the stability and eletrophilicity of carbonyl carbon. Furthermore, the structures of the synthesized 1,2,4,5-tetrasubstituted imidazoles bearing 4-amino phenyl were confirmed by FT-IR, ^1H and ^{13}C NMR and HRMS analysis (Table 3). The resonances of aryl-NH_2 proton of the synthesized compounds exhibited at 5.29–5.47 ppm, while the resonances for the aryl-N–RC = N–carbon atom on imidazole ring were observed at 145.4–147.9 ppm (DMSO as the solvent).

Table 2 Synthesis of compounds of 1,2,4,5-tetrasubstituted imidazoles bearing 4-amino phenyl



Entry	R–	R_1	Produce	Yield [b] (%)	M.p. (°C)
1		H	**2a**	71.2	224-226
2		Br	**2b**	56.6	220-222
3		CH_3	**2c**	67.0	237-239
4		NO_2	**2d**	53.8	244-246
5		H	**2e**	79.1	225-227
6		Cl	**2f**	60.9	218-220
7		Br	**2g**	46.4	217-218
8		CH_3	**2h**	74.3	241-243
9		NO_2	**2i**	58.9	234-236
10		H	**2j**	62.4	244-246
11		Cl	**2k**	56.4	198-201
12		Br	**2l**	48.7	212-214

Reaction conditions: p-phenylenediamine (1 mmol), aryl diketone (1 mmol), benzaldehyde derivatives (1 mmol), ammonium acetate (4 mmol), silica gel (1 g), $H_3[PW_{12}O_{40}]$ (0.7%), MW heating 15 min

[a] Isolated product yield

Luminescence properties of the synthesized compounds

Substituted groups effects on the spectral properties

The absorbance and fluorescence properties of compounds **2a**–**2l** (1.0×10^{-6} mol/L) in 0.05 M H_2SO_4 aqueous solution and in dichloromethane (DCM) excited at corresponding excitation wavelength were measured and are summarized in Table 4. Besides, Φ_u were measured and calculated against quinine sulfate as a standard (Table 4) according to the literature (Gill 1969; Fletcher 1969; Ci and Jia 1986). The maximum emission wavelengths of **2a**–**2l** in 0.05 M H_2SO_4 aqueous solution red-shifted, and their Φ_u decreased comparing with that of in DCM. The main reason was that H_2SO_4 protonated amino

