Efficient Synthesis of Transition-Metal Phthalocyanines in Functional Ionic Liquids

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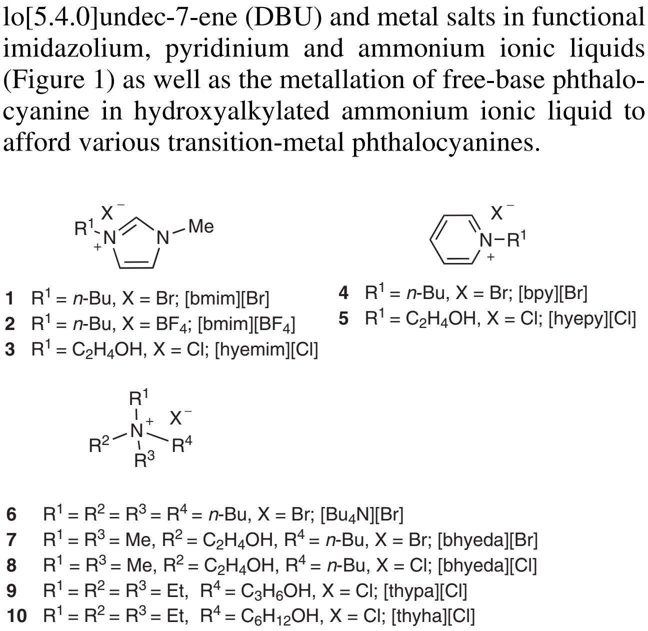
Abstract: The synthesis of transition-metal phthalocyanines by the reaction of substituted and unsubstituted phthalonitriles in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and metal salts in functional imidazolium, pyridinium and ammonium ionic liquids at 100–140 °C, is reported. The best yields of metallated phthalocyanines were achieved in butyl(2-hydroxyethyl)dimethylammonium bromide ionic liquid. Metallation of free-base phthalocyanines with different metal salts in the above ionic liquid has also been achieved in good yields.

Key words: phthalocyanines, ionic liquids, 1,8-diazabicyclo[5.4.0]undec-7-ene, DBU, metallations, complexes

Metallophthalocyanines and their derivatives are widely used as dyes and pigments,[1]chemical sensors,[2] photodynamic therapy agents,[3] non-linear optical materials,[4] catalysts,[5] liquid crystals[6] and other newer materials[7] owing to their high thermal stability and distinct physiochemical properties.[8] The reactions of phthalonitriles, 1,3-diiminoisoindolines, phthalic anhydrides or phthalimides in the presence of metal salts in dimethylformamide, dichlorobenzene, pentanol, ethyleneglycol and other high-boiling solvents yield metallophthalocyanines under basic or neutral conditions.[1,9] The irradiation of phthalogens[10] or metal-free phthalocyanines[11] in the presence of metal salts, affords metallophthalocyanines under microwave conditions. Further, the metallation of free-base phthalocyanines has also been achieved with different metal salts in refluxing high boiling solvents such as pentanol and quinoline.[12] However, the above methods suffer from certain disadvantages, such as slow reaction rate, low yields, troublesome workup procedures, tedious isolation and purification of products, drastic reaction conditions and the formation of various linear oligomers and other side products.[13]

Ionic liquids (ILs) have gained wide recognition as potential environmentally benign solvents for a variety of reactions.[5,14] In particular, functional imidazolium-, pyridinium- and ammonium-based ionic liquids are receiving a considerable upsurge of interest due to their applications in various reactions such as the Knoevenagel condensation,[15] the aldol condensation,[16] the Heck reaction[17] and Diels–Alder reactions.[18] Recently, tetrabutylammonium bromide[19] and 1,1,3,3-*N*,*N*,*N*′,*N*′-tetramethylguanidinium trifluoroacetate[20] have been used as ionic liquids for the synthesis of metal-free and metallated phthalocyanines. We have also highlighted the importance of butyl(2-hydroxyethyl)dimethylammonium bromide ionic liquid for the synthesis of metal-free phthalocyanines under environmental benign reaction conditions.[21] In a continuation of our ongoing research into the application of ionic liquids as green solvents in organic syntheses,[5,14a,21,22] herein we report the reactions of phthalonitriles in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and metal salts in functional imidazolium, pyridinium and ammonium ionic liquids (Figure 1) as well as the metallation of free-base phthalocyanine in hydroxyalkylated ammonium ionic liquid to afford various transition-metal phthalocyanines.



1 R^1 = *n*-Bu, X = Br; [bmim][Br]
2 R^1 = *n*-Bu, X = BF_4; [bmim][BF_4]
3 R^1 = C_2H_4OH, X = Cl; [hyemim][Cl]
4 R^1 = *n*-Bu, X = Br; [bpy][Br]
5 R^1 = C_2H_4OH, X = Cl; [hyepy][Cl]
6 R^1 = R^2 = R^3 = R^4 = *n*-Bu, X = Br; [Bu_4N][Br]
7 R^1 = R^3 = Me, R^2 = C_2H_4OH, R^4 = *n*-Bu, X = Br; [bhyeda][Br]
8 R^1 = R^3 = Me, R^2 = C_2H_4OH, R^4 = *n*-Bu, X = Cl; [bhyeda][Cl]
9 R^1 = R^2 = R^3 = Et, R^4 = C_3H_6OH, X = Cl; [thypa][Cl]
10 R^1 = R^2 = R^3 = Et, R^4 = $C_6H_{12}OH$, X = Cl; [thyha][Cl]

Figure 1

The reaction of phthalonitrile **11a** in the presence of DBU and $Zn(OAc)_2·2H_2O$ in 1-butyl-3-methylimidazolium bromide [bmim][Br] (**1**) gave phthalocyaninatozinc(II) (**12a**) in 31% yield at 140 °C after one hour (Scheme 1, Table 1, entry 1). The appearance of a characteristic Soret band at 340 nm and an intense Q band at 671 nm in the UV/Vis spectrum, indicated the formation of metallated phthalocyanine **12a**.[1] In the IR spectrum, the absence of CN and NH stretching bands at ~2200 cm^{-1} and ~3200–3300 cm^{-1}, respectively, suggested the complete conversion of **11a** into **12a**. The appearance of four unsplit signals at δ = 157.12, 139.58, 128.16 and 123.47 ppm in the ^{13}C NMR spectrum and a peak at *m*/*z* 577.91, corresponding to [M + H$^+$] in the ESI-MS spectrum, further confirmed the formation of **12a** in the reaction.

