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Synthesis of unsymmetrical benzoporphyrazines in functional ionic liquids and formation of self-aggregates of zinc(II) pyridino[3,4]tribenzoporphyrazines in solutions☆

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ABSTRACT

Unsymmetrically substituted metal-free and metallated benzoporphyrazines including pyridino[3,4]-tribenzoporphyrazinic macrocycles have been synthesized in good yields by ring expansion reactions of boron(III) subphthalocyanines with phthalonitriles in functional ammonium ionic liquids in the presence of 1,8-diazabicyclo-[5,4,0]-undec-7-ene (DBU) under different reaction conditions. The concentration dependent UV/vis, fluorescence, NMR and ESI-MS spectroscopic data indicate that zinc(II) pyridino[3,4]tribenzoporphyrazines exist as head-to-tail self-aggregates in the solution phase.

1. Introduction

Tetrabenzoporphyrazines, particularly the unsymmetrically substituted benzoporphyrazines with their special chemical, physical and optical properties[1] have gained importance for its potential application in non-linear optical materials,[2] photodynamic therapy agents,[3] antimicrobials[4] and other newer materials.[5] The applications of metallated benzoporphyrazines in materials chemistry as semiconductors, Langmuir–Blodgett thin films and artificial light harvesting systems are often sensitive to molecular stacking in their aggregates.[6] The self-assembly via metal coordination has been well constructed for porphyrin systems[7] and Zn^{II}–salpyr complex.[8] In comparison to other macrocyclic systems, few such works have been reported on such assemblies in metallated benzoporphyrazines.[9]

Different methods are available for the preparation of non-centrosymmetric benzoporphyrazines[10] and the most common one being the ring expansion reaction of boron(III) subphthalocyanines with various 1,3-diiminoisoindolines[2,11] or phthalonitriles.[1b] The ring expansion reaction of subphthalocyanine though is a selective method for the synthesis of A_3B type benzoporphyrazines, it suffers from various drawbacks ranging from slow reaction rate, low yields, tedious workups and the formation of other unwanted substituted benzoporphyrazines, resulting from the statistical condensation of the ring opening fragments from subphthalocyanine. Usually these ring expansion reactions are widely carried out at an elevated temperatures with high boiling solvents like dimethylsulfoxide (DMSO), DMSO/1-chloronaphthalene, DMSO/chlorobenzene, DMSO/*o*-dichlorobenzene and *N*,*N*-dimethylaminoethanol. In this work we have overcome many of the above-mentioned drawbacks and offered simple purification process for the synthesis of unsymmetrically substituted benzoporphyrazines with high selectivity. In comparison to many of the organic solvents used in the synthesis of benzoporphyrazines, ionic liquids can be thought of as a greener alternative. Ionic liquids as solvents find their application in various chemical and biochemical transformations.[12] In our previous work, we have explored the usefulness of functional ammonium, pyridinium and imidazolium ionic liquids in the synthesis of various metal-free and metallated phthalocyanines.[13] As an emphasize on ionic liquids as a greener solvent in our ongoing work,[12a,13,14] we report a simple and efficient method to synthesize unsymmetrically substituted metal-free and metallated benzoporphyrazines by the ring expansion reaction of corresponding boron(III) subphthalocyanines with phthalonitriles in functional

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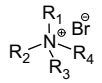
ammonium ionic liquids in the presence of 1,8-diazabicyclo-[5,4,0]-undec-7-ene (DBU) under different reaction conditions. We also report the formation of self-aggregates of zinc(II) pyridino[3,4]-tribenzoporphyrazines in solution via metal–nitrogen coordination involving the pyridyl nitrogen atom of one molecule and the metal ion of a second molecule.



1a R_1= R_2= R_3= R_4= n-Bu, X= Br; [Bu_4N][Br]
1b R_1= R_3= Me, R_2= C_2H_4OH, R_4= n-Bu, X= Br; [bhyeda][Br]

Figure 1. Structure of functional ionic liquids.

2. Results and discussion

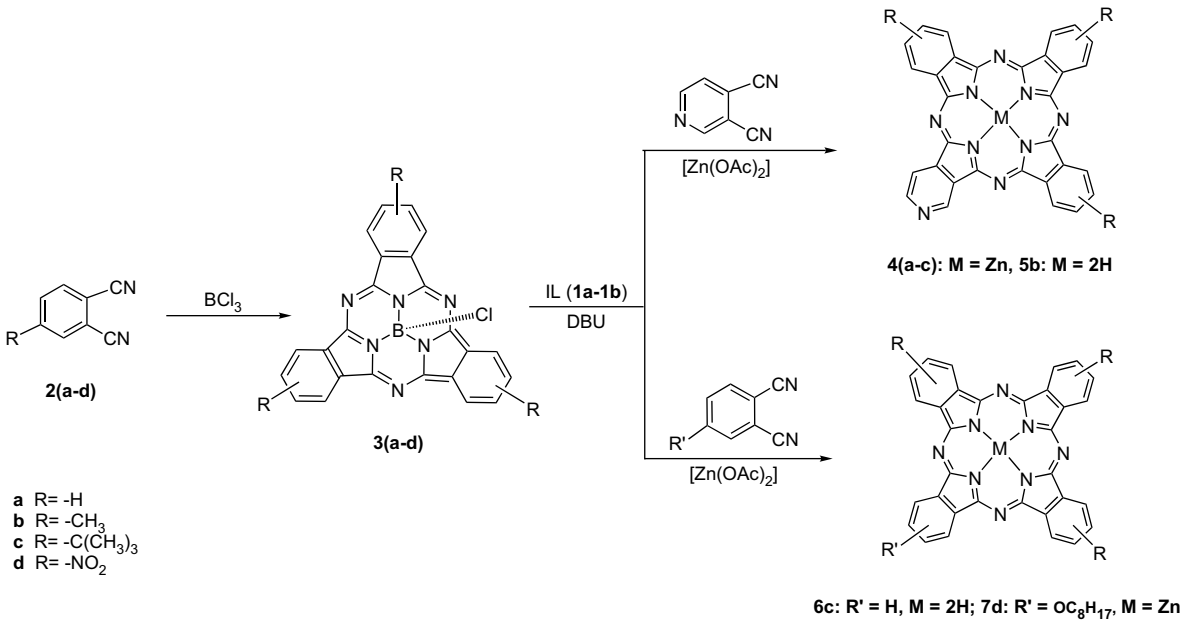
The cyclotrimerization of dry phthalonitrile (**2a**) with boron trichloride (1 M solution in *p*-xylene) at reflux temperature under nitrogen atmosphere gave chloro[subphthalocyaninato]boron(III) (**3a**) in 75% yield (Scheme 1). The UV/vis spectrum of **3a** showed characteristic absorption pattern,[15] a Soret band at 304 nm and an intense Q band at 564 nm. The appearance of a band at 950 cm^{-1} for –B–Cl stretching in the IR spectrum and two multiplets at 8.91 ppm and 7.96 ppm in the ^1H NMR spectrum of **3a** indicated the formation of a cyclotrimerized product of **2a** in the reaction. The presence of a peak at *m*/*z* 454.36 corresponding to [M+Na^+] in ESI-MS spectrum further confirmed the structure of **3a**. Similarly, chloro[2,9,16(17)-trimethylsubphthalocyaninato]boron(III) (**3b**), chloro[2,9,16(17)-tri-*tert*-butylsubphthalocyaninato]boron(III) (**3c**) and chloro[2,9,16(17)-trinitrosubphthalocyaninato]boron(III) (**3d**) were synthesized in good yields and their structures were identified by different spectroscopic analyses. The nucleophilic attack of polarized –CN to another cyano group and subsequent formation of open trimer intermediate followed by template directed cyclization is responsible for the formation of boron(III) subphthalocyanine.[16]

