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The synthesis and preliminary optical study of 1-alkyl-2,4,5-triphenylimidazole derivatives

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Abstract

A series of 1-alkyl-2,4,5-triphenylimidazole derivatives were synthesized by the alkylation of corresponding 2,4,5-triphenylimidazole derivatives with alkyl bromide using tetra-*n*-butylammonium bromide as phase-transfer catalyst in the presence of 50% NaOH in butanone in a good yield and five 1-alkyl-2,4,5-triphenylimidazole derivatives containing benzimidazole or benzothiazole fragments in the 4′-position of 2-phenyl ring were prepared by condensation of 1-alkyl-4,5-diphenyl-2-(4-carboxyphenyl)imidazoles with *o*-benzenediamine or 2-aminothiophenol in PPA under microwave irradiation. These products were identified by ^{1}H NMR, ^{13}C NMR, MS, IR and elemental analysis. At the same time, their UV–visible absorption coefficient (ε), maximum absorption wavelengths (λ_a), fluorescence emission wavelengths (λ_e), quantum yields (Φ), fluorescence lifetime in solution and solid state were measured. Single crystal of 1-*n*-butyl-4,5-diphenyl-2-(4-carboxyphenyl)imidazoles was obtained and the structure was determined by X-ray diffraction technique, based on which the relationships between spectral behaviors and molecular structure were discussed. The alkylation method of 2,4,5-triphenylimidazole derivatives and synthetic pathway for 1-alkyl-2,4,5-triphenylimidazole derivatives containing benzimidazole or benzothiazole fragments could provide an attractive and alternative, even a convenient and efficient approach to the preparation of some useful dyes and pigments.

Keywords: Triphenylimidazole; Alkylation; Synthesis; Spectra

1. Introduction

2,4,5-Triphenylimidazole derivatives were widely used as organic materials, such as resist composition on textile [1], fluorescent whiteners on textile [2,3], photographic materials [4–6], electroluminescent materials [7,8] and optical materials [9,10]. Meantime, it was found that this kind of compounds possesses many kinds of biological activities [11–13]. It was well known to all that these compounds possess a larger conjugated-system structure and they could not be dissolved well in most of common solvents, which limits their use in many fields. But the solubility of these compounds for common organic solvents or water could be improved by introducing some alkyl groups or carboxyl group and hydroxyl group into the molecules of these compounds, respectively. It was reported [14,15] that benzimidazole derivatives could be alkylized by reaction of benzimidazole with sodium, potassium or sodium hydride as deprotonation agent. However, this reaction operation was not easy to control, because the solvent for this reaction must be dried carefully and sodium or potassium is not easy to weight. Imidazole derivatives could be alkylized by the reaction of these compounds with alkyl bromide in the presence of 50% sodium hydroxide in DMF, the reported yield is 79% [12]. Using solid potassium hydroxide as deprotonation agent in THF, the alkylation of benzimidazole could be carried out [16], the yields are 24–81% and the reaction

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time is little longer. Jayachandran even completed the alkylation of 2,4,5-triphenylimidazole derivatives by using 2-benzylidene-*N*,*N*,*N*,*N*′,*N*′,*N*′-hexaethyl-1,3-propanediammonium dibromide as phase-transfer catalyst [17]. Youngblood [18] reported recently that the alkylation of benzimidazole could be effected using 1,8-diaza-bicyclo[5,4,0]undec-7-ene as deprotonation agent in acetonitrile or *N*-methyl pyrrolidinone and the yields are 35–76%. We were interested in the synthesis and optical spectral behaviors of those compounds possessing a large conjugated system [19–23], therefore, an alkylation reaction of imidazole derivatives was investigated in our laboratory by using tetra-*n*-butylammonium bromide (TBAB) as phase-transfer catalyst in butanone and water as solvent, in order to find a convenient and efficient method for the preparation of 1-alkyl-2,4,5-triphenylimidazole derivatives in large scale for industry. As benzimidazole or benzothiazole units are a good chromophore, the condensation of 1-alkyl-4,5-diphenyl-2-(4-carboxyphenyl)imidazole with 2-aminothiophenol or *o*-benzenediamine in PPA under microwave irradiation was studied for the synthesis of 1-alkyl-4,5-diphenyl-2-(4-(benzimidazol-2-yl)phenyl)imidazole and 1-alkyl-4,5-diphenyl-2-(4-(benzothiazol-2-yl)phenyl)imidazole. At the same time, UV–visible absorption coefficient (ε), maximum absorption wavelengths (λ_a), fluorescence emission wavelengths (λ_e), fluorescence quantum yields (Φ), fluorescence lifetime (T) in solution and solid state were measured, respectively. Single crystal of 1-*n*-butyl-4,5-diphenyl-2-(4-carboxyphenyl)imidazoles was obtained and the structure was determined by X-ray diffraction technique, based on which the relationships between spectral behaviors and molecular structure were discussed. The synthetic pathway and the structures of target molecules are shown in Fig. 1.

