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Introduction of a new bi-SO₃H ionic liquid based on 2,2'-bipyridine as a novel catalyst for the synthesis of various xanthene derivatives

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Introduction

Ionic liquids (ILs) are compounds with unique properties such as non-flammability, no miscibility with non-polar solvents, negligible vapor, reasonable thermal and chemical stability and the ability to be used many times without considerable decrease in their activity. Because of these important characteristics, the use of ILs in organic reactions is under the considerable attention of many organic chemists. These compounds have found three major applications in chemistry as eco-friendly solvents, catalysts and reagents.1 Among these types of compounds, acidic ionic liquids are the most important ones which have been successfully used in different types of organic transformations.² In the last decade, xanthenes and their derivatives have been the subject of considerable levels of interest because of their numerous applications in biological and pharmaceutical research such as antitumor, anticancer, antimicrobial and antiviral³⁻⁶ activities. In addition, these compounds can be used in fluorescent material for visualization of biomolecules and in laser technology.7,8 On the basis of the above mentioned applications the synthesis of xanthenes derivatives is of much importance. Xanthenes are in both symmetrical and asymmetrical forms and there are two ways to prepare them.

The reaction of aldehydes with cyclic 1,3-dicarbonyl compounds and/or β -naphthol for the preparation of symmetrical xanthenes.

The reaction of aldehydes with β -naphthol and cyclic 1,3dicarbonyl compounds for the preparation of asymmetrical xanthenes.

In this study, 1,1'-disulfo-[2,2'-bipyridine]-1,1'-diium chloride, $[BiPy](SO_3H)_2Cl_2$ as a new ionic liquid, is prepared, characterized and used as an efficient catalyst for the promotion of the synthesis of various symmetric and asymmetric xanthene derivatives under solvent free conditions. All products were formed in excellent yields over short reaction times. Easy preparation of the catalyst, simple and easy work-up, mild reaction conditions, low cost, excellent yields and short reaction times are some of the advantages of this work.

> To improve these reactions several methodologies were reported in the literature.^{9–25} Although these procedures provide an improvement, most of them suffer from disadvantages such as long reaction times, harsh reaction conditions, need to excess amounts of the reagent, use of organic solvents and use of toxic reagents. Additionally, only some of them are useful for the synthesis of all of the above mentioned xanthenes. Therefore, it is important to find more efficient catalysts and methods for the synthesis of these types of compounds.

> In recent years, preparation and use of ionic liquids in organic transformations became an important part of our ongoing research program.²⁶⁻²⁹

Herein and in continuation of these studies we wish to report the preparation and characterization of 1,1'-disulfo-[2,2'bipyridine]-1,1'-diium chloride, [BiPy](SO₃H)₂Cl₂, and its applicability in the promotion of the synthesis of different types of xanthenes derivatives. All reactions are performed under mild conditions during relatively short reaction time in good to high yields.

Experimental section

Reagents and materials

Chemicals were purchased from Fluka, Merck, and Aldrich chemical companies. All yields refer to the isolated products. Products were characterized by comparison of their physical constants and also their IR and NMR spectra with authentic samples and those reported in the literature. The purity determination of the substrate and reaction monitoring were accompanied by TLC on silicagel polygram SILG/UV 254 plates.

Characterization

The IR spectra were recorded on a Perkin Elmer 781 Spectrophotometer. In all the cases the ¹H NMR spectra were recorded

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with Bruker Avance 400 and 500 MHz instruments. All chemical shifts are quoted in parts per million (ppm) relative to TMS using deuterated solvent. The ¹³C NMR data were collected on BrukerAvance400 MHz instrument. MS studies were performed using 5973 network mass selective detector, Agilent Technology (HP) company (ion source: electronic (EI) 70 eV; ion source temperature: 230 °C; analyzer: quadrupole). Melting points were recorded on a Büchi B-545 apparatus in open capillary tubes.

