Synthesis and Optical Properties of Novel Fluorescence-Traced Benzimidazolium Bromides

Hong Shi,[a,b] Tao Wu,[a] Peng Jiang,[a] Xiaodong Jin,[a] and Hongjun Zhu[a,c]*

[a]Department of Applied Chemistry, College of Science, Nanjing University of Technology, Nanjing 210009, People's Republic of China

[b]Teaching and Research Department, Jiangsu College of Information Technology, Wuxi 214153, People's Republic of China

[c]Jiangsu Key Laboratory of Industrial Water-Conservation and Emission Reduction, Nanjing 210009, People's Republic of China

*E-mail: zhuhjnjut@hotmail.com

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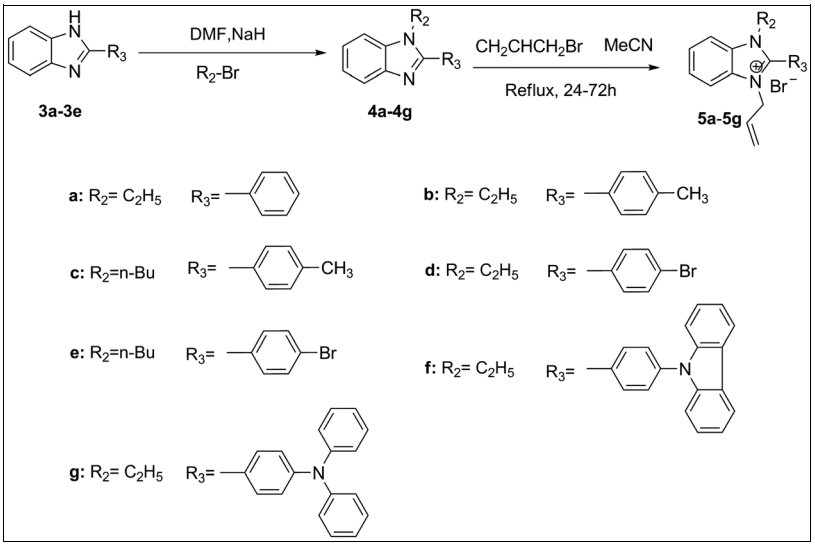

Seven novel fluorescence-traced 1-aryl-2-substituted-3-allyl-1*H*-benzimidazolium bromides (**5a–g**) were synthesized by alkylation and quaternization of compounds 1-aryl-2-substituted-1*H*-benzimidazoles (**4a–g**) with excess allyl bromide in acetonitrile at refluxing temperature. Their structures were characterized by ^{1}H-NMR, MS, and elemental analysis. They emit violet-blue light (λ_{max}^{Em} = 386–438 nm) with fluorescence quantum yields of 0.54 to 0.75 in aqueous solution.

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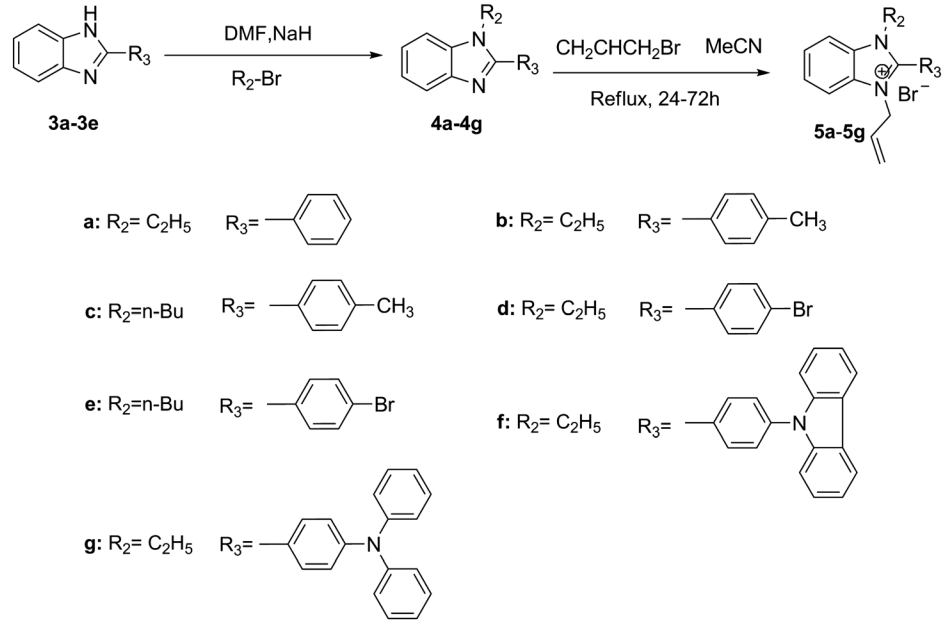
INTRODUCTION

The fluorescent tracer technique is an effective means to detect the residual quantity of water treatment agent [1]. Compared with other techniques of measurement, it has the advantages of high sensitivity, low detection limit, and multiple spectroscopy parameters [2,3]. Nowadays, synthesis and application of fluorescent water treatment agents are the front line of water treatment field, and the key to this technique is to synthesize the water treatment agent with improved fluorescence properties.