Table 3 Characterization data of synthesized compounds

Compound	Characterizing data
2a	IR(KBr) ν (cm^{-1}): 3445, 3053, 1599, 1514, 1287, 1169, 1072, 961, 835, 692, 538.
	^{1}H NMR (500 MHz, DMSO) δ (ppm): 7.46 (dd, J = 6.2, 3.5 Hz, 4H), 7.30 (dd, J = 7.1, 5.5 Hz, 6H), 7.26–7.20 (m, 4H), 7.15 (t, J = 7.9 Hz, 1H), 6.86 (d, J = 8.6 Hz, 2H), 6.42 (d, J = 8.6 Hz, 2H), which were ascribed to H on benzene rings. 5.30 (s, amino 2H)
	^{13}C NMR (125 MHz, DMSO) δ (ppm): 149.3 (1-phenyl–C4), 146.5 (imidazole–C2), 137.0 (2-phenyl–C1), 135.2 (imidazole–C5, 4-phenyl–C1), 132.2 (5-phenyl–C1), 131.6 (2-phenyl–C4), 129.5 (imidazole–C4), 128.8, 128.6, 128.5, 126.8 (ascribed to non-quaternary carbon of 2-phenyl, 4-phenyl and 5-phenyl.), 126.7 (1-phenyl–C3, C5) 125.0 (1-phenyl–C1), 114.1 (1-phenyl–C2, C6)
	HRMS, m/z: $(M + H)^+$ calcd for $C_{27}H_{22}N_3$ 388.1814, found 388.1791
2b	IR(KBr) ν (cm^{-1}): 3441, 3319, 3207, 3040, 1638, 1516, 1442, 1294, 1167, 1074, 964, 822, 777, 700, 640, 536
	^{1}H NMR (500 MHz, DMSO) δ (ppm): 7.52 (d, J = 8.6 Hz, 2H), 7.46 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 8.7 Hz, 2H), 7.35–7.29 (m, 3H), 7.28–7.19 (m, 4H), 7.16 (t, J = 7.3 Hz, 1H), 6.87 (d, J = 8.6 Hz, 2H), 6.43 (d, J = 8.6 Hz, 2H), which were ascribed to H on benzene rings. 5.33 (s, amino 2H).^{13}C NMR (125 MHz, DMSO) δ(ppm): 149.38(1-phenyl–C4), 145.36 (imidazole–C2), 137.08 (2-phenyl–C1), 134.96 (imidazole–C5), 133.29 (4-phenyl–C1), 132.52 (5-phenyl–C1), 131.10 (2-phenyl–C4), 130.07 (imidazole–C4), 131.56, 130.02, 129.45, 128.82, 128.71, 128.71, 128.65, 126.82(ascribed to non-quaternary carbon of 2-phenyl, 4-phenyl and 5-phenyl.) 126.77 (1-phenyl–C3, C5), 124.68(1-phenyl–C1), 114.15 (1-phenyl–C2, C6)
	HRMS, m/z: $(M + H)^+$ calcd for $C_{27}H_{21}BrN_3$ 466.0919, found 466.1142
2c	IR(KBr) ν (cm^{-1}): 3441, 3321, 3207, 3049, 2957, 2875, 1628, 1514, 1477, 1290, 1139, 1010, 961, 827, 750, 696, 518
	^{1}H NMR (500 MHz, DMSO) δ (ppm): 7.49–7.44 (m, 2H), 7.36–7.28 (m, 5H), 7.25–7.19 (m, 4H), 7.15 (t, J = 7.3 Hz, 1H), 7.10 (d, J = 8.1 Hz, 2H), 6.83 (d, J = 8.6 Hz, 2H), 6.42 (d, J = 8.6 Hz, 2H), which were ascribed to H on benzene rings. 5.29 (s, amino 2H), 2.27 (s, 3H)
	^{13}C NMR (125 MHz, DMSO) (ppm): 149.18(1-phenyl–C4), 146.65 (imidazole–C2), 137.92 (2-phenyl–C1), 136.76 (imidazole–C5), 135.21 (4-phenyl–C1), 131.97 (5-phenyl–C1), 131.59 (2-phenyl–C4), 131.37 (imidazole–C4), 128.46 (2-phenyl–C4), 129.52, 129.11, 128.78, 128.57, 128.52, 126.76(ascribed to non-quaternary carbon of 2-phenyl, 4-phenyl and 5-phenyl.), 126.65(1-phenyl–C3, C5), 125.10(1-phenyl–C1), 114.08(1-phenyl–C2, C6), 21.22(CH_3–C)
	HRMS, m/z: $(M + H)^+$ calcd for $C_{28}H_{24}N_3$ 402.1970, found 402.1961
