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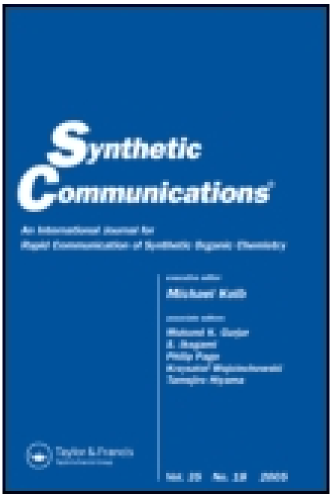

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Convenient and Efficient Method for the Synthesis of Phthalocyanines and Metallophthalocyanines in Task-Specific 2-Hydroxyethyl Ionic Liquids

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CONVENIENT AND EFFICIENT METHOD FOR THE SYNTHESIS OF PHTHALOCYANINES AND METALLOPHTHALOCYANINES IN TASK-SPECIFIC 2-HYDROXYETHYL IONIC LIQUIDS

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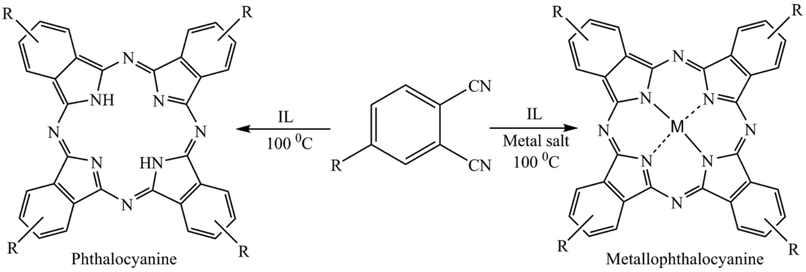
GRAPHICAL ABSTRACT



Abstract *Tetramerization of substituted phthalonitriles in task-specific 2-hydroxylethyl-based imidazolium and ammonium ionic liquids at 100 °C gave corresponding phthalocyanines in moderate yield. Further the reaction of substituted phthalonitriles in the presence of transition-metal salts in ionic liquids gave the corresponding metallophthalocyanines. The 2-hydroxylethyl ammonium ionic liquids gave better yields of phthalocyanines than 2-hydroxylethyl imidazolium and nonhydroxyl functionalized ionic liquids. The isolation and separations of different phthalocyanines were accomplished by silica-gel column chromatography, and products were characterized by various spectroscopic techniques.*

Keywords 2-Hydroxyethyl ionic liquids; metal salts; phthalocyanines; phthalonitriles; tetramerization

INTRODUCTION

Ionic liquids are widely used as a green reaction media to replace the conventional organic solvents in chemical and catalytic reactions,[1,2] separation and purification processes,[3] and biomedical fields.[4] The appropriate combination of organic cations and anions may modify the property, specificity, and reactivity of ionic liquids[5] to serve the dual roles of catalyst and reaction media. The replacement

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of conventional organic bases with basic ionic liquids are due to their flexible, nonvolatile, noncorrosive, immiscible, highly catalytic efficient, environmentally friendly, and reusable properties.[6] Basic ionic liquids are important task-specific ionic liquids used in base-catalyzed processes such as Michael addition,[7] Markovnikov addition,[8] Knoevenagel condensation,[9] Mannich reactions,[10] and various other base-catalyzed reactions. The basic ionic liquids enhance the nucleophilicity and the rate of reaction for nucleophilic substitution reactions in comparison to organic solvents.[11,12] The 2-hydroxylethyl ionic liquids are an important class of task-specific ionic liquids. They have increased solvent polarity and solvation properties similar to volatile alcohols in many organic transformations such as preparation of nonmaterial[13,14] and material chemistry.[15] The use of task-specific ionic liquids as a green reaction medium offers an efficient solution to both the solvent emission and catalytic recycling problems.[16]

