Investigation of Suitable Structure of Ionic Liquids for the Synthesis of Phthalocyanines

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The preparation of phthalocyanines are difficult because of their poor reactivity of reactants. In order to improve the reactivity, safety, and green technology in the preparation of the phthalocyanine (4-tBuPcH₂), several types of ionic liquids were applied as reaction medium. In the case of using [C₂-OHm₂im][Br] as a reaction media, 4-tBuPcH₂ was obtained in the highest yield (38%). These results suggested that the hydroxy groups, anion species, and stability of cations of ionic liquids are important to synthesis of 4-tBuPcH₂. In addition, [C₂-OHm₂im][Br] was reused without any loss of its catalytic activity.

Key words: ionic liquids, phthalocyanine, green chemistry, porphyrin

1. INTRODUCTION

The phthalocyanine and its derivatives are widely used in various fields, such as dyes and pigments,¹ chemical sensors,² photosensitizer for photodynamic therapy,³ non-linear optical materials,⁴ liquid crystals,⁵ and catalysts⁶ due to their high thermal stability and attractive chemical properties. There are two general approaches to the synthesis of some phthalocyanines and its derivatives. One is a condensation of phthalonitriles by refluxing with metal alkoxide or DBU in alcohol, and the other is fusion methods with phthalic anhydrides or its derivatives.⁷ These methods often requires high reaction temperature (100-300 °C), prolonged reaction time, strong basic condition and troublesome workup procedures. In order to achieve favorable reaction conditions such as more gentle, safe and lower energy, it is expected the development of the green phthalocyanine synthesis.

Ionic liquids (ILs) could be suitable and environmentally safer replacements for the volatile, toxic, and flammable organic solvents. In addition, ILs can easily dissolve many compounds involving some porphyrins. In fact, there are various reports about using ILs as reaction media and catalysis.⁸⁻⁹ We have studied the utilization of ILs to prepare porphyrins.¹⁰⁻¹³ The synthetic method of phthalocyanine is greatly different from other porphyrin derivatives, though phthalocyanines are one of the porphyrin derivatives. Base is necessary for the preparations the phthalocyanines, while acid is necessary for the preparations of other porphyrins. Tetrabutylammonium bromide^{14,15} and 1,1,3,3-*N*, *N*, *N*, *N*'-tetramethylguanidium bromide¹⁶ have been used as ILs for phthalocyanines and metallophthalocyanines synthesis. In addition, hydroxylated ammonium based ILs have been used for synthesis of phthalocyanines¹⁷ and metallophthalocyanines.¹⁸ In particular, the methods utilizing hydroxylated ammonium based ILs^{17,18} are worthy of attention, because hydroxylated ammonium based ILs act as basic catalyst by combining with DBU. While the effects of ILs structure on the preparation of

Fig.1 Structures of Ionic Liquids used in this study

metallophthalocyanines have been studied, the effect on the preparation of free base phthalocyanines has not been clarified. Because the preparation of free base phthalocyanines is not metal template synthesis, its reactivity is lower than that of metallophthalocyanines. In addition, the reactivity of the substituted phthalonitriles used in the preparation of phthalocyanines having substituents which improve their solubility in various solvents are lower than that of unsubstituted phthalonitrile. In this paper, we focused on the 4,4',4'',4'''-tetra-*tert*-butylphthalocyanine (4-tBuPcH₂), because 4-tBuPcH₂ can be dissolved in the many kinds of solvents and be useful in many fields. The purpose of this study was investigation of the suitable ILs structure for the phthalocyanine preparation, and to improve the yield of the phthalocyanines. We focused our attention on the following points of ILs structures. (1) hydroxy group, (2) C₂-H of imidazolium, (3) cation skeletons, (4) anion species, (5) spacer length between imidazolium ring and hydroxy group (Fig.1).

2. EXPERIMENTAL

All reagents were reagent grade and were used as received from Aldrich without further purification. All the ILs were dried *in vacuo* (under 0.1 mbar) at 60°C for 1 day prior to use. TLC analyses was performed on 0.25 mm

Silica gel Merck 60 F254 plates. NMR spectra were recorded on a 400 MHz spectrometer. Chemical shifts (δ ppm) in DMSO- d_6 were reported downfield from TMS (0 ppm) for ^1H NMR.