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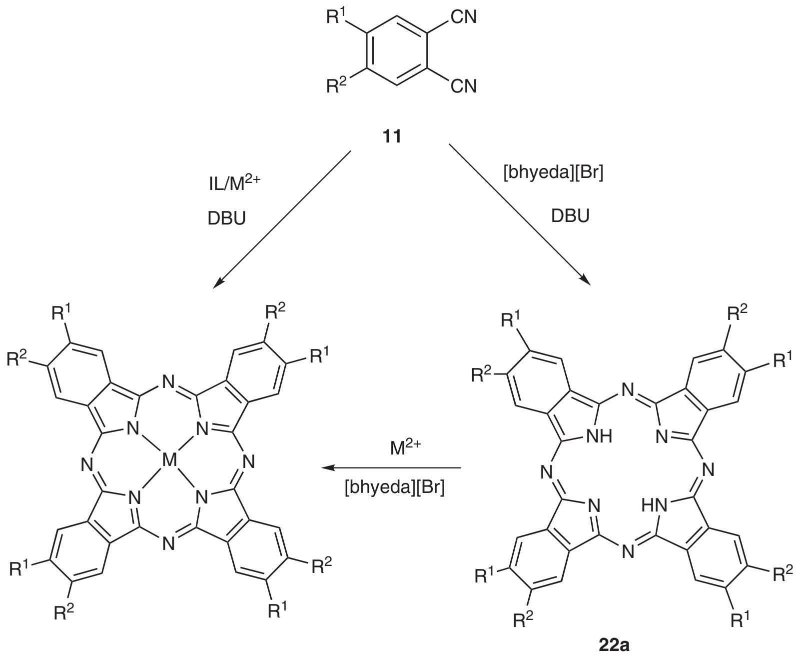


a) $R^1 = R^2 = H$
b) $R^1 = H, R^2 = Me$
c) $R^1 = H, R^2 = OMe$
d) $R^1 = H, R^2 = OC_5H_{11}$
e) $R^1 = H, R^2 = OC_8H_{17}$
f) $R^1 = H, R^2 = OC_{12}H_{25}$
g) $R^1 = R^2 = OC_{16}H_{33}$
h) $R^1 = R^2 = OC_{18}H_{37}$
i) $R^1 = H, R^2 = OCH_2C_6H_4$-4-OMe
j) $R^1 = H, R^2 = NO_2$

12 M = Zn **13** M = Co
14 M = Cu **15** M = Fe
16 M = Pd **17** M = Ni

Scheme 1

The reaction of **11a** with $Zn(OAc)_2 \cdot 2H_2O$ in the presence of DBU in 1-butyl-3-methylimidazolium tetrafluoroborate $[bmim][BF_4]$ (**2**) gave **12a** in 47% yield in 20 minutes (Table 1, entry 2), whereas the use of 1-(2-hydroxyethyl)-3-methylimidazolium chloride [hyemim][Cl] (**3**) gave **12a** in 42% yield (Table 1, entry 3). It was observed that during the reaction of **11a** in imidazolium ionic liquids **1**, **2** and **3**, the reaction mixture turned red within five minutes. The red-colored species were formed by the reaction of **1**, **2** or **3** with **11a** in the presence of DBU, irrespective of the presence of $Zn(OAc)_2 \cdot 2H_2O$.

The reaction of **11a** in the presence of $Zn(OAc)_2 \cdot 2H_2O$ and DBU in 1-butylpyridinium bromide [bpy][Br] (**4**) did not give **12a**, even after 24 hours, whereas the same reaction in 1-(2-hydroxyethyl)pyridinium chloride [hyepy][Cl] (**5**) afforded **12a** in 8% yield after one hour (Table 1, entry 4). It is worth mentioning that pyridinium ionic liquids **3** and **4** decomposed in the presence of DBU even at room temperature and turned brown. The base-instability of pyridinium ionic liquids **3** and **4** could be responsible for their poor activity.

The use of tetrabutylammonium bromide $[Bu_4N][Br]$ (**6**) in the reaction of **11a** gave **12a** in 53% yield, which was improved to 59% using butyl(2-hydroxyethyl)dimethylammonium bromide [bhyeda][Br] (**7**) in the reaction (Table 1, entries 5 and 6). The same reaction in butyl(2-hydroxyethyl)dimethylammonium chloride [bhyeda][Cl] (**8**), resulted in a significant decrease in yield of **12a** (39%; Table 1, entry 7), indicating the role of anions in the reaction. Introduction of long hydroxyalkylated chains on the nitrogen of the ammonium ionic liquids (**9** and **10**) showed a significant effect on the yield of **12a** (Table 1, entries 8 and 9).

Different ionic liquids (**1**–**10**) were further compared in order to synthesize lipid-soluble zinc(II) phthalocyanine **12f** by the reaction of 4-dodecyloxyphthalonitrile (**11f**) in the presence of DBU and $Zn(OAc)_2 \cdot 2H_2O$. The results with **11f** were similar to those obtained with **11a** (Table 1). Unlike **11a**, the reaction of **11f** in the presence of DBU and $Zn(OAc)_2 \cdot 2H_2O$ in imidazolium ionic liquids (**1**, **2** and **3**) did not yield any red-colored species in the reaction. Although ionic liquid **6** is known to promote the synthesis of various metallophthalocyanines,[19] the reaction of **11f** in ionic liquid **6** did not give **12f** under the experimental conditions. Further, the reaction of **11f** in ionic liquids **4**, **9** and **10** also failed to yield **12f** under similar reaction conditions. These differences in the course of the reaction could be attributed to deactivation of the cyano group by the electron-donating alkoxy group in **11f**, which makes it less reactive towards nucleophilic attack and, therefore, needs strongly nucleophilic conditions in order to undergo the reaction. Similar to **12a**, the best yield of **12f** (65%) was obtained using ionic liquid **7**. The tetrasubstituted metallophthalocyanine **12f** showed broad signals in the ^1H NMR and split signals in the ^{13}C NMR spectra due to the formation of four constitutional isomers (C_{4h}, C_{2v}, C_s and D_{2h}).[23] Further, the phthalonitrile containing two electron-donating octadecyloxy groups (**11h**) was also cyclized to **12h** more efficiently in ionic liquid **7** than in **3** (Table 1, entries 18 and 19). Unlike **12f**, the ^1H NMR and ^{13}C NMR spectra of **12h** showed sharp peaks (see experimental section).

Table 1 Reactions of Phthalonitriles **11a**, **11f** and **11h** in the Presence of DBU and $Zn(OAc)_2{\cdot}2H_2O$ in Different Ionic Liquids (**1**–**10**) at 140 °C[a]

Entry	Phthalonitrile	Phthalocyanine	Ionic liquid	Time	Yield (%)[b]
1	**11a**	**12a**	**1**	1 h	31
2	**11a**	**12a**	**2**	20 min	47
3	**11a**	**12a**	**3**	1 h	42
4	**11a**	**12a**	**5**	1 h	8
5	**11a**	**12a**	**6**	1 h	53[c]
6	**11a**	**12a**	**7**	10 min	59
7	**11a**	**12a**	**8**	30 min	47
8	**11a**	**12a**	**9**	2.5 h	18
9	**11a**	**12a**	**10**	2 h	23
10	**11f**	**12f**	**1**	10 min	5
11	**11f**	**12f**	**2**	3 h	28
12	**11f**	**12f**	**3**	1 h	45
13	**11f**	**12f**	**5**	3 h	20
14	**11f**	**12f**	**7**	1 h	65[d]
15	**11f**	**12f**	**8**	1 h	39
16	**11f**	**12f**	**7**	3 h	13[e]
17	**11f**	**12f**	**7**	2 h	39[f]
18	**11h**	**12h**	**3**	20 h	31
19	**11h**	**12h**	**7**	16 h	67

[a] Reaction conditions: phthalonitrile (1 mmol), DBU (2 equiv), $Zn(OAc)_2{\cdot}2H_2O$ (0.25 equiv), ionic liquid (1.5 g for 250 mg of phthalonitrile).