The ring expansion of **3a** with 3,4-dicyanopyridine in tetrabutylammonium bromide ionic liquid (**1a**) (Fig. 1) in presence of zinc acetate and DBU gave tribenzo[b.g.l]pyrido[3,4,q] porphyrazinatozinc(II) (**4a**) in 51% yield (Scheme 1, Table 1, entry 1). The similar reaction of **3a** in butyl-(2-hydroxyethyl)dimethylammonium bromide ionic liquid (**1b**) afforded **4a** in relatively high yield (59%) (Table 1, entry 2). The ring expansion reactions of **3b** and **3c** were also compared in **1a** and **1b** ionic liquids. Interestingly, the yields of **4b** and **4c** were found to be better in ionic liquid **1b** than **1a** under the condition of experiment (Table 1, entries 3, 4, 6 and 7). The yield of **4b** and the rate of ring expansion reaction of **3b** with 3,4-dicyanopyridine were affected greatly by reducing the reaction temperature and amount of DBU (Table 1, entry 4). The use of 1 to 1.5 equiv of ionic liquid **1b** in the ring enlargement reaction was found to be sufficient to proceed the reaction, however, reaction was fast and yield was high when ionic liquid was taken in excess (results not shown). The sequence of addition of phthalonitriles, subphthalocyanines and DBU in the reaction is not very specific to yield benzoporphyrazines except in the case of **5b** due to the tendency of the formation of DBU–phthalonitrile adduct[17] in the reaction.

The reaction of **3b** with 3,4-dicyanopyridine in presence of DBU and in absence of metal salt in ionic liquid **1b** gave metal-free benzoporphyrazine **5b** in 41% yield. Unlike zinc metallated benzoporphyrazine **4b**, the UV/vis spectrum of **5b** showed two distinct Q bands at 687 and 659 nm, and –NH stretching band appeared at 3393 cm^{-1} in the IR spectrum. It is noteworthy that the presence of metal ion is not crucial to yield benzoporphyrazines although its presence affords benzoporphyrazines in short time and better yields. The present method can be utilized for the synthesis of various metallated benzoporphyrazines using different metal salts such as cobalt acetate.

The recyclability of ionic liquid **1b** was examined in ring expansion reaction of **3a** with 3,4-dicyanopyridine. The ionic liquid **1b** was recovered from the reaction mixture and was reused three times for the synthesis of **4a**. In second run, **4a** was obtained in 48% yield that reduced to 41% in third run. The ionic liquid **1b** could be used for conducting further runs.

To investigate the mode of transformation of boron(III) subphthalocyanine into benzoporphyrazine, UV/vis spectroscopic analysis of the reaction was carried out. The UV/vis spectra of **3c** on heating in ionic liquid **1b** for 5 min at 140 °C exhibited absorption spectrum similar to that observed in chloroform with a Q band at 569 nm and a Soret band at 298 nm (see Supplementary data, Fig. S1). On addition of 3,4-dicyanopyridine, DBU and zinc acetate



Scheme 1. Ring expansion of boron(III) subphthalocyanines **3a**–**3d** in ionic liquids **1a**,**1b**.

Table 1
Synthesis of unsymmetrically substituted metal-free and metallated benzoporphyrazines (**4**–**7**) using functional ammonium ionic liquids (**1a**,**1b**) at 140 °C[a]

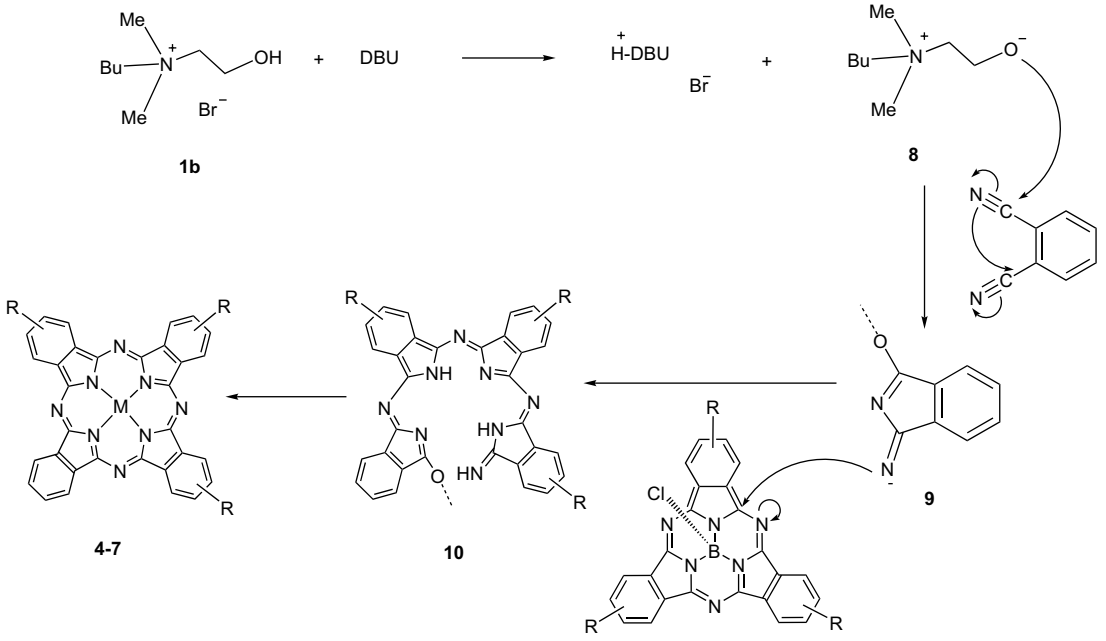
Entry	SubPc	Porphyrazine	Ionic liquid	Time	Yield[b] (%)
1	**3a**	**4a**	**1a**	10 h	51
2	**3a**	**4a**	**1b**	5 h	59, 48,[c] 41[c]
3	**3b**	**4b**	**1a**	30 min	49
4	**3b**	**4b**	**1b**	20 min	58[d]
5	**3b**	**5b**	**1b**	35 min	41
6	**3c**	**4c**	**1a**	25 min	53
7	**3c**	**4c**	**1b**	20 min	58
8	**3c**	**6c**	**1b**	25 min	45
9	**3d**	**7d**	**1b**	20 min	47