2. Experimental

2.1. Reagents and instruments

All melting points were determined on a X4 melting point microscope. ^{1}H NMR and ^{13}C NMR spectra were run on a Bruker AVANCE-300 NMR spectrometer. Ultraviolet spectra were recorded on a SHIMADZU UV-1601 spectrophotometer. Fluorescence spectra were taken with a SHIMADZU RF-5301PC spectro-fluorophotometer. Element analysis was taken with an Elementar Vario EL. Mass spectra were taken with a SHIMADZU LCMS-2010A. Single crystal was characterized by Bruker Smart 1000 CCD X-ray single crystal diffractometer. All the chemicals are commercially available and they were used without further purification. All the solvents were dried using standard methods before use.

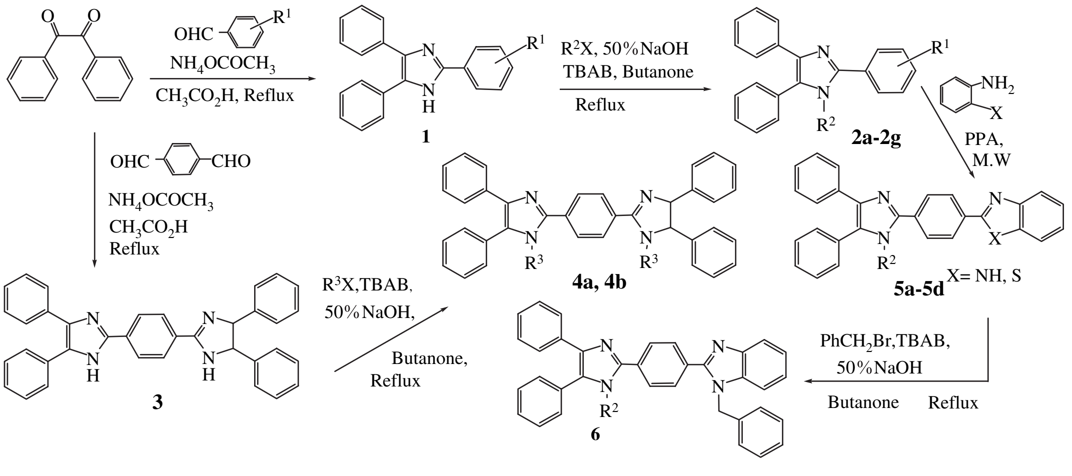
2.2. Alkylation of 2,4,5-triphenylimidazole derivatives

2.2.1. Preparation of 4,5-diphenyl-2-substituted-phenylimidazoles

4,5-Diphenyl-2-substituted-phenylimidazole compounds were prepared according to Ref. [12].

2.2.2. General procedure for alkylation of 2,4,5-triphenylimidazoles

The mixture of 2.5 mmol of 4,5-diphenyl-2-substituted-phenylimidazole, 3.0 mmol of alkyl bromide, 0.20 g of TBAB, 5 mL of 50% sodium hydroxide and 10 mL of butanone was refluxed for 1.5–3.5 h and the mixture was monitored by TLC. After butanone was evaporated under reduced



2a R^1 = 2-Nitrophenyl, R^2 = n-butyl; **2b** R^1 = 4-Dimethylaminophenyl, R^2 = n-butyl; **2c** R^1 = 3,4-(Methylenedioxy)phenyl, R^2 = n-butyl; **2d** R^1 = 4-Bromophenyl, R^2 = n-butyl; **2e** R^1 = 4-Carboxyphenyl, R^2 = n-butyl; **2f** R^1 = Carboxyphenyl, R^2 = n-dodecyl; **2g** R^1 = 2-Styryl, R^2 = n-butyl; **4a** R^3 = n-Butyl; **4b** R^3 = n-Dodecyl; **5a** R^2 = n-Butyl, X = NH; **5b** R^2 = n-Butyl, X = S; **5c** R^2 = n-Dodecyl, X = HN; **5d** R^2 = n-Dodecyl, X =S; **6** R^2 = n-Butyl, X = BenzylN.

Fig. 1. The synthetic pathway and the structures of target molecules.

pressure, the residue was poured into 100 mL of water, the solid was filtrated and recrystallized from ethanol or dichloromethane to offer the pure product.

*2.2.2.1. 1-n-Butyl-4,5-diphenyl-2(2-nitrophenyl)imidazole (**2a**).* Yield 86.1%; m.p. 146–147 °C. (DMSO-d_6): 0.58 (t, $J = 7.5$ Hz, 3H), 0.93–0.97 (m, 2H), 1.00–1.31 (m, 2H), 3.68 (t, $J = 7.8$ Hz, 2H), 7.11–7.20 (m, 3H), 7.43–7.47 (m, 7H), 7.48–7.51 (m, 1H), 7.64–7.68 (m, 2H), 8.15–8.17 (m, 1H). ESI-MS (*m/z*): 398 $(M + H)^+$.

*2.2.2.2. 1-n-Butyl-4,5-diphenyl-2(4-dimethylaminophenyl) imidazole (**2b**).* Yield 93.3%; m.p. 143–145 °C. (DMSO-d_6): 0.63 (t, $J = 7.3$ Hz, 3H), 0.94–1.02 (m, 2H), 1.29–1.35 (m, 2H), 3.00 (s, 6H), 3.84 (t, $J = 7.2$ Hz, 2H), 6.77 (d, $J = 2.0$ Hz, 1H), 7.10–7.19 (m, 3H), 7.28 (d, $J = 4.4$ Hz, 1H), 7.37–7.56 (m, 8H), 7.75 (d, $J = 4.4$ Hz, 1H). ESI-MS (*m/z*): 396 $(M + H)^+$.