[b] Isolated yields of zinc(II) phthalocyanines **12**.

[c] Product **12a** was isolated in 4% yield when the reaction was carried out in the absence of DBU.

[d] Product **12f** was isolated in 5% and 30% yields after 16 h and 1 h when the reaction was performed at 100 °C and 120 °C, respectively.

[e] Reaction was performed in the absence of DBU.

[f] Reaction was performed in presence of 1 equiv of DBU.

The effect of temperature and the amount of DBU on the course of the reaction of **11f** was also examined (Table 1). The reaction was sluggish at 100 °C and a remarkable decrease in the yield of **12f** (30%) was observed when the reaction was carried out at 120 °C (Table 1, entry 14). On decreasing the amount of DBU to one equivalent in the reaction of **11f** in ionic liquid **7** at 140 °C, **12f** was afforded in 39% yield in one hour; the same reaction performed in the absence of DBU gave only 13% yield of **12f** after three hours (Table 1, entries 16 and 17). A similar effect of DBU on the yield of **12a** was observed in ionic liquids **6** (Table 1, entry 5). Thus, changes to the reaction temperature and the amount of DBU in the reactions significantly influenced both the yield and the rate of metallophthalocyanine formation.

The present method worked well with a range of transition-metal salts (M = Zn, Co, Ni, Fe, Cu, Pd) and different metallophthalocyanines with electron-donating as well as electron-withdrawing substituents; all were synthesized in good yields in ionic liquid **7** under mild conditions (Table 1 and Table 2). It was observed that the reaction time and the yields were affected by the nature and number of substituents on the phthalonitriles (Table 1 and Table 2). The structures of all products were characterized by spectroscopic analyses.

Recyclability of ionic liquid **7** was examined for the synthesis of **13a** (Table 2, entry 1). The ionic liquid **7** was recovered from the reaction mixture by washing the crude product with distilled water. Water was evaporated at 70 °C under reduced pressure and the resulting ionic liquid was reused three times for the synthesis of **13a**. In a second run using the recovered ionic liquid **7**, **13a** was obtained in 54% yield from **11a** in the presence of DBU and cobalt(II) chloride. No substantial decrease in the yield of **13a** was observed in a third run (42% yield). The ionic liquid **7** could be used for conducting further runs.

Table 2 Synthesis of Metallophthalocyaniones **11**–**17** in Ionic Liquid **7** in the Presence of Metal Salts and DBU at 140 °C[a]

Entry	Phthalonitrile	Phthalocyanine	Metal salt	Time	Yield (%)[b]
1	**11a**	**13a**	$CoCl_2$	5 min	63 (run 1) 54 (run 2)[c] 42 (run 3)[c]
2	**11a**	**14a**	$Cu(OAc)_2$	5 min	76
3	**11a**	**15a**	$FeCl_3$	5 min	58
4	**11b**	**12b**	$Zn(OAc)_2{\cdot}2H_2O$	30 min	67
5	**11b**	**13b**	$CoCl_2$	30 min	69
6	**11c**	**12c**	$Zn(OAc)_2{\cdot}2H_2O$	3 h	58
7	**11c**	**13c**	$CoCl_2$	3 h	59
8	**11d**	**12d**	$Zn(OAc)_2{\cdot}2H_2O$	2 h	72
9	**11e**	**12e**	$Zn(OAc)_2{\cdot}2H_2O$	1 h	74
10	**11f**	**13f**	$Co(OAc)_2$	20 min	63
11	**11f**	**14f**	$Cu(OAc)_2$	30 min	32
12	**11f**	**16f**	$Pd(OAc)_2$	30 min	24
13	**11g**	**12g**	$Zn(OAc)_2{\cdot}2H_2O$	16 h	62
14	**11i**	**12i**	$Zn(OAc)_2{\cdot}2H_2O$	2 h	59
15	**11j**	**12j**	$Zn(OAc)_2{\cdot}2H_2O$	10 min	40
16	**11j**	**12j**	$CoCl_2$	10 min	43

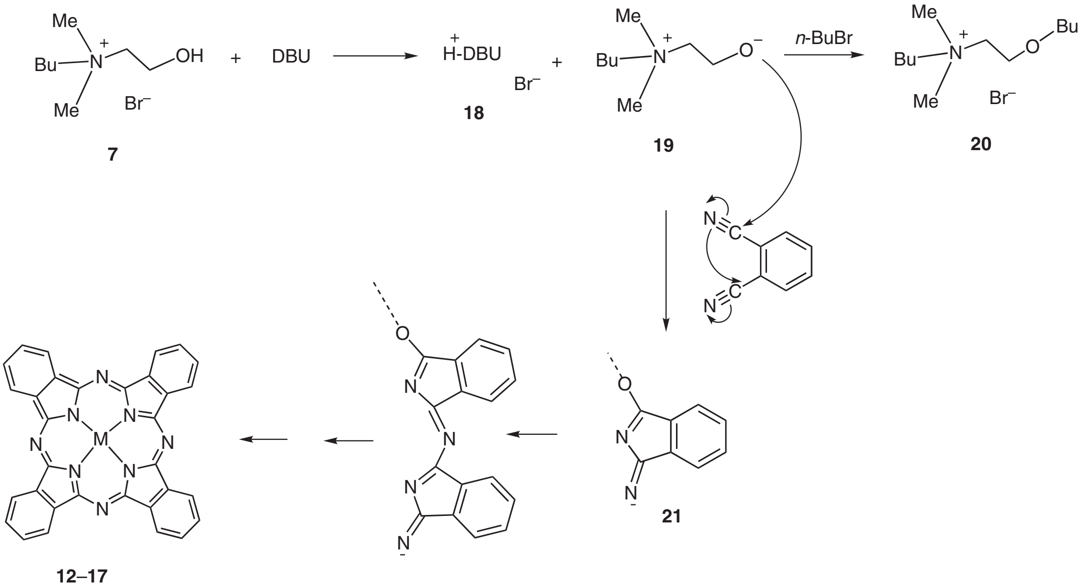
[a] Reaction conditions: phthalonitrile (1 mmol), DBU (2 equiv), metal salt (0.25 equiv), ionic liquid **7** (1.5 g for 250 mg of phthalonitriles).

[b] Isolated yields.

[c] The same recovered ionic liquid **7** was used for each of the three runs. The reaction time for the third run was 10 min.