Previous studies indicate that various heterocyclic compounds could be used as fluorescent tracer, such as naphthazine [4], acridine [5], pyrazoline [6], and benzoxazine [7]. The common characteristics of these compounds are the strong absorptions in both near ultraviolet and far infrared regions, as well as their relatively high fluorescence quantum efficiencies. Benzimidazole-based compounds are such kinds of heterocyclic compounds that have received much attention in the past few decades for their intense luminescence and high fluorescence quantum efficiency. They are widely used as fluorescent probes [8,9], fluorescent brightening agents [10], and nonlinear optical materials [11,12]. They also bear electron withdrawing imine nitrogen (C═N) moieties, which behave as electron-accepting molecules that can facilitate electrochemical reduction, a feature that renders them suitable electron carriers [13].

As we know, phenyl rings, triphenyl amino, and carbazole can increase the conjugated degree of the molecule. Also, triphenyl amino and carbazole are famous organic light-emitting diode (OLED) materials because of their high fluorescence quantum efficiency [14] and good hole-transporting abilities [15]. In this study, a series of novel fluorescence-traced benzimidazolium bromides (**5a–g**) containing the substituted groups previously mentioned was designed and synthesized (Scheme 1). The photophysical properties of these compounds were also investigated.

Scheme 1. The molecular structures and synthetic route of **5a–g**.



RESULTS AND DISCUSSION

The synthesis of compounds **5a–g** is outlined in Scheme 1. Compounds **3a**, **3c**, and **3e** were synthesized by the condensation of **1a–c** with o-phenylenediamine (OPDA) using air as oxidizing agent, and compounds **3b** and **3d** were synthesized by the condensation of **2d** and **2e** with OPDA using phosphoric acid and polyphosphoric acid as activator; the synthetic route is outlined in Scheme 2. By alkylation reactions of the 2-substituted benzimidazoles (**3a–e**) with ethyl bromide or *n*-butyl bromide as electrophilic reagent [16], compounds **4a–g** were obtained. The yields were all 90% above. Compounds **5a–g** were synthesized by alkylation and quaternization of compounds **4a–g** with excess allyl bromide in acetonitrile at refluxing temperature [17,18]. The ^{1}H-NMR spectra, MS spectra, and elemental analysis confirmed the proposed structures.

Compounds **5a–g** are found to have melting points higher than 310°C. In order to seek a better reacting condition, the effect of solvents on the yields was studied for comparison, and the results are listed in Table 1. For acetone, methanol, and ethyl acetate as solvent, the yields were lower. This is because the boiling points of the three solvents are not high to meet the needs of the reaction. Because compounds of **5a–g** are soluble in ethylene glycol monomethyl ether and DMF, the yields are still unsatisfactory. Compared with all of these solvents, acetonitrile is the best one.

Because the fluorescent tracer technique is used widely in water treatment fields, it is important to study and discuss the optical properties of these compounds in aqueous solution.

The UV–vis absorption spectra of compounds **5a–g** in aqueous solution ($10^{-5}\,M$) are displayed in Figure 1. Their photophysical properties are summarized in Table 2. The lowest energy absorption bands are from the π–π* transitions by virtue of their large molar extinction coefficients ($\varepsilon \approx 10^4\,M^{-1}\,\mathrm{cm}^{-1}$). All seven compounds showed strong absorptions, with maximum wavelengths in the range of 280–343 nm ($\lambda_{\max}^{\mathrm{Abs}}$). The increase in conjugation length and the increased electron density associated with carbazolyl groups in **5f** and triphenylamine groups in **5g** lead to a large bathochromic shift of absorption maximum. Ethyl and *n*-butyl had almost no influence on absorption maxima.

