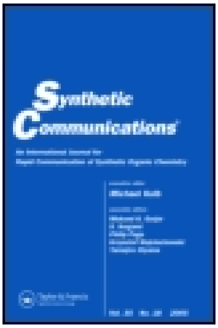

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Synthesis and Luminescence of 14-Aryl- or Alkyl-14*H*-dibenzo[*a,j*]xanthenes Catalyzed by 2-1′-Methylimidazolium-3-yl-1-ethyl Sulfate

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Abstract: A facile and efficient synthesis of 14-aryl or alkyl-14*H*-dibenzo[*a,j*] xanthenes has been accomplished by treatment of β-naphthol with aryl or alkyl aldehydes catalyzed by 2-1′-methylimidazolium-3-yl-1-ethyl sulfate in ionic liquid [BMIM][BF_4] at 80°C. The luminescence of products was studied in detail.

Keywords: Luminescence, 2-1′-methylimidazolium-3-yl-1-ethyl sulfate, synthesis, xanthenes

INTRODUCTION

The synthesis of xanthenes, especially benzoxanthenes, has received significant attention because they possess diverse biological and therapeutic properties, such as antiviral,[1] antibacterial,[2] and anti-inflammatory[3] activities. Furthermore, these compounds have emerged as sensitizers in photodynamic therapy[4] and are used as leuco-dyes[5] in laser technology and pH-sensitive fluorescent materials for the visualization of biomolecular assemblies.[6]

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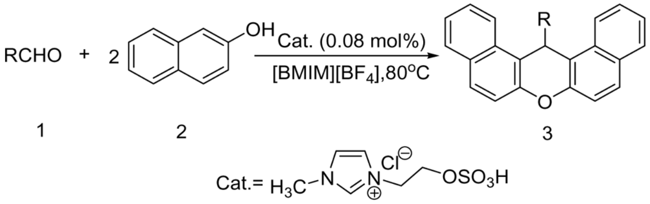

Scheme 1. Synthesis of 14-aryl or alkyl-14*H*-dibenzo[*a,j*]xanthenes.

Various methods are available for the preparation of benzoxanthenes involving the reaction of β-naphthol with formamide, 2-naphthol-1-methanol,[7] or carbon monoxide.[8] However, these methods have some drawbacks such as poor yields, prolonged reaction times, toxic organic solvents, excess reagents/catalysts, and harsh reaction conditions. Some catalysts such as *p*-toluenesulfonic acid (*p*-TSA),[9] sulfamic acid,[10] AcOH/H_2SO_4,[11] iodine,[12,13] $K_5CoW_{12}O_{40} \cdot 3H_2O$,[14] cyanuric chloride,[15] LiBr,[16] $HClO_4 \cdot SiO_2$,[17] $KAl(SO_4)_2 \cdot 12H_2O$,[18] silica sulfuric acid,[19] and $Yb(OTf)_3$[20] have been used to improve the condensation of β-naphthol with aldehydes. Even now, searching for new catalysts and green solvents for this reaction is still highly desirable.

2-1′-Methylimidazolium-3-yl-1-ethyl sulfate, which was synthesized in our laboratory, is a stable, nonvolatile, cheap, and safe reagent. Here we report a simple and facile synthesis of 14-aryl- or alkyl-14*H*-dibenzo[*a,j*]xanthenes by treatment of β-naphthol with aryl or alkyl aldehydes in ionic liquid 1-n-butyl-3-methyl-imidazolium tetrafluoroborate ([BMIM][BF_4]) catalyzed by 2-1′-methylimidazolium-3-yl-1-ethyl sulfate (Scheme 1).