4.1 Preparations of ILs

Preparation of 1-(2'-hydroxyethyl)-2,3-dimethylimidazolium bromide, $[\text{C}_{2-\text{OH}}\text{m}_2\text{im}][\text{Br}]$ (1)

A mixture of 1,2-dimethylimidazole (5.0 g, 52 mmol) and 2-bromoethanol (4.4 mL, 62 mmol) in acetonitrile (20 mL) was refluxed with stirring 7 hours. After removal of the solvent, the residue was diluted with water (50 mL) and washed with chloroform (3 X 50 mL). A spatula tip of activated charcoal was added to the aqueous phase and stirred 1 hour. The activated charcoal was removed by filtration, and the solvent was removed under reduced pressure. The residue was further dried *in vacuo* (under 0.1 mbar) at 60 °C for 24 hours, which gave a white solid (yield: 10.2 g, 46 mmol, 88%). ^1H NMR(400 MHz, DMSO- d_6 -TMS): δ =7.61 (d, 2H, C4-H + C5-H), 5.08 (t, 1H, OH), 4.18(t, 2H, $\text{NCH}_2\text{CH}_2\text{OH}$), 3.75(s, 3H, N-CH₃) 3.75-3.66 (m, 2H, $\text{NCH}_2\text{CH}_2\text{OH}$), 2.58(s, 3H, C2-CH₃). ESI-MS (CH_3OH), positive ion 141 [$\text{C}_{2-\text{OH}}\text{m}_2\text{im}$], negative ion 81 [Br].

Preparation of 1-butyl-2,3-dimethylimidazolium bromide, $[\text{C}_4\text{m}_2\text{im}][\text{Br}]$ (2)

A mixture of 1,2-dimethylimidazole (10.0 g, 104 mmol) and 1-bromobutane (13.0 mL, 125 mmol) in acetonitrile (50 mL) was refluxed with stirring 4 hours. After removal of the solvent, the residue was diluted with water (50 mL) and washed with chloroform (3 X 50 mL). A spatula tip of activated charcoal was added to the aqueous phase and stirred one hour. The activated charcoal was removed by filtration, and the solvent was removed under reduced pressure. The residue was further dried *in vacuo* (under 0.1 mbar) at 60 °C for 24 hours, which gave a white solid (yield: 24.1 g, 104 mmol, 99%). ^1H NMR(400 MHz, DMSO- d_6 -TMS): δ =7.64 (s, 1H, C4-H), 7.61 (s, 1H, C5-H), 4.11(t, 2H, N-CH₂), 3.73(s, 3H, N-CH₃), 2.57(2, 3H, C2-CH₃), 1.71(m, 2H, N-CH₂CH₂CH₂CH₃), 1.32 (m, 2H, N-CH₂CH₂CH₂CH₃), 0.91(t, 3H, N-CH₂CH₂CH₂CH₃). ESI-MS (CH_3OH), positive ion 153 [$\text{C}_4\text{m}_2\text{im}$], negative ion 81 [Br].

Preparation of 1-butyl-2,3-dimethylimidazolium chloride, $[\text{C}_4\text{m}_2\text{im}][\text{Cl}]$ (3)

A mixture of 1,2-dimethylimidazole (5.0 g, 52 mmol) and 2-chloroethanol (4.2 mL, 62 mmol) in acetonitrile (20 mL) was refluxed with stirring 42 hours. After removal of the solvent, the residue was diluted with water (50 mL) and washed with chloroform (3 X 50 mL). A spatula tip of activated charcoal was added to the aqueous phase and stirred one hour. The activated charcoal was removed by filtration, and the solvent was removed under reduced pressure. The residue was further dried *in vacuo* (under 0.1 mbar) at 60 °C for 24 hours, which gave a white solid (yield: 7.04 g, 40 mmol, 78%). ^1H NMR(400 MHz, DMSO- d_6 -TMS): δ =7.64 (d, 2H, C4-H + C5-H), 5.25 (t, 1H, OH), 4.18(t, 2H, $\text{NCH}_2\text{CH}_2\text{OH}$), 3.75(s, 3H, N-CH₃) 3.70-3.68 (m, 2H, $\text{NCH}_2\text{CH}_2\text{OH}$), 2.58(s, 3H, C2-CH₃). ESI-MS (CH_3OH), positive ion 141 [$\text{C}_{2-\text{OH}}\text{m}_2\text{im}$], negative ion 35 [Br].

