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SYNTHESIS OF PHTHALOCYANINE FUSED WITH BICYCLO[2.2.2]OCTADIENES AND THERMAL CONVERSION INTO NAPHTHALOCYANINE

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Abstract – Mg complex of phthalocyanine fused with bicyclo[2.2.2]octadiene (BCOD) units is prepared by the reaction of BCOD-fused phthalonitrile with $Mg(OPr)_2$ in PrOH at 100 ºC overnight in 42% yield. Subsequent heating the product at 250 ºC results in clean formation naphthalocyanine *via* the retro Diels-Alder reaction. An attempt to the synthesis of BCOD-fused tetraazaporphyrin by the similar cyclization of the Diels-Alder adduct of dicyanoacetylene with 1,3-cyclohexadiene was unsuccessful.

Dedicated to Prof. Dr. Ekkehard Winterfeldt on the occasion of his 75th birthday.

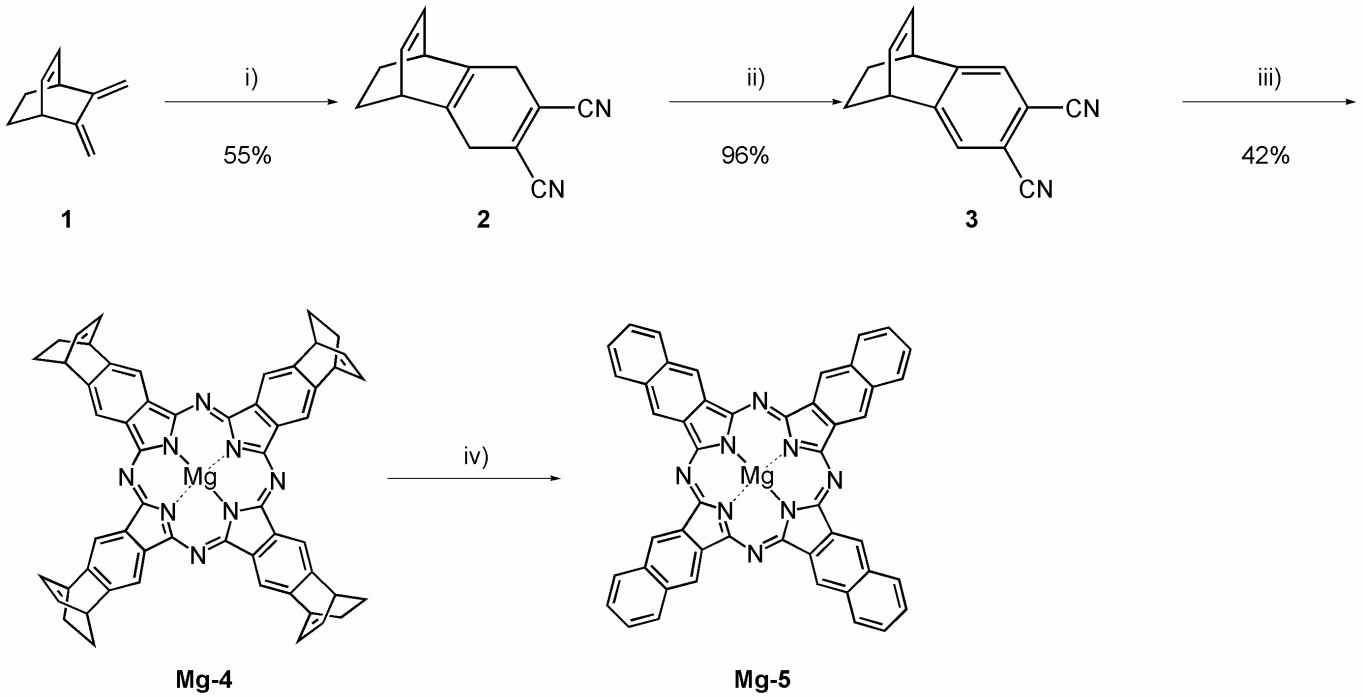
INTRODUCTION

Phthalocyanines (Pcs) and their homologues exhibit a remarkable range of optical and electronic properties that lend them to applications in electro photography, CD-Rs, sensors, optical limiters and photodynamic therapy.[1] As parent Pcs are generally insoluble in organic solvents, solubilizing groups such as alkyl or alkoxy groups are required to increase their solubility. However, these groups can not be removed after purification by column chromatography or recrystallization. Thus, it is extremely difficult to get pure samples of unsubstituted Pcs by the usual procedures of purification such as column chromatography. We have developed a simple solution of this problem by the introduction of thermally removal groups into porphyrins.[2] For example, soluble precursors of tetrabenzoporphyrin (TBP) or tetranaphthoporphyrin (TNP) are available by fusing BCOD rings into porphyrins, which are readily