[a] Reaction condition: subphthalocyanine, phthalonitrile and DBU in 1:1:1 molar ratio. $Zn(OAc)_2 \cdot 2H_2O$ for **4a**–**4c** and **7d** in equimolar amount. Functional ammonium ionic liquids (**1a**,**1b**): 1.5 g for 300 mg of subphthalocyanine.
[b] Isolated yields.
[c] The same recovered ionic liquid **1b** was used for each of the three runs. The reaction time for second and third run was 10 h.
[d] The product **4b** was isolated in 42% after 2 h when the reaction was performed in absence of DBU and only 21% yield was recorded when the reaction was carried out at 100 °C after 24 h.

in the reaction mixture, the optical spectra exhibited clear appearance of absorption bands for **4c** with the concomitant gradual disappearance of bands for **3c**, indicating the ring expansion of **3a**–**3d** via ring opening by nucleophilic attack of a species generated by phthalonitriles under the experimental conditions. This is in accordance with the nucleophilic attack of selected anionic species such as fluoride and cyanide on the π-delocalized polyimine framework of subphthalocyanine macrocycle.[18] The theoretical calculations and studies on ring expansion of boron(III) subphthalocyanines also support the above observations.[19] As subphthalocyanines do not exhibit any fluoro-chromogenic sensing ability for bromide ion and metal ions such as Zn^{2+},[18,20] their attack on imine type core and involvement in ring opening of subphthalocyanines has been ruled out. Rather, metal template effect may play an important role in cyclization leading to give final benzoporphyrazines products.[13b]

Based on above facts, it is believed that the alkoxide ion of ionic liquid **1b** (**8**), generated by proton abstraction with DBU,[13] attacks on phthalonitrile leading to the formation of an imidoisoindoline type of intermediate (**9**). The nucleophilic attack of **9** on highly strained imine core of subphthalocyanines (**3a**–**3c**) results in an open tetrameric intermediate (**10**), which on cyclization gives metal-free benzoporphyrazines. However, in the presence of metal ion **10** cyclizes rapidly and efficiently to yield metallobenzoporphyrazines, indicating the template effect of metal ion (Scheme 2). Consequently, selective ring opening of **3a**–**3d** by **9** in ionic liquid **1b** could be accountable for the formation of desired unsymmetrically substituted benzoporphyrazines (**4**–**7**) in good yields. Further, nucleophilicity,[21] high moisture and thermal stability of ionic liquid **1b**[22] offer an additional advantage and act as a promising promoter for the ring enlargement reaction of boron(III) subphthalocyanines. These results justify the versatility of ionic liquid **1b** in ring expansion reaction of different subphthalocyanines bearing electron withdrawing as well as electron donating groups with various phthalonitriles affording different unsymmetrically substituted metal-free and metallated benzoporphyrazines in good yields. Ionic liquid **1b** can be used in statistical condensation of two different phthalonitriles affording different unsymmetrically substituted benzoporphyrazines in good yields (please refer Supplementary data, Scheme S1, Fig. S2).

The self-aggregation behaviour of unsymmetrically substituted zinc(II) benzoporphyrazines (**4a**–**4c**) in solutions were analyzed by UV/vis, fluorescence, ^{1}H NMR and ESI-MS spectroscopic analyses. The UV/vis spectrum of **4c** (2.54×10^{-5} M) in chloroform showed a Soret band at 345 nm, a splitted Q band at 685 (Q_x) and 667 nm (Q_y) with two vibronic satellites at 632 and 608 nm (see Supplementary data, Fig. S3). At high concentrations (61.38×10^{-5} M), the form and position of peaks in the spectrum changed, Soret band being red shifted to 356 nm and split Q band to 695 and 664 nm. This red shift in the spectrum is ascribed to generation of head-to-tail self-aggregates of **4c** in solution as the formation of their aggregates cause significant spectral perturbations, owing to coupling between the electronic states of individual monomeric benzoporphyrazine units.[23] It is worth mentioning that the ratio of intensities of Q_x and Q_y bands was found to be sensitive to the concentration of **4c** in solution, which may be due to head-to-tail self-organization tendency of **4c**. Similar effect has been reported for dimerization of triazole-functionalized phthalocyaninatozinc(II) complex in the solution phase.[24] Additionally, the concentration



Scheme 2. Proposed mechanism for ring expansion of subphthalocyanines **3a**–**3d** in ionic liquid **1b**.

dependent UV/vis spectra of zinc(II) tetrapyridinoporphyrazine (see Supplementary data, Fig. S4), showed a great change in the ratio of intensities of split Q bands at 672 and 662 nm in DMF, which could be attributed to higher order zinc-coordinated self-aggregates of the macrocycle in the solution phase.

To investigate the de-aggregation of **4c**, a coordinating solvent, methanol was added, which caused a substantial increase in absorption concomitant a blue shift in the spectrum (Q band absorptions from 695 and 664 nm to 686 and 664 nm, and Soret band absorption from 355 to 352 nm) (see Supplementary data, Fig. S5). In addition, the vibrational satellites corresponding to monomeric species became more distinct. The appearance of isosbestic points at 700, 650, 625 and 375 nm further suggested the existence of molecular self-aggregates in the solution phase. Similar results were obtained on addition of pyridine in solution of **4c**, indicating the destruction of self-coordination from pyridyl nitrogen atom of one molecule to central zinc ion of a second molecule, owing to ligation of pyridine or methanol with central zinc ion. Similar concentration dependent absorption spectrum with red shift was recorded for **4b** (see Supplementary data, Fig. S6), which exhibited similar blue shift with distinct isosbestic points in the spectrum on addition of methanol or pyridine (see Supplementary data, Figs. S7 and S8). The change in the ratio of intensities of Q_x and Q_y bands in the absorption spectrum of **4b** in *o*-dichlorobenzene was more apparently observed on addition of pyridine (see Supplementary data, Fig. S9). No such concentration and disrupting effects were observed in metal-free benzoporphyrazine **5b** on increasing the concentration, and thus suggesting the involvement of metal ion in the self-assembly generation. Recently, the interaction of pyridine and other coordinating solvents with central metal ion in tetrabenzoporphyrazines have been reported.[25]