2d	IR(KBr) ν ($cm^{-1)}$: 3441, 3327, 3211, 3026, 1622, 1514, 1475, 1290, 1167, 1090, 1010, 829, 773, 635, 509
	^{1}H NMR (500 MHz, DMSO) δ (ppm): 8.20–8.16 (m, 2H), 7.73–7.69 (m, 2H), 7.50–7.47 (m, 2H), 7.36–7.32 (m, 3H), 7.28–7.23 (m, 4H), 7.19 (t, J = 7.3 Hz, 1H), 6.92 (d, J = 8.6 Hz, 2H), 6.46 (d, J = 8.7 Hz, 2H), which were ascribed to H on benzene rings 5.39 (s, amino 2H)
	^{13}C NMR (125 MHz, DMSO) δ (ppm): 149.67(2-phenyl–C4), 146.93 (1-phenyl–C4), 144.31 (imidazole–C2), 138.01 (imidazole–C5), 137.15 (4-phenyl–C1), 134.63 (2-phenyl–C1), 133.78 (5-phenyl–C1), 130.73 (imidazole–C4), 131.54, 129.38, 128.99, 128.84, 128.88, 128.65 127.10 (ascribed to non-quaternary carbon of 2-phenyl, 4-phenyl and 5-phenyl.), 126.83((1-phenyl–C3, C5), 124.32(1-phenyl–C1), 123.90 (2-phenyl–C3, C5), 114.24 (1-phenyl–C2, C6)
	HRMS, m/z: $(M + H)^+$ calcd for $C_{27}H_{21}N_4O_2$ 433.1665, found 433.1685
2e	IR (KBr) ν (cm^{-1}): 3474, 3385, 3041, 1618, 1514, 1285, 1285, 1136, 1090, 957, 831, 773, 692, 500
	^{1}H NMR (500 MHz, DMSO) δ (ppm): 7.49–7.43 (m, 4H,), 7.39 (d, J = 8.4 Hz, 2H,), 7.34 (d, J = 8.6 Hz, 2H), 7.32–7.29 (m, 3H,), 7.25 (d, J = 8.4 Hz, 2H), 6.87 (d, J = 8.6 Hz, 2H), 6.44 (d, J = 8.6 Hz, 2H), which were ascribed to H on benzene rings. 5.35 (s, amino 2H)
	^{13}C NMR (125 MHz, DMSO) δ(ppm): 149.43 (1-phenyl–C4), 147.00 (imidazole–C2,), 136.11(2-phenyl–C1), 133.80(4-phenyl–C1), 133.61(imidazole–C5), 131.44 and 131.21(4,5-phenyl–C4), 130.92(2-phenyl–C4), 129.85 (5-phenyl–C1), 133.30, 129.50, 129.06, 128.78, 128.57, 128.56 and 128.55(ascribed to non-quaternary carbon of 2-phenyl, 4-phenyl and 5-phenyl.), 128.42(1-phenyl–C3, C5), 124.60(1-phenyl–C1), 114.14(1-phenyl–C2, C6)
	HRMS, m/z: $(M + H)^+$ calcd for $C_{27}H_{20}Cl_2N_3$ 456.1034, found 456.1023
2f	IR (KBr) ν (cm^{-1}): 3441, 3319, 3206, 3040, 1638, 1516, 1443, 1294, 1167, 1074, 964, 822, 777, 700, 640, 536
	^{1}H NMR (500 MHz, DMSO) δ (ppm): 7.53 (d, J = 1.9 Hz, 1H), 7.52–7.51 (m, 1H), 7.46 (d, J = 2.0 Hz, 1H), 7.46–7.44 (m, 1H), 7.39 (dd, J = 7.0, 1.6 Hz, 4H), 7.35 (*d*, J = 2.1 Hz, 1H), 7.33 (s, 1H), 7.25 (s, 1H), 7.23 (s, 1H), 6.88 (d, J = 8.6 Hz, 2H), 6.45 (d, J = 8.7 Hz, 2H), which were ascribed to H ascribe to on benzene rings. 5.38 (s, amino 2H)
	^{13}C NMR (125 MHz, DMSO) δ(ppm): 149.58 (1-phenyl–C4), 145.92(imidazole–C2,), 136.32 (2-phenyl–C1), 133.72 (imidazole–C5), 133.62 (4-phenyl–C1), 131.55 (2-phenyl–4C), 130.08 (4-phenyl–4C, 5-phenyl–4C), 129.67 (imidazole–C4), 133.29, 131.62, 130.38, 129.42, 129.09 and 128.81(ascribed to non-quaternary carbon of 2-phenyl, 4-phenyl and 5-phenyl.), 128.43 (1-phenyl–C3, C5), 124.27 (5-phenyl–C1), 122.25 (1-phenyl–C1), 114.20 (1-phenyl–C2, C6)
	HRMS, m/z: $(M + H)^+$ calcd for $C_{27}H_{19}Cl_3N_3$ 490.0645, found 490.1003