RESULTS AND DISCUSSION

Synthesis of 14-Aryl or Alkyl-14*H*-dibenzo[*a,j*]xanthenes

In our initial endeavor, the reaction of 4-chlorobenzaldehyde (1.0 mmol), β-naphthol (2.0 mmol), and catalyst 2-1′-methylimidazolium-3-yl-1-ethyl sulfate were carried out in [BMIM][BF_4] at 80°C for the given time to screen optimum reaction conditions (Table 1). Among the eight tested solvents, such as methanol, ethanol, dimethylformamide (DMF), CH_3CN, tetrahydrofuren (THF), 1,2-dichloroethane, [BMIM][BF_4], and [BPY][BF_4], the best result was obtained in [BMIM][BF_4], which may be attributed to its strong basicity and solubility (entries 1–8). An increase

Table 1. Optimization of the reaction between 4-chlorobenzaldehyde and β-naphthol[a]

Entry	Solvent	Amount of catalyst (mol %)	Time (h)	Yield[b] (%)
1	MeOH	0.08	12	68
2	EtOH	0.08	12	56
3	DMF	0.08	16	N*r*[c]
4	CH_3CN	0.08	12	37
5	THF	0.08	12	58
6	$ClCH_2CH_2Cl$	0.08	12	72
7	[BPY][BF_4][d]	0.08	8	79
8	[BMIM][BF_4]	0.08	6	89
9	[BMIM][BF_4]	0.04	6	63
10	[BMIM][BF_4]	0.06	6	76
11	[BMIM][BF_4]	0.10	6	82
12	[BMIM][BF_4]	0.12	6	78

[a] Reaction conditions: 4-chlorobenzaldehyde (1.0 mmol), β-naphthol (2.0 mmol), and catalyst 2-1′- methylimidazolium-3-yl-1-ethyl sulfate (0.08 mol%) in [BMIM][BF_4] at 80°C.

[b] Yield of isolated products.

[c] No reaction.

[d] [BPY] = 1-n-butylpridinum.

in the quantity of catalyst from 0.04 mol% to 0.08 mol% improved the product yield from 63% to 89% (entries 8–10), which showed that the catalyst concentration plays a major role in the optimization of the product yield. However, when an excess amount (0.12 mol%) of catalyst was used in the reaction, the product yields unexpectedly decreased to 72% (entries 11 and 12); thus 0.08 mol% catalyst is the best choice for optimum yield of compound **3**.

In our initial experiments, we found that aldehydes **1** (1.0 mmol) and β-naphthol **2** (2.0 mmol) in [BMIM][BF_4] were stirred in the presence of a catalytic amount (0.08 mol%) of 2-1′-methylimidazolium-3-yl-1-ethyl sulfate at 80°C for 5–8 h to give compound **3** with good yields. As shown in Table 2, compared with the previous methods,[11,16,20] this method takes less reaction time with about equal yields, which indicated the efficient catalysis of this new catalyst as a strong acid. Aromatic aldehydes bearing both electron-rich and electron-deficient groups worked well. However, fatty aldehydes gave somewhat lower yields than aromatic aldehydes as a result of their higher volatility.

Table 2. Synthesis of 14-aryl or alkyl-14*H*-dibenzo[*a, j*]xanthenes

		Time (h)		Yield (%)		Mp (°C)	
Product	R	Found	Reported	Found	Reported	Found	Reported
3a	4-$CH_3C_6H_4$	7	18[11]	92	90[11]	227.9–229.0	229[11]
3b	4-$OCH_3C_6H_4$	7	22[11]	88	90[11]	203.4–204.7	204[11]
3c	4-FC_6H_4	6	18[11]	90	92[11]	238.1–238.8	239[11]
3d	4-BrC_6H_4	6	15[11]	91	95[11]	297.2–298.4	297[11]
3e	4-CNC_6H_4	5	20[20]	90	91[20]	291.6–292.5	291[20]
3f	4-ClC_6H_4	6	18[11]	89	93[11]	289.1–290.7	289[11]
3g	4-$NO_2C_6H_4$	6	20[11]	90	93[11]	>300.0	310[11]
3h	3-$NO_2C_6H_4$	6	24[11]	88	89[11]	211.8–212.7	211[11]
3i	3-FC_6H_4	7	2[16]	86	93[16]	259.7–260.3	260[16]
3j	3-BrC_6H_4	6	21[11]	90	90[11]	192.6–193.5	192[11]
3k	2-ClC_6H_4	8	21[11]	89	87[11]	215.1–216.3	215[11]
3l	2-$OCH_3C_6H_4$	8	24[11]	89	88[11]	260.4–261.8	260[11]
3m	2,4-ClC_6H_3	6	1.5[16]	88	95[16]	253.8–255.1	253[16]
3n	3,4-$OCH_2OC_6H_3$	5		91		233.8–235.1	
3o	4-IC_6H_4	6		92		284.2–285.1	
3p	CH_3CH_2	8	30[11]	86	85[11]	150.8–151.2	152[11]