The emission spectra of **5a–g** in aqueous solution ($10^{-8}\,M$) are shown in Figure 2. The fluorescence properties of the compounds are also summarized in Table 2. All the compounds emitted violet-blue light with a maximum emission in the 386–438-nm range. The variation of *N*-alkyl side chains did not have any significant effects on the emission maximum, indicating that fluorescence emission originate from the benzimidazolium backbone and 2-substituted groups. Compared with **5c** and **5e**, **5c** was blue-shifted by 5 nm, whereas **5e** was red-shifted by 8 nm. This observation may be due to the electron-withdrawing effect of the bromine atom substituted in phenyl ring [19,20].

The fluorescence quantum yields (Φ_F) of these compounds in aqueous solution were determined by the standard method (using quinine sulfate as the standard) [21]. The fluorescence quantum yields were in the range from 0.54 to 0.75, as can be seen from Table 2. Comparing **5b** with **5c** and **5d** with **5e**, it is noted that their fluorescence quantum

Scheme 2. The synthetic route of **3a–e**.

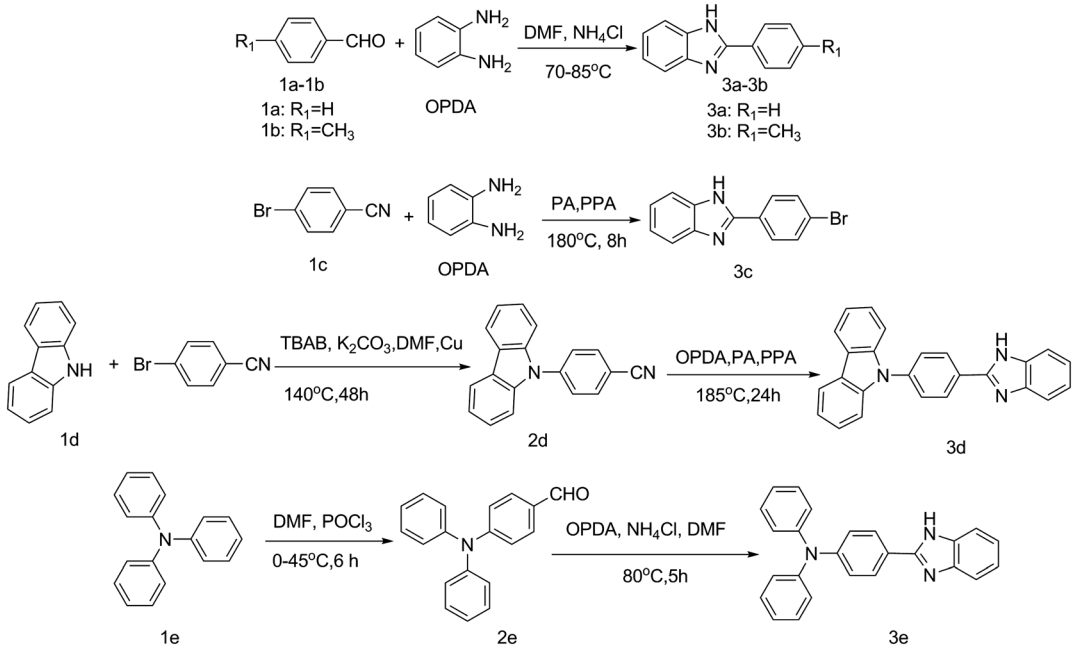


Table 1

Effect of solvent on the yields.

	Solvent					
	Acetone	Ethyl acetate	Ethylene glycol monomethyl ether	Acetonitrile	DMF	Methanol
Yield (%)	22.7	20.5	67.1	93.0	77.4	23.9

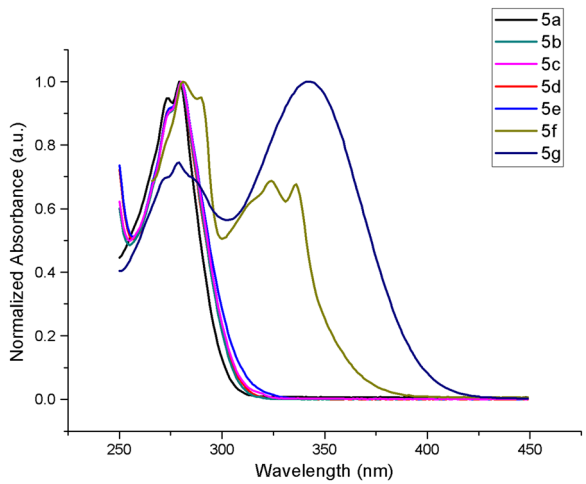


Figure 1. UV–vis absorption spectra of **5a–g** in aqueous solution (10^{-5} *M*). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

yields increase with the extension of the *N*-alkyl side chains. These results indicated that large side chains provide the benzimidazolium backbone better protection from the effect of the solvent molecules or other benzimidazolium molecules [22].