Preparation of [BiPy](HSO₃)₂Cl₂

Chlorosulfonic acid (1.75 g, 15 mmol) was added dropwise to a round-bottomed flask (100 mL) containing 2,2'-bipyridine (1.17 g, 7.5 mmol) in dry CH_2Cl_2 (50 mL), over a period of 5 min in an ice bath. After the addition was completed, the reaction mixture was stirred for 2 h at room temperature, then stood for 5 min, and the solvent was decanted. The residue was washed with dry diethylether (3 × 50 mL) and dried under vacuum to give [BiPy](HSO₃)₂Cl₂ as a white solid in 98% yield (Scheme 1).

Spectroscopic data for [BiPy](SO₃H)₂Cl₂ are as

Mp 86 °C; MS: 81, 155, 162, 191, 228, 272, 389 *m/z*; FT-IR (KBr, cm⁻¹) v_{max} : 3402, 1604, 1513, 1437, 1281, 1232, 1174, 877. ¹H NMR (400 MHz, DMSO-d6): δ = 7.92 (1H, ddd, J_1 = 8, J_2 = 5.2, J_3 = 1.2), 8.46 (1H, td, J_1 = 8, J_2 = 1.6), 8.70 (1H, d, J = 8), 8.91 (1H, ddd, J_1 = 5.2, J_2 = 1.6, J_3 = 0.8), 9.58 (1H, OH, s) ppm; ¹³C NMR (100 MHz, DMSO-d6) δ = 147.84, 147.02, 143.39, 127.66, 124.23 ppm; elemental analysis: C, 29.52; H, 3.93; N, 6.39; O, 26.22; S, 14.65. The amount of chloride in [BiPy](SO₃H)₂Cl₂ was determined by potentiometric titration method (titration of 50 mL 0.01 M [BiPy](SO₃H)₂Cl₂ with 0.1 M AgNO₃, that was 1.91 mmol Cl per mol of catalyst.

Synthesis of symmetric xanthenes derivatives: a typical procedure

A mixture of aldehyde (1 mmol), 2-naphthol and/or diketone (2 mmol) and [BiPy](SO₃H)₂Cl₂ (10 mg) was stirred in an oil-bath at 90 °C under solvent-free conditions. After completion of the reaction [monitored by TLC: EtOAc–*n*-hexane (2 : 8)], the reaction mixture was cooled, H₂O (5 mL) was added and filtered to separate the catalyst. Then the product was recrystallized from EtOH to give the pure product.

Synthesis of asymmetric xanthenes derivatives: a typical procedure

A mixture of 2-naphthol (1 mmol), diketone (1 mmol), aldehyde (1 mmol) and $[BiPy](SO_3H)_2Cl_2$ (10 mg, 2.5 mol%) was stirred in



Scheme 1 Preparation of [BiPy](HSO₃)₂Cl₂.

an oil-bath at 90 °C for an appropriate time. After completion of the reaction, as monitored with TLC [EtOAc–n-hexane (2 : 8)], the reaction mixture was cooled to room temperature, H₂O (5 mL) was added and filtered to separate the catalyst. Then the product was recrystallized from EtOH to give the pure product.

Result and discussions

Catalyst characterization

The infrared spectra of 2-(pyridin-2-yl) pyridine and $[BiPy](SO_3H)_2Cl_2$ are shown in Fig. 1. The IR spectrum of the product shows a broad peak at 2690–3600 cm⁻¹ which can be related to the OH stretching of the SO₃H groups.^{29,30} Moreover, the two peaks observed at 1174 cm⁻¹ and 1281 cm⁻¹ correspond to the O–SO₂ symmetric and asymmetric stretching, respectively and other band at 1068 cm⁻¹ is assigned to N–SO₂ stretching. In addition, C=N and C=C vibrations are observed at 1604 and 1513 cm⁻¹ correspondingly.³⁰

The ¹H NMR spectrum of $[BiPy](HSO_3)_2Cl_2$ in addition to the other protons, shows the SO₃H acidic hydrogen peak at 9.58 ppm. This observation clarifies that $[BiPy](HSO_3)_2Cl_2$ is exactly synthesized (Fig. 2).

The mass spectrum of $[BiPy](SO_3H)_2Cl_2$ is shown in Fig. 3. In this spectrum the correct molecular ion peak appears at 389. Other ion peaks are also observed at 272 (M⁺ – SO₃H and Cl), 228 (M⁺ – 2SO₃H), 191 (M⁺ – 2SO₃H and Cl), 162 (2SO₃H), 155 (M⁺ – 2SO₃H and 2Cl) and 81 (SO₃H) as well.