purified by column chromatography. Heating these soluble precursors gives TBP and TNP in quantitative yields accompanying by eliminating four ethylene units. TBP and TNP are pure enough without further purification, if the precursors are pure. This method is useful not only as a synthetic method but also as a fabrication method of the electronic devices such as organic thin film transistors (OTFTs)[3] or solar cells.[4] In this paper we report the synthesis of Pcs fused with BCOD rings and its thermal conversion into naphthalocyanines (Ncs). This is the first report of the Nc pigment from its soluble precursor (dye), which may be useful as a method to get pure Ncs and for fabrication of electronic devices as demonstrated in the case of TBP in applications for OTFTs.[3]

RESULTS AND DISCUSSION

Synthesis of Mg-Pc fused with BCOD is shown in Scheme 1. Diels-Alder reaction of dicyanoacetylene with 5,6-dimethylenebicyclo[2.2.2]oct-2-ene (**1**) proceed at room temperature to give the adduct **2** in 55% yield. Compound **2** was oxidized to the corresponding phthalonitrile **3** by DDQ in 96% yield. Treatment of **3** with $Mg(OPr)_2$ in PrOH at 100 ºC overnight gives Mg salt of phthalocyanine (**Mg-4**) fused with BCOD in 42% yield. Purification of **Mg-4** was carried out by column chromatography on alumina with THF.



Reagents and conditions; i) dicyanoacetylene, dry CH_2Cl_2, rt, 12 h; ii) DDQ, dry 1,4-dioxane, 60 °C, 2 days iii) $Mg(OPr)_2$, dry PrOH, 100 °C, overnight; iv) 250 °C.

Scheme 1. Synthesis of Mg-Pc (**Mg-4**) fused with BCOD and Thermal Conversion into Mg-**5**

Thermogravimetric analysis (TGA) of **Mg-4** verified the expected retro Diels-Alder reaction (Figure 1). 20 % loss of the total mass, corresponding to a loss of four ethylene units and $2H_2O$, initiates at 200 ºC and is complete by 250 ºC. The retro Diels-Alder reaction was also monitored by MALDI TOF showing the expected mass loss upon heating the sample **Mg-4** (Figure 2). Elimination of ethylene units takes places stepwise under conditions of measurement of MALDI TOF MS. MALDI TOF MS shows one peak of **Mg-5** after heating **Mg-4** at 250 ºC for 20 min which suggests that clean retro Diels-Alder reaction takes place at 250 ºC to give pure **Mg-5**. The UV-Vis spectra of **Mg-4** and **Mg-5** in DMF are shown in Figure 3, which are in good agreement of those of Pcs and Ncs. As byproduct of this thermal conversion is only ethylene, **Mg-5** obtained from purified **Mg-4** is pure enough without further purification. This is the first success of preparing Ncs from a soluble precursor.

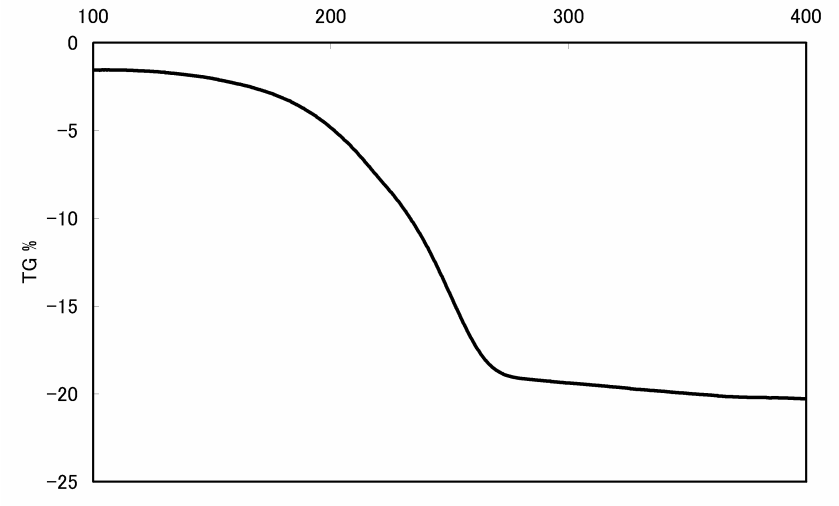


Figure 1. TG analysis of **Mg-4** heating at 10 ºC/min. The expected loss of the mass occurs between 200 and 250 ºC.