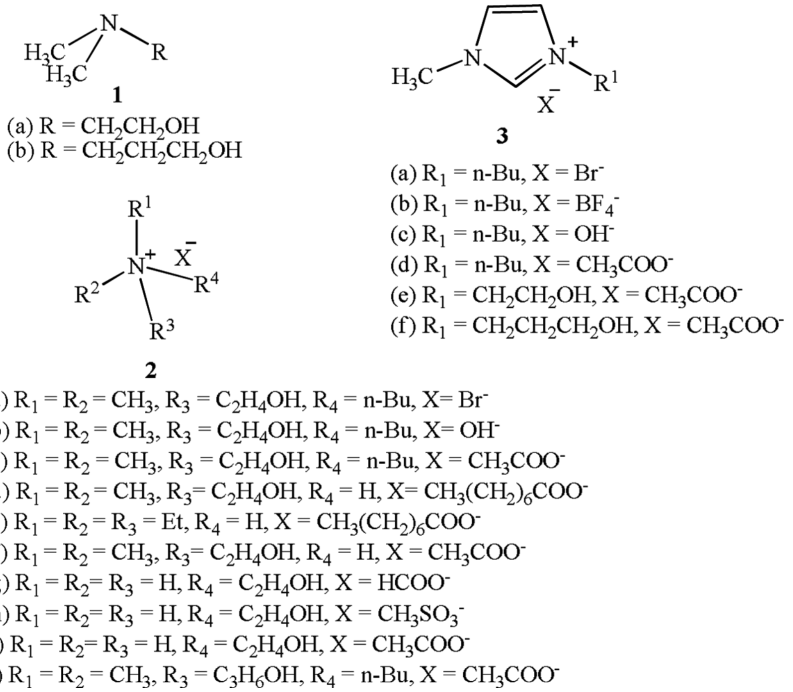
Phthalocyanines are well known because of their wide applications including use in chemical sensors, dyes, catalysts, liquid crystals, and biomedical fields.[17,18] A decisive disadvantage of phthalocyanines is their poor solubility in organic solvents and water. To increase the solubility, alkyl or alkyloxy substituents are introduced at peripheral positions of phthalocyanine framework. The tetramerization of phthalonitriles in high boiling solvents such as, dimethylformamide, pentanol, dichlorobenzene, and ethylene glycol are general methods for the synthesis of phthalocyanines. These methods require strong base and metal salts as a catalyst.[19,20] Previously, we have explored the synthesis of metal-free[21] and metallated phthalocyanines using functional imidazolium-, ammonium-, and pyridinium-based ionic liquids in combination with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a strong base. The use of such organic bases in reaction causes additional cost and environmentally hazardous conditions;[22] hence it is desirable to use task-specific basic ionic liquids[23] instead of hazardous organic bases.

Herein, we report the synthesis of phthalocyanines in task-specific basic ionic liquids, avoiding the use of strong and expensive DBU and related organic bases, thereby preventing the reaction from various disadvantages such as no catalyst recovery, corrosion, and waste production. This method involves a greener approach for the synthesis of highly valuable phthalocyanines at lower temperature in high purity than other methods[24] and offers a trouble-free workup procedure.

RESULTS AND DISCUSSION

The required task-specific ammonium (**2**) and imidazolium (**3**) ionic liquids are synthesized by modification of known methods and purified by crystallization in suitable solvents and various other purification processes. The characterizations of these task-specific ionic liquids are done by infrared (IR), NMR, and other spectroscopic techniques (Figure 1).

Phthalonitrile **4a** in dimethylaminoethanol (**1a**) with $Co(OAc)_2 \cdot 4H_2O$ tetramerizes to form phthalocyanine (**6a**) in 10% yield (Table 1), whereas the tetramerization of phthalonitrile **4a** in dimethylaminopropanol (**1b**) gave **6a** in 2% yield only. The appearance of a characteristic soret band at 337 nm and intense Q bands at 602 nm and 665 nm in ultraviolet–visible (UV-vis) spectrum indicates the formation of phthalocyanine **6a** in the reaction.[21] In the infrared (IR) spectrum, the absence of



