Convenient and efficient method for the synthesis of phthalocyanines and metallophthalocyanines in task specific 2-hydroxyethyl ionic liquids

Kumar Karitkey Yadav, Poonam and Shive Murat Singh Chauhan*

Bioorganic research laboratory, Department of chemistry, University of Delhi, Delhi-110007 India; Fax: +91-11-

27666845; E-mail: smschauhan@chemistry.du.ac.in

Contents

	Page
1. General information	2
2. Synthesis and characterization of ionic liquids	2-10
3. Synthesis and characterization of metal free phthalocyanines	10-12
4. Synthesis and characterization of metallophthalocyanines	12-16
5. Synthesis of metallophthalocyanines from metal free phthalocyanines	17
6. References	17-18
7. ¹ H NMR and Mass Spectra	19-20

General

The ^1H NMR spectra were recorded on Jeol 400 MHz spectrometer using TMS as internal standard and the chemical shifts (δ) are expressed in 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-methylphthalonitrile (**4b**) was obtained from Aldrich. N,N'-dimethylaminopropanol (**1b**) was obtained from Alfa-Aesar. The 4-methoxyphthalonitrile (**4c**), 4-butyloxyphthalonitrile (**4d**), 4-octyloxyphthalonitrile (**4e**), 4-dodecyloxyphthalonitrile (**4f**), 4-octadecyloxyphthalonitrile (**4g**) and 4-(p-tert-butylphenoxy)phthalonitrile (**4h**) are synthesized from 4-nitrophthalonitrile by following the literature procedures. Ionic liquids **2-3** 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.

Synthesis of ionic liquids

The task specific ionic liquids were synthesized by slightly modifying the literature procedures. All ionic liquids are known compounds and their purities were confirmed by comparison with literatures. The literatures are cited in the manuscript.

Butyl(2-hydroxyethyl)dimethylammonium bromide [bhveda][Br] (**2a**)¹

Freshly distilled 2-dimethylaminoethanol (4.42g, 0.0496mol) in 25 mL benzene was placed in a 250 mL two necked round bottom flask equipped with a dropping funnel and reflux condenser. The flask was putted in an ice bath. Under vigorous stirring with a magnetic stirring bar solution of n-butyl bromide (0.0496mol) in 25 mL benzene was added drop wise (at 0°C) in about 45 minute. The reaction mixture was refluxed for 16h to obtain a viscous liquid. Benzene was removed using rotavapour and light yellow solid was obtained. The yellowish solid product was washed with diethyl ether (3×30mL) and dried under vacuum for 48h at 80°C to obtain a white solid.

Yield: 95%, IR (nujol): ν (cm⁻¹) 3254, 2965, 2876, 2462, 1652, 1487, 1464, 1380, 1238, 1049, 920, 754. ¹H NMR (400 MHz, CDCl₃ δ): 5.0(brs, 1H), 4.10(t, 2H), 3.73(t, 2H), 3.55(t, 2H), 3.35(s, 6H), 1.73(m, 2H), 1.38-1.43(m, 2H), 0.97(t, 3H). ¹³C(400 MHz, CDCl₃ δ): 65.86(CH₂), 65.64(CH₂), 55.88(CH₂), 52.17(CH₃), 24.71(CH₂), 19.61(CH₂), 13.69(CH₃).

Butyl(2-hydroxyethyl)dimethylammonium hydroxide [bhyeda][OH] (2b)¹

To a solution of [bhyeda][Br] (9g, 40mmol) (**2a**) in dry methylene chloride (20 mL), powdered potassium hydroxide (2.3g, 40mmol) was added and the reaction mixture was stirred vigorously at room temperature for 24 h. The precipitated KBr was filtered off, and the filtrate was evaporated to leave the crude [bhyeda][OH] as a viscous liquid that was washed with diethyl ether (3×20 mL) and dried at 90°C for 10 h to prepare the pure colorless ionic liquid for use.

Yield: 96%, IR (nujol): ν (cm⁻¹) 3435, 3247, 1486, 1047, 1027, 991, 959, 918.; ¹H NMR (400 MHz, D₂O, δ): 4.1(t, 2H), 3.65(t, 4H), 3.50(t, 2H), 3.30 (s, 6H), 1.76(m, 2H), 1.34(m, 2H), 0.93(t, 3H).

Butyl(2-hydroxyethyl)dimethylammonium acetate [bhyeda][CH₃COO] (2c)¹

To a solution of [bhyeda][Br] (4.87g, 0.0215mol) in dry acetonitrile (20mL), powdered ammonium acetate (1.66g, 0.0215mol) was added and the reaction mixture was stirred vigorously at room temperature for 36 h. The precipitated NH_4Br was filtered off, and the filtrate was evaporated to leave the crude [bhyeda][CH_3COO] as a viscous solid that was washed with diethyl ether (3×20 mL) and dried at 90°C for 10 h to prepare the pure colorless ionic liquid for use.