It is interesting to note that imidazolium-based ionic liquids promote the synthesis of metallophthalocyanines more efficiently than pyridinium-based ionic liquids (Table 1). This could be attributed to generation of carbenes (ylides) by deprotonation at the second position of the imidazolium nucleus of the ionic liquids under basic condition, making it nucleophilic in nature.[24] The fact that better yields of metallophthalocyanines were obtained in hydroxylated imidazolium-, pyridinium- and ammonium-based ionic liquids (**3**, **5**, **7** and **8**) than in other ionic liquids, could be explained by the formation of alkoxide ions in the presence of a base.[25] The generation of the alkoxide ion **19** with DBU in ionic liquid **7** was supported by ^1H NMR analysis, which indicated the presence of H^+-DBU (**18**) in the reaction mixture; trapping **19** with butyl bromide gave butyl(2-butoxyethyl)dimethylammonium bromide (**20**; Scheme 2).[25,26] Thus, DBU generates alkoxide (in hydroxylated ionic liquids) or ylide type nucleophilic species (in imidazolium-based ionic liquids) which are believed to attack one of the cyano groups of the phthalonitrile, leading to formation of imidoisoindoline-type intermediates (**21**), which further react with other phthalonitriles and finally, due to a template effect of the metal ion, cyclization takes place to give the metallophthalocyanines **12**–**17** (Scheme 2).[27]

The influence of ionic liquids on the course of metallophthalocyanine formation has emerged as being associated with the Coulombic interaction between the cations and anions in ionic liquids as well as the nucleophilicity of the anions.[28] The bulkiness of the ammonium cations renders their anions more nucleophilic and available to promote the synthesis of phthalocyanines than the planar imidazolium and pyridinium cations. The effect of the size of the anion on the Coulombic interaction with the cationic nucleus of ionic liquids is also remarkable.[28] Better yields of metallophthalocyanines in ionic liquid **2** compared to **1** or in ionic liquid **7** compared to **8** could be attributed to the larger size of tetrafluoroborate than bromide or bromide than chloride ions, which results in weaker Coulombic interactions between the cationic and anionic parts of the ionic liquids, thereby improving the nucleophilicity of the anionic partner. Based on the above observations, ionic liquids with large counter anions (such as BF_4 and PF_6) could be promising promoters for the synthesis of phthalocyanines; however, since generation of HF under the reaction conditions limited their application,[25] no further attempts were made to prepare such ionic liquids. The high thermal and moisture stability of ionic liquid **7** offers an additional advantage for the synthesis of metallophthalocyanine under the experimental conditions.[25,29]



Scheme 2

Table 3 Metallation of Free-Base Phthalocyanine **22a** with Different Metal Salts in Ionic Liquid **7**

Entry	Phthalocyanine	Metal salt	Temp (°C)	Time	Yield (%)[a]
1	**12a**	$Zn(OAc)_2\cdot 2H_2O$	140	30 min	69
2	**13a**	$Co(OAc)_2$	180	16 h	72
3	**13a**	$CoCl_2$	140	24 h	0[b,c]
4	**14a**	$Cu(OAc)_2$	140	6 h	99
5	**17a**	$Ni(OAc)_2\cdot 4H_2O$	140	16 h	95
6	**17a**	$NiCl_2\cdot 6H_2O$	140	24 h	0[b,c]

[a] Isolated yields.

[b] No metallation of **22a** was observed when the reaction temperature was increased from 140 °C to 180 °C.

[c] No metallation of **22a** was observed when the reaction was carried out in the presence of DBU (1 equiv) at 140 °C and 180 °C.

The use of ionic liquid **7** was further explored for the metallation of free-base phthalocyanine **22a**, which was prepared by cyclotetramerization of **11a** in ionic liquid **7** under mild conditions (Scheme 1, Table 3).[21] Quantitative yields of metallophthalocyanines were obtained in relatively short reaction times, without using any base. It is worth noting that the metallation of **22a** was achieved in good yields with acetate salts of transition metals; neither an increase in temperature nor the addition of DBU to the reaction mixture affected the metallation of **22a** with chloride salts of transition metals.

In conclusion, the synthesis of metallophthalocyanines by the reaction of a range of phthalonitriles, in the presence of metal salts, in hydroxylated-ammonium-based ionic liquid **7** is simple and efficient. Moreover, hydroxylated ammonium ionic liquids are UV/Vis transparent, biodegradable, cost-effective and can be easily synthesized from bulk precursors. Furthermore, the metallation of free-base phthalocyanines can be achieved in excellent yields in this ionic liquid under mild conditions. The method offers various advantages such as fewer side products, easy isolation, good to excellent yields of products, tolerance of a variety of substituents and metals, and recyclability of the ionic liquid.

UV/Vis spectra were recorded on a Perkin–Elmer Lambda 35 UV/Vis Spectrophotometer. IR spectra were recorded on a Perkin–Elmer Spectrum 2000 infrared spectrophotometer. The ^1H NMR and ^{13}C NMR spectra were recorded on Bruker 300 MHz or 400 MHz spectrometers using TMS as internal standard and the chemical shifts (δ) are expressed in ppm. The mass spectra (EI-MS) were recorded on a Jeol SX-102DA-6000 (6 kV, 10 ma) spectrometer and ESI-MS spectra were recorded on a Micromass LCT KC 455 spectrometer (+ve mode). Phthalonitrile (**11a**), 4-nitrophthalonitrile (**11j**) and tetrabutylammonium bromide (**6**) were obtained from Spectrochem Pvt. Ltd. and 4-methylphthalonirile (**11b**) was obtained from Aldrich. 4-methoxyphthalonitrile (**11c**),[3] 4-pentyloxyphthalonitrile (**11d**),[30] 4-octyloxyphthalonitrile (**11e**)[19a] 4-dodecyloxylphthalonitrile (**11f**),[30] 4,5-hexadecyloxylphthalonitrile (**11g**),[31] 4,5-octadecyloxylphthalonitrile (**11h**)[31] and ionic liquids **1**,[32] **2**,[5] **3**,[33] **4**,[34] **5**,[35] **7**[28] and **8**[36] were prepared by minor modifications of literature procedure. The metal-free phthalocyanine (**22a**) was prepared according to the method reported by us.[21] All reactions were carried out under an N_2 atmosphere except where mentioned. All other solvents and reagents were used as received.

Triethyl(3-hydroxypropyl)ammonium Chloride (9)

A mixture of 3-chloro-1-propanol (4.2 mL, 5.0 mmol) and Et_3N (7 mL, 5.0 mmol) was heated to reflux for 24 h under anhydrous conditions. On cooling, two layers formed in the reaction mixture. The lower layer was taken and washed repeatedly with Et_2O and the resulting syrup was recrystallized ($EtOH–Et_2O$).

Yield: 5.8 g (59%); mp 155–158 °C.

IR (neat): 3391, 2991, 2891, 2115, 1645, 1488, 1457, 1396, 1162, 1059, 936 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.4–1.6$ (t, $J = 7.5$ Hz, 9 H, $3 \times CH_3$), 2.2–1.9 (m, 2 H, $N^+CH_2CH_2CH_2OH$), 3.4–3.6 (m, 6 H, $CH_3CH_2N^+$), 3.7 (m, 2 H, $N^+CH_2CH_2CH_2OH$), 3.8 (m, 2 H, CH_2OH), 4.2–4.3 (s, 1 H, OH).

MS (ESI): *m/z* calcd for $C_9H_{22}ClNO$: 195.73; found: 160.18 [M^+ – Cl].

Triethyl(6-hydroxyhexyl)ammonium Chloride (10)

Starting from Et_3N (6.95 mL, 5.0 mmol) and 6-chloro-1-hexanol (6.7 mL, 5.0 mmol), the title compound **10** was synthesized as described above.

Yield: 10.0 g (84%).