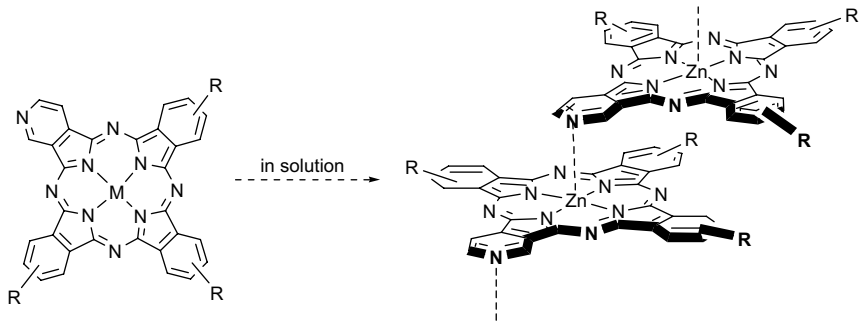
The Q band in UV/vis spectra of tetrabenzoporphyrazines corresponds to the lowest energetic π–π^* ligand transition.[26] The Q bands can be influenced by both the metal centre and the axial ligands. In metallotetrabenzoporphyrazines there is a π-back-donation of electrons from the metal d orbitals to the macrocycle ligand π^* orbitals.[27] The π–π^* transition energy, and therefore the Q band, is strongly influenced by this π-back-donation.[28] The introduction of axial ligands modifies the π-back-donation to the macrocycle, and therefore the π–π^* transition energy is affected.[29] Owing to this effect, the generation of self-coordinating assemblies in **4a**–**4c** via coordination of nitrogen with zinc metal caused the changes in Q band absorbance. This suggested the existence of metal-directed self-assembled molecular species of **4a**–**4c** in solution.

The fluorescence spectrum of **4c** in chloroform showed maximum fluorescence intensity at 687 nm, which shifted to 681 nm with a great intensity loss as the concentration was varied from 1.47×10^{-6} to 1.205×10^{-5} M (see Supplementary data, Fig. S10). These changes are in accordance with the existence of an aggregate of zinc(II) tetrabenzoporphyrazines in solution.[9c] Upon gradual addition of disruptor methanol or pyridine, a slight red shift with a substantial increase in fluorescence intensity at 687 nm was observed (see Supplementary data, Fig. S11). Similar changes were observed in the fluorescence spectrum of **4b** on addition of methanol or pyridine (see Supplementary data, Fig. S12). However, the concentration dependent fluorescence spectrum of **5b** did not show such changes in the spectrum. These results support the formation of self-aggregates via pyridine-to-zinc metal coordination in **4a**–**4c** as reported in porphyrinic systems.[6f]

Further confirmation of the formation of self-aggregates by **4a**–**4c** was obtained by the ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum of **4c** in $CDCl_3$ showed broad signals with two upfield signals for α-pyridyl protons at δ 5.20 and 3.90, and no signal downfield of δ 9.32 was observed (see Supplementary data, Fig. S13). Upon addition of pyridine-d_5 the spectrum simplified and in particular, the α-pyridyl protons of **4c** now appeared at δ 10.71. It is believed that higher oligomers may be present at the higher solution concentrations used in the NMR experiment. No such aggregation studies were possible for **4a** and **4b** as their poor solubility in $CDCl_3$ makes it difficult to record their well-resolved ^{1}H NMR spectra and addition of coordinating solvents such as DMSO-d_6, pyridine-d_5 in order to solubilize them may disrupt their self-coordinate assemblies. However, the ^{1}H NMR spectrum of monomeric **4a** and **4b** in DMSO-d_6 exhibited the pyridyl protons at δ 9.95 and 10.08, respectively.

The existence of self-assembled molecular species of **4a**–**4c** was also detected by ESI-MS analysis. The solutions of **4a**–**4c** were injected for mass analysis, which showed the presence of monomeric species at high cone voltage (>50 V) as the peaks appeared at *m*/*z* 579.96, 621.99, 748.26, respectively, in the ESI-MS spectra. At moderate cone voltage with tuning of other parameters like resolution gas flow, capillary voltage, dissolution temperature and source temperature, the peaks corresponding to dimeric species of **4a**–**4c** were observed at *m*/*z* 1158.86, 1242.98 and 1495.46, respectively (see Supplementary data, Figs. S14, S15 and S16). Further, no peaks corresponding to monomeric and dimeric species of **4a**–**4c** could be recorded with their very dilute solutions ($\sim10^{-7}$ M) even by changing any parameter. Using $\sim10^{-5}$ M solutions of **4a**–**4c**, the peaks corresponding to their dimeric species were recorded in the ESI-MS spectra in the solution phase. These dimeric species could exist in the form as shown in Scheme 3. On the other hand, the ESI-MS spectrum of **5b** (see Supplementary data, Fig. S17) exhibited the peak at *m*/*z* corresponding to its monomeric form at equivalent concentration by adjusting any parameter.

Further, the zinc metallated benzoporphyrazine **7d** bearing an octyloxy substituent also exhibited similar type of aggregation behaviour in the solution phase. A blue shift in the absorption spectrum of **7d** in chloroform was observed on addition of coordination disruptor methanol (see Supplementary data, Fig. S18). It is believed that oxygen atom of alkoxy substituent coordinates with zinc metal in **7d** as reported in the literature.[9c,d] Addition of methanol disrupts the metal-directed self-assembly of **7d** by



Scheme 3. Possible interactions in **4a**–**4c** in the solution phase.

forming coordination bond with zinc metal, which results in improved solubility of **7d** in chloroform.

In conclusion, the ring enlargement of subphthalocyanines with phthalonitriles in presence of DBU (and metal salt) yielding various unsymmetrically substituted metal-free and metallated benzoporphyrazines, in hydroxylated ammonium based ionic liquid (**1b**), is simple and efficient. Moreover, hydroxylated ammonium ionic liquids are biodegradable, cost-effective and UV/vis transparent making the study of the reaction convenient by UV/vis spectroscopic analysis. The present method offers various advantages such as short reaction time, less side products, easy isolation, good yield of products, survival of a variety of substituents and recyclability of ionic liquid. Different substituted zinc(II) pyridino[3,4]-tribenzoporphyrazines exist in the form of head-to-tail self-aggregates generated by nitrogen-to-zinc metal coordination in solutions.

3. Experimental

3.1. General

The IR spectra were recorded on a Perkin–Elmer 1710 FTIR spectrometer and the ν_{max} is expressed in cm^{-1}. The electronic spectra were recorded on a Perkin–Elmer Lambda-35 UV/vis spectrophotometer and the λ_{max} are expressed in nanometers. The ^1H NMR and ^{13}C NMR spectra were recorded on Bruker Avance-300 spectrometer using TMS as internal standard (chemical shifts in ppm). The mass spectra (ESI-MS) were recorded on Micromass LCT KC455 using electron spray positive ion mass spectra. Elemental analyses were obtained on GmbH Vario EL-III elemental analyzing system [CHN analyzer laboratory, University Science Instrumentation Centre (USIC), University of Delhi, Delhi]. Fluorescence spectra were recorded on Shimadzu RF-5301 spectrofluorometer. The excitation and emission bandwidths were set at 3 nm. The R_f of products (**4a**–**4c** and **5b**) (10% solution chloroform/methanol, v/v) (for **7d**, 1% solution $CHCl_3$/DMF) were recorded on TLC plates, Kieselgel 60 F_{254}, 25 folien 20×20 cm, 0.2 mm obtained from Merk. Phthalonitrile (**2a**), 4-methylphthalonitrile (**2b**), 4-*tert*-butylphthalonitrile (**2c**), 4-nitrophthalonitrile (**2d**), 3,4-dicyanopyridine, BCl_3 (1 M solution in *p*-xylene) and 1,8-diazabicyclo-[5,4,0]-undec-7-ene (DBU) were obtained from Aldrich. Tetrabutylammonium bromide was obtained from Spectrochem Pvt. Ltd. The butyl-(2-hydroxyethyl)dimethylammonium bromide ionic liquid (**1b**) and zinc(II) tetrapyridinoporphyrazine were prepared according to the methods reported by us[13b] and characterized by different spectroscopic data that concur with published data.[22a,30] All reactions were carried out under N_2 atmosphere except mentioned. All other solvents and reagents were used as received.