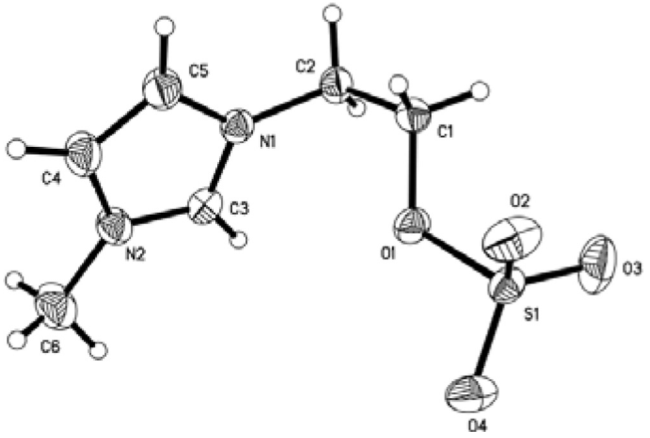

Figure 1. Single-crystal x-ray structure of 2-1′-methylimidazolium-3-yl-1-ethyl sulfate.

Luminescence Properties of 14-Aryl or Alkyl-14*H*-dibenzo[*a,j*]xanthenes

The luminescence properties of products are shown in Fig. 2 and Table 3. From Table 3, we can clearly see that (1) compared with the fluorescence emission of β-naphthol at 352 nm, the emission of all products moved to

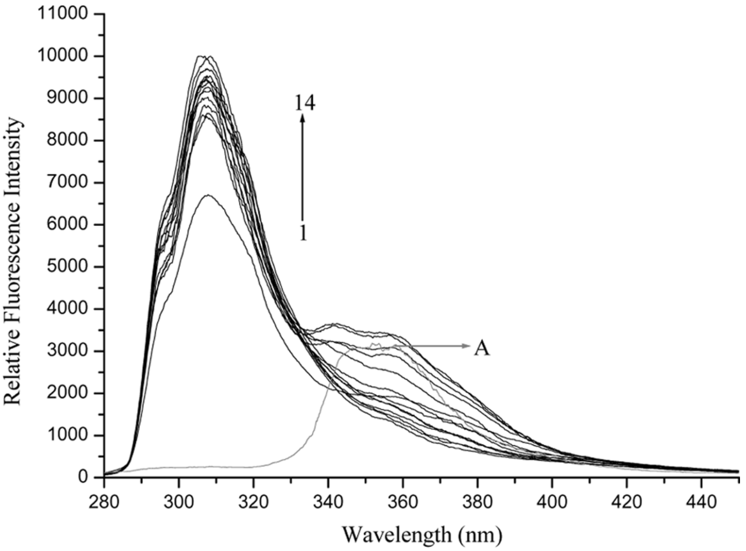

Figure 2. Fluorescent emission spectrum of 14-aryl or alkyl-14*H*-dibenzo[*a,j*] xanthenes. (A-β-naphthol; 1–14: **3b, 3a, 3c, 3d, 3e 3n, 3h, 3f, 3j, 3o, 3g, 3i, 3m, 3k**).