IR (neat): 3368, 2936, 2861, 1647, 1461, 1395, 1309, 1159, 1055, 729 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.5–1.6$ (m, 17 H, CH_2), 1.9 (m, 2 H, $N^+CH_2CH_2$), 3.5–3.8 (m, 8 H, N^+CH_2).

MS (ESI): *m/z* calcd for $C_{12}H_{28}ClNO$: 237.81; found: 202.23 [M – Cl].

4-[1-(4-Methoxyphenyl)methoxy]phthalonitrile (11i)

To a mixture of 4-nitrophthalonitrile (**11j**; 865.65 mg, 5 mmol) and K_2CO_3 (1.38 g, 10 mmol) in anhyd DMF (5 mL), 4-methoxyphenylmethanol (1.38 g, 10 mmol) was added and the reaction mixture was stirred at r.t. for 48 h under a nitrogen atmosphere. The crude reaction mixture was poured into distilled H_2O (60 mL) and extracted with $CHCl_3$ (3 × 20 mL). The organic layer was washed with H_2O (3 × 20 mL) and dried over anhydrous Na_2SO_4. After evaporating the solvent, the residue was purified by column chromatography on neutral alumina (PE–$CHCl_3$, 8:2) to give the title compound **11i**.

Yield: 793 mg (60%).

IR (nujol): 2228, 1596, 1558, 1514, 1295, 1247, 1175, 1092, 1032, 988, 828 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.7$ (d, $J = 8.7$ Hz, 1 H, ArH), 7.15–7.55 (m, 4 H, ArH), 7.0 (m, 2 H, ArH), 5.1 (s, 2 H, OCH_2), 3.85 (s, 3 H, OCH_3).

MS (EI): *m/z* = 264 [M^+], 173, 121, 100, 89, 77, 62.

Preparation of metallophthalocyanines

Reaction of Phthalonitriles 11a and 11j in Functional Ionic Liquids (1–10); Procedure A

To a mixture of phthalonitrile **11a** or **11j** (250 mg), metal salt (0.25 equiv) and functional ionic liquid **1**–**10** (1.5 g), DBU (304 μL, 2.0 equiv) was added and the reaction mixture was stirred at 140 °C under a nitrogen atmosphere for the appropriate time (see Table 1 and Table 2). The progress of the reaction was monitored by TLC and UV/Vis spectroscopic analysis. After the reaction was complete, the mixture was washed with distilled H_2O (50 mL) and filtered. The solid green product was washed thoroughly with H_2O–MeOH (1:1, 100 mL) to yield the product. In the case of phthalonitrile **11a**, the product was further purified using concd H_2SO_4 and washed thoroughly with distilled H_2O (150 mL). The filtrate was collected and dried at 70 °C using a rotary evaporator to recover the ionic liquid which was reused for the further synthesis of metallophthalocyanines.

Phthalocyaninatozinc(II) (12a)[37]

IR (nujol): 1646, 1602, 1459, 1318, 1195, 1116, 1089, 723 cm^{-1}.

^{13}C NMR (100 MHz, DMSO-d_6): $\delta = 157.12$ (8 × C), 139.58 (8 × C), 128.16 (8 × C), 123.47 (8 × C).

MS (ESI): *m/z* calcd for $C_{32}H_{16}N_8Zn$: 577.91; found: 578.91 [M + H^+].

UV-vis (DMF): λ_{max} (log ε) = 265 (4.01), 342 (3.37), 604 (3.19), 641 (3.15), 669 nm (3.96).

Phthalocyaninatocobalt(II) (13a)[37]

IR (nujol): 1579, 1526, 1162, 1120, 1090, 764, 733 cm^{-1}.

MS (ESI): *m/z* calcd for $C_{32}H_{16}CoN_8$: 571.48; found: 572.53 [M + H^+].

UV-vis (DMF): λ_{max} (log ε) = 273 (3.99), 418 (2.82), 604 (2.63), 664 (2.73), 692 nm (2.65).

Phthalocyaninatocopper(II) (14a)[37]

IR (nujol): 1648, 1578, 1525, 1289, 1119, 1092, 728, 766, 729 cm^{-1}.

MS (ESI): *m/z* calcd for $C_{32}H_{16}CuN_8$: 576.08; found: 577.85 [M + H^+].

UV-vis (DMF): λ_{max} (log ε) = 274 (5.57), 601 (3.77), 668 (3.80), 692 nm (3.70).

Phthalocyaninatoiron(III) Chloride (15a)[38]

IR (nujol): 3148, 3042, 1724, 1610, 1514, 1422, 1333, 1288, 1165, 1119, 1080, 893, 773, 753, 725 cm^{-1}.

MS (ESI): *m/z* calcd for $C_{32}H_{16}ClFeN_8$: 603.82; found: 568.38 [M – Cl].

UV-vis (DMF): λ_{max} (log ε) = 300 (3.72), 600 (2.58), 662 nm (2.91).

[2(3),9(10),16(17),23(24)-Tetrakis(nitro)phthalocyaninato]zinc(II) (12j)[39]

IR (nujol): 1652, 1608, 1520, 1340, 1136, 1084, 848, 728 cm^{-1}.

^1H NMR (300 MHz, DMSO-d_6): $\delta = 8.40–7.28$ (m, 12 H, PcH).

^{13}C NMR (75 MHz, DMSO-d_6): $\delta = 161.16$ (4 × C), 146.48 (8 × C), 136.0 (4 × C), 135.62 (4 × C), 125.39 (4 × C), 123.34 (4 × C), 120.33 (4 × C).

MS (ESI): *m/z* calcd for $C_{32}H_{12}N_{12}O_8Zn$: 757.38; found: 758.48 [M + H^+].

UV-vis (DMF): λ_{max} (log ε) = 345 (4.36), 648 (4.12), 684 (4.38), 703 nm (4.30).

[2(3),9(10),16(17),23(24)-Tetrakis(nitro)phthalocyaninato]cobalt(II) (13j)[40]

IR (nujol): 3070, 3000, 1654, 1612, 1543, 1502, 1471, 1426, 1342, 1286, 919, 875, 777 cm^{-1}.

MS (ESI): *m/z* calcd for $C_{32}H_{12}CoN_{12}O_8$: 750.93; found: 751.94 [M + H^+].

UV-vis (DMF): λ_{max} (log ε) = 273 (4.50), 606 (3.74), 667 nm (3.83).

Reaction of Phthalonitriles 11b–11i in Functional Ionic Liquids 1–10; Procedure B

Procedure B was conducted as described for procedure A; the workup was performed as follows: The reaction mixture was quenched with H_2O (50 mL) and extracted with $CHCl_3$ (4 × 20 mL). The organic layer was washed with H_2O (3 × 30 mL), dried over anhyd Na_2SO_4, concentrated and purified by column chromatography over neutral alumina [$CHCl_3$ to $CHCl_3$–MeOH (98:2)] to give pure metallophthalocyanines.

[2(3),9(10),16(17),23(24)-Tetrakis(dodecyloxy)phthalocyaninato]zinc(II) (12f)[41]
IR (nujol): 1608, 1491, 1464, 1339, 1241, 1120, 1090, 1051, 744 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.79– 6.76 (m, 12 H, PcH), 3.98 (br, 8 H, OCH_2), 1.96 (br, 8 H, OCH_2CH_2), 1.59–1.27 (m, 72 H, CH_2), 0.97 (m, 12 H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$–CS_2; 3:1 v/v): δ = 156.47 (4 × C), 152.94 (8 × C), 132.94 (4 × C), 125.88 (4 × C), 122.35 (4 × C), 116.47 (4 × C), 104.5 (4 × C), 68.30 (4 × C), 32.06–22.85 (40 × C), 14.21 (4 × C).