CONCLUSION

In summary, a new series of fluorescence-traced benzimidazolium bromides were synthesized and characterized. Acetonitrile is the best solvent that could lead to higher yields while synthesizing. The optical properties studied on UV–vis absorption and fluorescence emission spectroscopy showed that *N*-alkyl side chains did not have any significant effects on the absorption maxima as well as emission maximum. These compounds emitted violet-blue light ($\lambda_{max}^{Em} = 386–438$ nm) with fluorescence quantum yields of 0.54–0.75 when diluted in water. Thus, these new

Table 2

Photophysical properties of **5a–g** in aqueous solution.

Compounds	ε (10^4 mol^{-1} cm^{-1})	λ_{max}^{Abs} (nm)	λ_{max}^{Em} (nm)	Stokes shift (nm)	Φ_F[a]
5a	5.02	280	391	111	0.67
5b	5.43	281	391	100	0.54
5c	5.56	281	386	105	0.58
5d	5.29	281	391	100	0.71
5e	5.41	281	399	118	0.73
5f	6.17	281	426	145	0.70
5g	6.24	343	438	95	0.75

[a]Determined in aqueous solution ($A < 0.05$) at room temperature using quinine sulfate ($\Phi_F = 0.55$ in 0.1 *M* H_2SO_4) as standard.

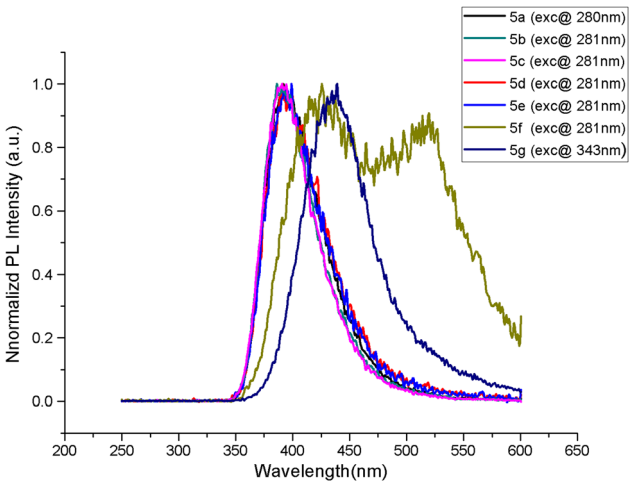


Figure 2. PL spectra of **5a–g** in aqueous solution (10^{-8} *M*). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

compounds have potential applications as fluorescence-traced materials. Further studies of their copolymers' application are underway in our laboratory.

EXPERIMENTAL

Melting points were measured on an X-4 microscope electrothermal apparatus (Taike, Beijing Taike Instrument Company, Beijing, China) and remained uncorrected. ^{1}H-NMR spectra were recorded on either a Bruker AV-500 spectrometer at 500 MHz or a Bruker AV-300 spectrometer at 300 MHz (Bruker AXS Inc., Madison, WI), using CD_3OD, D_2O, and $CDCl_3$ as the solvents, with TMS as the internal standard. Electrospray ionization mass spectroscopy measurements were carried out with an Agilent 1100 series LC/MSD Trap SL mass spectrometer (Agilent Inc., Santa Clara, CA). Elemental analyses were performed with a Vario EL III elemental analyzer (Elementar Analysensysteme GmbH, Hanau, Germany). Optical absorption spectra were obtained using an HP-8453 UV/vis/near-IR spectrophotometer (Agilent Inc., Santa Clara, CA). Photoluminescence spectra were carried out on an LS-55 spectrofluorometer (PerkinElmer Inc., Fremont, CA).

All the chemicals not recalling for synthesis were purchased either from the Sinopharm Chemical Reagent Co. Ltd. or the Shanghai Lingfeng Chemical Company, and the solvents were purified according to standard procedures. 4-(Carbazole-9-yl)benzonitrile (**2d**) was synthesized from carbazole and 4-bromobenzonitrile according to methods described in the literature [23]. 4-(*N*,*N*-Diphenylamino)benzaldehyde (**2e**) was synthesized by formylation of triphenyl amine using DMF and $POCl_3$ according to the reported method [24]. 2-Substituted-1*H*-benzimidazoles (**3a–e**) were synthesized by condensation of *o*-phenylenediamine with aromatic carboxylic aldehydes (**2a–e**) in the presence of DMF or in the presence of phosphoric acid and polyphosphoric acid according to the reported methods [25–27].