Table 3. Luminescence of products

Compound	E_{max} (abs) ($M^{-1} \cdot cm^{-1}$)	$\lambda_{max(ex)}$ (nm)	$\lambda_{max(em)}$ (nm)	RFI[a]	Stokes (nm)	Φ_F[b]
9,10-Diphenylanthracence	2.221	261	408	9989	147	0.660
β-naphthol (A)	0.067	231	352	3191	121	0.006
3a	0.056	254	307	8576	53	0.014
3b	0.085	254	308	6714	54	0.018
3c	0.055	254	308	8650	54	0.014
3d	2.236	254	307	8838	53	0.588
3e	1.978	254	308	9033	54	0.532
3f	2.294	254	308	9397	54	0.641
3g	2.291	253	307	9583	54	0.653
3h	1.653	254	307	9265	53	0.456
3i	2.067	254	308	9705	54	0.597
3j	2.353	255	307	9530	52	0.634
3k	2.077	252	308	10000	56	0.618
3m	2.235	255	307	9929	52	0.660
3n	2.173	253	308	9190	55	0.594
3o	2.231	254	308	9535	54	0.633

[a] Relative fluorescence intensity.

[b] Relative fluorescence quantum yield.

about 308 nm (Fig. 2); the blue-shifted $\lambda_{max(ex)}$ of products means that they can emit fluorescence easier than β-naphthol. Meanwhile, the OH group of β-naphthol joined the reaction to give a different framework with β-naphthol. The stronger fluorescence emission of products than that of β-naphthol showed the formation of a longer conjugated system in the skeleton of products. (2) The electro and steric effects of the substituted group on aromatic aldehydes have little influence on the fluorescence properties, which clearly showed that the luminescence of products come from their framework directly. (3) Besides **3a, 3b**, and **3c**, other products exhibited stronger fluorescence in ethanol (EtOH) with the about equal fluorescence quantum yield to that of 9,10-diphenylanthracence ($\Phi_F = 0.660$, EtOH), which showed their potential application as new fluorescent probes or luminescence material.

EXPERIMENTAL

General Procedure

All reagents were purchased from commercial sources and used without further purification. Thin-layer chromatographic (TLC) analysis was performed with glass-backed plates precoated with silica gel and examined under ultraviolet (UV) light (254 nm). NMR spectra were measured in $CDCl_3$ with Me_4Si as the internal standard on a Bruker Advance DPX-400 instrument at room temperature. Infared (IR) spectra were recorded on a Bruker Fourier transform (FT)-IRspectrometer; absorbance are reported in centimeters^{-1}. Fluorescence properties were reported on a F-4500 fluorescence spectrophotometer (Hitachi, Japan). The absorption spectrum was measured with a Tu-1201 uv spectrophotometer (Shimadzu).

General Procedure for the Preparation of 2-1′-Methylimidazolium-3-yl-1-ethyl Sulfate

1-Methylimidazole (0.3 mol) and chloroethanol (0.3 mol) were added in a flask containing 10 mL of $CHCl_3$; the mixture was refluxed for 8 h. $CHCl_3$ was removed under vacuum and the unreacted 1-methylimidazole was extracted with ether to give 1-methyl-3-(2-hydroxylethyl)imidazolium chloride. Then chlorosulfonic acid was added dropwise at 0–5°C; when the mixture became solid, a suitable single crystal was obtained after 3 days by recrystallization with dimethylformamide (DMF). Its structure was further confirmed by x-ray crystallographic analysis (Fig. 1). This solid inner salt reacted with chlorosulfonic acid continuously until it became a ropy liquid to afford acidic ionic liquid 2-1′-methylimidazolium-3-yl-1-ethyl sulfate.