Table 3 continued

Compound	Characterizing data
2g	IR(KBr) v (cm^{-1}): 3458, 3319, 3204, 3053, 1622, 1516, 1296, 1138, 1094, 1015, 837, 759, 640
	^{1}H NMR (500 MHz, DMSO) δ (ppm): 7.53 (d, J = 1.9 Hz, 1H), 7.52–7.51 (m, 1H), 7.46 (d, J = 2.0 Hz, 1H), 7.46–7.44 (m, 1H), 7.40 (d, J = 2.0 Hz, 1H), 7.39 (d, J = 1.1 Hz, 2H), 7.38–7.36 (m, 1H), 7.35 (d, J = 2.1 Hz, 1H), 7.33 (s, 1H), 7.24 (d, J = 8.5 Hz, 2H), 6.88 (d, J = 8.6 Hz, 2H), 6.45 (d, J = 8.7 Hz, 2H), which were ascribed to H on benzene rings. 5.38 (s, amino 2H)
	^{13}C NMR (125 MHz, DMSO) δ(ppm): 149.58(1-phenyl–C4), 145.87 (imidazole–C2,), 136.29 (2-phenyl–C1), 133.71 (imidazole–C5), 133.63 and 133.52(4-phenyl–C4 and 5-phenyl–C4), 131.55 (4-phenyl–C1), 131.51 (imidazole–C4), 129.73 (5-phenyl-C1), 129.68 (2-phenyl-C4), 133.29, 130.12, 129.43, 129.09, 128.81, 128.71, 128.43 (ascribed to non-quaternary carbon of 2-phenyl, 4-phenyl and 5-phenyl.), 124.29 (1-phenyl–C1), 114.20(1-phenyl–C2,C6)
	HRMS, m/z: $(M + H)^+$ calcd for $C_{27}H_{19}BrCl_2N_3$ 534.0139, found 534.0175
2h	IR (KBr) v (cm^{-1}): 3431, 3341, 3233, 3052, 2931, 2873, 1597, 1516, 1342, 1093, 1013, 833, 719, 624, 514
	^{1}H NMR (500 MHz, DMSO) δ (ppm): 7.46 (d, J = 8.7 Hz, 2H), 7.38 (d, J = 8.5 Hz, 2H), 7.33 (d, J = 8.8 Hz, 4H), 7.23 (d, J = 8.5 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 6.85 (d, J = 8.6 Hz, 2H), 6.44 (d, J = 8.7 Hz, 2H), which were ascribed to H on benzene rings. 5.34 (s, amino 2H), 2.27 (s, 3H, CH_3 H)
	^{13}C NMR (125 MHz, DMSO) δ(ppm): 149.39 (1-phenyl–C4), 147.17 (imidazole–C2), 138.19 (2-phenyl–C1), 135.98 (imidazole–C5), 133.87 and 133.57 (4,5-phenyl–C1), 131.38 and 130.98 (4,5-phenyl–C4), 129.93 (imidazole–C4), 133.31, 129.51, 129.05, 128.76 and 128.50 (ascribed to non-quaternary carbon of 2-phenyl, 4-phenyl and 5-phenyl.), 128.42 (1-phenyl–C3,C5), 128.14 (2-phenyl–C1), 124.70 (1-phenyl–C1), 114.14 (1-phenyl–C2,C6), 21,23 (CH_3–C)
	HRMS, m/z: $(M + H)^+$ calcd for $C_{28}H_{22}Cl_2N_3$ 470.1191, found 470.1109
2i	IR (KBr) v (cm^{-1}): 3474, 3381, 3053, 1624, 1518, 1477, 1292, 1169, 1092, 1074, 961, 831, 729, 698, 500
	^{1}H NMR (500 MHz, DMSO) δ(ppm): 8.18 (d, J = 9.0 Hz, 2H), 7.70 (d, J = 9.1 Hz, 2H), 7.48 (d, J = 8.7 Hz, 2H), 7.42 (d, J = 8.5 Hz, 2H), 7.37 (d, J = 8.6 Hz, 2H), 7.27 (d, J = 8.5 Hz, 2H), 6.93 (d, J = 8.6 Hz, 2H), 6.48 (d, J = 8.6 Hz, 2H), which were ascribed to H on benzene rings. 5.44 (s, amino 2H)
	^{13}C NMR (125 MHz, DMSO) δ (ppm): 149.84 (1-phenyl–C4, 2-phenyl–C4), 147.09 (2-phenyl–C1), 144.80(imidazole–C2), 137.14 (imidazole–C5), 136.85(4-phenyl–C1), 133.95 and 133.31 (4,5-phenyl–C4), 132.70 (imidazole–C4), 131.83 (5-phenyl–C1), 129.32 (1-phenyl–C1), 133.29, 129.11, 128.89 and 123.93 (ascribed to non-quaternary carbon of 2-phenyl, 4-phenyl and 5-phenyl.), 128.49 (1-phenyl–C3, C5), 114.29 (1-phenyl–C2, C6)