The synthesis of 1-ethyl-2-phenylbenzimidazole (4a). 2-Phenyl-1*H*-benzimidazole (**3a**) (1.94 g, 10 mmol) and DMF (30 mL) were put into a 50-mL four-necked flask equipped with a temperature probe and magnetic stirrer and stirred to dissolve. The whole mixture was cooled to 0°C using ice bath. After adding NaH (1.44 g, 60 mmol), the mixture was warmed to room temperature and stirred for 1.5 h. Then, ethyl bromide (1.31 g, 12 mmol) was added, and the mixture was heated to 45°C. After reacting for 6–10 h at that temperature, saturated salt water (10 mL) was added dropwise, and the reaction stopped. The mixture was extracted with ethyl acetate (3 × 10 mL), washed with saturated salt water, and separated. The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give **4a** with the following properties: white crystal; mp 89–91°C (reference [28]: 88–88.5°C); yield: 93.1%. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ 1.46 (t, $J = 7.6$ Hz, 3H, CH_3), 4.26 (q, $J = 7.6$ Hz, 2H, CH_2), 7.42–7.48 (m, 3H, Ar-H), 7.50–7.56 (m, 3H, Ar-H), 7.71–7.81 (m, 3H, Ar-H). *Anal.* Calcd for $C_{15}H_{14}N_2$: C, 81.05; H, 6.35; N, 12.60. Found: C, 81.09; H, 6.33; N, 12.58.

1-Ethyl-2-(4-methylphenyl)benzimidazole (4b). Following the same procedure described for the synthesis of **4a**. 2-(4-Methylphenyl)-1*H*-benzimidazole (**3b**) and ethyl bromide were used to obtain product **4b**. White crystal; mp 104–106°C; yield: 92.0%. ^{1}H-NMR ($CDCl_3$, 500 MHz, ppm): δ 1.46 (t, $J = 7.25$ Hz, 3H, CH_3), 2.44 (s, 3H, CH_3), 4.28 (q, $J = 7.25$ Hz, 2H, CH_2), 7.33–7.29 (m, 4H, Ar-H), 7.43–7.40 (m, 1H, Ar-H), 7.62 (d, $J = 8.05$ Hz, 2H, Ar-H), 7.84–7.81 (m, 1H, Ar-H); MS: *m/z* 237.1 ($M + H^+$), 238.1 ($M + 2H^+$), 359.1 ($M + Na^+$). *Anal.* Calcd for $C_{16}H_{16}N_2$: C, 81.32; H, 6.82; N, 11.85. Found: C, 81.35; H, 6.78; N, 11.87.

1-Butyl-2-(4-methylphenyl)benzimidazole (4c). Compound **4c** was obtained from 2-(4-methylphenyl)-1*H*-benzimidazole (**3b**) and *n*-butyl bromide. White crystal; mp 62–63°C; yield: 91.4%. ^{1}H-NMR ($CDCl_3$, 500 MHz, ppm): δ 0.87 (t, $J = 7.35$ Hz, 3H,

CH_3), 1.31–1.25 (m, 2H, CH_2), 1.83–1.77 (m, 2H, CH_2), 2.44 (s, 3H, CH_3), 4.22 (t, J = 7.65 Hz, 2H, CH_2), 7.30–7.27 (m, 4H, Ar-H), 7.41–7.39 (m, 1H, Ar-H), 7.61 (d, J = 8.1 Hz, 2H, Ar-H), 7.83–7.81 (m, 1H, Ar-H); MS: *m/z* 265.2 ($M + H^+$), 266.2 ($M + 2H^+$). *Anal*. Calcd for $C_{18}H_{20}N_2$: C, 81.78; H, 7.63; N, 10.60. Found: C, 81.75; H, 7.61; N, 10.63.