Preparation of 1-(2'-hydroxyethyl)-2,3-dimethylimidazolium dicyanamide, $[\text{C}_{2-\text{OH}}\text{m}_2\text{im}][\text{N}(\text{CN})_2]$ (4)

To a solution of sodium dicyanamide (4.5 g, 51 mmol) in water (30 mL) was added the silver nitrate (8.58 g, 51 mmol), and the reaction mixture was stirred for 2 hours at room temperature. The precipitate (silver dicyanamide) was collected by filtration. To a solution of [$\text{C}_{2-\text{OH}}\text{m}_2\text{im}$] [Br] (10.1 g, 46 mmol) in water (30 mL) was added the silver dicyanamide, and the reaction mixture was stirred overnight at room temperature. The precipitate was removed by filtration. A spatula tip of activated charcoal was added and the mixture was stirred 1 hour at room temperature. The activated charcoal was removed by filtration, and the solvent was removed under reduced pressure. The residue was further dried *in vacuo* (under 0.1mbar) at 60 °C for 24 hours, which gave a pale yellow liquid (yield: 7.1 g, 34 mmol, 86%). ^1H NMR(400 MHz, DMSO- d_6 -TMS): δ =8.22(s, 1H, C4-H), 7.51 (s, 1H, C5-H), 5.00 (t, 1H, OH), 4.09(t, 2H, $\text{NCH}_2\text{CH}_2\text{OH}$), 3.67(s, 3H, N-CH₃) 3.60 (m, 2H, $\text{NCH}_2\text{CH}_2\text{OH}$), 2.45(s, 3H, C2-CH₃). ESI-MS (CH_3OH), positive ion 141 [$\text{C}_{2-\text{OH}}\text{m}_2\text{im}$], negative ion 66 [$\text{N}(\text{CN})_2$].

Preparation of 1-(2'-hydroxyethyl)-3-methylimidazolium bromide, $[\text{C}_{2-\text{OH}}\text{mim}][\text{Br}]$ (5)

A mixture of 1-methylimidazole (5.0 mL, 63 mmol) and 2-bromoethanol (5.3 mL, 75 mmol) in acetonitrile (20 mL) was refluxed with stirring 4 hours. After removal of the solvent, the residue was diluted with water (50 mL) and washed with chloroform (3 X 50 mL). A spatula tip of activated charcoal was added to the aqueous phase and stirred 1 hour. The activated charcoal was removed by filtration, and the solvent was removed under reduced pressure. The residue was further dried *in vacuo* (under 0.1 mbar) at 60 °C for 24 hours, which gave a white solid (yield: 11.3 g, 55 mmol, 88%). ^1H NMR(400 MHz, DMSO- d_6 -TMS): δ =9.08 (s, 1H, C2-H), 7.72 (s, 1H, C4-H), 7.69(s, 1H, C5-H), 5.18 (t, 1H, OH), 4.21(t, 2H, $\text{NCH}_2\text{CH}_2\text{OH}$), 3.85(s, 3H, N-CH₃) 3.72-3.68(m, 2H, $\text{NCH}_2\text{CH}_2\text{OH}$). ESI-MS (CH_3OH), positive ion 127 [$\text{C}_{2-\text{OH}}\text{mim}$], negative ion 81 [Br].

Preparation of N-(2'-hydroxyethyl)-pyridinium bromide, $[\text{C}_{2-\text{OH}}\text{Py}][\text{Br}]$ (6)

A mixture of pyridine (5.0 mL, 60 mmol) and 2-bromoethanol (5.0 mL, 70 mmol) in acetonitrile (20 mL) was refluxed with stirring 19 hours. After removal of the solvent, the residue was diluted with water (50 mL) and washed with chloroform (3 X 50 mL). A spatula tip of activated charcoal was added to the aqueous phase and stirred one hour. The activated charcoal was removed by filtration, and the solvent was removed under reduced pressure. The residue was further dried *in vacuo* (under 0.1 mbar) at 60 °C for 24 hours, which gave a white solid (yield: 11.1 g, 54 mmol, 91%). ^1H NMR(400 MHz, DMSO- d_6 -TMS): δ =9.01 (d, 2H, *o*-H), 8.62 (t, 1H, *p*-H), 8.16(t, 2H, *m*-H), 5.25(br, 1H, OH) 4.66 (t, 2H, $\text{NCH}_2\text{CH}_2\text{OH}$), 3.85(t, 2H, $\text{NCH}_2\text{CH}_2\text{OH}$). ESI-MS (CH_3OH), positive ion 124 [$\text{C}_{2-\text{OH}}\text{Py}$], negative ion 81 [Br].

