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Synthesis of Metal-Free Phthalocyanines in Functionalized Ammonium Ionic Liquids

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Abstract: A convenient, fast, efficient, and ecofriendly synthesis of metal-free phthalocyanines from various substituted phthalonitriles in different hydroxyalkylammonium ionic liquids in the presence of 1,8-diazabicyclo-[5,4,0]-undec-7-ene (DBU) is reported in moderate yields. The effect of concentration of DBU and temperature on the synthesis of phthalocyanine in N-(2-hydroxyethyl)-N,N-dimethylbutylammonium bromide ionic liquid has been examined, and the ionic liquid has been recovered and reused conveniently.

Keywords: 1,8-diazabicyclo-[5,4,0]-undec-7-ene (DBU), ionic liquids, liquid crystals, metal-free phthalocyanines, thermal heating

INTRODUCTION

Phthalocyanines are 18π-electron-conjugated macrocycles with unique physiochemical properties, and they have been used as dyes,[1] chemical sensors,[2] photodynamic cancer drugs,[3] nonlinear optical materials,[4] catalysts,[5] liquid crystals,[6] and other newer materials.[7] These versatile features have stimulated attempts on the synthesis of different functionalized phthalocyanines. Metal-free phthalocyanines have been obtained from cyclocondensation of diverse precursors such as phthalonitriles,[8,9] 1,3-diiminoisoindolines,[10] phthalic anhydrides and phthalimides[11] under basic conditions in high-boiling nonaqueous solvents such as pentanol, N,N-dimethylformamide, and N,N-dimethylaminoethanol. Metal-free phthalocyanines have also been prepared by an electrochemical method,[12] UV irradiation,[13] and microwave

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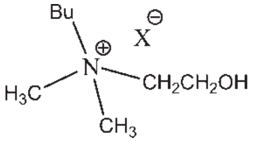
irradiation.[14] These routes are not very common for peripherally functionalized phthalocyanines. Moreover, these methods suffer from certain disadvantages such as slow reaction rate, low yields, use of high-boiling solvents, and tedious isolation of products, and generally employed drastic reaction conditions often cause contamination with undesired side products.[15]

Ionic liquids offer an environmentally benign reaction media in place of conventional organic solvents because of their low vapor pressure, thermal stability, high ionic conductivity, and ease of recyclability. Different functionalized ionic liquids have been used in various chemical transformations including Knoevenagel condensation,[16] aldol condensation,[17] and Heck reaction.[18] Tetrabutylammonium bromide[19,20] and 1,1,3,3-N,N,N′,N′-teteramethylguanidinium trifluoroacetate[21] have been used as ionic liquids for phthalocyanines synthesis. Recently, hydroxylated quaternary ammonium salts[22] have attracted increasing interest because they are less expensive, moisture stable, and base stable and have been used effectively in the electrodeposition of thick, crack-free films[23] and Diels-Alder reactions.[24] Herein, we report a simple, efficient, and ecofriendly synthesis of free-base phthalocyanines from corresponding phthalonitriles in the presence of 1,8-diazabicyclo-[5,4,0]-undec-7-ene (DBU) in N-(2-hydroxyethyl)-N,N-dimethylbutyl amonium bromide (**1a**) and N-(2-hydroxyethyl)-N,N-dimethylbutylamonium hexafluorophosphate (**1b**) ionic liquids (Fig. 1) at 140°C.

RESULTS AND DISCUSSION

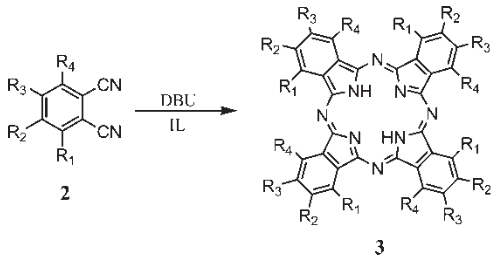
Different metal-free phthalocyanines have been prepared by cyclotetramerization of various phthalonitriles in the presence of DBU in hydroxyalkylammonium ionic liquids (**1a** and **1b**) at 140°C (Scheme 1). The presence of DBU is important for the synthesis of free-base phthalocyanines under the condition of the experiment, as no phthalocyanine formation was observed in the reaction of phthalonitrile (**2a**) in ionic liquid **1a** in the absence of DBU at 140°C (Table 1). Further, the concentration of DBU in the reaction of **2a** affected not only the rate of cyclotetramerization of **2a** but also the yield of phthalocyanine (**3a**) (Table 1). The reaction of **2a** in presence of 2 equivalents of DBU in ionic liquid **1a** at 140°C gave **3a** in 47% yield in 10 min, whereas only 27% yield of **3a** was obtained with 1 equivalent of DBU in 30 min. The rate of phthalocyanine formation as



1a $X = Br^-$

1b $X = PF_6^-$

Figure 1. Structure of ionic liquids.