1-Ethyl-2-(4-bromophenyl)benzimidazole (4d). Compound **4d** was obtained from 2-(4-bromophenyl)-1*H*-benzimidazole (**3c**) and ethyl bromide. Yellow crystal; mp 137–138°C; yield: 94.8%. ^{1}H-NMR ($CDCl_3$, 500 MHz, ppm): δ 1.44 (t, J = 7.2 Hz, 3H, CH_3), 4.25 (q, J = 7.2 Hz, 2H, CH_2), 7.33–7.29 (m, 2H, Ar-H), 7.42–7.40 (m, 1H, Ar-H), 7.59 (d, J = 8.15 Hz, 2H, Ar-H), 7.65 (d, J = 8.4 Hz, 2H, Ar-H), 7.83–7.81 (m, 1H, Ar-H); MS: *m/z* 301.0 ($M + H^+$), 304.0 ($M + 4H^+$), 323.0 ($M + Na^+$). *Anal*. Calcd for $C_{15}H_{13}BrN_2$: C, 59.82; H, 4.35; N, 9.30. Found: C, 59.86; H, 4.31; N, 9.35.

1-Butyl-2-(4-bromophenyl)benzimidazole (4e). Compound **4e** was obtained from 2-(4-bromophenyl)-1*H*-benzimidazole (**3c**) and *n*-butyl bromide. Yellow crystal; mp 81–83°C; yield: 93.3%. ^{1}H-NMR ($CDCl_3$, 500 MHz, ppm): δ 0.88 (t, J = 7.35 Hz, 3H, CH_3), 1.31–1.24 (m, 2H, CH_2), 1.82–1.76 (m, 2H, CH_2), 4.21 (t, J = 7.65 Hz, 2H, CH_2), 7.33–7.29 (m, 2H, Ar-H), 7.47–7.40 (m, 1H, Ar-H), 7.58 (d, J = 8.3 Hz, 2H, Ar-H), 7.65 (d, J = 8.2 Hz, 2H, Ar-H), 7.82–7.80 (m, 1H, Ar-H); MS: *m/z* 329.1 ($M + H^+$), 332.1 ($M + 4H^+$), 351.0 ($M + Na^+$). *Anal*. Calcd for $C_{17}H_{17}BrN_2$: C, 62.02; H, 5.20; N, 8.51. Found: C, 62.04; H, 5.19; Br, 24.23; N, 8.54.

1-Ethyl-2-{4-(9*H*-carbazole-9-yl)phenyl}benzimidazole (4f). Compound **4f** was obtained from 2-{4-(9*H*-carbazole-9-yl) phenyl}-1*H*-benzimidazole (**3d**) and ethyl bromide. Yellow crystal; mp 166–168°C; yield: 88.7%. ^{1}H-NMR ($CDCl_3$, 500 MHz, ppm): δ 1.58 (t, J = 7.25 Hz, 3H, CH_3), 4.45–4.40 (q, J = 7.25 Hz, 2H, CH_2), 7.38–7.30 (m, 4H, Ar-H), 7.51–7.43 (m, 5H, Ar-H), 7.76 (d, J = 8.35 Hz, 2H, Ar-H), 7.89–7.87 (m, 1H, Ar-H), 8.00 (d, J = 8.35 Hz, 2H, Ar-H), 8.16 (d, J = 7.7 Hz, 2H, Ar-H); MS: *m/z* 388.2 ($M + H^+$), 389.2 ($M + 2H^+$), 410.2 ($M + Na^+$). *Anal*. Calcd for $C_{27}H_{21}N_3$: C, 83.69; H, 5.46; N, 10.84. Found: C, 83.72; H, 5.44; N, 10.84.

4-(1-Ethyl-1*H*-benzimidazol-2-yl)-*N*,*N*-diaphenylbenzenamine (4g). Compound **4g** was obtained from 4-(*N*,*N*-diphenylaminophenyl)-1*H*-benzimidazole (**3e**) and ethyl bromide. Light yellow crystal; mp 170–172°C; yield: 90.2%. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ 1.48 (t, J = 7.17 Hz, 3H, CH_3), 4.30 (q, J = 7.17 Hz, 2H, CH_2), 7.10–7.05 (m, 2H, Ar-H), 7.24–7.15 (m, 6H, Ar-H), 7.32–7.26 (m, 6H, Ar-H), 7.41–7.38 (m, 1H, Ar-H), 7.59 (d, J = 8.46 Hz, 2H, Ar-H), 7.81–7.78 (m, 1H, Ar-H); MS: *m/z* 390.3 ($M + H^+$), 391.3 ($M + 2H^+$), 412.3 ($M + Na^+$). *Anal*. Calcd for $C_{27}H_{23}N_3$: C, 83.26; H, 5.95; N, 10.79. Found: C, 83.28; H, 5.90; N, 10.82.