The Hammett acidity method is an effective way to the acidity strength of an acid in organic solvents, using UV-vis technique.³¹ The Hammett function is defined as:

$$H_0 = pK(I)_{aq} + \log([I]_s/[IH^+]_s)$$



Fig. 1 FT-IR spectra of 2-(pyridin-2-yl) pyridine (up) and [BiPy]-(SO_3H)_2Cl_2 (down).







Fig. 3 Mass spectra of $[BiPy](SO_3H)_2Cl_2$.

Table 1 Calculation of Hammett acidity function (H_0) for [BiPy](HSO_3)₂Cl₂^{*a*}

Entry	Catalyst	A _{max}	[I] _s %	$[IH^+]_s$ %	H_0
1	_	2.2261	100	0	_
2	[BiPy](HSO ₃) ₂ Cl ₂	1.5984	71.80	28.2	1.40

 a Condition for UV-visible spectrum measurement: solvent: CCl₄, indicator: 4-nitroaniline (p*K*(I)_{aq} = 0.99), 1.44 × 10⁻⁴ mol L⁻¹ (10 mL); catalyst: [BiPy](HSO₃)₂Cl₂ (10 mg), 25 °C.



Fig. 4 Absorption spectra of 4-nitroaniline (indicator) (a) and [BiPy](HSO_3)_2Cl_2 (catalyst) (b) in CCl_4.



Scheme 2 Synthesis of various xanthene derivatives catalyzed by [BiPy](SO_3H)_2Cl_2.

Table 2	Optimization of the reaction conditions for the synthesis of
xanthen	es derivative of 4-chlorobenzaldehyde and 2-naphthol

Entry	Catalyst $(mg mol^{-1} \%)$	Temperature (°C)	Time (min)	Conversion (%)
1	5/1.25	90	24	70
2	10/2.5	110	25	98
3	10/2.5	90	10	98
4	10/2.5	80	30	40
5	20/5	90	5	70

where the $pK(I)_{aq}$ is the pK_a value of aqueous solution of indicator, $[IH^+]_s$ and $[I]_s$ are the molar concentrations of protonated and unprotonated forms of the indicator in the solvent, respectively. According to Lambert–Beer's Law, the value of $[I]_s/[IH^+]_s$ can be determined and calculated through UV-visible spectrum.

For this purpose, 4-nitroaniline $(pK(I)_{aq} = 0.99)$ as the basic indicator and CCl₄ as the solvent were chosen. As can

be seen in Fig. 4, the maximal absorbance of the unprotonated form of the indicator was observed at 328 nm in CCl_4 . When [BiPy](HSO₃)₂Cl₂ as the ionic liquid catalyst was added to the indicator solution, the absorbance of the unprotonated form of the indicator decreased, which indicated that the indicator was partially in the form of [IH⁺]. These results that have listed in Table 1, show the acidity strength of [BiPy](HSO₃)₂Cl₂.

Catalytic activity

On the basis of the obtained information, we anticipated that $[BiPy](HSO_3)_2Cl_2$ can be used as an efficient catalyst for the acceleration of the reactions which need the use of an acidic catalyst to speed-up. So we were interested to investigate the applicability of this reagent in the promotion of the synthesis of xanthenes derivatives.

At first, we focused our attention to study the synthesis of 14aryl-14*H*-dibenzo $[a_j f]$ xanthenes. For optimization of the reaction conditions, the condensation of 4-chlorobenzaldehyde