General Synthesis of 14-Aryl or Alkyl-14*H*-dibenzo[*a,j*]xanthenes

The reaction mixture of aldehyde (1.0 mmol) and β-naphthol (2.0 mmol) in [BMIM][BF_4] (2.0 mL) and 2-1′-methylimidazolium-3-yl-1-ethyl sulfate (0.08 mol%) was stirred at 80°C for the given time (Table 2). After completion of the reaction, as indicated by TLC, the reaction mixture was cooled to room temperature, filtered, washed with water, and recystallized from EtOH and DMF to afford the pure product.

General Preparation Solution of 14-Aryl or Alkyl-14*H*-dibenzo[*a,j*]xanthenes

The EtOH solution of 9,10-diphenylanthracence, β-naphthol, and **3a–o** (1.0×10^{-6} mol/L) were measured on an uv and fluorescence spectrophotometer to give their absorption and emission spectra, respectively.

Spectral Data of New Products

14-(Benzo[*d*][1,3]dioxol-5-yl)-14*H*-dibenzo[*a,j*]xanthene (**3n**)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.36 (d, $J = 8.4$ Hz, 2H), 7.78–7.84 (m, 4H), 7.58 (t, $J = 7.6$ Hz, 2H), 7.40–7.48 (m, 4H), 7.10 (d, $J = 8.0$ Hz, 1H), 6.87 (s, 1H), 6.61 (d, $J = 8.4$ Hz, 1H), 6.42 (s, 1H), 5.74 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.67, 147.87, 145.95, 139.06, 131.36, 131.07, 128.85, 126.82, 124.28, 122.65, 121.23, 118.05, 117.27, 108.87, 107.79, 100.84, 37.64; IR (KBr, ν, cm^{-1}): 3005, 1621, 1592, 1265.

14-(4-Iodophenyl)-14*H*-dibenzo[*a,j*]xanthene (**3o**)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.30 (d, $J = 8.4$ Hz, 2H), 7.78–7.84 (m, 4H), 7.57 (t, $J = 8.0$ Hz, 2H), 7.40–7.48 (m, 6H), 7.27 (d, $J = 2.0$ Hz, 2H), 6.43 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.68, 144.68, 137.55, 131.25, 131.06, 130.18, 129.12, 128.92, 126.94, 124.39, 122.39, 118.02, 116.62, 113.22, 91.81, 37.60; IR (KBr, ν, cm^{-1}): 3071, 1620, 1591, 1239.

Crystal Data for 2-1′-Methylimidazolium-3-yl-1-ethyl Sulfate

The single-crystal growth was carried out in DMF at room temperature. Crystal data: Empirical formula $C_6H_{10}N_2O_4S$, yellow, crystal dimension 0.48 × 0.46 × 0.43 mm, orthorhombic, space group P2(1)2(1)2(1), a = 7.4262 (13) Å, b = 10.0243 (15) Å, c = 12.0997 (18) Å, α=90.00°, β=90.00°, γ=90.00°, $V = 900.7$ (2) Å^3, $Mr = 206.22$, $Z = 4$, $Dc = 1.521$ Mg/m^3, $\lambda = 0.71073$ Å, μ (Mo $K\alpha$) = 0.345 mm^{-1}, F(000) = 432, S = 1.089, R = 0.0328, and wR = 0.0795. Crystallographic data for the structures of 2-1′-methylimidazolium-3-yl-1-ethyl sulfate reported in this letter have been deposited with the Cambridge Crystallographic Date Centre as supplementary publication no. CCDC-655836.

CONCLUSION

In summary, we have discovered that a novel and highly efficient catalyst 2-1′-methylimidazolium-3-yl-1-ethyl sulfate, can promote the condensation reaction of aldehydes and β-naphthol to construct 14-aryl- or alkyl-14*H*-dibenzo[*a,j*]xanthenes in [BMIM][BF_4]. Furthermore, the screening for optical properties showed that some products may have a good future as new luminescence material's or fluorescence probes.

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