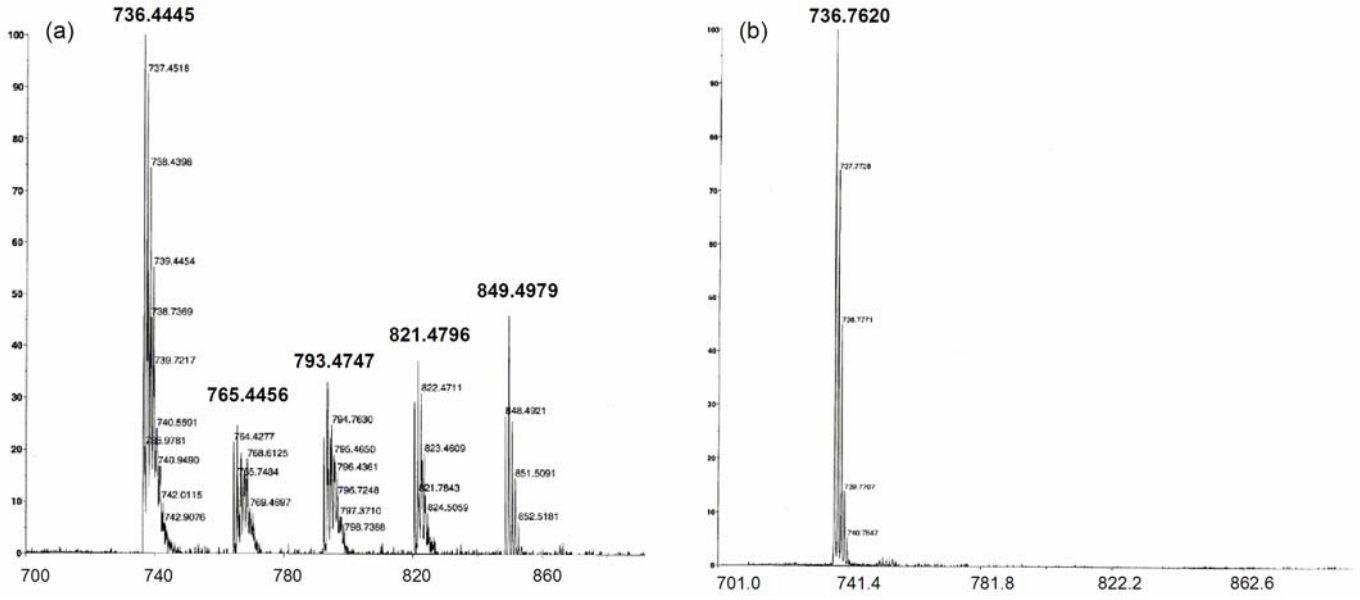


Figure 2. MALDI TOF MS of **Mg-4** (a) before heating (calc MW = 848.3226) and (b) after heating at 250 ºC for 20 min (calc MW = 736.1974)