Preparation of 1-(6'-hydroxyhexyl)-2,3-dimethylimidazolium bromide, $[\text{C}_{6-\text{OH}}\text{m}_2\text{im}][\text{Br}]$ (7)

A mixture of 1,2-dimethylimidazole (5.0 g, 52 mmol) and

6-bromohexanol (8.1 mL, 62 mmol) in acetonitrile (50 mL) was refluxed with stirring 18 hours. After removal of the solvent, the residue was diluted with water (50 mL) and washed with chloroform (3 X 50 mL). A spatula tip of activated charcoal was added to the aqueous phase and stirred one hour. The activated charcoal was removed by filtration, and the solvent was removed under reduced pressure. The residue was further dried *in vacuo* (under 0.1 mbar) at 60 °C for 24 hours, which gave a pale yellow liquid (yield: 12.2 g, 44 mmol, 85%). ¹H NMR(400 MHz, DMSO-*d*₆-TMS) : δ=7.60 (d, 2H, C4-H), 7.55 (d, 2H, C5-H), 4.31(s, 1H, OH), 4.06(t, 2H, NCH₂), 3.34(m, 2H, N-CH₂CH₂CH₂(CH₂)₂CH₂OH), 2.53(s, 3H, C2-CH₃), 1.68(m, 2H, N-CH₂CH₂CH₂(CH₂)₂CH₂OH), 1.38(m, 2H, N-CH₂CH₂CH₂(CH₂)₂CH₂OH), 1.25(m, 4H, N-CH₂CH₂CH₂(CH₂)₂CH₂OH). ESI-MS (CH₃OH), positive ion 197 [C₆-OHm₂im], negative ion 81 [Br].

4.2 Preparations of phthalocyanine in ILs

Preparation of 4,4',4''-tetra-*tert*-butylphthalocyanine, 4-tBuPcH₂ in [C₂-OHm₂im][Br]

2 mL of [C₂-OHm₂im][Br] was melted at 80 °C in the test tube. 4-*tert*-butylphthalonitrile (360 mg, 1.95 mmol) and DBU (0.304 mL, 2.03 mmol) were added in to [C₂-OHm₂im][Br]. After stirring for 5 hours at 120 °C, the reaction mixture was dissolved in the chloroform (100 mL) and distilled water (100mL). After the water phase including [C₂-OHm₂im][Br] was separated, the chloroform phase including 4-tBuPcH₂ was washed with distilled water (3 X 50 mL). The chloroform phase was dried over anhydrous sodium sulfate and the chloroform was removed under reduced pressure. The residue was dissolved in dichloromethane and chromatographed on silica gel with dichloromethane elution to get deep blue powder (90 mg, 0.12 mmol, 38 %). UV-vis(CHCl₃): λ_{max} (nm) 701, 664, 644, 602, 341.

Preparations of 4-tBuPcH₂ in other ILs were conducted on the same procedure in [C₂-OHm₂im][Br].

3. RESULTS AND DISCUSSION

First, 4-tBuPcH₂ was prepared in ILs, [C₂-OHm₂im][Br] (Table 1). [C₂-OHm₂im][Br] was heated until liquid state (80 °C), because [C₂-OHm₂im][Br] is solid at room temperature. 4-*tert*-butylphthalonitrile (0.9 M) and DBU (1.0 M) was added in the liquid [C₂-OHm₂im][Br]. After reaction mixture was heated at 120 °C for 6 hours, 4-tBuPcH₂ was obtained in 38% yield. In contrast, 4-tBuPcH₂ was obtained in 4.4% yield by refluxing with ethanol as a molecular solvent. Although reaction temperature is different, the yield of 4-tBuPcH₂ was higher in ILs than in molecular solvent. These results suggested that the phthalocyanine synthesis maybe accelerated in ILs. Therefore, we investigated the key structure of ILs in the phthalocyanine synthesis by 4-tBuPcH₂ preparation in various ILs.