*2.2.2.3. 1-n-Butyl-4,5-diphenyl-2(3,4-(methylenedioxy)phenyl) imidazole (**2c**).* Yield 92.1%; m.p. 86–88 °C. (DMSO-d_6): 0.61 (t, $J = 7.6$ Hz, 3H), 0.93–1.02 (m, 2H), 1.27–1.35 (m, 2H), 3.85 (t, $J = 7.6$ Hz, 2H), 6.02 (s, 2H), 6.91 (d, $J = 7.6$ Hz, 1H), 7.08–7.13 (m, 1H), 7.15–7.19 (m, 4H), 7.38–7.40 (m, 2H), 7.42–7.45 (m, 3H), 7.48–7.51 (m, 2H). ESI-MS (*m/z*): 397 $(M + H)^+$.

*2.2.2.4. 1-n-Butyl-4,5-diphenyl-2(4-bromophenyl)imidazole (**2d**).* Yield 91.6%; m.p. 108.0–109.5 °C [107–110 °C] [12]. (DMSO-d_6): 0.62 (t, $J = 7.2$ Hz, 3H), 0.93–1.02 (m, 2H), 1.28–1.34 (m, 2H), 3.86 (t, $J = 8.6$ Hz, 2H), 7.09–7.13 (m, 1H), 7.15–7.20 (m, 2H), 7.37–7.39 (m, 2H), 7.44–7.49 (m, 5H), 7.55–7.61 (m, 4H); 13.4, 19.6, 32.6, 44.7, 123.0, 126.2, 126.6, 127.9, 128.6, 128.9, 129.9, 130.3, 130.5, 130.8, 131.2, 131.7, 134.2, 137.8, 146.2. ESI-MS (*m/z*): 431.1 $(M + H)^+$.

*2.2.2.5. 1-n-Butyl-4,5-diphenyl-2(4-carboyphenyl)imidazole (**2e**).* Yield 50.5%; m.p. 124–126 °C. ^{1}H NMR (DMSO-d_6): 0.55 (t, $J = 7.2$ Hz, 3H), 0.90–1.02 (m, 2H), 1.28–1.38 (m, 2H), 4.11 (t, $J = 6.9$, 2H), 7.36–7.44 (m, 5H), 7.57–7.63 (m, 5H), 8.06 (d, $J = 8.4$ Hz, 2H), 8.25 (d, $J = 8.1$ Hz, 2H). ESI-MS (*m/z*): 397 $(M + H)^+$.

*2.2.2.6. 1-n-Dodecyl-4,5-diphenyl-2(4-carboyphenyl)imidazole (**2f**).* Yield 64.9%; m.p. 93–95 °C. ^{1}H NMR (DMSO-d_6): 0.84–1.19 (m, 23H), 3.93 (t, $J = 7.2$ Hz, 2H), 7.10–7.21 (m, 3H), 7.38–7.54 (m, 7H), 7.86 (dd, $J_1 = 8.4$ Hz, $J_2 = 2.1$ Hz, 2H), 8.07 (d, $J = 8.4$ Hz, 2H). ESI-MS (*m/z*): 510 $(M + H)^+$.

*2.2.2.7. 1-n-Butyl-4,5-diphenyl-2-styrylimidazole (**2g**).* Yield 53.06%; m.p. 123.5–124.5 °C. ^{1}H NMR (CDCl$_3$): 0.72 (t, $J = 7.5$ Hz, 3H), 1.07–1.19 (m, 2H), 1.46–1.56 (m, 2H), 3.78 (t, $J = 7.5$ Hz, 2H), 6.89 (d, $J = 16.0$ Hz, 1H), 7.01–7.17 (m, 3H), 7.19–7.31 (m, 5H), 7.34–7.36 (m, 3H), 7.41 (d, $J = 7.8$ Hz, 2H), 7.48 (d, $J = 7.5$ Hz, 2H), 7.65 (d, $J = 15.9$ Hz, 1H). ^{13}C NMR (CDCl$_3$): 14.0, 20.3, 33.8, 43.8, 114.2, 126.8, 127.3, 127.4, 128.6, 128.7, 129.2, 129.3, 129.5, 130.1, 131.6, 131.6, 133.2, 135.0, 137.4, 138.8, 145.2. IR (KBr) ν: 3429, 2959, 1500, 1462, 761, 697 cm^{-1}. ESI-MS (*m/z*): 379 $(M + H)^+$. Element analysis for $C_{27}H_{26}N_2$, Calc.: C, 85.68; H, 6.92; N, 7.40; Found: 85.47; H, 7.44; N, 7.43.

*2.2.2.8. 1-Butyl-2-(4-(1-butyl-4,5-diphenylimidazol-2-yl)-phenyl)-4,5-diphenylimidazole (**4a**).* Yield 61.1%; m.p. 300.5–301.5 °C. ^{1}H NMR (CDCl$_3$): 0.65 (t, $J = 7.2$ Hz, 6H), 1.02–1.08 (m, 4H), 1.35–1.42 (m, 4H), 3.97 (t, $J = 7.5$ Hz, 4H), 7.13–7.22 (m, 6H), 7.42–7.55 (m, 14H), 7.89 (s, 4H). IR (KBr) ν: 3432, 2956, 1462, 773, 701 cm^{-1}. ESI-MS (*m/z*): 628 $(M + H)^+$.