	Product		Time (min)		Mp (°C)	
Entry		Aldehydes		Yield (%)	Found	Reported ²⁴
1		C ₆ H ₅ CHO	15	95	185-184	185-186
2	Ar Ar	4-ClC ₆ H ₄ CHO	10	98	280	280-283
3		2-ClC ₆ H ₄ CHO	30	95	206-207	206-209
4		4-BrC ₆ H ₄ CHO	18	95	294-295	294-295
5		4-NO ₂ C ₆ H ₄ CHO	25	95	310-312	310-311
6		3-NO ₂ C ₆ H ₄ CHO	23	90	212	212-214
7	• 0 •	4-MeOC ₆ H ₄ CHO	30	90	199-201	199-201
8		2-MeOC ₆ H ₄ CHO	50	80	258-259	258-259
9		4-HOC ₆ H ₄ CHO	45	80	130-132	130-133
10		C ₆ H ₅ CHO	2	98	197-198	197-198
11	0 4 7 0	4-ClC ₆ H ₄ CHO	4	98	225-229	227-229
12		2-ClC ₆ H ₄ CHO	3	98	220-223	224-225
13		4-BrC ₆ H ₄ CHO	4	98	240-242	240-242 (ref. 26)
14		3-BrC ₆ H ₄ CHO	8	96	280-282	281-282
15	Me I I I I I I I I I I I I I I I I I I I	4-NO ₂ C ₆ H ₄ CHO	2	95	223-224	223-224
16	$Me' \sim 0' \sim Me$	3-NO ₂ C ₆ H ₄ CHO	5	90	162-163	164-165
17	1110	4-MeOC ₆ H ₄ CHO	5	98	241-242	243-245
18		3-MeOC ₆ H ₄ CHO	1	98	190-191	190-191
19		2-MeOC ₆ H ₄ CHO	2	98	209-210	209-210
20	O Ar O	C ₆ H ₅ CHO	1	98	203-205	203-204
21		4-ClC ₆ H ₄ CHO	2	98	228-230	228-229
22		2-ClC ₆ H ₄ CHO	3	95	247-248	248-249
23		4-BrC ₆ H ₄ CHO	2	98	227-229	227-228
24		3-BrC ₆ H ₄ CHO	2	98	280-281	280-281
25	\sim 0 \sim	4-NO ₂ C ₆ H ₄ CHO	3	95	260-261	263-264
26		C ₆ H ₅ CHO	15	90	150-151	150-151
27	<u>^</u>	4-ClC ₆ H ₄ CHO	10	98	170-171	173-174
28	Ar O	2-ClC ₆ H ₄ CHO	15	80	220-224	221-224
29		4-BrC ₆ H ₄ CHO	20	98	180-182	180-182
30		3-BrC ₆ H ₄ CHO	25	85	164-166	164-165
31	Me	4-NO ₂ C ₆ H ₄ CHO	20	90	175-176	175-178
32		3-NO ₂ C ₆ H ₄ CHO	15	95	166-169	166-169
33	Me	2-NO ₂ C ₆ H ₄ CHO	20	80	218-220	218-220
34		4-MeOC ₆ H ₄ CHO	16	90	205-207	205-208
35		3-MeOC ₆ H ₄ CHO	20	95	218-220	218-220
36		2-Naphthaldehyde	15	80	213-214	213-215

^a Isolated yields.

with 2-naphthol to the corresponding product was selected as a model reaction in different conditions in the presence of different amounts of [BiPy](SO₃H)₂Cl₂. The results are tabulated in Table 1.

The obtained results showed that the reaction using 10 mg of the catalyst at 90 °C proceeded with highest yield in shortest reaction times (Scheme 2).

It should be noted that using lower or higher amounts of the catalyst lead to the product in longer times. On the other hand by decreasing of the temperature, the reaction became slower (Table 2, entry 4). It is also important to note that by increasing of the temperature, the mixture became sticky which resulted in the increasing of the reaction time (Table 2, entry 2).

After optimization of the reaction conditions, we explored the protocol with a variety of simple readily available substrates under the optimal conditions. As presented in Table 3, different aromatic aldehydes were condensed with 2-naphthol under the selected conditions with high yields in very short reaction times. As can be seen, the strict effect of the substituents on the aromatic ring led to the addition of the reaction times (Table 3, entries 1-9).

In the next step, this ionic liquid was used as a catalyst in the condensation of dimedone or cyclohexadione with aldehydes leading to 1,8-dioxo-octahydroxanthenes (Scheme 2). Our

investigations clarified that under the same optimal conditions, the products can be obtained in high yields in very short reaction times (Table 3, entries 10-25).