MS (ESI): *m*/*z* calcd for $C_{80}H_{112}N_8O_4Zn$: 1315.20; found: 1338.23 [M + Na$^+$].

UV-vis ($CHCl_3$): λ_{max} (log ε) = 284 (4.47), 350 (4.72), 350 (4.40), 615 (4.34), 683 nm (5.03).

[2(3),9(10),16(17),23(24)-Tetrakis(dodecyloxy)phthalocyaninato]cobalt(II) (13f)
IR (nujol): 1580, 1526, 1288, 1163, 1120, 1092, 857, 766, 728 cm^{-1}.

MS (ESI): *m*/*z* calcd for $C_{80}H_{112}CoN_8O_4$: 1308.76; found: 1331.40 [M + Na$^+$].

UV-vis ($CHCl_3$): λ_{max} (log ε) = 291 (4.45), 326 (4.38), 385 (3.95), 614 (4.19), 676 nm (4.52).

[2(3),9(10),16(17),23(24)-Tetrakis(dodecyloxy)phthalocyaninato]copper(II) (14f)
IR (film): 2923, 2853, 1744, 1609, 1509, 1461, 1391, 1347, 1243, 1121, 1112, 1059, 826, 747 cm^{-1}.

^{13}C NMR (75 MHz, $CDCl_3$–CS_2; 3:1 v/v): δ = 155.88 (4 × C), 153.52 (8 × C), 138.3 (4 × C), 124.7 (4 × C), 122.35 (4 × C), 117.8 (4 × C), 102.94 (4 × C), 68.73 (4 × C), 32.11–22.96 (4 × C), 14.26 (4 × C).

MS (ESI): *m*/*z* calcd for $C_{80}H_{112}CuN_8O_4$: 1315.38; found: 1338.07 [M + Na$^+$].

UV-vis ($CHCl_3$): λ_{max} (log ε) = 338 (4.74), 379 (4.35), 619 (4.57), 682 nm (4.97).

[2(3),9(10),16(17),23(24)-Tetrakis(dodecyloxy)phthalocyaninato]palladium(II) (16f)
IR (film): 2921, 2852, 1609, 1510, 1467, 1391, 1246, 1133, 1063, 821, 747 cm^{-1}.

^{13}C NMR (100 MHz, $CDCl_3$–CS_2; 3:1 v/v): δ = 159.81 (4 × C), 153.64 (8 × C), 136.2 (4 × C), 129.55 (4 × C), 123.71 (4 × C), 117.33 (4 × C), 104.36 (4 × C), 68.36 (4 × C), 32.28–23.01 (40 × C), 14.32 (4 × C).

MS (ESI): *m*/*z* calcd for $C_{80}H_{112}N_8O_4Pd$: 1356.24; found: 1379.42 [M + Na$^+$].

UV-vis ($CHCl_3$): λ_{max} (log ε) = 289 (4.25), 329 (4.01), 387 (3.65), 602 (3.91), 667 nm (4.46).

[2,3,9,10,16,17,23,24-Octakis(octadecyloxy)phthalocyaninato]zinc (12h)
IR (film): 2919, 2851, 1599, 1498, 1467, 1384, 1280, 1203, 1050, 743, 720 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.19 (s, 8 H, PcH), 4.01–3.95 (m, 16 H, OCH_2), 2.10 (s, 16 H, OCH_2CH_2), 1.78–0.79 [m, 264 H, $(CH_2)_{15}CH_3$].

^{13}C NMR (100 MHz, $CDCl_3$–CS_2; 3:1 v/v): δ = 154.01 (8 × C), 125.66 (8 × C), 115.77 (8 × C), 106.45 (8 × C), 69.58 (8 × C), 31.93–22.69 (128 × C), 14.10 (8 × C).

MS (ESI): *m*/*z* calcd for $C_{176}H_{304}N_8O_8Zn$: 2725.77; found: 860.70 [$C_{40}H_{32}N_8O_8Zn$ + Na].

UV-vis ($CHCl_3$): λ_{max} (log ε) = 294 (4.61), 355 (4.66), 390 (4.30), 613 (4.16), 648 (4.18), 679 nm (4.94).

[2(3),9(10),16(17),23(24)-Tetrakis(methyl)phthalocyaninato]zinc(II) (12b)[42]
IR (nujol): 1723, 1610, 1489, 1459, 1341, 1237, 1120, 1092, 1055, 744 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.75–7.26 (m, 12 H, PcH), 2.52 (m, 12 H, CH_3).

MS (ESI): *m*/*z* calcd for $C_{36}H_{24}N_8Zn$: 634.02; found: 635.08 [M + H$^+$].

UV-vis (DMF): λ_{max} (log ε) = 348 (4.77), 609 (4.49), 674 nm (5.26).

[2(3),9(10),16(17),23(24)-Tetrakis(methyl)phthalocyaninato]cobalt(II) (13b)[43]
IR (nujol): 1707, 1615, 1523, 1323, 1276, 1167, 1094, 1066, 941, 817, 749 cm^{-1}.

MS (ESI): *m*/*z* calcd for $C_{36}H_{24}CoN_8$: 627.59; found: 628.48 [M + H$^+$].

UV-vis (DMF): λ_{max} (log ε) = 337 (3.57), 602 (3.09), 665 nm (3.71).

[2(3),9(10),16(17),23(24)-Tetrakis(methoxy)phthalocyaninato]zinc(II) (12c)[3]
IR (nujol): 1613, 1460, 1333, 1273, 1162, 1090, 1049, 741 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.0–7.3 (m, 12 H, PcH), 3.7 (br, 12 H, OCH_3).

MS (ESI): *m*/*z* calcd for $C_{36}H_{24}N_8O_4Zn$: 698.02; found: 699.02 [M + H$^+$].

UV-vis (DMF): λ_{max} (log ε) = 355 (5.02), 610 (4.67), 678 nm (5.37).

[2(3),9(10),16(17),23(24)-Tetrakis(methoxy)phthalocyaninato]cobalt(II) (13c)[44]
IR (nujol): 3189, 3066, 1764, 1723, 1619, 1489, 1460, 1295, 1237, 1111, 1053, 1021, 897, 844, 749 cm^{-1}.

MS (ESI): *m*/*z* calcd for $C_{36}H_{24}CoN_8O_4$: 691.58; found: 692.65 [M + H$^+$].

UV-vis (DMF): λ_{max} (log ε) = 318 (3.96), 601 (2.66), 667 nm (3.07).

[2(3),9(10),16(17),23(24)-Tetrakis(pentyloxy)phthalocyaninato]zinc(II) (12d)[45]
IR (nujol): 1607, 1489, 1464, 1338, 1293, 1230, 1117, 1090, 1054, 745 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.06– 6.03 (m, 12 H, PcH), 3.41 (br, 8 H, OCH_2), 1.61–1.38 (m, 24 H, CH_2), 0.99 (br, 12 H, CH_3).