3.2. General procedure for the synthesis of boron(III) subphthalocyanines (3a–3d)

A solution of BCl_3 (5 ml, 1 M solution in *p*-xylene) was added to dry phthalonitrile (**2a**–**2d**) (5 mmol) under nitrogen atmosphere. The reaction mixture was refluxed for 30 min with stirring. The products were isolated and purified following the literature procedures.

3.2.1. Chloro[subphthalocyaninato]boron(III) (3a)[31]

Yield: 75%; purple solid; UV/vis (CH_2Cl_2, λ_{max}/log ε): 304 (3.74), 485 (3.10), 522 (3.45), 546 (3.72), 564 nm (3.96); IR (Nujol, ν): 3046, 1730, 1687, 1604, 1444, 1382, 1305, 1050, 950, 808, 748, 714 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 8.91 (m, 6H, ArH), 7.96 (m, 6H, ArH). ESI-MS (*m*/*z*): found ($M+Na^+$) 454.36; $C_{24}H_{12}BClN_6$ requires 430.66.

3.2.2. Chloro[2,9,16(17)-trimethylsubphthalocyaninato]-boron(III) (3b)[32]

Yield: 60%; purple solid, UV/vis ($CHCl_3$, λ_{max}/log ε): 261 (4.02), 307 (3.93), 512 (3.71), 547 (4.02), 566 nm (4.23); IR (Nujol, ν): 3062, 1724, 1614, 1461, 1217, 1170, 1128, 1044, 960, 820, 783, 722 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 8.43 (d, *J*=8.1 Hz, 3H, ArH), 8.37 (m, 3H, ArH), 7.58 (d, *J*=7.8 Hz, 3H, ArH), 2.67 (s, 9H, CH_3). ESI-MS (*m*/*z*): found ($M+K^+$) 511.26; $C_{27}H_{18}BClN_6$ requires 472.74.

3.2.3. Chloro[2,9,16(17)-tri-tert-butylsubphthalocyaninato]-boron(III) (3c)[33]

Yield: 58%; purple solid; UV/vis ($CHCl_3$, λ_{max}/log ε): 301 (3.80), 514 (3.17), 548 (4.41), 568 nm (3.62); IR (Nujol, ν): 3144, 1749, 1619, 1462, 1409, 1365, 1306, 1257, 1119, 1083, 1042, 975, 749, 721 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 8.87–8.86 (m, 3H, ArH), 8.81–8.80 (m, 3H, ArH), 8.01 (m, 3H, ArH), 1.54 (s, 27H, *t*-Bu). ESI-MS (*m*/*z*): found ($M+Na^+$) 621.98; $C_{36}H_{36}BClN_6$ requires 598.97.

3.2.4. Chloro[2,9,16(17)-trinitrosubphthalocyaninato]-boron(III) (3d)[31]

Yield: 82%; violet solid; UV/vis ($CHCl_3$, λ_{max}/log ε): 301 (4.14), 526 (3.73), 543 (3.83), 575 (4.14), 585 nm (4.14). IR (Nujol, ν): 3207, 1780, 1625, 1606, 1538, 1462, 1346, 1307, 1185, 1104, 1078, 1040, 976, 840, 801, 742, 721 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 9.78 (m, 3H, ArH), 9.07 (m, 3H, ArH), 8.85 (m, 3H, ArH). ESI-MS (*m*/*z*): found ($M+H^+$) 566.65; $C_{24}H_9BClN_9O_6$ requires 565.65.

3.3. General procedure for the synthesis of unsymmetrically substituted metallated benzoporphyrazines

A sample of boron(III) subphthalocyanine (**3a**–**3d**) (2 mmol) in functional ammonium ionic liquid (**1a**,**1b**) (1.5 g for 300 mg of **3a**–**3d**) was heated at 140 °C under nitrogen atmosphere for 5 min. To the reaction mixture, phthalonitriles (2 mmol), DBU (304 µl, 2 mmol) and zinc acetate (2 mmol) were added and heating was continued for appropriate time as mentioned in Table 1. The progress of the reaction was monitored by TLC and UV/vis spectroscopic analysis. After the reaction, the mixture was washed with distilled water (2×100 ml) and filtered. The solid green product was subjected to column chromatography on silica gel (230–400 mesh) eluting with chloroform/methanol (varying ratio) to yield pure products. The filtrate was collected and dried at 70 °C using a rotary evaporator to recover ionic liquid **1b**, which was reused for the synthesis of unsymmetrically substituted benzoporphyrazines.

3.3.1. Zinc(II) tribenzo[b.g.l]pyrido[3,4,q]porphyrazine (4a)

Green solid; [Found: C, 64.78; H, 3.01; N, 21.88. $C_{31}H_{15}N_9Zn$ requires: C, 64.32; H, 2.61; N, 21.78%]; R_f (50% $CHCl_3$/MeOH) 0.75; UV/vis (DMF, λ_{max}/log ε): 365 (3.15), 603 (2.95), 625 (2.94), 662 (3.57), 673 nm (3.59); IR (Nujol, ν): 1620, 1463, 1380, 1248, 1152, 1054, 884, 749 cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6) δ: 9.95 (m, 2H, ArH), 9.26–8.12 (m, 13H, ArH); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 162.50, 158.7, 152.5, 145.0, 138.9, 137.2, 134.6, 134.2, 132.7, 130.28, 129.9, 128.8, 128.3, 126.7, 122.9. ESI-MS (*m*/*z*): found ($M+H^+$) 579.96, [2×M+H^+] 1158.86; $C_{31}H_{15}N_9Zn$ requires 578.90.

3.3.2. Zinc(II) 2(3),9(10),16(17)-trimethyltribenzo[b.g.l]-pyrido[3,4,q]porphyrazine (4b)

Green solid; [Found: C, 65.92; H, 3.51; N, 20.19. $C_{34}H_{21}N_9Zn$ requires: C, 65.76; H, 3.41; N, 20.30%]; R_f (50% $CHCl_3$/MeOH) 0.82; UV/vis (DMF, λ_{max}/log ε): 351 (4.23), 605 (3.88), 631 (3.87), 665 (4.54), 679 nm (4.56); IR (Nujol, ν): 1609, 1461, 1378, 1324, 1258, 1136, 1080, 924, 823, 742, 721 cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6) δ: 10.08 (m, 2H, ArH), 9.09–7.67 (m, 10H, ArH), 2.96–2.89 (m, 9H,

CH_3); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 161.6, 154.7, 151.2, 143.5, 138.2, 134.9, 132.1, 130.2, 128.9, 122.8, 122.1, 107.6, 102.3, 22.1–21.0. ESI-MS (m/z): found ($M+H^+$) 621.99, ($2\times M+H^+$) 1242.98; $C_{34}H_{21}N_9Zn$ requires 620.98.