Yield: 93%, IR (nujol): ν (cm^{-1}) 3253, 3013, 2965, 2876, 2362, 2084, 1718, 1653, 1487, 1380, 1238, 1049, 920, 753. ^1H NMR (400 MHz, CDCl_3 , δ): 5.01(brs, 1H), 4.11(t, 2H), 3.73(t, 2H), 3.54(t, 2H), 3.35(s, 6H), 2.05(s, 3H), 1.69-1.77(m, 2H), 1.36-1.45(m, 2H), 0.97(t, 3H).

(2-hydroxyethyl)dimethylammonium octanoate [hyeda][$\text{C}_7\text{H}_{15}\text{COO}$] (2d)¹

Distilled 2-dimethylaminoethanol (4.42g, 0.0496mol) was placed in a 100 ml two necked round bottom flask equipped with a dropping funnel and reflux condenser. The flask was putted in an ice bath. Under vigorous stirring with a magnetic stirring bar octanoic acid (5 mmol) was added drop wise (at 0°C) in about 15 minute. The reaction mixture was refluxed for 24h to obtain a viscous liquid. The oily-viscous liquid was washed with acetone ($3 \times 30\text{mL}$) and dried under vacuum for 24h at 80°C to obtain a colorless viscous ionic liquid.

Yield: 93%, IR (nujol): ν (cm^{-1}) 3393, 2925, 2856, 2728, 1736, 1557, 1460, 1414, 1304, 1169, 1081, 992, 923.; ^1H NMR (400 MHz, D_2O , δ): 4.8(t, 2H), 3.45(t, 4H), 3.25(brs, 1H), 2.88(s, 6H), 1.2-1.6(m, 12H), 0.68(t, 3H).

Triethylammonium octanoate (2e)²

Triethylamine (0.50g, 5mmol) was placed in a 100 ml round bottom flask equipped with a dropping funnel. The flask was putted in an ice bath. Under vigorous stirring with a magnetic stirring bar octanoic acid (5 mmol) was added drop wise (at 0°C) in about 15 minute. The reaction mixture was refluxed for 24h to obtain a viscous liquid. The oily-viscous liquid was washed with acetone (3×30mL) and dried under vacuum for 48h at 80°C to obtain a colorless viscous ionic liquid.

Yield: 91%, IR (nujol): ν (cm⁻¹) 3422, 2956, 2857, 2649, 2510, 1717, 1560, 1401, 1267, 1106, 1034, 838. ¹H NMR (400 MHz, D₂O, δ): 3.2(q, 6H), 3.14(brs, 1H), 2.3(t, 9H), 1.2-1.5 (m, 12H), 0.72(t, 3H).

2-Hydroxyethyltrimethylammonium acetate (2f)³

Distilled 2-dimethylaminoethanol (4.43g, 0.0498 mol) was placed in a 100 mL round bottom flask equiped with a dropping funnel. The flask was putted in an ice bath. Under vigorous stirring with a magnetic stirring bar acetic acid (0.0498mol) was added drop wise (at 0°C) in about 45 minute. At room temperature stirring was continued for 24h to obtain a viscous clear liquid. The oily-viscous liquid was washed with diethyl ether (3×30mL) and dried under vacuum for 48h at 80°C to obtain a colorless viscous ionic liquid.

Yield: 96%, IR (nujol): ν (cm⁻¹) 3392, 2738, 1641, 1568, 1409, 1342, 1173, 1081, 1016, 924, 882; ¹H NMR (400 MHz, D₂O, δ): 3.70(t, 2H), 3.15(brs, 1H), 3.09(t, 2H), 2.73(s, 6H), 1.73(s, 3H).

2-Hydroxyethyltrimethylammonium formate (2g)³

Distilled 2-aminoethanol (20.24g, 0.3313mol) was placed in a 250 mL round bottom flask equipped with a dropping funnel. The flask was mounted in an ice bath. Under vigorous stirring with a magnetic stirring bar formic acid (0.3313mol) was added drop wise (at 0°C) to the flask in about 30 minute. At room temperature stirring was continued for 24h to obtain a viscous clear liquid. The oily-viscous liquid was washed with diethyl ether (3×30mL) and dried under vacuum for 24h at 80°C to obtain a colorless viscous liquid.

Yield: 95%, IR (nujol): ν (cm⁻¹) 3367, 2946, 2889, 1668, 1542, 1389, 1252, 1069, 753; ¹H NMR (400 MHz, D₂O, δ): 8.1(s, 1H), 4.03(brs, 3H), 3.41(t, 2H), 3.12(t, 2H).

2-Hydroxyethylammonium methansulfonate (2h)³

Distilled 2-aminoethanol (9.40g, 0.154mol) was placed in a 250 ml round bottom flask equipped with a dropping funnel. The flask was mounted in an ice bath. Under vigorous stirring with a magnetic stirring bar methane sulfonic acid (0.154mol) was added drop wise (at 0°C) to the flask in about 45 minute. At room temperature stirring was continued for 24h to obtain a viscous clear liquid. The oily-viscous liquid was washed with diethyl ether (3×30mL) and dried under vacuum for 24h at 80°C to obtain a colorless viscous ionic liquid.