The influence of hydroxy group was investigated by using [C₄m₂im][Br]. In [C₂-OHm₂im][Br] with hydroxy group, 4-tBuPcH₂ was obtained in 38% yield (Table 2, Entry 1), whereas in [C₄m₂im][Br] without hydroxy group, only 4% of 4-tBuPcH₂ was obtained (Table 2, Entry 2). Thus, the plausible mechanism of 4-tBuPcH₂ synthesis in ILs is the same as the method using molecular solvent

Table 1 Comparison of reaction solvent (ILs vs molecular solvent) for the preparation of 4-tBuPcH₂

Solvent	Temp./ °C	Time / h	Yield / %
[C ₂ -OHm ₂ im][Br]	120	6	38
EtOH	78	24	4.4

[4-*tert*-butylphthalonitrile] = 0.9 M, [DBU] = 1.0 M.

alcohol.¹⁹ (1) Alkoxide is formed from alcohol by DBU. (2) The alkoxide accelerates the reaction by nucleophilic attack on the carbon of the cyano group of 4-*tert*-butylphthalonitrile.

The effect of C₂-H of imidazolium ring was investigated by using [C₂-OHmim][Br]. 4-BuPcH₂ was obtained in 38% yield in [C₂-OHm₂im][Br] in which the C₂ position of imidazolium ring was substituted with a methyl group (Table 2, Entry 1), while 4-BuPcH₂ was obtained in 20% yield in [C₂-OHmim][Br] with C₂-H. Both reactions are carried out in the presence of stronger base DBU. The acidity of the imidazolium C₂-H is relatively high (pK_a = 21 – 23), and its value was roughly intermediate between the acidities of acetone (pK_a = 19.3) and ethyl acetate (pK_a = 25.6).²⁰ It is well known from the seminal work of Arduengo that deprotonation at the C₂ position of the imidazolium salt generates N-heterocyclic carbene.²¹ Therefore, it is reasonable to surmise that the carbene generated by deprotonation of the acidic C₂-H by DBU interferes with the phthalocyanine formation.

The influence of cation skeleton was investigated by [C₂-OHPy][Br]. In [C₂-OHm₂im][Br] with imidazolium skeleton, 4-tBuPcH₂ was obtained in 38% yield (Table 2,

Table 2 The preparations of 4-tBuPcH₂ in several ILs

Entry	Ionic liquids	Time / h	Yield / %
1	[C ₂ -OHm ₂ im][Br]	6	38
2	[C ₄ m ₂ im][Br]	7	4
3	[C ₂ -OHmim][Br]	6	20
4	[C ₂ -OHPy][Br]	20	trace
5	[C ₂ -OHm ₂ im][Cl]	6	14
6	[C ₂ -OHm ₂ im][N(CN) ₂]	6	6
7	[C ₆ -OHm ₂ im][Br]	7	18

[4-*tert*-butylphthalonitrile] = 0.9 M, [DBU] = 1.0 M.

Entry 1). In $[\text{C}_{2\text{-OH}}\text{Py}][\text{Br}]$ with pyridinium skeleton, only a trace amount of 4-*t*BuPcH₂ was generated, and could not be isolated (Table 2, Entry 4). Chauhan and coworkers pointed out the possibility that the pyridinium ILs was decomposed in the presence of DBU in the metallophthalocyanines synthesis using pyridinium ILs.¹⁸ For the same reason, 4-*t*BuPcH₂ cannot be generated in $[\text{C}_{2\text{-OH}}\text{Py}][\text{Br}]$.