*3.3.3. Zinc(II) 2(3),9(10),16(17)-tri-tert-butyltribenzo[b.g.l]-pyrido[3,4,q]porphyrazine (**4c**)*

Green solid; [Found: C, 69.32; H, 5.18; N, 16.94. $C_{43}H_{39}N_9Zn$ requires: C, 69.12; H, 5.26; N, 16.87%]; R_f (2.5% $CHCl_3$/MeOH) 0.85; UV/vis (DMF, λ_{max}/log ε): 350 (4.00), 606 (3.57), 632 (3.56), 666 (4.22), 681 nm (4.24); IR (Nujol, ν): 2921, 2852, 1613, 1485, 1393, 1257, 1139, 1081, 920, 833, 749 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$/pyridine-d_5, 3:1) δ: 10.71 (m, 2H, ArH), 9.52–8.28 (m, 10H, ArH), 1.81 (m, 27H, *t*-Bu); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 169.5, 154.9, 148.1, 143.7, 135.1, 130.8, 129.6, 128.3, 127.2, 125.4, 122.7, 122.5, 119.3, 115.0, 20.5–18.5. ESI-MS (m/z): found ($M+H^+$) 748.26, ($2\times M+H^+$) 1495.46; $C_{43}H_{39}N_9Zn$ requires 747.22.

*3.3.4. Zinc(II) 2(3),9(10),16(17)-trinitro-23(24)-octyloxytetrabenzoporphyrazine (**7d**)*

Green solid; [Found: C, 57.88; H, 4.23; N, 18.77. $C_{40}H_{29}N_{11}O_7Zn$ requires: C, 57.12; H, 3.48; N, 18.32%]; R_f (50% $CHCl_3$/MeOH) 0.89; UV/vis (DMF, λ_{max}/log ε): 285 (4.39), 349 (4.33), 647 (4.34), 684 nm (4.39); IR (Nujol, ν): 2925, 1611, 1522, 1486, 1335, 1137, 1086, 1040, 846, 757, 728 cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6) δ: 8.44–7.29 (m, 12H, ArH), 4.10 (m, 2H, $-OCH_2$), 1.73–1.29 (m, 12H, $-CH_2-$), 0.88 (m, 3H, $-CH_3$); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 164.4, 158.7, 157.5, 155.6, 150.0, 138.7, 135.0, 133.7, 130.0, 125.0, 122.5, 119.3, 106.2, 103.7, 68.6, 31.2, 28.6, 25.3, 22.0, 13.9.

3.4. General procedure for the synthesis of unsymmetrically substituted metal-free benzoporphyrazines

A mixture of functional ammonium ionic liquid (**1b**) (1.5 g for 300 mg of **3b**,**3c**) and DBU (304 μl, 2 mmol) was heated at 140 °C under nitrogen atmosphere for 5 min. To the reaction mixture, phthalonitrile (2 mmol) followed by boron(III) subphthalocyanine (**3b**,**3c**) (2 mmol) were added and heating was continued for appropriate time as mentioned in Table 1. The products were isolated and purified as mentioned above for metallobenzoporphyrazines.

*3.4.1. 2(3),9(10),16(17)-Trimethyltribenzo[b.g.l]pyrido[3,4,q]porphyrazine (**5b**)*

Green solid; [Found: C, 70.75; H, 4.39; N, 21.88. $C_{34}H_{23}N_9\cdot H_2O$ requires: C, 70.94; H, 4.38; N, 21.90%]; R_f (50% $CHCl_3$/MeOH) 0.41; UV/vis (THF, λ_{max}/log ε): 340 (4.86), 606 (4.49), 635 (4.63), 659 (4.97), 687 nm (4.98); IR (Nujol, ν): 3393, 1618, 1032, 1099, 743, 722 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ: 10.11–7.55 (m, 12H, ArH), 2.31 (m, 9H, CH_3), −3.89 to −2.57 (m, 2H, –NH); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 167.5, 148.4, 145.4, 144.8, 136.4, 134.7, 129.0, 123.5, 122.9, 115.9, 113.1, 105.2, 21.4. ESI-MS (m/z): found ($M+H^+$) 558.63; $C_{34}H_{23}N_9$ requires 557.61.

*3.4.2. 9(10),16(17),23(24)-Tri-tert-butyltetrabenzoporphyrazine (**6c**)*[34]

Green solid; [Found: C, 77.08; H, 6.04; N, 16.68. $C_{44}H_{42}N_8$ requires: C, 77.39; H, 6.20; N, 16.41%]; UV/vis ($CHCl_3$, λ_{max}/log ε): 337 (4.98), 602 (4.45), 643 (4.64), 662 (5.04), 694 nm (5.07). IR (Film, ν): 3419, 2957, 2919, 2850, 1540, 1489, 1463, 1394, 1362, 1215, 1190, 108, 908, 848, 759 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 9.12–8.32 (m, 8H, ArH), 8.20–8.01 (m, 3H, ArH), 1.92–1.81 (m, 27H, *t*-Bu), −4.00 to −2.70 (m, 2H, –NH). ESI-MS (m/z): found ($M+H^+$) 683.87; $C_{44}H_{42}N_8$ requires 682.86.

3.5. General procedure for the study of self-aggregation in zinc(II) pyridino[3,4]tribenzoporphyrazines (4b,4c) by UV/vis spectroscopy

Stock solutions of **4b** (7.085×10^{-4} M), **4c** (1.296×10^{-3} M) and **5b** (7.086×10^{-4} M) were prepared in chloroform. An aliquot of 50 μl from the stock solution of **4b** was added to 2.5 ml of chloroform solution taken in a quartz cell and its UV/vis spectrum was recorded. Further, 50 μl stock solution of **4b** was added in stages to the quartz cell and the absorption spectra were recorded in each case. To study the effect of pyridine or methanol on head-to-face assembly of **4b**, pyridine (0.72 M) or methanol (20 μl) was added in stages to 1.242×10^{-4} M solution of **4b** in chloroform (3 ml) in a quartz cell and the changes in the absorption spectra were recorded each time. Similar experiments were performed with **4c** and **5b**. Further, this study was repeated for zinc(II) tetrapyridinoporphyrazine in DMF and for **7d** in chloroform.