	HRMS, m/z: $(M + H)^+$ calcd for $C_{27}H_{19}Cl_2N_4O_2$ 501.0885, found 501.1028
2j	IR (KBr) v (cm^{-1}): 3421, 3325, 3221, 3043, 3128, 1631, 1516, 1469, 1292, 1168, 1072, 1010, 887, 775, 740, 594, 540
	^{1}H NMR (300 MHz, DMSO) δ (ppm): 7.71–7.66 (m, 1H), 7.66–7.61 (m, 1H), 7.45 (dd, J = 6.6, 3.2 Hz, 2H), 7.34–7.29 (m, 3H), 6.94–6.89 (m, 2H), 6.49 (ddd, J = 11.1, 3.4, 1.8 Hz, 5H), 6.27 (d, J = 3.1 Hz, 1H), which were ascribed to H on benzene rings and furan rings. 5.42 (s, amino 2H)
	^{13}C NMR (125 MHz, DMSO) δ(ppm): 149.75 and 149.29 (4-furyl–C2, 5-furyl–C2), 147.89(1-phenyl–C4), 142.96 (imidazole–C2), 132.43 (2-phenyl–C1), 130.53(imidazole–C4), 129.12, 128.97 (4-furyl–C5, 5-furyl–C5), 128.66 128.65 (1-phenyl–C2, C6),128.60 (imidazole–C5), 122.40 (1-phenyl–C1), 114.18 (1-phenyl–C2, C6), 112.64, 111.73, 111.57, 107.15(4-furyl–C3,C4 and 5-furyl–C3,C4)
	HRMS, m/z: $(M + H)^+$ calcd for $C_{23}H_{18}N_3O_2$ 368.1399, found 368.1398
2k	IR (KBr) v (cm^{-1}): 3448, 3317, 3212, 3136, 3037, 1635, 1519, 1300, 1168, 1090, 1014, 833, 736, 594, 520
	^{1}H NMR (300 MHz, DMSO) δ (ppm): 7.69 (dd, J = 1.9, 0.8 Hz, 1H), 7.65 (dd, J = 1.8, 0.9 Hz, 1H), 7.42 (d, J = 6.6 Hz, 4H), 6.93 (d, J = 8.7 Hz, 2H), 6.55–6.47 (m, 5H), 6.27 (dd, J = 3.4, 0.8 Hz, 1H), which were ascribed to H on benzene rings and furan rings.5.46 (s, amino 2H)
	^{13}C NMR (125 MHz, DMSO) δ(ppm): 149.89 and 149.13(4-furyl–C2, 5-furyl–C2), 146.77 (1-phenyl–C4), 142.79 (imidazole–C2), 133.82 (1-phenyl–C1), 132.53(imidazole–C4), 130.27 (5-furyl–C5, 4-furyl–C5), 129.35 (2-phenyl–C2,C6), 129.06 (imidazole–C5), 128.74 (2-phenyl–C3,C5), 124.31 (2-phenyl–C4), 122.65 (1-phenyl–C1), 114.24 (1-phenyl–C2, C6), 112.73, 111.75, 111.59, 107.27 (4-furyl–C3,C4 and 5-furyl–C3,C4)
	HRMS, m/z: $(M + H)^+$ calcd for $C_{23}H_{17}ClN_3O_2$ 402.1009, found 402.1023
2l	IR (KBr) v (cm^{-1}): 3441, 3309, 3209, 3136, 3051, 1635, 1519, 1296, 1165, 1068, 1010, 829, 748, 594, 516
	^{1}H NMR (300 MHz, DMSO) δ (ppm): 7.70 (dd, J = 1.9, 0.7 Hz, 1H), 7.65 (dd, J = 1.7, 0.8 Hz, 1H), 7.56–7.52 (m, 2H), 7.40–7.34 (m, 1H), 6.97–6.90 (m, 2H), 6.55–6.46 (m, 3H), 6.28 (d, J = 0.8 Hz, 1H), which were ascribed to H on benzene rings and furan rings.5.47 (s, amino 2H)
	^{13}C NMR (125 MHz, DMSO) δ(ppm): 149.90 and 149.11 (4-furyl–C2, 5-furyl–C2), 146.78 (1-phenyl–C4), 142.78 (imidazole–C2), 132.56 (1-phenyl–C1), 131.65 and 130.51 (5-furyl–C5, 4-furyl–C5), 129.70 (imidazole–C4), 129.05 (2-phenyl–C3,C5), 128.7 (2-phenyl–C2,C6) 124.30 (imidazole–C5), 122.69 (1-phenyl–C1), 122.57 (2-phenyl–C4), 114.23 (1-phenyl–C2, C6), 112.74, 111.76, 111.60, 107.28 (4-furyl–C3,C4 and 5-furyl–C3,C4)
	HRMS, m/z: $(M + H)^+$ calcd for $C_{23}H_{17}BrN_3O_2$ 446.0504, found 446.0532