Yield: 94%, IR (nujol): ν (cm⁻¹) 3434, 2362, 2093, 1632, 1383, 1350, 1191, 1049, 784; ¹H NMR (400 MHz, D₂O, δ): 5.33(brs, 3H), 3.69(t, 2H), 3.01(t, 2H), 2.68(s, 3H).

2-Hydroxyethylammonium acetate (2i)³

Distilled 2-aminoethanol (20.24g, 0.3313mol) was placed in a 250 mL round bottom flask equipped with a dropping funnel. The flask was mounted in an ice bath. Under vigorous stirring with a magnetic stirring bar acetic acid (0.3313mol) was added drop wise (at 0°C) to the flask in

about 30 minute. At room temperature stirring was continued for 24h to obtain a viscous clear liquid. The oily-viscous liquid was washed with diethyl ether (3×30mL) and dried under vacuum for 24h at 80°C to obtain a colorless viscous ionic liquid.

Yield: 93%, IR (nujol): ν (cm⁻¹) 3392, 1640, 1557, 1410, 1343, 1071, 1018, 925, 840.; ¹H NMR (400 MHz, D₂O, δ): 5.26 (brs, 3H), 3.61 (t, 2H), 2.93 (t, 2H), 1.71 (s, 3H).

Butyl(3-hydroxypropyl)dimethylammonium acetate [bhypda][CH₃COO] (2j)³

Solution of distilled 3-dimethylaminopropanol (4.42g, 0.0429mol) in 25 mL benzene was placed in a 250 mL two necked round bottom flask equipped with a dropping funnel and reflux condenser. The flask was putted in an ice bath. Under vigorous stirring with a magnetic stirring bar solution of n-butyl bromide (0.0429mol) in 25 mL benzene was added drop wise (at 0°C) in about 45 minute. The reaction mixture was refluxed for 16h to obtain a viscous liquid. Benzene was removed using rotavapour and light yellow solid was obtained. The yellowish solid product was washed with diethyl ether (3×30mL) and dried under vacuum for 48h at 80°C to obtain a white solid.

To a solution of [bhypda][Br] (4.87g, 0.0204mol) in dry acetonitrile (20mL), powdered ammonium acetate (2.96g, 0.0306mol) was added and the reaction mixture was stirred vigorously at room temperature for 36 h. The precipitated NH₄Br was filtered off, and the filtrate was evaporated to leave the crude [bhypda][CH₃COO] as a viscous solid that was washed with diethyl ether (3×20 mL) and dried at 90°C for 10 h to prepare the pure colorless ionic liquid for use.

Yield: 82%, IR (nujol): ν (cm⁻¹) 3254, 3011, 2963, 2878, 2362, 2086, 1716, 1654, 1485, 1382, 1237, 1045, 924, 753.; ¹H NMR (400 MHz, D₂O, δ): 4.78(brs, 1H), 3.76(t, 2H), 3.56(t, 2H),

3.54(t, 2H), 3.30(s, 6H), 2.05(s, 3H), 1.86-1.94(m, 2H), 1.69-1.77(m, 2H), 1.36-1.45(m, 2H), 0.97(t, 3H).

1-Butyl-3-methylimidazolium bromide [bmim][Br] (3a)⁴

Freshly distilled 1-methylimidazole (8.21g, 0.1mol) and n-butylbromide (13.7g, 0.1mol) were combined in 100 mL round bottom flask equipped with a reflux condenser. The reaction mixture was heated to reflux (90°C) under N₂ atmosphere for 24h. The product was washed with ethyl acetate (3×30 mL) to remove starting material. The residual ethyl acetate was removed from product under vacuum pressure. The yellow solid was dissolved in water (50 mL) and decolorizing charcoal (2g) was added. This solution was heated at 70°C for 24h, cooled and filtered. The water was removed using rotavapor. The resulting solid was heated under high vacuum for 48h at 70°C. The product was obtained as a white solid.

Yield: 94%, IR (nujol): ν (cm⁻¹) 3440, 3142, 3072, 2960, 1552, 1488, 800, 768, 624; ¹H NMR (400 MHz, CDCl₃ δ): 9.12(s, 1H), 7.53(d, 1H), 7.46(d, 1H), 4.13(t, 2H), 3.72(s, 3H), 1.83(m, 2H), 1.36(m, 2H), 0.92(t, 3H).