*2.2.2.9. 1-Dodecyl-2-(4-(1-dodecyl-4,5-diphenylimidazol-2-yl)-phenyl)-4,5-diphenylimidazole (**4b**).* Yield 57.0%; m.p. 187.5–188.5 °C. ^{1}H NMR (CDCl$_3$): 0.76 (t, $J = 6.3$ Hz, 6H), 0.87–0.88 (m, 14H), 1.13–1.18 (m, 22H), 1.23–1.29 (m, 4H), 3.84 (t, $J = 7.5$ Hz, 4H), 7.01–7.14 (m, 7H), 7.30–7.43 (m, 13H), 7.73 (s, 4H). ^{13}C NMR (CDCl$_3$): 12.4, 23.1, 26.7, 29.2, 29.7, 29.8, 29.9, 30.1, 30.9, 32.4, 45.6, 53.8, 67.6, 88.3, 109.1, 127.0, 127.4, 128.3, 128.6, 129.4, 129.6, 130.0, 130.6, 131.5, 147.2. IR (KBr) ν: 3438, 2922, 1470, 846, 699 cm^{-1}. ESI-MS (*m/z*): 427 $[(M + 2H)/2]^+$. Element analysis for $C_{60}H_{74}N_4$, Calc.: C, 84.66; H, 8.76; N, 6.58; Found: C, 84.87; H, 9.01; N, 6.32.

2.2.3. General procedure for the condensation of substituted-benzoic acid with o-benzenediamine and 2-aminothiophenol

The condensation of substituted-benzoic acid and *o*-benzenediamine or 2-aminothiophenol was carried out in a Galanz microwave oven; 3.4 mmol of 1-alkyl-4,5-diphenyl-2-(4-carboxyphenyl)imidazole, 3.4 mmol of *o*-benzenediamine (or 2-aminothiophenol) and 12 mL of PPA were mixed together at ambient temperature in a flask. The mixture was subjected to microwave irradiation for an optimized time and taken out for a few seconds and at the same time, the mixture was stirred carefully using a bar. The mixture was subjected to microwave irradiation for another optimized time and then taken out for stirring. The operation was repeated several times, and the reaction mixture was monitored by TLC; after the reaction was completed, the mixture was poured into 80 mL of water and neutralized with 5% sodium hydroxide. The solid product was filtrated and recrystallized form ethanol.

*2.2.3.1. 2-(4-(1-Butyl-4,5-diphenylimidazol-2-yl)phenyl)benzimidazole (**5a**).* Yield 66.7%. ^{1}H NMR (DMSO-d_6): 0.55 (t, $J = 7.8$ Hz, 3H), 0.87–1.01 (m, 2H), 1.22–1.38 (m, 2H), 3.98 (t, $J = 7.5$ Hz, 2H), 7.10–7.29 (m, 4H), 7.41 (t, $J = 6.9$ Hz, 2H), 7.45–7.47 (m, 2H), 7.54–7.59 (m, 3H), 7.62–7.63 (m, 1H), 7.87 (d, $J = 8.4$ Hz, 1H), 7.94 (d, $J = 8.1$ Hz, 2H), 8.08 (d, $J = 8.4$ Hz, 1H), 8.34 (d, $J = 8.4$ Hz, 2H). ESI-MS (*m/z*): 470 $(M + H)^+$. Element analysis for $C_{32}H_{28}N_4$, Calc.: C, 82.02; H, 6.02; N, 11.96; Found: C, 79.81; H, 6.13; N, 12.17.

*2.2.3.2. 2-(4-(1-Butyl-4,5-diphenylimidazol-2-yl)phenyl)benzothiazole (**5b**).* Yield 65.3%; m.p. 187.0–188.5 °C. ESI-MS (*m/z*): 486 $(M+H)^+$; Element analysis for $C_{32}H_{27}N_3S$, Calc.: C, 79.14; H, 5.60; N, 8.65; Found: C, 79.10; H, 5.73; N, 8.36.

*2.2.3.3. 2-(4-(1-Dodecyl-4,5-diphenylimidazol-2-yl)phenyl)-benzimidazole (**5c**).* Yield 60.3%; m.p. 180.5–181.5 °C. ^1H NMR ($CDCl_3$): 0.74–1.23 (m, 23H), 3.71–3.75 (m, 2H), 7.06–7.16 (m, 4H), 7.33–7.40 (m, 10H), 7.72–7.77 (m, 2H), 8.07 (d, $J=6.9$ Hz, 2H). ^{13}C NMR ($CDCl_3$): 14.6, 23.2, 26.7, 29.1, 29.7, 29.8, 29.9, 30.0, 31.0, 32.4, 45.3, 122.9, 127.3, 127.5, 127.9, 129.0, 129.5, 129.7, 130.2, 130.3, 131.3, 131.5, 131.8, 131.9, 134.5, 138.2, 148.0, 152.2. IR (KBr) ν: 3427, 2924, 1438, 744, 700 cm^{-1}. ESI-MS (*m/z*): 582 $(M+H)^+$. Element analysis for $C_{40}H_{44}N_4$, Calc.: C, 82.72; H, 7.64; N, 9.65; Found: 82.61; H, 7.63; N, 9.46.