Table 4 Fluorescence properties of compounds of 1,2,4,5-tetrasubstituted imidazoles bearing 4-amino phenyl

Compound	λ_{max} (nm)	F_{smax} (nm)	F^{W}_{lmax} (nm)	Φ^{W}_{u}	F^{D}_{lmax} (nm)	Φ^{D}_{u}
2a	276	384	405	0.273	381	0.406
2b	268	397	415	0.195	385	0.189
2c	267	385	417	0.332	381	0.468
2d	260	396	411	0.002	380	0.009
2e	286	389	418	0.215	392	0.406
2f	281	394	419	0.239	387	0.380
2g	286	394	419	0.134	388	0.125
2h	280	386	417	0.487	401	0.633
2i	283	394	414	0.004	400	0.011
2j	297	411	487	0.133	408	0.399
2k	299	393	486	0.115	419	0.334
2l	298	397	488	0.086	422	0.053
m	311	–	460	0.376	415	0.744
n	287	–	467	0.101	411	0.145

Φ^{W}_{u} and Φ^{D}_{u} are the fluorescence quantum yields in 0.05 M H_2SO_4 aqueous solution H_2SO_4 and in dichloromethane (DCM) using quinine sulfate as standard

F^{W}_{lmax}, F^{D}_{lmax} F_{smax} are the emission wavelengths excited at corresponding wavelength with gap 3 and 1 mm, respectively, in 0.05 M H_2SO_4 aqueous solution H_2SO_4, in dichloromethane (DCM) and in the solid state

group of 4-amino phenyl group in 0.05 M H_2SO_4 aqueous solution, which led to fluorescence quenching (Huang et al. 2012). Also, the emission of the synthesized compounds bearing furan rings redshifted about 20 nm compared to the corresponding compounds with 1-benzyl (Chen et al. 2013) in the above H_2SO_4 solution. This was because of the interaction of n–π and π–π electrons, along with coplanarity between 4-amino phenyl and trisubstituted imidazole (Huang, et al., 2012). In addition, compared to our previous work, Φ_u of **2j** (0.133 in 0.05 M H_2SO_4 aqueous solution and 0.399 in DCM) was lower than that of 4,5-di(furan-2-yl)-2-phenyl-1*H*-imidazole (Li et al. 2012) (**m**, Table 4) (0.376 in 0.05 M H_2SO_4 aqueous solution and 0.744 in DCM), but higher than that of 1-benzyl-4,5-di(furan-2-yl)-2-phenyl-1*H*-imidazole (Nagarapu et al. 2007) (**n**, Table 4) (0.101 and 0.145). This is likely because the coplanarity of trisubstituted imidazole is superior to tetrasubstituted imidazole. Also, the conjugate effect of amino phenyl is superior to benzyl, which improved the fluorescence properties and enhanced Φ_u of the synthesized compounds.

Furthermore, as shown in Table 4, the emission wavelengths of **2a**–**2l** in 0.05 M H_2SO_4 aqueous solution (F^{w}_{lmax}) and in DCM (F^{D}_{lmax}) were, respectively, from 405 to 488 nm and from 381 to 422 nm. They emitted purple light. Herein, Φ_u (from 0.002 to 0.487 and from 0.009 to 0.633) of **2a**–**2l**, respectively, in 0.05 M H_2SO_4 aqueous solution and in DCM changed depending on the substituents investigated. The effects of substituents on the maximal emission wavelength and Φ_u were mainly relative to the 2-position substituent groups of imidazoles when 4- and 5-substituted groups were the same, which was consistent with the literature (Chen et al. 2013). In H_2SO_4 aqueous solution, Φ_u of imidazole derivatives bearing furan rings on 4,5-position of imidazole (Table 4, entries **2j**–**2l**) were lower than that bearing the benzene ring and substituted benzene ring (Table 4, entries **2a**–**2i**). This was because the oxygen atom of furan rings contains a pair of non-bonding n-electron and π-electron engender n–π* and π–π* transitions in the excitation, whereas the n–π* and π–π* energy of the furan ring was much lower than the π–π* transition energy of benzene ring. In the **2e**–**2i** series, **2h** bearing $-CH_3$ similarly had the highest Φ_u (0.487) followed by **2f** (−Cl, 0.239) rather than **2e** (−H, 0.215) and then in turn **2g** (−Br, 0.134) and **2i**($-NO_2$, 0.004) (Table 3, entries **2e**–**2i**). The n-electron cloud of the chloro