1-Butyl-3-methylimidazolium tetrafluoroborate [bmim][BF₄] (3b)⁴

To a solution of [bmim][BF₄] (5.47g, 0.25mol) in dry acetone (50 mL), sodium tetrafluoroborate (5.0g) was added and reaction mixture was stirred vigorously at room temperature for 24h. The precipitated solid sodium bromide was filtered off, and the filtrate was evaporated to leave the crude [bmim][BF₄] as a viscous liquid. It was washed with diethyl ether (3×30 mL) and dried at 90°C for 10 h to afford the pure colorless ionic liquid

Yield: 95%, IR (nujol): ν (cm^{-1}) 3150, 3094, 2874, 1631, 1571, 1464, 1382, 1168, 753. ^1H NMR (400 MHz, CDCl_3 , δ): 8.98 (s, 1H), 7.49 (s, 2H), 4.21 (t, 2H), 4.01 (s, 3H), 1.85 (m, 2H), 1.35 (m, 2H), 0.91 (t, 3H).

1-Butyl-3-methylimidazolium hydroxide [bmim][OH] (3c)⁵

To a solution of [bmim][Br] (2g, 9.12mmol) in dry methylene chloride (20 mL), powdered potassium hydroxide (9.12mmol) was added and the reaction mixture was stirred vigorously at room temperature for 24 h. The precipitated potassium bromide was filtered off, and the filtrate was evaporated to leave the crude [bmim][OH] as a viscous liquid. It was washed with diethyl ether (3 $\times$ 30 mL) and dried at 90°C for 10 h to afford the pure colorless ionic liquid.

Yield: 95%, ^1H NMR (400 MHz, CDCl_3 , δ): 9.74 (s, 1H), 7.51 (d, 1H), 7.39 (d, 1H), 4.13 (t, 2H), 3.89 (s, 3H), 3.24 (brs, 1H), 1.68 (m, 2H), 1.16 (m, 2H), 0.72 (t, 3H).

1-Butyl-3-methylimidazolium acetate [bmim][CH₃COO] (3d)⁶

To a solution of [bmim][Cl] (0.700g, 4mmol) in water (10 mL), CH_3COOAg (0.67 g, 4mmol) was added and reaction mixture was stirred at room temperature for 4 h. The suspension was filtered to remove silver chloride. The water was removed in vacuum to afford 0.69g (85%) of a colorless oily ionic liquid.

Yield: 85%, IR (nujol): ν (cm^{-1}) 3147, 2875, 2067, 1630, 1573, 1339, 1169, 1022, 849, 755.; ^1H NMR (400 MHz, CDCl_3 , δ): 9.95(s, 1H), 7.53(d, 1H), 7.42(d, 1H), 4.18(t, 2H), 3.94(s, 3H), 2.80(s, 3H), 1.72(m, 2H), 1.20(m, 2H), 0.78(t, 3H).

1-(2'-hydroxyethyl)-3-methylimidazolium acetate [HOEMIM][CH₃COO] (3e)⁷

To a solution of [HOEMIM][Br] (1g, 4.82mmol) in dry acetonitrile (20mL), powdered ammonium acetate (0.3722g, 4.82mmol) was added and the reaction mixture was stirred vigorously at room temperature for 36 h. The precipitated NH₄Br was filtered off, and the filtrate was evaporated to leave the crude [HOEMIM][CH₃COO] as a viscous liquid that was washed with diethyl ether (3×20 mL) and dried at 90°C for 10 h to prepare the pure colorless ionic liquid for use.

Yield: 96%, ¹H NMR (400 MHz, D₂O, δ): 8.64(s, 1H), 7.39(d, 1H), 7.34(d, 1H), 4.19(t, 2H), 3.80(t, 2H), 3.78(s, 3H), 2.62(s, 3H).

1-(2'-hydroxypropyl)-3-methylimidazolium acetate [HOPMIM][CH₃COO] (3f)⁷

To a solution of [HOPMIM][Br] (3g, 0.0169mol) in dry acetonitrile (20mL), powdered ammonium acetate (1.309g, 0.0169mol) was added and the reaction mixture was stirred vigorously at room temperature for 36 h. The precipitated NH₄Br was filtered off, and the filtrate was evaporated to leave the crude [HOPMIM][CH₃COO] as a viscous liquid that was washed with diethyl ether (3×20 mL) and dried at 90°C for 10 h to prepare the pure colorless ionic liquid for use.

Yield: 94%, ¹H NMR (400 MHz, D₂O δ): 10.14(s, 1H), 7.34(d, 1H), 7.22(d, 1H), 3.77 (s, 3H), 3.72 (t, 2H), 2.60 (s, 3H), 1.78 (t, 2H), 1.32(t, 2H).

Synthesis of metal free phthalocyanines; Method A

A mixture of phthalonitrile (**4a-g**, 200 mg) and functional ionic liquid **2c** (1 equivalent) was stirred at 100°C under a nitrogen atmosphere for the appropriate time (Table 4). The progress of the reaction was monitored by 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 under reduced pressure to recover the ionic liquid pure enough for further use. The solid mass was further washed thoroughly with H₂O–MeOH (1:1, 100 mL) to remove the impurities and phthalocyanines are obtained in pure form. All of the phthalocyanines are known compounds and their purities were confirmed by comparison with literature.