MS (ESI): *m*/*z* calcd for $C_{52}H_{56}N_8O_4Zn$: 922.45; found: 923.45 [M + H$^+$].

UV-vis ($CHCl_3$): λ_{max} (log ε) = 287 (4.57), 350 (4.92), 615 (4.57), 682 nm (5.27).

[2(3),9(10),16(17),23(24)-Tetrakis(octyloxy)phthalocyaninato]zinc(II) (12e)[46]
IR (nujol): 1608, 1490, 1464, 1339, 1283, 1226, 1119, 1091, 1052, 743 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.03– 6.02 (m, 12 H, PcH), 3.36 (m, 8 H, OCH_2), 1.65–1.35 (m, 48 H, CH_2), 0.96 (br, 12 H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$–CS_2; 3:1 v/v): δ = 159.29 (4 × C), 158.99 (4 × C), 158.79 (4 × C), 137.28 (4 × C), 127.98 (4 × C), 121.17 (4 × C), 116.12 (4 × C), 103.16 (4 × C), 67.71 (4 × C), 32.05–22.87 (24 × C), 14.23 (4 × C).

MS (ESI): *m*/*z* calcd for $C_{64}H_{80}N_8O_4Zn$: 1090.77; found: 1091.77 [M + H$^+$].

UV-vis ($CHCl_3$): λ_{max} (log ε) = 287 (4.48), 350 (4.86), 615 (4.64), 682 nm (5.36).

[2,3,9,10,16,17,23,24-Octakis(hexadecyloxy)phthalocyaninato]zinc (12g)[47]

IR (film): 2919, 2851, 1597, 1500, 1467, 1383, 1355, 1281, 1219, 1050, 888, 743, 721 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.19 (s, 8 H, PcH), 4.01–3.99 (m, 16 H, OCH_2), 1.78–0.79 [m, 248 H, $(CH_2)_{14}CH_3$].

MS (ESI): *m/z* calcd for $C_{160}H_{272}N_8O_8Zn$: 2501.34; found: 841.79 [$C_{40}H_{32}N_8O_8Zn$ + Na].

UV-vis ($CHCl_3$): λ_{max} (log ε) = 295 (4.61), 354 (4.73), 612 (4.20), 650 (4.21), 678 nm (4.95).

[2(3),9(10),16(17),23(24)-Tetrakis{1-(4-methoxyphenyl)methoxy}phthalocyaninato]zinc(II) (12i)

IR (nujol): 3168, 1769, 1706, 1612, 1514, 1317, 1280, 1245, 1173, 1086, 1050, 818, 747 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.99–6.94 (m, 28 H, ArH), 5.10 (s, 8 H, OCH_2), 3.82 (s, 12 H, CH_3).

MS (ESI): *m/z* calcd for $C_{64}H_{48}N_8O_8Zn$: 1125.92; found: 1126.29 [$M + H^+$].

UV-vis (DMF): λ_{max} (log ε) = 354 (4.82), 613 (4.42), 681 nm (5.08).

Metallation of Free-Base Phthalocyanine 22a in Ionic Liquid 7

A mixture of metal-free phthalocyanine **22a** (1 mmol) and metal salt (1.5 mmol) in ionic liquid **7** (550 mg) was heated with stirring at 140–180 °C for the appropriate time (Table 3). The progress of the reaction was monitored by UV/Vis spectroscopic analysis of the reaction mixture. After the reaction was complete, the mixture was washed with distilled H_2O (50 mL) and filtered. The solid product was washed thoroughly with distilled H_2O.

Phthalocyaninatonickel(II) (17a)[37]

IR (nujol): 1523, 1336, 1159, 1118, 1093, 1006, 764, 732 cm^{-1}.

MS (ESI): *m/z* calcd for $C_{32}H_{16}NiN_8$: 571.23; found: 572.04 [$M + H^+$].

UV-vis (DMF): λ_{max} (log ε) = 272 (3.10), 612 (2.42), 668 nm (2.53).

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References

(1) (a) *Phthalocyanines - Properties and Applications*, Vol. 1-4; Lenzoff, C. C.; Lever, A. B. P., Eds.; VCH: New York, **1989-1996**. (b) McKeown, N. B. *Phthalocyanine Materials: Synthesis, Structure and Function*; Cambridge University Press: Cambridge, **1998**.

(2) Sülü, M.; Altindal, A.; Bekaroglu, Ö. *Synth. Met.* **2005**, *155*, 211.

(3) Yslas, E. I.; Rivarolab, V.; Durantinia, E. N. *Bioorg. Med. Chem.* **2004**, *13*, 39.

(4) Nalwa, H. S.; Engel, M. K.; Hanack, M.; Schultz, H. *Appl. Organomet. Chem.* **1996**, *10*, 661.

(5) Chauhan, S. M. S.; Kumar, A.; Srinivas, K. A. *Chem. Commun.* **2003**, *18*, 2348.

(6) (a) Sleven, J.; Cardinaels, T.; Binnemans, K.; Nelis, D.; Mullens, J.; Hinz-Huebner, D.; Meyer, G. *Liq. Cryst.* **2003**, *30*, 143. (b) Maeda, F.; Hatsusaka, K.; Ohta, K.; Kimura, M. *J. Mater. Chem.* **2003**, *13*, 243.

(7) Engelkamp, H.; Middelbeek, S.; Nolte, R. J. M. *Science* **1999**, *284*, 785.

(8) Leznoff, C. C.; Lever, A. B. P.; Bonnet, R. *Chem. Soc. Rev.* **1995**, 19.

(9) (a) Hanack, M.; Lang, M. *Chemtracts* **1995**, *8*, 131. (b) Uchida, H.; Reddy, P. Y.; Nakamura, S.; Toru, T. *J. Org. Chem.* **2003**, *68*, 8736.

(10) (a) Villemin, D.; Hammadi, M.; Hachemi, M.; Bar, N. *Molecules* **2001**, *6*, 831. (b) Ungurenasu, C. *Synthesis* **1999**, 1729.

(11) Liu, L. C.; Lee, C. C.; Hu, A. T. *J. Porphyrins Phthalocyanines* **2001**, *5*, 806.

(12) (a) Swarts, J. C.; Langner, E. H. G.; Krokeide-Hove, N.; Cook, M. J. *J. Mater. Chem.* **2001**, *11*, 434. (b) Nolte, R. J. M.; van der Pol, J. F.; Neeleman, E.; Zwikker, J. W.; Nolte, R. J. M.; Drenth, W.; Aerts, J.; Visser, R.; Picken, S. J. *Liq. Cryst.* **2006**, *33*, 1373. (c) Kantekin, H.; Rakap, M.; Gok, Y.; Sahinbas, H. Z. *Dyes Pigm.* **2007**, *74*, 21.

(13) (a) Yao, J.; Yonehara, H.; Pae, C. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1001. (b) Janczak, J.; Kubiak, R. *Acta Chem. Scand.* **1999**, *53*, 602. (c) Kim, I.-B.; Rixman, M. A.; Tsai, Z.-H.; Wu, D.; Njus, J. M.; Stark, J. C.; Hankins, J.; Sandman, D. J. *Macromolecules* **2001**, *34*, 7576.