2a, 3a $R_1=R_2=R_3=R_4=H$
2b, 3b $R_1=R_3=R_4=H, R_2=OCH_3$
2c, 3c $R_1=R_3=R_4=H, R_2=OC_5H_{11}$
2d, 3d $R_1=R_3=R_4=H, R_2=OC_8H_{17}$
2e, 3e $R_1=R_3=R_4=H, R_2=OC_{12}H_{25}$
2f, 3f $R_1=R_4=H, R_2=R_3=OC_{16}H_{33}$
2g, 3g $R_1=R_4=H, R_2=R_3=OC_{18}H_{37}$

Scheme 1. Synthesis of phthalocyanines in ionic liquids.

well as the yield of **3a** enhanced with increasing DBU concentration in the reaction of **2a** in ionic liquid **1a** at 140°C. A decrease in reaction temperature affected more the rate of phthalocyanine formation than the yield of **3a** as the reaction of **2a** in the presence of DBU (2 equiv) in **1a** gave **3a** in 45% yield at 120°C after 2 h. Similarly, the reaction of **2a** in the presence of DBU (2 equiv) in ionic liquid **1b** gave **3a** in 24% yields at 140°C. The lower yield of **3a** in **1b** than in ionic liquid **1a** could be attributed to decomposition of PF_6 anion to hydrofluoric acid or fluoride in the presence of a base.[25]

The formation of phthalocyanine (**3a**) in the reaction of **2a** in the presence of DBU in different ionic liquids (**1a** and **1b**) was confirmed by different spectroscopic analysis.[1] The UV-visible spectrum of **3a** showed characteristic absorption pattern consisting of two Q bands at 656 nm and 693 nm in N,N-dimethylformamide. The disappearance of the band due to -CN stretching at $\sim$2200 cm^{-1} and the appearance of N-H stretching band at 3278 cm^{-1} in IR spectrum of **3a** suggested the formation of **3a** by cyclotetramerization of **2a** in the presence of DBU in ionic liquids. The appearance of a peak at m/z 514.1470 in the ESI-MS spectrum of **3a** corresponding to its [M^+] molecular

Table 1. Synthesis of phthalocyanine (**3a**) in different ionic liquids (**1a** and **1b**) from phthalonitrile (**2a**) under different reaction conditions

Entry	Ionic liquid	Conc. of DBU	Temp (°C)	Time	Yield of **3a**^{a}(%)
1	**1a**	0 equ.	140	24 h	0
2	**1a**	Catalytic amount	140	2 h	11
3	**1a**	0.5 equ.	140	1 h	17
4	**1a**	1 equ.	140	30 min	27
5	**1a**	2 equ.	140	10 min	47
6	**1a**	2 equ.	120	2 h	45
7	**1b**	2 equ.	140	1 h	24

^{a}Isolated yield.

Table 2. Synthesis of different phthalocyanines in the presence of DBU in ionic liquid **1a**

Entry	Phthalonitriles (**2**)	Time (h)	Product	Yield of **3**[a] (%)
1	**2b**	5	**3b**[b]	18
2	**2c**	3	**3c**[b]	25
3	**2d**	3	**3d**[b]	24
4	**2e**	6	**3e**[b]	20
5	**2f**	48	**3f**	17
6	**2g**	48	**3g**	12

[a] Isolated yield.
[b] Mixture of constitutional isomers.

mass further confirmed the structure of **3a**. The reaction of 4-methoxyphthalonitrile (**2b**) at 140°C in the presence of DBU in ionic liquid **1a** gave **3b** in 18% yield (Table 2). Similarly other phthalocyanines (**3c**–**3g**) were prepared in moderate yields (Table 2) by the reaction of corresponding phthalonitriles in the presence of DBU in ionic liquid **1a** at 140°C. It has been observed that on increasing the chain length of the alkoxy group of phthalonitrile, yields of phthalocyanines decreased, but in this series, yield of 2(3),9(10),16(17),23(24)-tetramethoxyphthalocyaine **(3b)** is less than that of 2(3),9(10),16(17),23(24)-tetrapentoxyphthalocyaine (**3c**) (18% and 25 % yields, respectively). The structures of various phthalocyanines (**3b**–**3g**) were characterized by different spectroscopic techniques.