Phthalocyanine (5a) C₃₂H₁₈N₈^{8,9}

IR (nujol): 3410, 3396, 1608, 1499, 1320, 1276, 1157, 1118, 1093, 1004, 873, 735, 714 cm⁻¹. UV-Vis (DMF): λ_{max} (A_{max}) 276.76 (2.45), 603.82 (0.06), 639.39 (0.088), 656.39 (0.18), 693.29 nm (0.19). Analysis: calcd for C₃₂H₁₈N₈ C, 74.70; H, 3.53; N, 21.78; Found: C, 74.96; H, 3.61; N, 22.08. MS (ESI): m/z calcd for C₃₂H₁₈N₈: 514.54; found: 515.62 [M+H⁺].

2(3),9(10),16(17),23(24)-Tetrakis(methyl)phthalocyanine C₃₆H₂₆N₈ (5b)¹⁰

IR (nujol): 3366, 3082, 1643, 1502, 1319, 1155, 873 cm⁻¹. UV-Vis (DMF): λ_{max} (A_{max}) 332 (0.82), 598 (0.24), 663 (1.4), 692 nm (1.6). Analysis: calcd for C₃₆H₂₆N₈ C, 75.77; H, 4.59; N, 19.64; Found: C, 75.97; H, 4.86; N, 19.86.

2(3),9(10),16(17),23(24)-Tetrakis(methoxy)phthalocyanine C₃₆H₂₆N₈O₄ (5c)^{8a}

IR (nujol): 3286, 1613, 1345, 1242, 1098, 1012, 821, 743, 721 cm⁻¹. UV-Vis (CHCl₃): λ_{max} (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 nm (0.55). Analysis: calcd for C₃₆H₂₆N₈O₄ C, 68.13; H, 4.13; N, 17.66; Found: C, 68.42; H, 4.58; N, 17.87.

2(3),9(10),16(17),23(24)-Tetrakis(butoxy)phthalocyanine C₄₈H₅₀N₈O₄ (5d)¹⁰

IR (neat): 3274, 3056, 2935, 1607, 1489, 1464, 1338, 1293, 1230, 1117, 1090, 1054, 745 cm^{-1} . UV-Vis (CHCl_3): λ_{max} (A_{max}) 296.99 (2.18), 306.74 (2.18), 608.16 (0.06), 639 (0.08), 689.17 (0.17), 705.23 nm (0.19). Analysis: calcd for $\text{C}_{48}\text{H}_{50}\text{N}_8\text{O}_4$ C, 71.80; H, 6.28; N, 13.96; Found: C, 71.96; H, 6.49; N, 14.21.

2(3),9(10),16(17),23(24)-Tetrakis(octoxy)phthalocyanine $\text{C}_{64}\text{H}_{82}\text{N}_8\text{O}_4$ (5e)^{8a}

IR (nujol): 3294, 2988, 1663, 1611, 1349, 1242, 1100, 1023, 832, 750 cm^{-1} . UV-Vis (CHCl_3): λ_{max} (A_{max}) 289.51 (0.25), 343.93 (0.44), 389.77 (0.22), 607.81 (0.17), 646.37 (0.29), 668.78 (0.69), 705.80 nm (0.81). Analysis: calcd for $\text{C}_{64}\text{H}_{82}\text{N}_8\text{O}_4$ C, 74.82; H, 8.04; N, 10.91; Found: C, 74.64; H, 8.35; N, 11.08.

2(3),9(10),16(17),23(24)-Tetrakis(dodecyloxy)phthalocyanine $\text{C}_{80}\text{H}_{114}\text{N}_8\text{O}_4$ (5f)^{8a}

IR (nujol): 3293, 1612, 1345, 1244, 1116, 1097, 1010, 824, 748, 721 cm^{-1} . UV-Vis (CHCl_3): λ_{max} (A_{max}) 289.55 (0.31), 343.72 (0.50), 389.78 (0.27), 608.10 (0.20), 668.88 (0.77), 705.78 nm (0.90). Analysis: calcd for $\text{C}_{80}\text{H}_{114}\text{N}_8\text{O}_4$ C, 76.76; H, 9.18; N, 8.95; Found: C, 76.98; H, 9.47; N, 9.32.

2(3),9(10),16(17),23(24)-Tetrakis(octadecyloxy)phthalocyanine $\text{C}_{104}\text{H}_{162}\text{N}_8\text{O}_4$ (5g)^{8a}

IR (nujol): 3437, 2919, 2850, 1591, 1467, 1382, 1279, 1096, 1023, 854, 742, 721 cm^{-1} . UV-Vis (CHCl_3): λ_{max} (A_{max}) 290.28 (0.65), 347.96 (0.49), 421.17 (0.11), 603.18 (0.11), 648.36 (0.24), 664.72 (0.54), 702.41 nm (0.67). Analysis: calcd for $\text{C}_{104}\text{H}_{162}\text{N}_8\text{O}_4$ C, 78.64; H, 10.28; N, 7.05; Found: C, 78.94; H, 10.57; N, 7.36.