Procedure for the synthesis of 5a–5g. 1-Alkyl-2-aryl-1*H*-benzimidazole (**4a–g**) (5 mmol) and acetonitrile (20 mL) were put into a 50-mL four-necked flask and stirred to dissolve. After heated to 60°C, the mixed liquid of allyl bromide (0.6 g, 5 mmol) and acetonitrile (20 mL) was added dropwise, and the mixture was heated at refluxing temperature for 24 h. After the reaction, the mixture was washed with acetonitrile (20 mL) and then concentrated under reduced pressure to give crude products. The crude products were purified by recrystallization from acetonitrile to give pure **5a–g** with the following properties:

1-Ethyl-2-phenyl-3-allyl-1H-benzimidazolium bromide (5a). Yield: 93.0%; white crystals; mp >310°C; ^{1}H-NMR (D_2O, 300 MHz, ppm): δ 1.47 (t, J = 7.05 Hz, 3H, CH_3), 4.40 (q, J = 7.05 Hz, 2H, CH_2), 4.96 (d, J = 3.95 Hz, 2H, CH_2), 5.12 (d, J = 15.39 Hz, 1H, CH_2=), 5.34 (d, J = 10.38 Hz, 1H, CH_2=), 6.03–5.98 (m, 1H, -CH=), 7.74–7.41 (m, 6H, Ar-H), 7.93–7.84 (m, 2H, Ar-H), 8.00 (d, J = 7.47 Hz, 1H, Ar-H); MS: *m/z*: 261.3 $[M - Br]^+$. *Anal*. Calcd for $C_{18}H_{19}BrN_2$: C, 62.98; H, 5.58; N, 8.16. Found: C, 62.96; H, 5.60; N, 8.19.

1-Ethyl-2-(4-methylphenyl)-3-allyl-1H-benzimidazolium bromide (5b). Yield: 92.4%; white crystals; mp >310°C; ^{1}H-NMR (D_2O, 500 MHz, ppm): δ 1.47 (t, J = 7.15 Hz, 3H, CH_3), 2.54 (s, 3H, CH_3), 4.43–4.39 (q, J = 7.15 Hz, 2H, CH_2), 4.95 (d, J = 3.95 Hz, 2H, CH_2), 5.12 (d, J = 17.25 Hz, 1H, CH_2=), 5.34 (d, J = 10.5 Hz, 1H, CH_2=), 6.06–6.00 (m, 1H, -CH=), 7.67–7.62 (m, 4H, Ar-H), 7.79–7.74 (m, 2H, Ar-H), 7.91 (d, J = 7.75 Hz, 1H, Ar-H), 8.00 (d, J = 7.85 Hz, 1H, Ar-H); MS: *m/z*: 277.3 $[M - Br]^+$. *Anal*. Calcd for $C_{19}H_{21}BrN_2$: C, 63.87; H, 5.92; N, 7.84. Found: C, 63.84; H, 5.93; N, 8.21.

1-Butyl-2-(4-methylphenyl)-3-allyl-1H-benzimidazolium bromide (5c). Yield: 90.3%; yellow crystals; mp >310°C; ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ 0.84 (t, J = 7.35 Hz, 3H, CH_3), 1.33–1.28 (m, 2H, CH_2), 1.89–1.83 (m, 2H, CH_2), 2.52 (s, 3H, CH_3), 4.47–4.42 (t, J = 7.47 Hz, 2H, CH_2), 5.06 (d, J = 4.14 Hz, 2H, CH_2), 5.17 (d, J = 17.13 Hz, 1H, CH_2=), 5.35 (d, J = 10.17 Hz, 1H, CH_2=), 6.07–5.94 (m, 1H, -CH=), 7.52–7.49 (m, 2H, Ar-H), 7.69–7.61 (m, 2H, Ar-H), 7.86–7.81 (m, 4H, Ar-H); MS: *m/z*: 305.1 $[M - Br]^+$. *Anal*. Calcd for $C_{21}H_{25}BrN_2$: C, 65.46; H, 6.54; N, 7.27. Found: C, 65.43; H, 6.58; N, 8.20.

1-Ethyl-2-(4-bromophenyl)-3-allyl-1H-benzimidazolium bromide (5d). Yield: 87.2%; yellow crystals; mp >310°C; ^{1}H-NMR (D_2O, 500 MHz, ppm): δ 1.43 (t, J = 7.5 Hz, 3H, CH_3), 4.40–4.36 (q, J = 7.5 Hz, 2H, CH_2), 4.93 (d, J = 4.0 Hz, 2H, CH_2), 5.08 (d, J = 16.5 Hz, 1H, CH_2=), 5.31 (d, J = 10.5 Hz, 1H, CH_2=), 6.02–5.95 (m, 1H, -CH=), 7.65 (d, J = 8.5 Hz, 2H, Ar-H), 7.77–7.71 (m, 2H, Ar-H), 7.90–7.88 (m, 1H, Ar-H), 7.99–7.94 (m, 3H, Ar-H); MS: *m/z*: 341.0 $[M - Br]^+$. *Anal*. Calcd for $C_{18}H_{18}Br_2N_2$: C, 51.21; H, 4.30; N, 6.64. Found: C, 51.25; H, 4.29; N, 6.61.