1

(a) R = CH_2CH_2OH
(b) R = $CH_2CH_2CH_2OH$

2

(a) $R_1 = R_2 = CH_3$, $R_3 = C_2H_4OH$, R_4 = n-Bu, $X = Br^-$
(b) $R_1 = R_2 = CH_3$, $R_3 = C_2H_4OH$, R_4 = n-Bu, $X = OH^-$
(c) $R_1 = R_2 = CH_3$, $R_3 = C_2H_4OH$, R_4 = n-Bu, $X = CH_3COO^-$
(d) $R_1 = R_2 = CH_3$, $R_3 = C_2H_4OH$, $R_4 = H$, $X = CH_3(CH_2)_6COO^-$
(e) $R_1 = R_2 = R_3$ = Et, $R_4 = H$, $X = CH_3(CH_2)_6COO^-$
(f) $R_1 = R_2 = CH_3$, $R_3 = C_2H_4OH$, $R_4 = H$, $X = CH_3COO^-$
(g) $R_1 = R_2 = R_3 = H$, $R_4 = C_2H_4OH$, $X = HCOO^-$
(h) $R_1 = R_2 = R_3 = H$, $R_4 = C_2H_4OH$, $X = CH_3SO_3^-$
(i) $R_1 = R_2 = R_3 = H$, $R_4 = C_2H_4OH$, $X = CH_3COO^-$
(j) $R_1 = R_2 = CH_3$, $R_3 = C_3H_6OH$, R_4 = n-Bu, $X = CH_3COO^-$

3

(a) R_1 = n-Bu, $X = Br^-$
(b) R_1 = n-Bu, $X = BF_4^-$
(c) R_1 = n-Bu, $X = OH^-$
(d) R_1 = n-Bu, $X = CH_3COO^-$
(e) $R_1 = CH_2CH_2OH$, $X = CH_3COO^-$
(f) $R_1 = CH_2CH_2CH_2OH$, $X = CH_3COO^-$

Figure 1. Structure of functional ionic liquids.

Table 1. Tetramerization of phthalonitrile **4a** in different ionic liquids (**1**–**3**) at 100 °C in the presence of $Co(OAc)_2 \cdot 4H_2O^a$

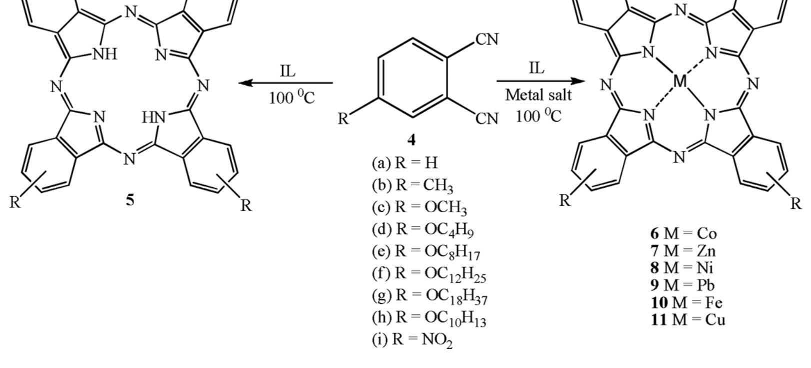
S. no.	Phthalonitrile	Phthalocyanine	Ionic liquid	Yield (%)^b
1	**4a**	**6a**	**la**	10
2	**4a**	**6a**	**lb**	2
3	**4a**	**6a**	**2a**	6
4	**4a**	**6a**	**2b**	62
5	**4a**	**6a**	**2c**	84, 81^c, 76^c
6	**4a**	**6a**	**2d**	61
7	**4a**	**6a**	**2e**	0
8	**4a**	**6a**	**2f**	60
9	**4a**	**6a**	**2g**	30
10	**4a**	**6a**	**2h**	22
11	**4a**	**6a**	**2i**	44
12	**4a**	**6a**	**2j**	25
13	**4a**	**6a**	**3a**	9
14	**4a**	**6a**	**3b**	6
15	**4a**	**6a**	**3c**	30
16	**4a**	**6a**	**3d**	12
17	**4a**	**6a**	**3e**	72
18	**4a**	**6a**	**3f**	22

[a] Reaction condition ratio, phthalonitrile (**4a**)–ionic liquid–metal salt = 1:1:0.25 in 2 h.
[b] Isolated yields.
[c] The same ionic liquid was reused for each consecutive run.