Synthesis of metallophthalocyanines; Method B

A mixture of desired phthalonitrile (**4a-i**, 200mg) and corresponding metal salts (0.25 equivalents) were stirred at 100°C with functional ionic liquid **2c** (1 equivalent) for the appropriate time (Table 1, 2 and 3). The progress of the reaction was monitored by 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 H₂O–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) C₃₂H₁₆N₈Co (6a)^{8c}

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 C₃₂H₁₆N₈Co 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 C₃₂H₁₆N₈Co: 571.08; found: 572.32 [M+H⁺].

[2(3),9(10),16(17),23(24)-Tetrakis(methyl)phthalocyaninato] cobalt(II) C₃₆H₂₄N₈Co (6b)^{8c}

IR (nujol): 3068, 3024, 2986, 1615, 1523, 1323, 1276, 1167, 1094, 1066, 941, 817, 749 cm⁻¹. UV-Vis (DMF): λ_{max} (log e) 337 (3.57), 602 (3.09), 665 nm (5.28). Analysis: calcd for C₃₆H₂₄N₈Co C, 68.90; H, 3.85; N, 17.86; Found: C, 69.21; H, 3.63; N, 17.98.

[2(3),9(10),16(17),23(24)-Tetrakis(methoxy)phthalocyaninato] cobalt(II) C₃₆H₂₄N₈O₄Co (6c)^{8c}

IR (nujol): 3189, 3066, 2942, 1619, 1489, 1460, 1295, 1237, 1111, 1053, 1021, 897, 844, 749 cm^{-1} . UV-Vis (DMF): λ_{max} (log ϵ) 318 (3.96), 601 (2.66), 667 nm (5.37). Analysis: calcd for $\text{C}_{36}\text{H}_{24}\text{N}_8\text{O}_4\text{Co}$ C, 62.52; H, 3.50; N, 16.20; Found: C, 62.82; H, 3.74; N, 16.56.

[2(3),9(10),16(17),23(24)-Tetrakis(butoxy)phthalocyaninato] cobalt(II) $\text{C}_{48}\text{H}_{48}\text{N}_8\text{O}_4\text{Co}$ (6d)¹¹

IR (nujol): 3169, 3056, 2935, 1607, 1489, 1464, 1338, 1293, 1230, 1117, 1090, 1054, 745 cm^{-1} . UV-Vis (DMF): λ_{max} (log ϵ) 287 (4.57), 350 (4.92), 615 (4.57), 682 nm (5.27). Analysis: calcd for $\text{C}_{48}\text{H}_{48}\text{N}_8\text{O}_4\text{Co}$ C, 67.05; H, 5.63; N, 13.03; Found: C, 67.33; H, 5.82; N, 13.31.

[2(3),9(10),16(17),23(24)-Tetrakis(octoxy)phthalocyaninato] cobalt(II) $\text{C}_{64}\text{H}_{80}\text{N}_8\text{O}_4\text{Co}$ (6e)^{8c}

IR (nujol): 3043, 2944, 2835, 1608, 1490, 1464, 1339, 1283, 1226, 1119, 1091, 1052, 743 cm^{-1} . UV-Vis (DMF): λ_{max} (log ϵ) 287 (4.48), 350 (4.86), 615 (4.64), 682 nm (5.36). Analysis: calcd for $\text{C}_{64}\text{H}_{80}\text{N}_8\text{O}_4\text{Co}$ C, 70.89; H, 7.44; N, 10.33; Found: C, 70.98; H, 7.67; N, 10.57.

[2(3),9(10),16(17),23(24)-Tetrakis(dodecyloxy)phthalocyaninato] cobalt(II) $\text{C}_{80}\text{H}_{112}\text{N}_8\text{O}_4\text{Co}$ (6f)^{8c}

IR (nujol): 3037, 2972, 2912, 1606, 1482, 1454, 1336, 1233, 1124, 1082, 1042, 754 cm^{-1} . UV-Vis (DMF): λ_{max} (log ϵ) 285 (4.46), 350 (4.78), 616 (4.44), 681 nm (5.23). Analysis: calcd for $\text{C}_{80}\text{H}_{112}\text{N}_8\text{O}_4\text{Co}$ C, 73.42; H, 8.63; N, 8.56; Found: C, 73.78; H, 8.98; N, 8.96.