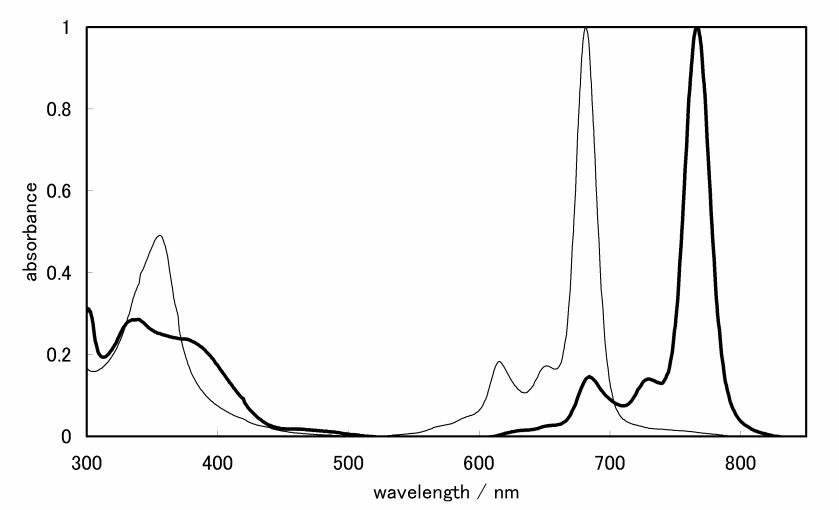
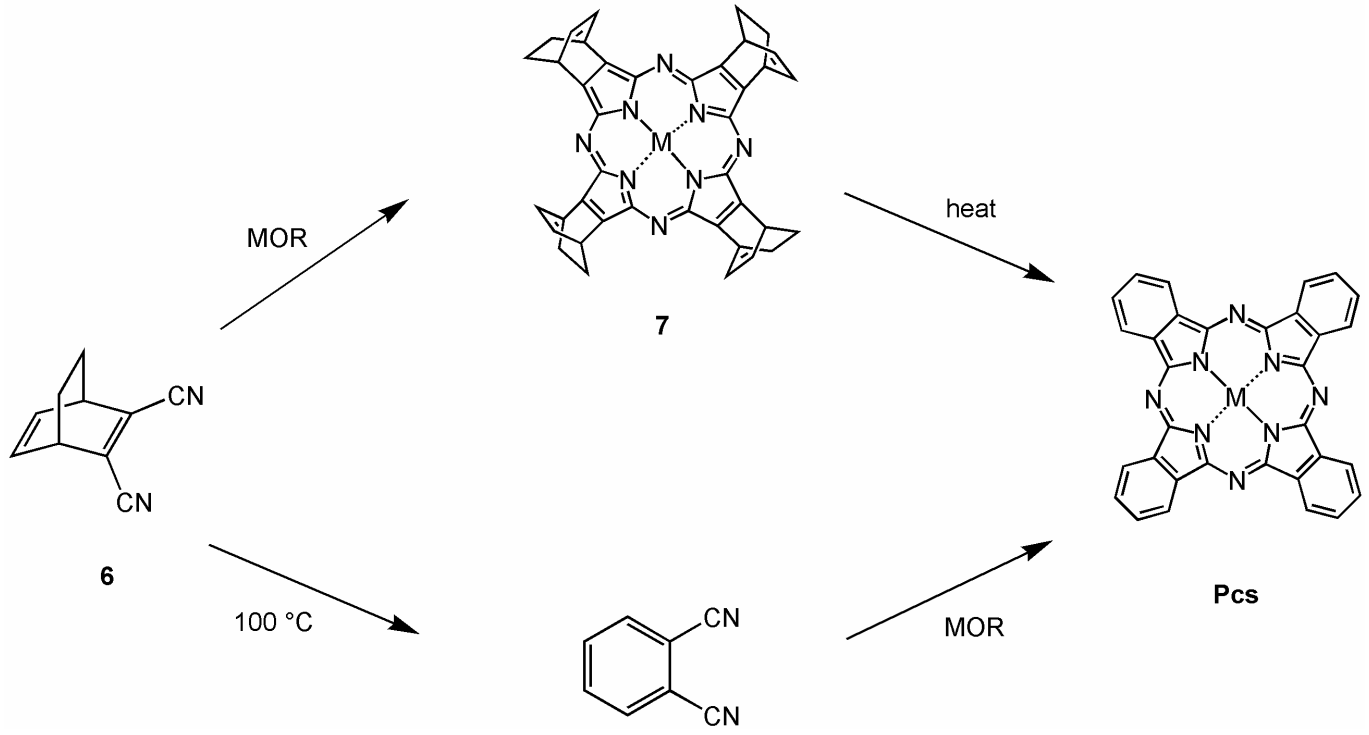


Figure 3. UV-Vis spectra of **Mg-4** (solid line) and **Mg-5** (bold line)



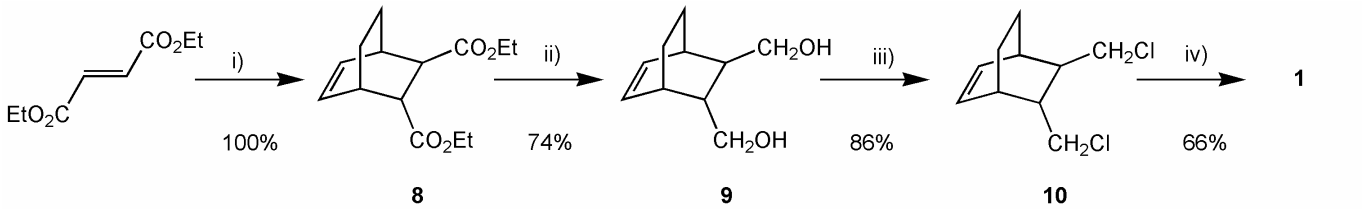
Scheme 2. Attempts to prepare soluble precursor **7** for Pcs.