*2.2.3.4. 2-(4-(1-Dodecyl-4,5-diphenylimidazol-2-yl)phenyl)-benzothiazole (**5d**).* Yield 48.3%; m.p. 111.5–112.0 °C. ^1H NMR ($CDCl_3$): 0.86 (t, $J=6.3$ Hz, 3H), 0.98–1.39 (m, 20H), 3.96 (t, $J=7.5$ Hz, 2H), 7.13–7.24 (m, 3H), 7.41–7.54 (m, 9H), 7.86–7.94 (m, 3H), 8.09 (d, $J=8.1$ Hz, 1H), 8.21 (d, $J=7.5$ Hz, 2H). ^{13}C NMR ($CDCl_3$): 14.6, 23.1, 26.6, 29.1, 29.6, 29.8, 29.9, 30.0, 30.1, 30.8, 32.3, 45.5, 122.2, 123.8, 125.9, 126.9, 127.0, 127.4, 128.2, 128.6, 129.3, 129.6, 130.1, 130.8, 131.5, 134.3, 135.6, 146.9, 154.6, 167.7. IR (KBr) ν: 3431, 2924, 1468, 765, 702 cm^{-1}. ESI-MS (*m/z*): 599 $(M+H)^+$. Element analysis for $C_{40}H_{43}N_3S$, Calc.: C, 80.36; H, 7.25; N, 7.03; Found: 80.05; H, 7.30; N, 6.98.

*2.2.3.5. 1-Benzyl-2-(4-(1-butyl-4,5-diphenylimidazol-2-yl)phenyl)benzimidazole (**6**).* The benzylation of **5a** was carried out following the method described above to give **6**. Yield 54.7%; m.p. 193.5–195.0 °C. ^1H NMR ($CDCl_3$): 0.65 (t, $J=7.8$ Hz, 3H), 0.93–1.05 (m, 2H), 1.27–1.40 (m, 2H), 3.93 (t, $J=7.8$ Hz, 2H), 5.51 (s, 2H), 7.12–7.22 (m, 5H), 7.25–7.28 (m, 2H), 7.31–7.37 (m, 4H), 7.40–7.43 (m, 2H), 7.47–7.52 (m, 5H), 7.81–7.82 (m, 4H), 7.89 (d, $J=7.8$ Hz, 1H). ^{13}C NMR ($CDCl_3$): 13.8, 19.9, 33.0, 45.2, 48.9, 111.0, 120.5, 123.4, 123.8, 126.4, 126.9, 127.3, 128.3, 128.6, 129.3, 129.6, 129.9, 130.0, 130.7, 131.5, 131.6, 136.6, 136.7, 147.0, 153.9. IR (KBr) ν: 3427, 2955, 1455, 738, 701 cm^{-1}. LC/MS (*m/z*): 560 $(M+H)^+$. Element analysis for $C_{39}H_{34}N_4$, Calc.: C, 83.84; H, 6.13; N, 10.03; Found: C, 83.67; H, 6.02; N, 9.89.

2.3. The determination of spectra and fluorescence lifetime (*T*)

The concentrations of samples were about $10^{-6}\ mol\ l^{-1}$ in ethanol, DMSO or ethyl acetate. The UV absorption spectra and emission spectra were, respectively, recorded; data for λ_a, ε, λ_e values are presented in Table 1. The Stokes shift values were calculated according to Eq. (1) and they are listed in Table 1.

$$\text{Stokes shift} = \frac{1}{\lambda_a} - \frac{1}{\lambda_e} \tag{1}$$

The Φ values of samples in ethanol or in DMSO were determined according to comparative methods [24,25], using coumarin as a standard sample and its Φ value is 99% in ethyl acetate [26]. The Φ values for **2e**, **2f**, **2g**, **4b**, **5c**, **5d** and **6** are listed in Table 1.

The *T* values were determined [27–29] in solid state and in DMSO, the obtained data are shown in Table 2.

2.4. Single crystal preparation of sample **2e** and crystal structure

Sample **2e** was dissolved in 95% of ethanol, the solution was allowed to evaporate the solvent contained in it at room temperature. Good quality and colorless single crystals would be obtained in 3–4 days, crystals of size 2 mm × 2 mm × 2 mm were chosen for the experiments. The crystal structure is determined based on the diffraction data, the cell parameters obtained are the following: $\alpha = 18.706(7)$ Å, $J = 9.115(3)$ Å, $c = 15.197(6)$ Å, cell volume $V = 2590.7(16)$ Å^3 and $\beta = 91.061(7)$. The crystal structure, cell structure and dihedral structure of **2e** are shown in Figs. 2–4, respectively.