[2(3),9(10),16(17),23(24)-Tetrakis(octadecyloxy)phthalocyaninato] cobalt(II) $\text{C}_{104}\text{H}_{160}\text{N}_8\text{O}_4\text{Co}$ (6g)^{8c}

IR (nujol): 3033, 2982, 2922, 1608, 1491, 1464, 1339, 1241, 1120, 1090, 1051, 744 cm^{-1} . UV-Vis (DMF): λ_{max} (log ϵ) 284 (4.47), 350 (4.72), 615 (4.34), 683 nm (5.03). Analysis: calcd for $\text{C}_{104}\text{H}_{160}\text{N}_8\text{O}_4\text{Co}$ C, 75.92; H, 9.80; N, 6.81; Found: C, 76.32; H, 9.62; N, 7.13.

[2(3),9(10),16(17),23(24)-Tetrakis(4-tert-butylphenoxy)phthalocyaninato] cobalt(II)
 $\text{C}_{72}\text{H}_{64}\text{N}_8\text{O}_4\text{Co}$ (6h)¹²

IR (nujol): 3023, 2980, 2926, 1619, 1522, 1321, 1279, 1164, 1092, 1031, 942, 813, 748, 684 cm^{-1} . UV-Vis (DMF): λ_{max} (log ϵ) 607 (1.68), 672 nm (5.05). Analysis: calcd for $\text{C}_{72}\text{H}_{64}\text{N}_8\text{O}_4\text{Co}$ C, 74.28; H, 5.54; N, 9.62; Found: C, 74.56; H, 5.98; N, 9.93.

[2(3),9(10),16(17),23(24)-Tetrakis(nitro)phthalocyaninato]cobalt(II) $\text{C}_{32}\text{H}_{12}\text{N}_{12}\text{O}_8\text{Co}$ (6i)^{8c}

IR (nujol): 3070, 3000, 1654, 1612, 1543, 1502, 1471, 1426, 1342, 1286, 919, 875, 777 cm^{-1} . UV-Vis (DMF): λ_{max} (log ϵ) 274 (4.96), 606 (3.74), 667 nm (5.10). Analysis: calcd for $\text{C}_{32}\text{H}_{12}\text{N}_{12}\text{O}_8\text{Co}$ C, 51.15; H, 1.61; N, 22.37; Found: C, 51.46; H, 1.97; N, 22.62.

Phthalocyaninatozinc(II) $\text{C}_{32}\text{H}_{16}\text{N}_8\text{Zn}$ (7a)^{8c}

IR (nujol): 3106, 3086, 1646, 1602, 1591, 1574, 1508, 1446, 1318, 1195, 1116, 1089, 1084, 906, 768, 723 cm^{-1} . UV-Vis (DMF): λ_{max} (log ϵ) 279 (4.23), 343 (4.44), 604 (4.23), 669 nm (5.05). Analysis: calcd for $\text{C}_{32}\text{H}_{16}\text{N}_8\text{Zn}$ C, 66.50; H, 2.79; N, 19.39; Found: C, 66.96; H, 2.61; N, 19.68. MS (ESI): m/z calcd for $\text{C}_{32}\text{H}_{16}\text{N}_8\text{Zn}$: 577.91; found: 578.96 $[\text{M}+\text{H}^+]$.

Phthalocyaninatonicle(II) $\text{C}_{32}\text{H}_{16}\text{N}_8\text{Ni}$ (8a)^{8c}

IR (nujol): 3104, 3076, 3024, 2970, 2935, 1642, 1599, 1523, 1484, 1412, 1336, 1220, 1159, 1118, 1093, 1006, 962, 857, 764, 732 cm^{-1} . UV-Vis (DMF): λ_{max} (log ϵ) 275 (3.28), 637 (2.68),

665 nm (5.06). Analysis: calcd for $C_{32}H_{16}N_8Ni$ C, 67.28; H, 2.82; N, 19.62; Found: C, 67.54; H, 2.98; N, 19.88. MS (ESI): m/z calcd for $C_{32}H_{16}N_8Ni$: 571.21; found: 572.28 $[M+H^+]$.

Phthalocyanitolead(II) $C_{32}H_{16}N_8Pb$ (9a)¹³

IR (nujol): 3098, 3049, 2925, 2855, 1668, 1590, 1509, 1474, 1332, 1290, 1208, 1110, 1074, 966, 915, 868, 727 cm^{-1} . UV-Vis (DMF): λ_{max} (log e) 333 (4.16), 632 (2.3), 670 (4.72), 701 nm (5.29). Analysis: calcd for $C_{32}H_{16}N_8Pb$ C, 53.40; H, 2.24; N, 15.57; Found: C, 53.82; H, 2.44; N, 15.73.

Phthalocyaninatoiron(III) chloride $C_{32}H_{16}N_8FeCl$ (10a)^{8c}

IR (nujol): 3108, 3082, 2925, 1652, 1529, 1474, 1420, 1333, 1289, 1120, 1089, 1026, 908, 880, 755, 724 cm^{-1} . UV-Vis (DMF): λ_{max} (log e) 296 (4.79), 599 (4.38), 661 nm (5.01). Analysis: calcd for $C_{32}H_{16}N_8FeCl$ C, 63.65; H, 2.67; N, 18.56; Found: C, 63.94; H, 2.86; N, 18.83.