For phthalocyanine **3a**, recyclability of ionic liquid **1a** was examined. The ionic liquid **1a** 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 phthalocyanine synthesis. In the second run, phthalocyanine **3a** was obtained in 42% yield by cyclotetramerization of **2a** in the presence of DBU in recovered ionic liquid **1a**. The reactivity of ionic liquid reduced appreciably in the third run as **3a** was isolated in 20% yield.

The results suggested that ionic liquid is playing an important role in cyclotetramerization of phthalonitriles. It was believed that DBU, like other bases, abstracts protons from the hydroxyalkylammonium ionic liquid, and the resulting alkoxide ion[25] attacks one of the cyano groups of phthalonitrile, leading to formation of phthalocyanine under the conditions of the reaction.[8]

In conclusion, the synthesis of metal-free phthalocyanines by cyclotetramerization of different phthalonitriles in the presence of DBU in hydroxyalkylammonium ionic liquids is simple and efficient. The method offers various advantages such as fewer side products, easy isolation of products, and recyclability of ionic liquid. The moderate yields of various functionalized phthalocyanines have been obtained under the condition of the experiment.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Brucker 300-MHz spectrometer using TMS as internal standard and $CDCl_3$ as solvent, and the chemical shifts were expressed in parts per million (ppm). IR spectra were recorded on a Perkin-Elmer Spectrum 2000 infrared in nujol and $CHCl_3$, and ν_{max} were expressed in cm^{-1}. UV-visible spectra were recorded on a Perkin-Elmer Lambda 35 UV/VIS spectrophotometer, and absorption maxima have been expressed in nm. ESI-MS spectra were recorded on a Micromass LCT KC 455 using electrospray positive ion mass spectra. Melting points were taken on a Thomas Hoover capillary melting-point apparatus, and all the melting points are uncorrected. All reactions were carried out under an N_2 atmosphere except where mentioned. The phthalonitriles **2b** [3], **2c** [26], **2d** [23], **2e** [26], **2f** [27], and **2g** [27] and ionic liquid **1a** [24] were prepared by minor modifications of literature procedures. Phthalonitrile and 4-methylphthalonirile were obtained from Spectrochem. Pvt. Ltd. and Aldrich, respectively. All other solvents and reagents were used as received.

Preparation of Butyl-(2-hydroxyethyl)-dimethylammonium Hexafluorophosphate (1b)

Butyl-(2-hydroxyethyl)-dimethylammonium bromide (**1a**) (2.26 g, 10 mmol) was dissolved in dry acetone (30 mL) and stirred with KPF_6 (2.42 g, 11 mmol) at room temperature for 24 h to exchange the anion. The reaction mixture was filtered, evaporated, and dried under vacuum for 6 h. Yield: 94.2% (3.08 g). IR (neat) ν_{max} (cm^{-1}): 3397, 2969, 1659, 1485, 1421, 1389, 1132, 1087, 977, 922, 838, 440. ^{1}H NMR δ ($CDCl_3$): 3.0–3.2 (m, 2H, $C\underline{H}_2OH$), 2.8 (m, 2H, $N^+C\underline{H}_2CH_2OH$), 2.3 (m, 6H, $2C\underline{H}_3$), 1.9–2.1 (m, 2H, $C_3H_7C\underline{H}_2N^+$), 1.7–1.8 (m, 2H, $N^+CH_2C\underline{H}_2C_2H_5$), 1.5 (s, 5H, 3 $C\underline{H}_3C\underline{H}_2$). ESI-MS (m/z): 146.2468 (M^+-PF_6).

Preparation of Phthalocyanines

Procedure A: For Phthalocyanine (**3a**)

A mixture of phthalonitrile (**2a**) (200 mg, 1.56 mmol) and ionic liquid (**1a** and **1b**) (1.0 g) was heated at 140°C for 10 min. After addition of DBU (470 μL, 3.12 mmol), the reaction mixture was further heated for additional 10 min with stirring under a nitrogen atmosphere to give a deep green color. The reaction mixture was cooled to room temperature, and distilled water (50 ml) was added to it. The product was separated by filtration as a green solid, and the filtrate (**A**) was collected in a round-bottomed flask. The green solid was washed with aqueous methanol (50:50) followed by methanol (30 ml) until the washings were colorless. The solid was air dried to give 94 mg (47%) of phthalocyanine (**3a**). Water was evaporated from filtrate (**A**) at 70°C by rotatory evaporator to recover the ionic liquid, which was reused for phthalocyanine synthesis.