3. Results and discussion

3.1. For the alkylization of 4,5-diphenyl-2-substituted-phenylimidazoles

The reaction was carried out in one-step by refluxing the mixture at 80 °C for 1.5–3.5 h, and the solvent butanone could be recycled. The product yields for alkylation of 2,4,5-triphenylimidazole is from 50.5% to 93.3% (**2a**–**2g**), and for benzylation of benzimidazole (**6**) is 54.7%. The products are easily purified just by recrystallization from ethanol or dichloromethane. Therefore, the reaction condition is mild, reaction

Table 1
The λ_a, ε, λ_e, and Φ values

Sample	**2e**	**2f**	**2g**	**4b**	**5c**	**5d**	**6**
Solvent	Ethanol	Ethanol	DMSO	DMSO	DMSO	DMSO	DMSO
λ_a (nm)	307	305	350	310	331	345	310
ε ($\times 10^{-4}\ mol^{-1}$)	2.400	2.650	1.693	4.641	3.948	4.641	3.520
λ_e (nm)	397	392	431	417	435	457	429
Stokes shift	7384	7277	5370	8277	7223	7104	8948
Φ (%)	40	37	57	53	74	88	61

Table 2
The T values of some samples in DMSO and in solid state[a]

Sample	λ_a (nm)	λ_e (nm)	T_1[b] (ns)	T_1[c] (ns) (Rel.%)	T_2[c] (ns) (Rel.%)
2g	391	426	1.95		
4a	379	413	1.31		
4b	366	409	1.30	0.93 (79.4)	2.08 (20.6)
5c	382	428	1.56	2.39 (55.7)	7.35 (44.4)
5d	392	460	2.23	2.49 (25.2)	0.82 (74.8)
6	372	424	1.56		

[a] ns means second × 10^{-9}; T_1 and T_2 means lifetime diminished in first-order progression and second-order progression, respectively.

[b] Only first-order-progression diminishing of lifetime was found in DMSO.

[c] Both first-order-progression diminishing T_1 and second-order-progression diminishing T_2 were found in solid state; data in brackets are the ratio of the corresponding T_1 and T_2.

time and product yields are satisfactory, solvent could be simply recycled, this procedure is easy to be carried out and suitable to the preparation of 1-alkyl imidazole and 1-alkylbenzimidazole in a large scale for industry.

1-Alkyl imidazole derivatives, especially for 1-dodecylimidazole derivatives, possess good solubility for most solvents, such as dichloromethane, chloroform, 1,2-dichloroethane, ethyl acetate, acetonitrile, acetone, and butanone. Therefore, the solubility of imidazole derivatives could be improved by the alkylation of these compounds with alkyl bromide or alkyl iodide.

3.2. For the condensation of carboxylic acid with o-benzenediamine and 2-aminothiophenol

The condensation between substituted-benzoic acid and *o*-benzenediamine or 2-aminothiophenol could be finished efficiently with a satisfied to high yield in short reaction time under microwave irradiation. 2-(4-(1-Butyl-4,5-diphenyl-imidazol-2-yl)phenyl)benzimidazole and 2-(4-(1-butyl-4,5-diphenylimidazol-2-yl)phenyl)benzothiazole were isolated in the yields of 48.3–66.7%, they were easily collected and purified in this experiment. Therefore, this procedure could offer an efficient pathway to attach benzimidazole and benzothiazole unit by 2-position to the 4′-position of 2-phenyl ring of 2,4,5-triphenylimidazoles derivatives.

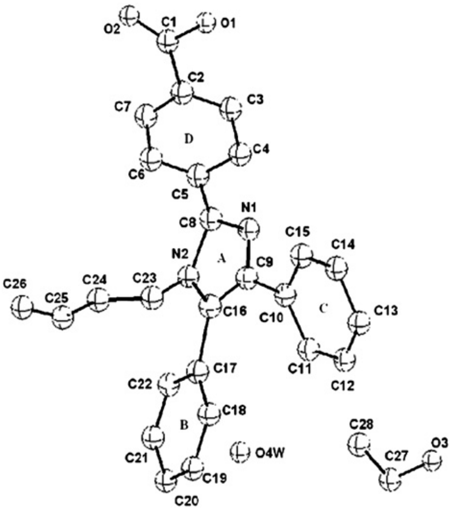


Fig. 2. The single crystal structure of 4,5-diphenyl-2-(4-carboxyphenyl)imidazole (**2e**).

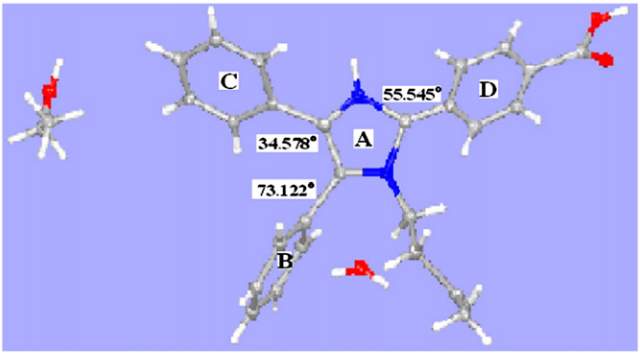


Fig. 3. The dihedral structure of 4,5-diphenyl-2-(4-carboxyphenyl)imidazole (**2e**). Dihedral angle values are the following: for plane of C_{17}, C_{18}, C_{19}, C_{20}, C_{21}, C_{22} (**B**) to that of C_9, C_{16}, N_2, C_8, N_1 (**A**) is 73.122°; for plane of C_{10}, C_{11}, C_{12}, C_{13}, C_{14}, C_{15} (**C**) to (**A**) is 34.578°; for plane of C_4, C_5, C_6, C_7, C_2, C_3 (**D**) to (**A**) is 55.545°.