The present method is not limited to the preparation of **Mg-4**, but it is applicable to metal free or other metal complexes of **4**. For example, heating of **3** with PrOLi in PrOH at reflux overnight gave metal free **4** in 25% yield. TGA and MALDI TOF of metal free **4** exhibits completely same behaviors as those of **Mg-4** to indicate the clean retro Diels-Alder reaction of **4**. Other metals can be introduced into **4** by the reaction of **4** with appropriate metal salts.[1] Application of this thermal conversion to a fabrication of solar cells or OTFTs using Ncs as semiconductors by a solution process is now under progress in our laboratory.

Next, we have extended the present strategy to prepare Pcs from soluble precursors as shown in Scheme 2. The Diels-Alder adduct **6** between dicyanoacetylene and 1,3-cyclohexadiene was treated with a base under various conditions to get tetraazaporphyrin **7** or its metal complexes. However, the retro Diels-Alder reaction of **6** takes place at 100 ºC to give phthalonitrile exclusively, which gives Pcs under cyclization conditions (PrOLi in PrOH or $Mg(OPr)_2$ in PrOH at 100 ºC). It was very difficult to get **7** from **6** without formation of Pcs. Cyclization of **6** at lower temperature or protection of the double bond in **6** is crucial to get **7** from **6**. Now we are trying to find such conditions, but we have not yet succeeded in preparing **7** from **6** or related compounds without formation of Pcs.

EXPERIMENTAL

General. Melting points were determined on a Yanaco micro melting point apparatus MP500D and are uncorrected. Mass spectra were measured on JEOL JMS-700 usually at 70 eV. MALDI TOF mass spectra were measured on an Applied Biosystems Voyager de Pro. UV-Vis spectra were measured on a JASCO V-570 spectrophotometer. ^{1}H NMR spectra (and ^{13}C NMR spectra) were recorded on JEOL GSX-270 at 270 MHz (67.5 MHz) and AL-400 at 400 MHz (100 MHz). Elemental analyses were performed at Integrated Center for Sciences, Ehime University. Dicyanoacetylene was prepared by dehydration of the corresponding amide with P_2O_5.[5] The requisite amide is commercially available, but it is very expensive. It can be prepared by the reaction of dimethyl acetylenedicarboxylate with NH_4OH.[5] Diene **1** was prepared according to the literature procedure as shown in Scheme 3.[6]



Reagents and conditions: i) 1,3-cyclohexadiene, 120 °C, 24 h; ii) $LiAlH_4$, dry THF, reflux, overnight; iii) $SOCl_2$, pyridine, 80 °C, 2h; iv) t-BuOK, dry THF, reflux, overnight.

Scheme 3. Synthesis of 5,6-dimethylenebicyclo[2.2.2]oct-2-ene (**1**)

5,8-Ethano-1,4,5,8-tetrahydronaphthalene-2,3-dicarbonitrile (2)

A solution of **1** (3.07 g, 23.2 mmol) in dry CH_2Cl_2 (20 mL) was poured into dicyanoacetylene (1.5 g, 20 mmol) at 0 ºC. The reaction mixture was stirred under N_2 atmosphere at rt for 12 h. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with $CHCl_3$ to give **2** as a white solid (2.24 g, 55%). mp 155 ºC (decomp); ^{1}H NMR ($CDCl_3$, 270MHz) δ 6.31 (m, 2H), 3.36 (m, 2H), 3.18 (s, 4H),1.28-1.35 (m, 4H); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 133.79, 131.01,

124.29, 115.59, 39.62, 30.77, 24.76; IR (KBr) ν_{max} 2225, 1425, 846, 692, 682 (CN) cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 208 (M^+, 7%), 180 (100), 153 (21), 140 (20); Anal. Calcd for $C_{14}H_{12}N_2$: C, 80.74; H, 5.81; N, 13.45. Found: C, 80.86; H, 5.98; N, 13.29.