(14) (a) Jain, N.; Kumar, A.; Chauhan, S.; Chauhan, S. M. S. *Tetrahedron* **2005**, *61*, 1015. (b) Olivier-Bourbigou, H.; Magna, L. *J. Mol. Catal. A: Chem.* **2002**, *182-183*, 419. (c) Welton, T. *Chem. Rev.* **1999**, *99*, 2071. (d) Chowdhury, S.; Mohan, R. S.; Scott, J. L. *Tetrahedron* **2007**, *63*, 2363.

(15) Xu, X. M.; Li, Y. Q.; Zhou, M. Y. *Youji Huaxue* **2004**, *24*, 1253.

(16) Abello, S.; Medina, F.; Rodriguez, X.; Cesteros, Y.; Salagre, P.; Sueiras, J. E.; Tichit, D.; Coq, B. *Chem. Commun.* **2004**, *9*, 1096.

(17) Zhou, L.; Wang, L. *Synthesis* **2006**, 2653.

(18) Abbott, A. P.; Capper, G.; Davies, D. L.; Rasheed, R. K.; Tambyrajah, V. *Green Chem.* **2002**, *4*, 24.

(19) (a) Lo, P. C.; Cheng, D. Y. Y.; Ng, D. K. P. *Synthesis* **2005**, 1141. (b) Safari, N.; Jamaat, P. R.; Shirvan, S. A.; Shoghpour, S.; Ebadi, A.; Darvishi, M.; Shaabani, A. *J. Porphyrins Phthalocyanines* **2005**, *9*, 256.

(20) (a) Shaabani, A.; Rezayan, A. H. *J. Porphyrins Phthalocyanines* **2005**, *9*, 617. (b) Shaabani, A.; Maleki, A. *J. Porphyrins Phthalocyanines* **2006**, *10*, 1253.

(21) Chauhan, S. M. S.; Agarwal, S.; Kumari, P. *Synth. Commun.* **2007**, *37*, 2917.

(22) (a) Jain, N.; Kumar, A.; Chauhan, S. M. S. *Tetrahedron Lett.* **2005**, *46*, 2599. (b) Kumar, A.; Jain, N.; Chauhan, S. M. S. *Synlett* **2007**, 411.

(23) (a) Hanack, M.; Meng, D.; Beck, A.; Sommerauer, M.; Subramanian, L. R. *J. Chem. Soc., Chem. Commun.* **1993**, 58. (b) Leznoff, C. C.; Hu, M.; McArthur, C. R.; Qin, Y. *Can. J. Chem.* **1994**, *72*, 1990.

(24) (a) Xu, L.-W.; Gao, Y.; Yin, J.-J.; Li, L.; Xia, C.-G. *Tetrahedron Lett.* **2005**, *46*, 5317. (b) Aggarwal, V. K.; Emme, I.; Mereu, A. *Chem. Commun.* **2002**, 1612.

(25) Earle, M. J.; Frohlich, U.; Huq, S.; Katdare, S.; Lukasik, R. M.; Bogel, E.; Plechkova, N. V.; Seddon, K. R. WO 2006072785 A2 20060713, **2006**; *Chem. Abstr.* **2006**, *145*, 145001.

(26) Ionic liquid **7** (1 mmol) was heated in the presence of DBU (1 mmol) in anhyd MeCN (5 mL) at 140 °C for 10 min under a nitrogen atmosphere. Analysis of the ^1H NMR spectrum of the reaction mixture showed a peak at δ = 7.7 ppm,

indicating the presence of protonated NH in H$^+$-DBU(**18**) and a downfield shift of 2–3 ppm was observed for all the protons of **18**. The reaction mixture was further reacted with butyl bromide (1 mmol) at 60 °C for 24 h under a nitrogen atmosphere, which resulted in the formation of butyl(2-butoxyethyl)dimethylammonium bromide(**20**) as identified by the presence of a peak (*m*/*z* 202), corresponding to [$C_{12}H_{28}NO$] in ESI-MS spectrum.

(27) Oliver, S. W.; Smith, T. D. *J. Chem. Soc., Perkin Trans. 1* **1987**, 1579.

(28) Calo, V.; Nacci, A.; Monopoli, A. *Eur. J. Org. Chem.* **2006**, 3791.

(29) (a) Domanska, U.; Bogel-Lukasik, R. *J. Phys. Chem. B* **2005**, *109*, 12124. (b) Domanska, U.; Bakala, I.; Pernak, J. *J. Chem. Eng. Data* **2007**, *52*, 309.

(30) Xie, W.; Xu, H.; Gan, C.; Pan, Z.; Yan, T.; Peng, B. *Huaxue Wuli Xuebao* **2003**, *16*, 491.

(31) Sleven, J.; Gorller-Walrand, C.; Binnemans, K. *Mater. Sci. Eng., C* **2001**, *18*, 229.

(32) Kamal, A.; Chouhan, G. *Adv. Synth. Catal.* **2004**, *346*, 579.

(33) Wang, L.; Zhang, Y.; Xie, C.; Wang, Y. *Synlett* **2005**, 1861.

(34) Deetlefs, M.; Seddon, K. R. *Green Chem.* **2003**, *5*, 181.

(35) Kuhnen-Clausen, D. *J. Med. Chem.* **1979**, *22*, 177.

(36) Ko, K.-H.; Kim, T.-S.; Yoon, Y.-K. WO 2003016448 A1 20030227, **2003**; *Chem. Abstr.* **2003**, *138*, 206892.

(37) Shaabani, A.; Maleki-Moghaddam, R.; Maleki, A.; Rezayan, A. H. *Dyes Pigm.* **2007**, *74*, 279.

(38) Villemin, D.; Hammadi, M.; Hachemi, M.; Bar, N. *Molecules* **2001**, *6*, 831.

(39) Ogunsipe, A.; Chenb, J.-Y.; Nyokong, T. *New J. Chem.* **2004**, *28*, 822.

(40) Shaabani, A.; Safari, N.; Bazgir, A.; Bahadoran, F.; Sharifi, N.; Jamaat, P. R. *Synth. Commun.* **2003**, *33*, 1717.

(41) Xu, J.; Lin, Y.; Xiao, X.; Deng, G.; Xu, H. *Ganguang Kexue Yu Guang Huaxue* **1992**, *10*, 253; *Chem. Abstr.* **1992**, 120, 81443.

(42) Del Sole, R. *J. Porphyrins Phthalocyanines* **2005**, *9*, 519.

(43) Sasaki, N.; Matsumoto, M.; Oi, R. JP 10059974, **1998**; *Chem. Abstr.* **1998**, *128*, 231617.

(44) Orihashi, Y.; Nishikawa, M.; Ono, H.; Tsuchida, E.; Matsuda, H.; Nakanishi, H.; Kato, M. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3731.

(45) Gu, Z. *Opt. Mater. (Amsterdam)* **2005**, *27*, 1618.

(46) Yang, S. *J. Phys. Chem. B* **2003**, *107*, 8403.

(47) Sleven, J.; Cardinaels, T.; Goerller-Walrand, C.; Binnemans, K. *ARKIVOC* **2003**, *(iv)*, 68.