3.3. Spectra properties and X-ray crystal structure

According to their conjugated system, the compounds reported here could be classed into three types, **2a–2g** (I), **4a–4b** (II), and **5a–5e** (III) (Fig. 5). According to the relationship between the conjugated-system structure and λ_a, λ_e or Φ values, all of the λ_a, λ_e and Φ values should become larger with the increase of conjugated system. Therefore, for the λ_a, λ_e and Φ values of these three kinds of compounds,

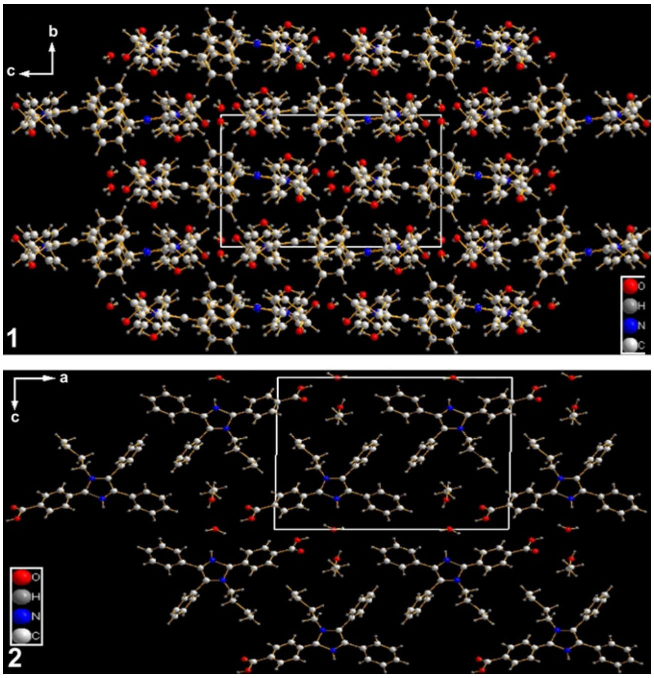
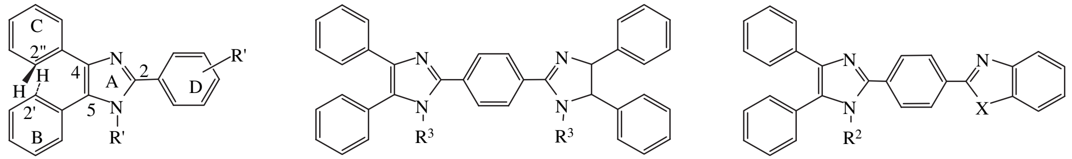


Fig. 4. The cell structure of 4,5-diphenyl-2-(4-carboxyphenyl)imidazole (**2e**).



2a-2g **4a, 4b** **5a-5d, 6**

I **II** **III**

Fig. 5. The structure of 4,5-diphenyl-2-(phenyl-substituted)imidazole derivatives synthesized in this work.

there should be a consequence: III ≈ II > I. However, this consequence of spectral data could not be found from Table 1. Actually, it could be found from the structure of 2,4,5-triphenylimidazole that two phenyl rings (**C** and **B**) in 4- and 5-position and imidazole ring (**A**) could not be coplanar, because two hydrogen atoms in 2′-position of ring **B** and 2″-position of ring **C** are too close to each other. The stereo relationship between two ring planes of **B** and **C** is just like that of two planes of two 2-naphthol in 2,2′-dihydroxy-1,1′-dinaphthyl. Then, how about the stereo relationships between the other ring planes, that is, ring **A** with ring **B**, ring **A** with ring **C**, ring **A** with ring **D**?

In order to investigate the real three-dimensional structure of 2,4,5-triphenylimidazole, the crystal of **2e** was obtained, fortunately, and X-ray diffraction data were obtained. It was found from the crystal structure in Figs. 2–4 that the four ring planes, ring **A**, ring **B**, ring **C** and ring **D**, were not coplanar, there is at least a 34.578° dihedral angle between the four ring planes. It could be found from picture 1 in Fig. 4 that the single crystals of **2e** belong to the layer structure and from picture 2 in Fig. 4 that there is a π–π stack effect between two phenyl rings (**B**) in different molecules and hydrogen-bonding effect between molecules of **2e** or between molecules of **2e** and water molecular or ethanol molecular, which could make out the plane of ring **B** twins from the plane of ring **A**, and the dihedral angle of ring **A** with ring **B** is 73.122°, both planes are nearly vertical to each other. For the other dihedral angle, ring **A** with ring **C** is 34.578°, ring **A** with ring **D** is 55.545°.

Therefore, the λ_a, λ_e or Φ values in solid state should be mainly determined by the conjugated system of imidazole ring **A** and phenyl ring **C**, as the dihedral angle for ring **A** with ring **C** is the smallest one among these three dihedral angles (ring **A** with ring **B**, with ring **C** or with ring **D**). For the stereo structure of **2e**, there is a certain difference between solid state and solution state, because there are π–π stack effect and hydrogen-bonding effect in crystal, and these effects would be destroyed and these three phenyl rings could twist around the single bond between imidazole ring (**A**) and three phenyl rings to a certain extent in solution. However, the plane of ring **C** could be the easiest one among the three planes to be turned to form a conjugated system with imidazole ring **A** in solution, after all, the dihedral angle for ring **A** with ring **C** is the smallest one among three dihedral angles. Therefore, it could be suggested that the λ_a, λ_e, or Φ values in solution also would be primarily determined by the conjugated system of imidazole ring **A** and phenyl ring **C**. So, for the three kinds of compounds reported here I, II and III, their λ_a, λ_e or Φ values in solution are close to each other, although these compounds possess different scales or sizes in conjugated system.