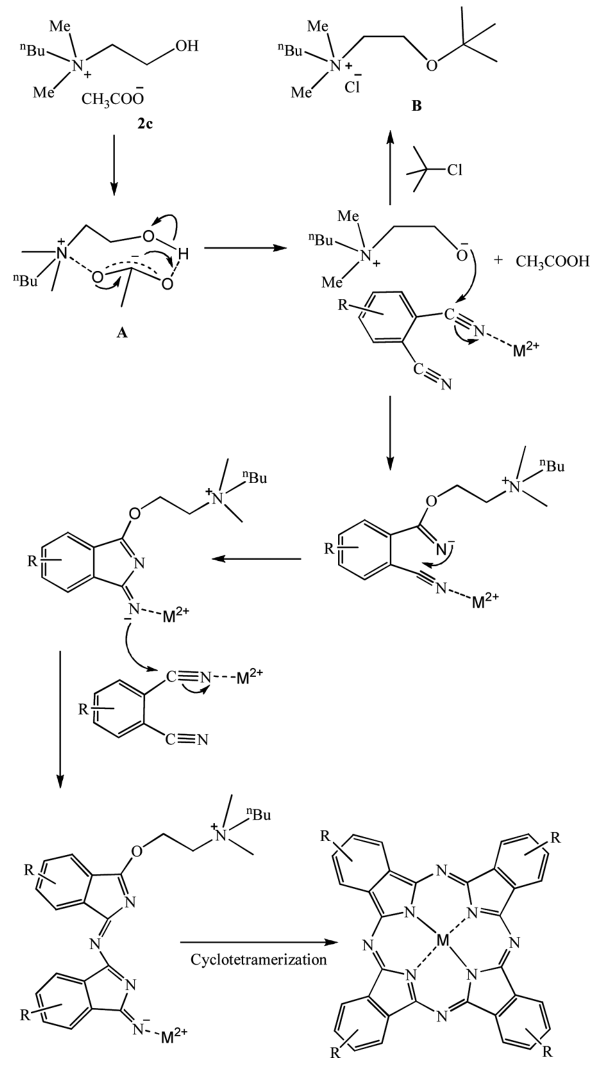
CN and NH stretching bands at ~2200 cm^{-1} and 3200–3300 cm^{-1} respectively confirmed the complete conversion of **4a** into **6a**. A peak at *m*/*z* 572.32, corresponding to $[M+H]^+$ in the electrospray ionization–mass spectrometry (ESI-MS) spectrum confirmed the formation of **6a** in the reaction (Scheme 1).

The roles of anions attached to ionic liquids were examined by carrying out the reaction in different ionic liquids. Tetramerization of phthalonitrile **4a** in 1-butyl-3-methylimidazolium bromide [bmim][Br] (**3a**) and 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF_4] (**3b**) gave phthalocyanine (**6a**) in 9% and 6% yields respectively. The same reaction in 1-butyl-3-methylimidazolium acetate [bmim][CH_3COO] (**3d**) (Table 1) gave phthalocyanine (**6a**) in 12% yield, signifying the role of anions in the reactions. As the anion was more basic, the yield of the product increased. The imidazolium ionic liquids in the absence of hydroxyalkyl group may catalyze the reaction either by direct involvement of anion in the reaction or its ability to show stronger hydrogen bonded interaction with cyano group of phthalonitriles. The [bmim][Br] and [bmim][BF_4] ionic liquids show hydrogen bonding interactions,[25] whereas the greater yield in ionic liquids **3c** and **3d** clearly indicates the direct involvement of more basic anion in the reaction.