1-Butyl-2-(4-bromophenyl)-3-allyl-1H-benzimidazolium bromide (5e). Yield: 86.3%; yellow crystals; mp >310°C; ^{1}H-NMR ($CDCl_3$, 500 MHz, ppm): δ 0.87 (t, J = 7.4 Hz, 3H, CH_3), 1.32–1.23 (m, 2H, CH_2), 1.89–1.83 (m, 2H, CH_2), 4.39 (t, J = 7.75 Hz, 2H, CH_2), 5.00 (d, J = 3.45 Hz, 2H, CH_2), 5.20 (d, J = 17.15 Hz, 1H, CH_2=), 5.37 (d, J = 10.45 Hz, 1H, CH_2=), 6.05–5.98 (m, 1H, -CH=), 7.68–7.64 (m, 2H, Ar-H), 7.80–7.76 (m, 2H, Ar-H), 7.85 (t, J = 4.20 Hz, 2H, Ar-H), 8.04 (d, J = 8.45 Hz, 2H, Ar-H); MS: *m/z*: 369.0 $[M - Br]^+$. *Anal*. Calcd for $C_{20}H_{22}Br_2N_2$: C, 53.36; H, 4.93; N, 6.22. Found: C, 53.39; H, 4.89; N, 8.22.

1-Ethyl-2-{4-(9H-carbazole-9-yl)phenyl}-3-allyl-1H-benzimidazolium bromide (5f). Yield: 64.1%; brown crystals; mp >310°C; ^{1}H-NMR (CD_3OD, 500 MHz, ppm): δ 1.60 (t, J = 7.35 Hz, 3H, CH_3), 4.57 (q, J = 7.35 Hz, 2H, CH_2), 5.12–5.10 (m, 2H, CH_2), 8.21–8.20 (m, 2H, Ar-H), 8.14–8.13 (m, 1H, Ar-H), 8.10–8.08 (m, 4H, Ar-H), 5.28 (d, J = 16.95 Hz, 1H, CH_2=), 5.41 (d, J = 10.5 Hz, 1H, CH_2=), 6.15–6.09 (m, 1H, -CH=), 7.37–7.34 (m, 2H, Ar-H), 7.50–7.47 (m, 2H, Ar-H), 7.62 (d, J = 8.25 Hz, 2H, Ar-H), 7.84–7.78 (m, 2H, Ar-H), 8.03–8.02 (m, 1H, Ar-H); MS: *m/z*: 428.3 $[M - Br]^+$. *Anal*. Calcd for $C_{30}H_{26}BrN_3$: C, 70.87; H, 5.15; N, 8.26. Found: C, 70.91; H, 5.16; N, 8.21.

1-Ethyl-2-{(4-N,N-diphenyl)aminophenyl}-3-allyl-1H-benzimidazolium bromide (5g). Yield: 64.1%; brown crystals; mp >310°C; ^{1}H-NMR (CD_3OD, 500 MHz, ppm): δ 1.51 (t, J = 7.3 Hz, 3H, CH_3), 4.48–4.44 (q, J = 7.3 Hz, 2H, CH_2), 5.01–4.99 (m, 2H, CH_2), 5.19 (d, J = 17.2 Hz, 1H, CH_2=), 5.36 (d, J = 10.45 Hz, 1H, CH_2=), 6.06–6.01 (m, 1H, -CH=), 7.18–7.16 (m, 2H, Ar-H), 7.27–7.23 (m, 6H, Ar-H), 7.44–7.40

(m, 4H, Ar-H), 7.54–7.52 (m, 2H, Ar-H), 7.76–7.70 (m, 2H, Ar-H), 7.93–7.91 (m, 1H, Ar-H), 8.04–8.02 (m, 1H, Ar-H); MS: *m/z*: 430.5 $[M - Br]^+$. *Anal*. Calcd for $C_{30}H_{28}BrN_3$: C, 70.59; H, 5.53; N, 8.23. Found: C, 70.62; H, 5.54; N, 8.19.

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