On the basis of these studies and after the successful application of $[BiPy](SO_3H)_2Cl_2$ in the preparation of symmetric xanthenes, we decided to use this reagent in the synthesis of 12aryl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-ones. The same reaction condition was applied for this purpose and the results showed that using this method the requested products were obtained under mild conditions in excellent yields during very short times (Table 3, entries 26-36).

Table 4 compares our results with the results reported in the literature using some of the other ionic liquids in the synthesis of xanthenes. This comparison indicates that in some cases, the reaction time is too long in the presence of the other catalysts (Table 4, ref. 18, 34 and 36-41). In addition, the amount of the catalyst in this work have been reduced relative to the other ILs and it is clear that [BiPy](HSO₃)₂Cl₂ is superior in terms of TOF (turnover frequency) to the compared ionic liquids.

To check the reusability of the catalyst, the reaction of 4chlorobenzaldehyde and dimedone under the optimized reaction conditions was studied again. When the reaction completed, H₂O (3 mL) was added to separate the catalyst. The solvent was evaporated under reduced pressure and resulting

Table 4 Comparison of the results obtained from the synthesis of xanthenes in the presence of [BiPy](HSO₃)₂Cl₂ with those obtained using other ionic liquids^a

Product	Catalyst loading (mol%)	Temperature (°C)	Time (min)	Yield (%)
\land	[Dsim]Cl (10)	110	5	90 (ref. 32)
	$[Et_3N-SO_3H]Cl$ (15)	120	30	96 (ref. 18)
\land	DSIMHS (25)	90	3	94 (ref. 26)
	$[H-NMP][HSO_4](10)$	110	20	96 (ref. 33)
	$[\text{Hmim}]\text{HSO}_4(12)$	125	90	85 (ref. 34)
$ \qquad \qquad$	$[MIMPS]HSO_4$ (25)	100 (Water)	7	93 (ref. 35)
	[BiPy](HSO ₃) ₂ Cl ₂ (2.57) ^a	90	15	95 (this work)
Br	[Dsim]Cl (10)	70	4	96 (ref. 32)
Ĭ	DSIMHS (25)	55	3	92 (ref. 26)
	[Hmim]TFA (100 mg)	80	180	91 (ref. 36)
	$[bmim]HSO_4$ (100 mg)	80	210	90 (ref. 37)
	$[Et_3NH][HSO_4](20)$	100	45	87 (ref. 38)
$\begin{array}{ccc} \mathbf{O} & \mathbf{T} & \mathbf{O} \\ \mathbf{O} & \mathbf{T} & \mathbf{O} \end{array}$	$[Et_3N-SO_3H]Cl(25)$	80	40	91 (ref. 18)
	[BiPy](HSO ₃) ₂ Cl ₂ (2.57) ^b	90	4	98 (this work)
Me Me				
Me				
Cl	$[Et_3N-SO_3H]Cl$ (25)	120	40	89 (ref. 39)
	DSIMHS (25)	55	12	93 (ref. 26)
	$Py(HSO_4)_2$ (10)	100	30	87 (ref. 40)
	$[NMP]H_2PO_4$ (20)	80	40	87 (ref. 41)
	$[Msim]BF_4$ (10)	110	7	95 (ref. 32)
	$[BiPy](HSO_3)_2Cl_2 (2.57)^c$	90	10	98 (this work)
Me				

^{*a*} TOF (h⁻¹): a = 147.8, b = 572, c = 228.8.

Table 5 Reusability of $[BiPy](SO_3H)_2Cl_2$ in the reaction of 4-chloro benzaldehyde and dimedone

Run	Time (min)	Yield (%)
1	4	98
2	7	95
3	10	92
4	20	85

ionic liquid was reused directly for the next run. It was found that the catalyst could be recovered and reused at least for three runs (Table 5).

Conclusions

In conclusion, in this study we have introduced $[BiPy](HSO_3)_2Cl_2$ as a highly powerful ionic liquid for the simple preparation of symmetric and asymmetric xanthenes derivatives. Ease of preparation and handling of the catalyst, high reaction rates, simple procedure, use of lower loading of the catalyst, high yield of the products without side reactions and solvent-free conditions are some of the advantages of this method.

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