The influence of anion species was investigated. 4-*t*BuPcH₂ was prepared in three type ILs with different anions, $[\text{C}_{2\text{-OH}}\text{m}_2\text{im}][\text{X}]$ (X = Br, Cl, N(CN)₂) (Table 2, Entry 1, 5, 6). In $[\text{C}_{2\text{-OH}}\text{m}_2\text{im}][\text{Br}]$, 4-*t*BuPcH₂ was obtained in 38% yield (Table 2, Entry 1), whereas in $[\text{C}_{2\text{-OH}}\text{m}_2\text{im}][\text{Cl}]$, $[\text{C}_{2\text{-OH}}\text{m}_2\text{im}][\text{N}(\text{CN})_2]$, 4-*t*BuPcH₂ was obtained in 20%, 6% respectively (Table 2, Entry 5, 6). The Lewis basicity of the anion seems to be influenced the reaction. As mentioned above, the formation of phthalocyanine is accelerated by the nucleophilic attack of alkoxide on the carbon of cyano group.¹⁹ These results suggested that not only alkoxide but also Lewis base of the anion participates in the reaction. Br⁻ and Cl⁻ has a higher Lewis basicity than that of N(CN)₂⁻. The high basicity of Br⁻ and Cl⁻ can greatly promote the phthalocyanine formation. Although there is little difference in Lewis basicity between Br⁻ and Cl⁻, the yields of 4-*t*BuPcH₂ in these two ILs are very different. The difference in yield can be explained by HSBA (hard and soft acids and bases) principle. The carbon of the cyano group in phthalonitrile was a soft acid, and it shows high affinity for the moderate hard base Br⁻ than hard base Cl⁻. Thus, it is reasonable surmised that the carbon of the cyano group can be attacked nucleophilically by Br⁻ anion than Cl⁻ anion.

The spacer length between the imidazolium ring and the hydroxy group was investigated. In $[\text{C}_{2\text{-OH}}\text{m}_2\text{im}][\text{Br}]$ with a short spacer (C2), 4-*t*BuPcH₂ was obtained in 38% yield (Table 2, Entry 1), whereas in $[\text{C}_{6\text{-OH}}\text{m}_2\text{im}][\text{Br}]$ with a long spacer (C6), 4-*t*BuPcH₂ was obtained in 18% yield (Table 2, Entry 7). As mentioned above, the formation of phthalocyanine is accelerated by alkoxide which generated by deprotonation of hydroxy group, and the stability of the generated alkoxide seems to have influenced the reactivity. It is expected that the alkoxide is stabilized when the negative charge of imidazolium cation. Therefore, $[\text{C}_{2\text{-OH}}\text{m}_2\text{im}][\text{Br}]$ with a short spacer can accelerate the reaction rate than $[\text{C}_{6\text{-OH}}\text{m}_2\text{im}][\text{Br}]$ with a long spacer.

Most effective catalysts for the 4-*t*BuPcH₂ preparation,

Table 3 Recycling of $[\text{C}_{2\text{-OH}}\text{m}_2\text{im}][\text{Br}]$ in the preparation of 4-*t*BuPcH₂

Cycle	Ionic liquids	1	2
Yield / %	$[\text{C}_{2\text{-OH}}\text{m}_2\text{im}][\text{Br}]$	33	32

[4-*tert*-butylphthalonitrile] = 0.9 M, [DBU] = 1.0 M.

$[\text{C}_{2\text{-OH}}\text{m}_2\text{im}][\text{Br}]$ was reused in second cycle of the reaction, as shown in Table 3. After first cycle of the reaction, $[\text{C}_{2\text{-OH}}\text{m}_2\text{im}][\text{Br}]$ was diluted with water and 4-*t*BuPcH₂ was extracted with chloroform. The water phase including $[\text{C}_{2\text{-OH}}\text{m}_2\text{im}][\text{Br}]$ was washed with chloroform, then it was decolorized using activated charcoal. After water was evaporated, it was confirmed by the ¹H NMR that $[\text{C}_{2\text{-OH}}\text{m}_2\text{im}][\text{Br}]$ does not contain impurities. 4-*tert*-butylphthalonitrile and DBU were added to the recovered ILs and the reaction was carried out again. The yields of first and second cycle were almost same as 33% and 32%, respectively. The use of recycled $[\text{C}_{2\text{-OH}}\text{m}_2\text{im}][\text{Br}]$ did not affect the productivity of phthalocyanine at all.

4. CONCLUSION

It was revealed that the optimum ILs structure for the preparation of 4-*t*BuPcH₂ is $[\text{C}_{2\text{-OH}}\text{m}_2\text{im}][\text{Br}]$. In addition, $[\text{C}_{2\text{-OH}}\text{m}_2\text{im}][\text{Br}]$ could be reused without any loss of its catalytic activity. The utilization of ILs enabled effective and green phthalocyanine synthesis. Further investigation to apply this method to other useful phthalocyanine derivatives are being made in our laboratory.

5. ACKNOWLEDGEMENTS

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