Spectroscopic Data for **3a**

Phthalocyanine (3a):[8] UV-VIS [DMF, λ_{max}/nm, (A_{max})]: 276.76 (2.45), 603.82 (0.06), 639.39 (0.088), 656.39 (0.18), 693.29 (0.19). IR (nujol) ν_{max} (cm^{-1}): 3278, 1608, 1499, 1320, 1276, 1157, 1118, 1093, 1004, 873, 735, 714. ESI-MS (m/z): 514.1470 (M^+).

Spectroscopic Data for **3b–3g**

The procedure is same as for phthalocyanine **3a**. For the workup of phthalocyanines (**3b–3g**), the reaction mixture was quenched with water and extracted with $CHCl_3$. The organic layer was washed with water, dried over anhydrous Na_2SO_4, concentrated, and purified by column chromatography over neutral alumina to give pure phthalocyanines (**3b–3g**).

Data

2(3),9(10),16(17),23(24)-Tetramethoxyphthalocyanine (3b):[8] UV-VIS [$CHCl_3$, λ_{max}/nm, (A_{max})]: 288.79 (0.18), 344.03 (0.32), 392.04 (0.16), 607.78 (0.12), 642.18 (0.22), 666.18 (0.48), 702.61 (0.55). IR (nujol) ν_{max} (cm^{-1}): 3286, 1613, 1345, 1242, 1098, 1012, 821, 743, 721. ESI-MS (m/z): 634.0889 (M^+).

2(3),9(10),16(17),23(24)-Tetrapentyloxyphthalocyanine (3c):[28] UV-VIS [$CHCl_3$, λ_{max}/nm, (A_{max})]: 289.7 (0.21), 344.04 (0.36), 389.28 (0.18), 607.78 (0.14), 668.98 (0.55), 706.03 (0.65). IR (nujol) ν_{max} (cm^{-1}): 3289, 1726, 1663, 1612, 1345, 1241, 1098, 1013, 835, 753. ESI-MS (m/z): 858.1573 (M^+).

2(3),9(10),16(17),23(24)-Tetraoctyloxyphthalocyanine (3d):[23] UV-VIS [$CHCl_3$, λ_{max}/nm, (A_{max})]: 289.51 (0.25), 343.93 (0.44), 389.77 (0.22), 607.79 (0.17), 646.35 (0.29), 668.76 (0.69), 705.80 (0.81). IR (nujol) ν_{max} (cm^{-1}): 3294, 1726, 1663, 1611, 1349, 1242, 1100, 1023, 832, 750. ESI-MS (m/z): 1026.2902 (M^+).

2(3),9(10),16(17),23(24)-Tetrakis(dodecyloxy)phthalocyanine (3e): UV-VIS [$CHCl_3$, λ_{max}/nm, (A_{max})]: 289.53 (0.31), 343.72 (0.50), 389.76 (0.26), 608.10 (0.20), 668.85 (0.76), 705.78 (0.90). IR (nujol) ν_{max} (cm^{-1}): 3293, 1612, 1345, 1244, 1116, 1097, 1010, 824, 748, 721. ^1H NMR δ ($CDCl_3$):

7.79–6.76 (m, 12H, ArH), 3.98 (m, 8H, $OC\underline{H}_2$), 1.96 (m, 8H, $OCH_2C\underline{H}_2$), 1.59–1.27 (m, 80H, $C\underline{H}_2$), 0.97 (m, 12H, $C\underline{H}_3$). ESI-MS (m/z): 1251.2595 (M^+).

2,3,9,10,16,17,23,24-Octakis(hexadecyloxy)phthalocyanine (3f):[27] UV-VIS [$CHCl_3$, λ_{max}/nm, (A_{max})]: 295.62 (0.21), 348.44 (0.22), 425.04 (0.08), 603.86 (0.05), 648.02 (0.10), 665.23 (0.26), 702.77 (0.32). IR (film) ν_{max} (cm^{-1}): 3204, 2919, 2851, 1594, 1466, 1383, 1283, 1094, 1026, 854, 743, 721. ESI-MS (m/z): 852.2440 ($M^{3+} + K$).

2,3,9,10,16,17,23,24-Octakis(octadecyloxy)phthalocyanine (3g):[27] UV-VIS [$CHCl_3$, λ_{max}/nm, (A_{max})]: 290.26 (0.65), 347.96 (0.49), 421.17 (0.11), 603.18 (0.11), 648.36 (0.24), 664.72 (0.54), 702.41 (0.67). IR (film) ν_{max} (cm^{-1}): 3437, 2919, 2850, 1591, 1467, 1382, 1279, 1096, 1023, 854, 742, 721. ESI-MS (m/z): 668.340 ($M^{4+} + 2H$).

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