5,8-Dihydro-5,8-ethanonaphthalene-2,3-dicarbonitrile (3)

To a solution of **2** (1.61 g, 7.75 mmol) in dry 1,4-dioxane (50 mL) was added DDQ (3.5 g, 15 mmol). The resulting mixture was stirred under N_2 atmosphere at 60 ºC for 2 days. The solvent was removed under a reduced pressure. The residue was dissolved in $CHCl_3$. The solution was washed with water and brine, and dried over anhydrous Na_2SO_4. After evaporation, the residue was purified by column chromatography on alumina with $CHCl_3$ to give **3** as a white solid (1.54 g, 96%). mp 129-131 ºC; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.57 (s, 2H), 6.52 (dd, 2H, *J* = 4.4, 2.9 Hz), 4.11 (m, 2H), 1.62-1.69 (m, 2H), 1.41-1.45 (m, 2H); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 150.39, 134.07, 127.22, 116.02, 112.57,40.12, 24.63; IR (KBr disk) ν_{max} 2229 (CN), 1477, 717 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 206 (M^+, 6%), 178 (100); Anal. Calcd for $C_{14}H_{10}N_2$: C, 81.53; H, 4.89; N, 13.58. Found: C, 81.46; H, 5.07; N, 13.43.

BCOD-fused phthalocyanine Mg-4

A mixture of magnesium (51.4 mg, 2.11 mmol) and a small amount of iodine in propanol (74 mL) was refluxed until magnesium was dissolved. After the solution was cooled to rt, **3** (800 mg, 3.88 mmol) was added to it. The resulting mixture was heated at 100 ºC overnight. The solvent was removed under reduced pressure. The residue was purified by column chromatography on alumina with THF and then washed with Et_2O to give **Mg-4** (381 mg, 42%). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 9.23 (m, 8H) 6.84 (m, 8H), 4.69 (m, 8H), 1.75-1.83 (m, 16H); MS (FAB) *m*/*z* (rel intensity) 1697 (2*M^++1, 8%), 849 (M^++1, 31), 763 (45), 737 (100); Anal. Calcd for $C_{56}H_{40}N_8Mg{\cdot}2H_2O$: C, 75.97; H, 5.01; N, 12.66. Found: C, 75.80; H, 4.91; N, 12.66.

Naphthalocyanine Mg-5

Mg-4 (9.3 mg 0.011 mmol) was heated in a grass tube under vacuum at 250 ºC for 20 min to give **Mg-5** (8.4 mg 0.011 mmol, 100%). MS (FAB) *m*/*z* (rel intensity) 737 (M^++1, 100%); Anal. Calcd for $C_{42}H_{24}MgN_8Mg{\cdot}3H_2O$: C, 72.87; H, 3.82; N, 14.16. Found: C, 73.17; H, 3.70; N, 14.07.

BCOD-fused phthalocyanine free base-4

A mixture of lithium (51.5 mg, 7.42 mmol) in butanol (8.0 mL) was refluxed until lithium was dissolved. After the solution was cooled to rt, **3** (350 mg, 1.68 mmol) was added to it. The resulting mixture was refluxed overnight. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with $CHCl_3$ and then recrystallized from hexane/$CHCl_3$ to give **Metal free-4** (87.4 mg, 25%). ^{1}H NMR (5% TFA/$CDCl_3$, 400 MHz) δ 9.17 (br, 8H), 6.83 (br, 8H), 4.62 (br, 8H), 1.75-1.94 (br, 16H); MS (MALDI TOF) *m*/*z* (rel intensity) 827 (M^++1), 799 (M^++1-C_2H_4), 770 (M^++1-2C_2H_4), 743 (M^++1-3C_2H_4), 715 (M^++1-4C_2H_4).

Attempt to prepare 7

Bicyclo[2.2.2]octa-2,5-diene-2,3-dicarbonitrile **6** was prepared by stirring a solution of dicyanoacetylene (1.74 g, 22.9 mmol) and 1,3-cyclohexadiene (2.5 mL, 26 mmol) in $CHCl_3$ (20 mL) at rt for 24 h. Removal of the solvent gave **6** (2.95 g, 83%). mp 101-102 ºC [lit.,[7] mp 105 ºC]; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 6.40 (dd, 2H, *J* = 4.4, 3.4), 4.04 (m, 2H), 1.54-1.58 (m, 4H); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ132.31, 131.86, 113.94, 41.13, 24.06; IR (KBr disk) ν_{max} 2221 (CN), 1585, 1342, 736, 686 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 156 (M^+, 8), 128 (100), 101 (10), 69 (14), 57 (13); Anal. Calcd for $C_{10}H_8N_2$: C, 76.90; H, 5.16; N, 17.94. Found: C, 76.85; H, 5.26; N, 17.61.

Treatment of **6** with $Mg(OPr)_2$ in PrOH or HMDS and $Zn(OAc)_2$ in DMF[8] at 100 ºC gave MgPc or ZnPc, respectively. The reaction using LiOR or DBU as a base at lower temperature (80 ºC) resulted in recovery of **6**.

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