Further to enhance the catalytic efficiency of the reaction, we have moved towards hydroxyl-based task-specific ionic liquids. The reaction medium plays an important role in determining the rate of a chemical reaction, mainly when anionic species are involved. We have synthesized the task-specific imidazolium ionic liquids **3e** and **3f** by introduction of hydroxyl alkyl groups. Phthalonitrile **4a** in the presence of ionic liquid **3e** and $Co(OAc)_2 \cdot 4H_2O$ tetramerizes to form phthalocyanine **6a** in 72% yield, whereas the same reaction in ionic liquid **3f** gave **6a** in 22% yield only (Table 1). From the literature[26,27] it is clear that the presence of hydroxyl group in imidazolium cation makes it a better hydrogen bond donor than C-2 hydrogen of imidazolium; therefore a strong hydrogen-bonded interaction is obtained between anion and hydroxyl of cation. These ionic liquids **3e–3f** may involve an alkoxide type of mechanism by showing the hydrogen bonding network (Scheme 2) and provide better yields than non-hydroxyl-based ionic liquid **3d**.



Scheme 1. Synthesis of phthalocyanines.



Scheme 2. Proposed mechanism.

The change of imidazolium ion with bulkier tetraalkylammonium cation is less prone to Coulomb interactions, which again increases the nucleophilicity of the anions. To explore the role of anions in ionic liquids, task-specific ionic liquids were designed and synthesized by introduction of the hydroxylethyl group as an ethanol group attached to the ammonium-based ionic liquids (Figure 1, **2a–2j**). The yields for the tetramerization of phthalonitrile **4a** at 100 °C in task-specific ammonium ionic liquids (**2a–2j**) are mentioned in Table 1. The trend for the anions giving the maximum yield of phthalocyanine (**6a**) in ionic liquids (**2a–2d**) follows the order $CH_3COO^- > C_7H_{15}COO^- > OH^- > Br^-$, corresponding to the nucleophilicity of the anion. The introduction of long-chain octanoate anion in (2-hydroxyethyl) dimethylammonium octanoate [hyeda][$C_7H_{15}COO$] (**2d**) gave lower yield in comparison to (2-hydroxyethyl)dimethylammonium acetate **(2f),** due to the presence of a bulky group, which reduced the nucleophilicity of octanoate ion (Table 1).

Further, the effect of change of anion in combination with hydroxylethyl group of ammonium cation was studied. Increase in the yield of the phthalocyanine **6a** was observed on changing the anion from methyl sulfate to formate to acetate in ionic liquids **2h, 2g,** and **2i,** which confirms the fact that ionic liquids that have a hydroxyl group in combination with strong basic anion (**2i**) (strong conjugate base) show better potential as organic solvents in comparison to the one having weak basic anion (**2g**) (weak conjugate base) (Table 1), which was further confirmed by using ionic liquid **2h** (possessing much weaker basic anion), thereby giving phthalocyanine in only 22% yield (Table 1). To compare the role of hydroxylethyl group attached to nitrogen atom in ammonium-based ionic liquids, the same reaction was carried out using ionic liquids **2d** and **2e**. It is interesting to observe that the reaction in ionic liquid **2d** gave phthalocyanine in 61% yield, while the reaction in ionic liquid **2e** (which does not contain any hydroxyl group) could not lead to the formation of the desired phthalocyanine. Similar results were obtained by using imidazolium-based ionic liquid **3d–3e** (Table 1). This clearly indicate the generation and involvement of alkoxide ion in the reaction (Scheme 2) as the most stable anion (least basic, i.e., methyl sulfate and formate) in combination with hydroxylethyl cation gives minimum yield. The least stable anion (most basic, i.e., acetate) in combination with hydroxylethyl cation gives maximum yield of phthalocyanine **6a** (Table 1). The 2-hydroxypropyl ionic liquids (**2j** and **3f**) gave lower yield of phthalocyanines as compared with their corresponding 2-hydroxyethyl ionic liquids (**2c** and **3e**) (Table 1). Thus the imidazolium ionic liquids show interactions with phthalonitriles in the reaction medium and give lower yields of phthalocyanines as compared with ammonium ionic liquids.