Phthalocyaninatocopper(II) $C_{32}H_{16}N_8Cu$ (11a)^{8c}

IR (nujol): 3108, 3078, 2988, 1648, 1578, 1525, 1484, 1442, 1289, 1119, 1092, 960, 804, 728, 766, 729 cm^{-1} . UV-Vis (DMF): λ_{max} (log e) 344 (4.93), 603 (4.48), 669 nm (5.08). Analysis: calcd for $C_{32}H_{16}N_8Cu$ C, 66.72; H, 2.80; N, 19.45; Found: C, 66.95; H, 2.98; N, 19.72. MS (ESI): m/z calcd for $C_{32}H_{16}N_8Cu$: 576.07; found: 577.18 $[M+H^+]$.

[2(3),9(10),16(17),23(24)-Tetrakis(nitro)phthalocyaninato]zinc(II) $C_{32}H_{12}N_{12}O_8Zn$ (7i)^{8c}

IR (nujol): 3098, 3042, 2982, 1652, 1608, 1520, 1342, 1136, 1084, 1042, 848, 726 cm^{-1} . UV-Vis (DMF): λ_{max} (log e) 345 (4.36), 647 (4.12), 684 (4.38), 703 nm (5.30). Analysis: calcd for $C_{32}H_{12}N_{12}O_8Zn$ C, 50.71; H, 1.60; N, 22.18; Found: C, 50.92; H, 1.42; N, 22.54.

Synthesis of metallophthalocyanines from metal free phthalocyanines; Method C

A mixture of metal free phthalocyanine (**5a**, 200mg) and corresponding metal salts (1 equivalents) were stirred at 100°C with functional ionic liquid **2c** (1 equivalent) for the appropriate time. The progress of the reaction was monitored by 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 H₂O–MeOH (1:1, 100 mL) to remove the colorless impurities and metallophthalocyanines are obtained in pure form in excellent yield.

References

1. Domanska, U. *Thermochimica Acta*. **2006**, *448*, 19-30.
2. Shen, Y.; Kennedy, D. F.; Greaves, T. L.; Weerawardena, A.; Mulder, R. J.; Kirby, N.; Song, G.; Drummond, C. J. *J. Phys. Chem. Chem. Phys.*, **2012**, *14*, 7981–7992
3. (a) Bicak, N. *J. Mol. Liq.* **2005**, *116*, 15-18; (b) Iranpoor, N.; Firouzabadi, H.; Ahmadi, Y. *Eur. J. Org. Chem.* **2012**, 305-311.
4. Burrell, A. K.; Sesto, R. E. D.; Baker, S. N.; Mccleskey, T. M.; Baker, G. A. *Green Chem.* **2007**, *9*, 449-454.
5. Peng, Y.; Li, G.; Li, J.; Yu, S. *Tetrahedron Lett.* **2009**, *50*, 4286-4288.
6. Chakraborti, A. K.; Roy, S. R. *J. Am. Chem. Soc.* **2009**, *131*, 6902-6903.
7. Zhang, S.; Qi, X.; Ma, X.; Lu, L.; Deng, Y. *J. Phys. Chem. B.* **2010**, *114*, 3912-3920.
8. (a) Chauhan, S. M. S.; Srinivas, K. A.; Srivastava, P. K.; Sahoo, B. *J. Porphyrins Phthalocyanines*. **2003**, *7*, 548-550; (b) Chauhan, S. M. S.; Agarwal, S.; Kumari, P. *Synth. Commun.* **2007**, *37*, 2917-2925; (c) Chauhan, S. M. S.; Kumari, P.; Agarwal, S. *Synthesis* **2007**, *23*, 3713-3721.

9. Shabbani, A.; Moghaddam, R. M.; Maleki, A.; Rezayan, A. H. *Dyes and Pigments* **2007**, *74*, 279-282.
10. Luzyanin, K. V.; Kukushkin, V. Y.; Kopylovich, M. N.; Nazarov, A. A.; Galanski, M.; Pombeiro, A. J. L. *Adv. Synth. Catal.* **2008**, *350*, 135-142.
11. Kobayashi, N.; Ogata, H.; Nonaka, N.; Luk'yanets, E. A. *Chem. Eur. J.* **2003**, *9*, 5123-5134.
12. Young, J. G.; Onyebuagu, W. *J. Org. Chem.* **1990**, *55*, 2155-2159.
13. Kumar, T. M. M.; Achar, B. N. *J. Phys. Chem. Solids.* **2006**, *67*, 2282-2288.

Figure S1: (A) ^1H NMR spectrum of pure ionic liquid **2c** in CDCl_3 ; (B) ^1H NMR spectrum of reaction mixture of ionic liquid **2c** with *t*-butyl chloride in CDCl_3 .

Figure S2: ESI-MS of reaction mixture of ionic liquid **2c** with t-butyl chloride.