3.6. General procedure for the study of self-aggregation in zinc(II) pyridino[3,4]tribenzoporphyrazines (4b,4c) by spectrofluorometry

2.5 ml solution of **4c** (1.47×10^{-6} M) in chloroform was taken in a quartz cell. Its concentration was slowly increased up to 1.205×10^{-5} M by further addition of **4c** stock solution in it. The fluorescence spectra were recorded in each case. The spectral changes on stepwise addition of pyridine solution (0.72 M) or methanol (20 μl) to **4c** solution in chloroform were also recorded. Similar experiments were performed with 4.97×10^{-5} M solution of **5b** in chloroform.

3.7. General procedure for the study of self-aggregation in zinc(II) pyridino[3,4]tribenzoporphyrazine (4c) by ^1H NMR spectroscopy

The benzoporphyrazine **4c** (15 mg, 0.020 mmol) was dissolved in $CDCl_3$ (600 μl) in a sample tube. This solution was transferred to an NMR tube and aliquots of pyridine-d_5 (1–3 equiv v/v) were added to the solution in the NMR tube. The change in chemical shift for each peak was recorded.

3.8. General procedure for the study of self-aggregation in zinc(II) pyridino[3,4]tribenzoporphyrazines (4a–4c) by ESI-MS spectroscopy

A sample of **4c** (1.64×10^{-5} M) was prepared in chloroform. The solutions of **4a** (2.43×10^{-5} M), **4b** (2.49×10^{-5} M) and **5b** (2.23×10^{-5} M) were prepared in chloroform/methanol (99:1, v/v). These samples were analyzed on electrospray mass spectrometer by tuning different parameters in the instrument. The resulting mass spectra were analyzed on the basis of m/z values.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.01.046.

References and notes

1. (a) Rodriguez-Morgade, M. S.; de la Torre, G.; Torres, T. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic: New York, NY, 2003; Vol. 15, pp 125–160; (b) Matlane, P.; Nyokong, T. *Polyhedron* **2002**, *21*, 2463–2472.
2. Sastre, A.; del Rey, B.; Torres, T. *J. Org. Chem.* **1996**, *61*, 8591–8597.