To explore the generality of this procedure, a series of substituted phthalocyanines were synthesized under the given reaction conditions by using 1 equivalent of ionic liquid **2c** (Scheme 1). Increasing the amount of ionic liquid does not affect the yield of phthalocyanine. Phthalonitriles (**4a–i**) were tetramerized in presence of cobalt acetate and ionic liquid **2c** to their corresponding phthalocyanine (**6a–i**) in moderate yield. These results are summarized in Table 2. The structures of all products were characterized by spectroscopic analysis and these results were in satisfactory agreement with their literature values.[21]

The core metal of phthalocyanine had been changed with various metals in the presence of corresponding metal salts. In the presence of 2-hydroxylethyl ammonium ionic liquid **2c** and metal salts, phthalonitrile **4a** tetramerizes to give corresponding metallophthalocyanines in efficient yield (Scheme 1). The results are summarized in Table 3. The structures of all metallophthalocyanines were confirmed by various spectroscopic techniques.[21] The tetramerizations of phthalonitriles in ionic liquid **2c** with metal salts depend on the substituent of phthalonitriles and types of metal salts. Metal ions in reaction media coordinate with cyano groups of phthalonitrile and facilitate the attack of ionic liquid on nitrile group (Scheme 2). Thus the metal ion in reaction acts as template and favors the cyclotetramerization of phthalonitrile, thus increasing the yields of the reaction.[28]

The efficient ionic liquid **2c** was further used to synthesize the unmetallated phthalocyanine. In the presence of 2-hydroxyethyl ammonium ionic liquid **2c**,

Table 2. Tetramerization of substituted phthalonitriles in ionic liquid **2c** at 100 °C in the presence of $Co(OAc)_2 \cdot 4H_2O$[a]

S. no.	Phthalonitrile	Phthalocyanine	Yield (%)[b]
1	**4a**	**6a**	84
2	**4b**	**6b**	82
3	**4c**	**6c**	82
4	**4d**	**6d**	80
5	**4e**	**6e**	78
6	**4f**	**6f**	72
7	**4g**	**6g**	70
8	**4h**	**6h**	60
9	**4i**	**6i**	78

[a] Reaction condition ratio, phthalonitrile (**4a–4i**)–ionic liquid (**2c**)–metal salt = 1:1:0.25 in 2 h.
[b] Isolated yields.

Table 3. Tetramerization of phthalonitrile **4a** in ionic liquid **2c** with different metal salts at 100 °C[a]

S. no.	Phthalonitrile	Phthalocyanine	Metal salt	Yield (%)[b]
1	**4a**	**6a**	$Co(OAc)_2 \cdot 4H_20$	84
2	**4a**	**7a**	$Zn(OAc)_2 \cdot 2H_20$	86
3	**4a**	**8a**	$Ni(OAc)_2 \cdot 4H_20$	76
4	**4a**	**9a**	$Pb(OAc)_2$	64
5	**4a**	**10a**	$FeCl_3$	62
6	**4a**	**11a**	$Cu(OAc)_2 \cdot H_2O$	74
7	**4a**	**7i**	$Zn(OAc)_2 \cdot 2H_2O$	80

[a] Reaction condition ratio, phthalonitrile–ionic liquid (**2c**)–metal salt = 1:1:0.25 in 2 h.
[b] Isolated yields.

phthalonitriles (**4a–g**) tetramerize to form unmetallated phthalocyanine (**5a**–**g**). The results are summarized in Table 4. The structures of all unmetallated phthalocyanines are confirmed by IR and UV-vis spectroscopy. According to the results, the tetramerization reactions in the absence of metal salts gave lower yields of phthalocyanines in comparison with metallophthalocyanines because there was no template effect of metal ions. Metallation of metal free phthalocyanine **5a** was also carried out

Table 4. Tetramerization of phthalonitrile **4a** in ionic liquid **2c** without metal salts at 100 °C[a]