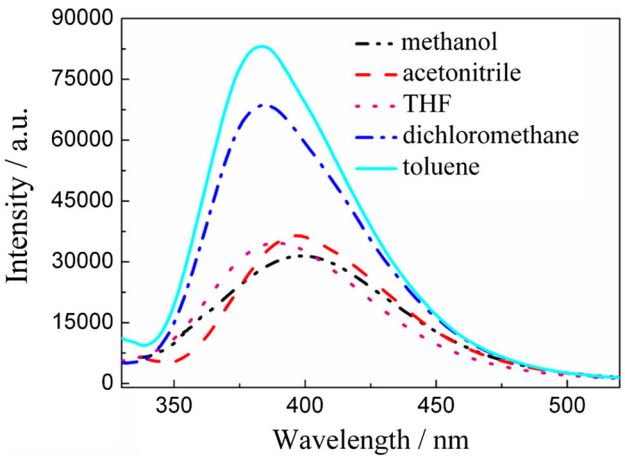


Fig. 1 The emission spectra of **2c** in the solvents with different polarities (λ_{ex} = 300 nm)

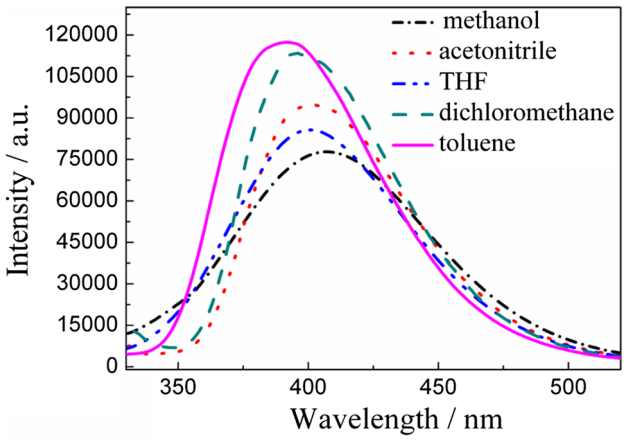


Fig. 2 The emission spectra of **2 h** in the solvents with different polarities (λ_{ex} = 300 nm)

group on 2-substituted phenyl of imidazole is almost parallel with that of the π orbit of aromatic rings, which increased the conjugated effect and coplanarity of the molecule (Table 3, entries **2e–2i**) (Xu and Wang 2006). In addition, the reason for fluorescence quenching (Table 4, entries **2d**, **2i**) was that compounds bearing nitro group could switch from the excited singlet (n, π_1^*) to triple state under light irradiation (Huang et al. 2012). However, when benzene was replaced by a low electron-withdrawing substituent, such as a halogen (entries **2f** and **2g**; **2j** and **2 k**), Φ_u gradually decreased with 2-position of tetrasubstituted imidazoles bearing 4-chlorophenyl and 4-bromophenyl, which was derived from the introduction of heavy atoms (Cl and Br) resulting in a great enhancement of the rate of S_1-T_1 spin-forbidden process (Chen et al. 1990; Chen and Tong 2014; Chandra et al. 1978). In DCM, Φ_u of the synthesized compounds was basically dependent on the electron-donating ability of the substituent. However, Φ_u of **2e** and **2f** showed abnormal change rule, and Φ_u of imidazole derivatives bearing 2-furyl on 4,5-position of imidazole (Table 4, entries **2j–2l**) were about equal to that of compounds bearing phenyl and substituted phenyl (Table 4, entries **2a–2i**). It was likely due to the repelling effect between n-electrons of oxygen atom on 2-furyl and that of chlorine atom on DCM which improved the molecular planarity. Additionally, compared with solid-state emission spectra, in the DCM solvent, the emission of the compounds redshifted 3–26 nm (Table 4, entries 5, 8, 9, 11, 12), indicating that there was a little interaction between DCM and the reported compounds (Ho et al. 2005). On the other hand, it also suggested that these compounds had strong π–π^* interaction in the solid state (Table 4, entries 1–4, 6, 7, 10).