3. Hu, M.; Brasseur, N.; Yildiz, S. Z.; van Lier, J. E.; Leznoff, C. C. *J. Med. Chem.* **1998**, *41*, 1789–1802.
4. Cosimelli, B.; Roncucci, G.; Dei, D.; Fantetti, L.; Ferroni, F.; Ricci, M.; Spinelli, D. *Tetrahedron* **2003**, *59*, 10025–10030.
5. (a) Ali-Adib, Z.; Clarkson, G. J.; McKeown, N. B.; Treacher, K. E.; Gleeson, H. F.; Stennett, A. S. *J. Mater. Chem.* **1998**, *8*, 2371–2378; (b) Cook, M. J. *Pure Appl. Chem.* **1999**, *71*, 2145–2151; (c) de la Torre, G.; Claessens, C. G.; Torres, T. *Chem. Commun.* **2007**, 2000–2015.
6. (a) Van Nostrum, C. F.; Picken, S. J.; Schouten, A. J.; Nolte, R. J. M. *J. Am. Chem. Soc.* **1995**, *117*, 9957–9965; (b) Piechocki, C.; Simon, J.; Skoulios, A.; Guillon, D.; Weber, P. *J. Am. Chem. Soc.* **1982**, *104*, 5245–5347; (c) Piechocki, C.; Simon, J. *Nouv. J. Chim.* **1985**, *9*, 159–166; (d) Cook, M. J. *Adv. Mater.* **1995**, *7*, 877–880; (e) Hanack, M. *Tr. J. Chem.* **1998**, *22*, 13–22; (f) Kobuke, Y. *Eur. J. Inorg. Chem.* **2006**, 2333–2351; (g) Flora, W. H.; Mendes, S. B.; Doherty, W. J., III; Saavedra, S. S.; Armstrong, N. R. *Langmuir* **2005**, *21*, 360–368; (h) Nostrum, C. F. V.; Nolte, R. J. M. *Chem. Commun.* **1996**, 2385–2392.
7. (a) Shachter, A. M.; Fleischer, E. B.; Haltiwanger, R. C. *J. Chem. Soc., Chem. Commun.* **1988**, 960–961; (b) Funatsu, K.; Kimura, A.; Imamura, T.; Sasaki, Y. *Chem. Lett.* **1995**, 765–766; (c) Alessio, E.; Macchi, M.; Heath, S.; Marzilli, L. G. *Chem. Commun.* **1996**, 1411–1412; (d) Anderson, S.; Anderson, H. L.; Bashall, A.; McPartlin, M.; Sanders, J. K. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1096–1099; (e) Fleischer, E. B.; Shachter, A. M. *Inorg. Chem.* **1991**, *30*, 3763–3769; (f) Kobuke, Y.; Miyaji, H. *J. Am. Chem. Soc.* **1994**, *116*, 4111–4112.
8. Kleij, A. W.; Kuil, M.; Tooke, D. M.; Spek, A. L.; Reek, J. N. H. *Inorg. Chem.* **2007**, *46*, 5829–5831.
9. (a) Cook, M. J.; Jafari-Fini, A. *J. Mater. Chem.* **1997**, *7*, 2327–2329; (b) Al-Raqa, S. Y.; Cook, M. J.; Hughes, D. L. *Chem. Commun.* **2003**, 62–63; (c) Huang, X.; Zhao, F.; Li, Z.; Huang, L.; Tang, Y. *Chem. Lett.* **2007**, *36*, 108–109; (d) Huang, X.; Zhao, F.; Li, Z.; Tang, Y.; Zhang, F.; Tung, C.-H. *Langmuir* **2007**, *23*, 5167–5172; (e) Rikukawa, M.; Matuzaki, D.; Nakagawa, M.; Sanui, K.; Ogata, N. *Synth. Met.* **1995**, *71*, 2279–2280; (f) Gao, B.; Li, Y.; Su, J.; Tian, H. *Supramol. Chem.* **2007**, *19*, 207–210.
10. (a) De la Torre, G.; Claessens, C. G.; Torres, T. *Eur. J. Org. Chem.* **2000**, 2821–2830; (b) Torres, T. *J. Porphyrins Phthalocyanines* **2000**, *4*, 325–330.
11. (a) Sharman, W. M.; van Lier, J. E. *Bioconjugate Chem.* **2005**, *16*, 1166–1175; (b) Geyer, M.; Plenzig, F.; Rauschnabel, J.; Hanack, M.; del Rey, B.; Sastre, A.; Torres, T. *Synthesis* **1996**, 1139–1151; (c) Ali, H.; Sim, S. K.; van Lier, J. E. *J. Chem. Res., Synop.* **1999**, 496–497; (d) Sastre, A.; Torres, T.; Hanack, M. *Tetrahedron Lett.* **1995**, *36*, 8501–8504.
12. (a) Jain, N.; Kumar, A.; Chauhan, S.; Chauhan, S. M. S. *Tetrahedron* **2005**, *61*, 1015–1060; (b) Olivier-Bourbigou, H.; Magna, L. *J. Mol. Catal. A: Chem.* **2002**, *182–183*, 419–437; (c) Welton, T. *Chem. Rev.* **1999**, *99*, 2071–2083; (d) Chowdhury, S.; Mohan, R. S.; Scott, J. L. *Tetrahedron* **2007**, *63*, 2363–2389.
13. (a) Chauhan, S. M. S.; Agarwal, S.; Kumari, P. *Synth. Commun.* **2007**, *37*, 2917–2925; (b) Chauhan, S. M. S.; Kumari, P.; Agarwal, S. *Synthesis* **2007**, 3713–3721.
14. (a) Jain, N.; Kumar, A.; Chauhan, S. M. S. *Tetrahedron Lett.* **2005**, *46*, 2599–2602; (b) Kumari, P.; Yathindranath, V.; Chauhan, S. M. S. *Synth. Commun.* **2008**, *38*, 637–648; (c) Kumar, A.; Jain, N.; Chauhan, S. M. S. *Synlett* **2007**, 411–414; (d) Chauhan, S. M. S.; Kumar, A.; Srinivas, K. A. *Chem. Commun.* **2003**, 2348–2349; (e) Angrish, C.; Kumar, A.; Chauhan, S. M. S. *Indian J. Chem., Sect. B* **2005**, *44B*, 1515–1518; (f) Jain, N.; Kumar, A.; Chauhan, S. M. S. *Synth. Commun.* **2005**, *35*, 1223–1230; (g) Kumar, A.; Jain, N.; Rana, S.; Chauhan, S. M. S. *Synlett* **2004**, 2785–2787; (h) Kumar, A.; Jain, N.; Chauhan, S. M. S. *Synth. Commun.* **2004**, *34*, 2835–2842; (i) Chauhan, S. M. S.; Jain, N.; Kumar, A.; Srinivas, K. A. *Synth. Commun.* **2003**, *33*, 3607–3614; (j) Srinivas, K. A.; Kumar, A.; Chauahn, S. M. S. *Chem. Commun.* **2002**, 2456–2457.
15. Claessens, C. G.; Gonzalez-Rodriguez, D.; Torres, T. *Chem. Rev.* **2002**, *102*, 835–853.
16. Claessens, C. G.; Gonzalez-Rodriguez, D.; McCallum, C. M.; Nohr, R. S.; Schuchmann, H.-P.; Torres, T. *J. Porphyrins Phthalocyanines* **2007**, *11*, 181–188.
17. The reaction of 3,4-dicyanopyridine or other phthalonitrile bearing electron withdrawing groups such as nitro or fluoro with DBU gives a reddish brown species at room temperature, which remains stable even on heating the reaction mixture for 24–48 h at 140 °C. This species is believed to be a DBU–phthalonitrile adduct and this adduct remains stable even on heating in the presence of metal salt such as zinc acetate and ionic liquid **1a**. No such adduct formation was observed when 3,4-dicyanopyridine was added in the reaction mixture of ionic liquid **1b** and DBU at 140 °C.
18. (a) Palomares, E.; Martínez-Díaz, M. V.; Torres, T.; Coronado, E. *Adv. Funct. Mater.* **2006**, *16*, 1166–1170; (b) Ros-Lis, J. V.; Mártinez-Máñez, R.; Soto, J. *Chem. Commun.* **2005**, 5260–5262.
19. Ferro, V. R.; de la vega, J. M. G.; Claessens, C. G.; Poveda, L. A.; Gonzalez-Jonte, R. H. *J. Porphyrins Phthalocyanines* **2001**, *5*, 491–499.
20. Xu, S.; Chen, K.; Tian, H. *J. Mater. Chem.* **2005**, *15*, 2676–2680.
21. Calo, V.; Nacci, A.; Monopoli, A. *Eur. J. Org. Chem.* **2006**, 3791–3802.
22. (a) Domanska, U.; Bogel-Lukasik, R. *J. Phys. Chem. B* **2005**, *109*, 12124–12132; (b) Domanska, U.; Bakala, I.; Pernak, J. *J. Chem. Eng. Data* **2007**, *52*, 309–314; (c) 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.
23. (a) Kroon, J. M.; Koehorst, R. B. M.; van Dijk, M.; Sanders, G. M.; Sudholter, E. J. R. *J. Mater. Chem.* **1997**, *7*, 615–624; (b) Kasha, M.; Rawls, H. R.; EL-Bayomi, M. A. *Pure Appl. Chem.* **1965**, *11*, 371–392; (c) Isago, H. *Chem. Commun.* **2003**, 1864–1865.
24. Vagin, S.; Frickenschmidt, A.; Kammerer, B.; Hanack, M. *Eur. J. Org. Chem.* **2005**, 3271–3278.
25. (a) Lebedeva, N. S.; Trofimova, E. V.; Pavlycheva, N. A.; Vyugin, A. I. *Russ. J. Org. Chem.* **2002**, *38*, 1195–1199; (b) Lebedeva, N. S.; Mal'kova, E. A.; V'yugin, A. I.; Maizlish, V. E.; Shaposhnikov, G. P. *Zh. Neorg. Khim.* **2005**, *50*, 336–339; *Chem. Abstr.* **2005**, *143*, 394085; (c) Sole, R. D.; Luca, A. D.; Mele, G.; Vasapollo, G. *J. Porphyrins Phthalocyanines* **2005**, *9*, 519–527.
26. Berkowitz, J. *J. Chem. Phys.* **1979**, *70*, 2819–2828.
27. Cariati, F.; Morazzoni, F.; Zocchi, M. *J. Chem. Soc., Dalton Trans.* **1978**, 1018–1024.
28. Barterman, P. S.; Davies, R. C.; Williams, R. J. P. *Adv. Chem. Phys.* **1964**, *7*, 359–407.
29. Ouedraogo, G. V.; More, C.; Richard, Y.; Benlian, D. *Inorg. Chem.* **1981**, *20*, 4387–4393.
30. (a) Dupouy, E. A. *Photochem. Photobiol. Sci.* **2004**, *3*, 992–998; (b) Sakamoto, K. *J. Photochem. Photobiol, A: Chem.* **2002**, *153*, 245–252.
31. Claessens, C. G.; Gonzalez-Rodriguez, D.; del Rey, B.; Torres, T.; Mark, G.; Schuchmann, H.-P.; von Sonntag, C.; MacDonald, J. G.; Nohr, R. S. *Eur. J. Org. Chem.* **2003**, 2547–2551.
32. Tsuchiya, M.; Shinkai, M.; Tanabe, J. Jpn. Kokai Tokkyo Koho JP2007063436 A20070315, 2007; *Chem. Abstr.* **2007**, *146*, 326489.
33. Yanagimoto, T.; Yamado, H. Jpn. Kokai Tokkyo Koho JP2005289854 A20051020, 2005; *Chem. Abstr.* **2005**, *143*, 378579.
34. Kobayashi, N.; Kondo, R.; Nakajima, S.-i.; Osa, T. *J. Am. Chem. Soc.* **1990**, *112*, 9640–9641.