S. no.	Phthalonitrile	Phthalocyanine	Time (h)	Yield (%)[b]
1	**4a**	**5a**	2	62
2	**4b**	**5b**	2.5	54
3	**4c**	**5c**	2.5	58
4	**4d**	**5d**	2.5	58
5	**4e**	**5e**	2.5	56
6	**4f**	**5f**	3	54
7	**4g**	**5g**	2.5	46
8	**4h**	**5h**	2.5	48

[a] Reaction condition ratio, phthalonitrile–ionic liquid (**2c**) = 1:1.
[b] Isolated yields.

in the efficient ionic liquid **2c**. The metallophthalocyanines **6a, 7a, 8a, 9a,** and **10a** are obtained in 99%, 92%, 98%, 94%, and 90% yields, respectively.

The recyclability of ionic liquid **2c** was examined for the synthesis of **6a** (Table 1). After the completion of reaction, the ionic liquid **2c** was recovered from the reaction mixture by washing the crude product with chloroform. Chloroform was evaporated at 40 °C under reduced pressure, and the resultant ionic liquid was reused three times for the synthesis of **6a** (Table 1). Further, the spectral data of recovered ionic liquid was found to be identical with unused ionic liquid. The results show that no substantial decrease in the yield of **6a** was observed in a second run (81%). In a third run, using the recovered ionic liquid **2c** by the same procedure, **6a** was obtained in 76% yield from **4a**. The other ionic liquids were recovered by washing the reaction mixture with water, and water was removed using reduced pressure. Therefore these ionic liquids can be easily used for further runs with an advantage of convenient and trouble-free workup.

A basic ionic liquid acting both as the solvent and base would make the procedure much easier to handle. The fact that better yields of phthalocyanines were obtained in strongly basic hydroxyl ionic liquids in comparison to other ionic liquids could be explained by the involvement of the anion present in the basic ionic liquid. The anion affects the reaction in two ways: (1) The anionic species present in the ionic liquid could directly attack one of the cyano groups of the phthalonitrile to form phthalocyanine. (2) The anion abstracts the proton from hydroxyl group to generate the alkoxide ion[29,30] (in hydroxylated ionic liquids) or ylide type nucleophilic species (in imidazolium-based ionic liquids) and attacks one of the cyano groups of the phthalonitrile, leading to the formation of imidoisoindoline-type intermediates, which further react with other phthalonitriles and tetramerizes to give the corresponding phthalocyanines (Scheme 2).

The greater yields of phthalocyanines in ammonium-based ionic liquid having the combination of both ethanolic group and acetate ion are due to the dual effect of the hydrogen-bonded interaction of acetate ion with the hydrogen present at hydroxyl terminal of ammonium cation and the stronger conjugate base of acetic acid in ionic liquid **2c** (species A in Scheme 2). The 2-hydroxyethyl ionic liquids form the favorable eight-membered stable cyclic transition state A (stable chair conformation) with acetate anion and generate the alkoxide ion more easily as compared to 2-hydroxypropyl ionic liquids (**2j** and **3f**), which forms less stable nine-membered cyclic transition state (Scheme 2). The involvement of alkoxyethyl anion in the reaction was further confirmed by treating the ionic liquid **2c** with t-butyl chloride for 5 h at 60 °C under N_2 atmosphere. The formation of species **B** in the medium proves the generation of alkoxide ion in the reaction medium. The species **B** in the reaction was characterized by the shifting of CH_2O proton of ionic liquid **2c** from 4.09 ppm to 3.96 ppm in ^1H NMR and the appearance of characteristic peak at 202.23 $[M\text{-}Cl]^+$ in ESI-MS. Based on these experimental results, a reaction mechanism for the tetramerization of phthalonitriles has been proposed using 2-hydroxylethyl ammonium ionic liquid (**2c**) (Scheme 2).