Effects of solvent polarity on photoluminescence

Furthermore, the fluorescence emission spectra of **2c** and **2h** (1.0×10^{-6} mol/dm^3) in the solvents with different polarity (toluene, dichloromethane, THF, methanol and acetonitrile) under the same test condition are shown in Fig. 1 and 2, respectively. The corresponding data are summarized in Table 5.

Notably, the Φ_u of compounds **2c** and **2h** were decreased significantly with increasing solvent polarity (toluene, dichloromethane, THF and methanol). In toluene, Φ_u of **2c** (0.587) and **2h** (0.648) was highest and decreased with increasing solvent polarity. In methanol, the values were reduced to 0.257 (**2c**) and 0.407 (**2h**), respectively. It suggested that the polarity of the ground state molecule was much lower than the singlet excited one in the course of an intramolecular charge transfer, and stronger electrostatic interactions between the excited molecule and polar solvent were proposed to result in a decrease in Φ_u. Higher polar acetonitrile showed an anomalous increase compared to methanol and THF, maybe because of intermolecular hydrogen bonding between the acidic hydrogen of compounds **2c** and **2h** and the cyano groups of acetonitrile (Shirai et al. 2000). However, the emission bands of compound **2c** and **2h** were redshifted slightly with an increase of the solvent polarity. In toluene, the emission of **2c** and **2h** were at 383 nm (Fig. 1) and 390 nm (Fig. 2), respectively. However, in methanol, they were, respectively, redshifted to 399 nm (**2c**) and 406 nm (**2h**) due to the stronger interaction between the solvent and the excited state molecules in π–π^* transition. The excited state was more stabilized in polar solvents than that in lower polar solvents. In acetonitrile, an anomalous decrease was shown

Table 5 The emission wavelength and Φ_u of **2c** and **2h** in the solvents with different polarities (λ_{ex} = 300 nm)

Solvents	Dipole moment (Debye)	**2c**		**2h**	
		Emission wavelength (nm)	Φ_u	Emission wavelength (nm)	Φ_u
Toluene	0.43	383	0.587	390	0.648
DCM	1.60	381	0.468	401	0.633
THF	1.63	389	0.288	399	0.456
Methanol	1.70	399	0.257	406	0.407
Acetonitrile	3.45	395	0.322	401	0.546

compared to methanol for intermolecular hydrogen bonding. Also, compounds **2c** and **2h** possessed higher Φ_u. Φ_u of **2h** was obviously higher for the chloro group introduced into the imidazole ring which made the coplanarity of tetrasubstituted imidazole better.

Conclusions

A facile and efficient one-pot MCRs microwave-irradiated method for synthesizing 1,2,4,5-tetrasubstituted imidazoles bearing auxochrome 4-amino phenyl (1-position) was revealed. Twelve 1,2,4,5-imidazoles bearing a 4-aminophenyl substituent were successfully synthesized in 56.8–74.3% using $H_3[PW_{12}O_{40}]$ as a catalyst and silica gel as solid support, and Φ_u values were measured against quinine sulfate in the 0.05 M H_2SO_4 aqueous solution and the different solvents. The effects of different substituted groups on the emission and Φ_u in the 0.05 M H_2SO_4 aqueous solution, in DCM and in the solid state, were investigated. The highest Φ_u was up to 0.487 in H_2SO_4 solution, 0.648 in toluene and 0.633 in DCM. It was found that 2- and 4,5-substituents of 1,2,4,5-tetrasubstituted imidazoles with a 4-aminophenyl substituent, respectively, had much influence on Φ_u, and the emission and Φ_u of tetraimidazole compounds in solution could be restricted by the polarity of the solvents. It suggested that the synthesized compounds would have potential applications in the metal ion detection, biological pharmaceutical and material fields. In addition, the applications of 1,2,4,5-trisubstituted imidazoles bearing 4-amino phenyl in metal ion detection is being studied in our laboratory.

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