The conclusion deduced above could be confirmed by obtained spectral data in Table 1. For example, as to the λ_a and λ_e values, **2e** (307 nm, 397 nm) and **2f** (305 nm, 392 nm) are very close, respectively, **4b** (310 nm, 417 nm) and **6** (310 nm, 429 nm) are close too, respectively; because **2e** is similar to **2f** and **4b** is similar to **6** in the conjugated-system structure. However, it could be found that **2e**, **2f**, **4b** and **6** are all close to each other with regard to λ_a or λ_e values, respectively. Even **2e**, **2f**, **4b**, **5c**, **5d** and **6** are all close to each other with regard to the λ_a or λ_e values, respectively, in general, even though it seems from the structures shown in Fig. 5 that **4b**, **5c**, **5d** and **6** possess a larger conjugated system than **2e**, **2f** and **2g**.

Compound **2g** possesses the largest λ_a or λ_e value among **2e**, **2f** and **2g**, the reason could be that **2g** is of a larger conjugated system than **2e** or **2f**, because there is a styrene group in 2-position of **2g** and there is a 4-carboxyphenyl group in 2-position of **2e** or **2f**.

The λ_a or λ_e value of **5d** is, respectively, larger than that of **5c**, although **5c** is very similar to **5d** in the structure, it was suggested that it could take part in an important role that sulfur atom possesses a stronger electron-donating ability than nitrogen atom. The λ_a or λ_e value of **6** is, respectively, smaller than that of **5c** and **5d**, although **6** is very similar to **5c** and **5d** in the conjugated-system structure. The reason suggested is that the bulk benzyl group in 1-position of benzimidazole in **6** would make the plane of benzimidazole ring rotate more violently, as compared with that in **5c** and **5d**.

Samples **5c** and **5d** possess a higher Φ value than **6**, the reason is the same thing as their λ_a or λ_e value. Samples **2e**, **2f**, **2g** and **4b** possess a medium strong fluorescence-emitting ability. The Φ value of **4b** is close to that of **2e**, **2f**, **2g**, the reason is similar to that of their λ_a or λ_e value.

Compared with 1,4-diphenylbuta-1,3-diene, 1,6-diphenylhexa-1,3,5-triene and 2,3,5-tri-substituted-furan derivatives [23] (Fig. 6), samples **4a**, **4b**, **5a**, **5b**, **5c**, **5d** and **6** showed lower Φ values, although these compounds possess a larger conjugated system. The reason suggested could be that samples **4a**, **4b**, **5a**, **5b**, **5c**, **5d** and **6** could not possess a desired planar structure for three phenyl ring planes and imidazole ring plane, which confirms further the conclusion that the planes of three phenyl rings of 2,4,5-triphenylimidazoles derivatives all twist out of the imidazole ring plane to a certain extent, respectively.

n = 2, Φ (%)= 68
n = 3, Φ (%)= 82

R^1= Methoxyformyl, R^2 = 4-CF_3, R^3 = n-butyl, Φ (%)= 91;
R^1= Methoxyformyl, R^2 = 2,4-dimethoxy, R^3 = n-butyl, Φ (%) = 101; R^1= 4-Biphenyl, R^2 = 4-F, R^3 = n-butyl, Φ (%)= 93

Fig. 6. The structures of 1,4-diphenylbuta-1,3-diene, 1,6-diphenyl-hexa-1,3,5-triene and some 2,3,5-tri-substituted-furan derivatives.

The fluorescence lifetime was determined in DMSO and in solid state, respectively. It was found that only first-order-progression diminishing of lifetime of samples in DMSO was obtained, their lifetime values in solution are in the region of 1.30–2.33 ns; first-order-progression diminishing and second-order-progression diminishing of samples **4b**, **5c** and **5d** in solid state were measured at the same time. In addition, some samples showed a longer lifetime in solution and some samples could show a longer lifetime in solid state, especially, for **5c**, it could perform a 7.35-ns lifetime in solid state in second-order-progression diminishing.

4. Conclusions

The approach reported here for alkylation of 2,4,5-triphenylimidazole derivatives could be an efficient method, especially for industry, as reaction condition is mild, the yield is high, solvent could be recycled, the product is easy to be purified. Meantime, the solubility of imidazole derivatives to most organic solvents could be improved by the alkylation of these compounds with alkyl bromide or alkyl iodide.

The procedure reported here could offer an efficient route to link benzimidazole and benzothiazole unit by 2-position up to 4′-position of 2-phenyl ring of 2,4,5-triphenylimidazoles derivatives, which could provide an attractive and even an efficient approach to the preparation of some useful dyes and pigments.

Because the planes of three phenyl rings of 2,4,5-triphenylimidazoles derivatives all twist out of the imidazole plane to a certain extent, respectively, the λ_a, λ_e or Φ values for these derivatives should be contributed mainly to the conjugated system of imidazole ring and 4-position phenyl ring, the extension of conjugated system could not obviously increase the λ_a, λ_e or Φ values for 2,4,5-triphenylimidazoles derivatives.

Acknowledgments

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