EXPERIMENTAL

The ^1H NMR spectra were recorded on a Jeol 400-MHz spectrometer using Tetramethylsilane (TMS) as internal standard, and the chemical shifts (δ) are expressed in parts per million (ppm). IR spectra were recorded on a Perkin–Elmer Spectrum 2000 infrared spectrophotometer. UV-visible spectra were recorded on a Perkin–Elmer Lambda 35 UV/vis spectrophotometer. The mass spectra (EI-MS) were recorded on a Jeol SX-102DA-6000 (6 kV, 10ma) spectrometer, and ESI-MS spectra were recorded on a Micromass LCT KC 455 spectrometer (+ve mode). Phthalonitrile (**4a**), 4-nitrophthalonitrile (**4i**), and N,N′-dimethylaminoethanol (**1a**) were obtained from Spectrochem Pvt. Ltd., and 4-methylphthalonirile (**4b**) was obtained from Aldrich. N,N′-Dimethylaminopropanol (**1b**) was obtained from Alfa-Aessar. The 4-methoxyphthalonitrile (**4c**), 4-butyloxyphthalonitrile (**4d**), 4-octyloxyphthalonitrile (**4e**), 4-dodecyloxylphthalonitrile (**4f**), 4-octadecyloxyphthalonitrile (**4g**), and 4-(p-*tert*-butylphenoxy)phthalonitrile (**4h**) are synthesized from 4-nitrophthalonitrile by following the literature procedures. Ionic liquids **2** and **3** were prepared by minor modifications of the literature procedure. All reactions were carried out under N_2 atmosphere except where mentioned. All other solvents and reagents were used as received. All phthalocyanines are known compounds, and their analytical data were identical to those reported in different literature studies.

Synthesis of Metallophthalocyanines

A mixture of desired phthalonitrile (**4a–i**, 200 mg) and corresponding metal salts (0.25 equivalents) were stirred at 100 °C with functional ionic liquid **2c** (1 equivalent) for the appropriate time (Tables 1–3). The progress of the reaction was monitored by thin-layer chromatography (TLC) and UV-visible spectroscopic analysis. When reaction was completed, the mixture was cooled to room temperature, and distilled water (50 mL) was added to dissolve the functional ionic liquid. The blue-green solid mass was filtered and the aqueous filtrate was evaporated using reduced pressure to recover the pure ionic liquid for further use. The solid mass was further washed thoroughly with H_2O–MeOH (1:1, 100 mL) to remove the colorless impurities and metallophthalocyanines are obtained in pure form. All of the phthalocyanines are known compounds and their purities were confirmed by UV-visible spectroscopic analysis and further comparison with literature.

Phthalocyaninatocobalt(II) $C_{32}H_{16}N_8Co$ (6a)[21c]

IR (nujol): 3076, 3021, 1654, 1608, 1479, 1426, 1162, 1270, 1090, 913, 805, 764, 733 cm^{-1}. UV-vis (DMF): λ_{max} (log e) 282.84 (4.71), 328.11 (4.71), 602.91 (4.42), 666.4 nm (5.09). Analysis: calcd. for $C_{32}H_{16}N_8Co$: C, 67.26; H, 2.82; N, 19.61. Found: C, 67.44; H, 2.96; N, 19.92. MS (ESI): *m/z* calcd. for $C_{32}H_{16}N_8Co$: 571.08. Found: 572.32 $[M+H^+]$.

CONCLUSION

A simple, efficient, convenient, and environmentally benign procedure for the synthesis of functionalized phthalocyanines by tetramerization of substituted phthalonitriles in different task-specific basic ionic liquids at lower temperature has been developed. In comparison with nonhydroxyl ionic liquids, hydroxyl functionalized ionic liquids give better yields. The 2-hydroxylethyl ammonium ionic liquids give better yields than 2-hydroxylethyl imidazolium ionic liquids. In the reaction medium metal ion acts as template and increases the tetramerization of phthalonitriles. Thus metallophthalocyanines are obtained in better yields than unmetallated phthalocyanines.

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SUPPORTING INFORMATION

Supplemental data for this article can be accessed on the publisher's website.

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