various solvents such as diethylether, tetrahydrofuran, and acetonitrile. Of them, acetonitrile gives the highest yields.

Based on the known facts and reports by others[17-18], a possible mechanism for carbamate formation is proposed in Scheme 1. In this reaction, two equivalents of amine per alkyne are required in order to get the better yields in 1,1-dimethyl-2-oxopropyl-N,N-dialkylcarbamates. This is consistent with the in situ formation of ammonium carbamates, according to proposed mechanism of two possible reaction paths can account for the formation of 1,1-dimethyl-2-oxopropyl-N,N-dialkylcarbamates. (i) The intermediate (A) has been isolated from the reaction of 2-methyl-3-butyn-2-ol with CO_2 in the presence of NEt_3 and $CoCp_2$ at 80°C, 50 atm, 5 hours.[17] Addition of a secondary amine to the carbonyl carbon of the carbonate (A) would then give the intermediate (B), the tautomeric form of (E).[18] (ii) First, $CeCl_2^+$ attacked terminal acetylene carbon and then carbamate ion [R_2NCOO^-] was added to the adjacent carbon. The transesterification of (C) into (D) would normally lead to (B), the precursor of (E).

The typical procedure of synthesis of 1,1-dimethyl-2-oxopropyl-N,N-dialkyl carbamates using lanthanide metal chloride as a catalyst; under the stream of nitrogen, secondary amine (20 mmol), 2-methyl-3-butyn-2-ol (10 mmol), acetonitrile (10 ml), and catalyst (0.2 mmol) were added with a magnetic stirring bar in a glass liner set in the reactor. After purging with CO_2 a few times, the reactor was pressurized to the desired pressure (P_{CO_2} = 20 atm). The system was heated to 160°C in 30 min in a heating mantle and thermostated at this temperature with stirring for 8 hours. This reaction was terminated by rapid cooling and reactor was discharged. At the bottom of the resulting clear dark brown solution, lanthanide chloride residue was precipitated and it was discarded. The reaction mixture was reduced in volume to minimum amount. The reduced reaction mixture was chromatographed to give 1,1-dimethyl-2-oxopropyl-N,N-dialkyl carbamates as a pure product. The products were identified by IR, ^{1}H-NMR, and mass spectra, respectively. Spectral data of carbamates are as follows:

1,1-Dimethyl-2-oxopropyl-N,N-tetramethylene carbamate. IR(neat) 1700 cm^{-1} (C=O), 1690 cm^{-1} (NCOO), ^{1}H-NMR (CDCl$_3$) δ 1.42 (s, 2CH$_3$), 1.90 (m, 2CH$_2$), 2.09 (s, CH$_3$CO), 3.38 (m, N(CH$_2$)$_2$): MS (*m/e*) 199 (rel. int., 12, M$^+$), 98 (100), 70 (12), 43 (14).

1,1-Dimethyl-2-oxopropyl-N,N-pentamethylene carbamate. IR (neat) 1722 cm^{-1} (C=O), 1688 cm^{-1} (NCOO); ^{1}H-NMR (CDCl$_3$) δ 1.31 (s, 2CH$_3$), 1.60 (m, 2CH$_2$), 2.01 (s, CH$_3$CO), 3.40 (m, N(CH$_2$)$_2$); MS (*m/e*) 214 (rel. int., 3, M$^+$ + 1), 112 (45), 70 (100), 43 (30).

1,1-Dimethyl-2-oxopropyl-N,N-hexamethylene carbamate. IR (neat) 1720 cm^{-1} (C=O), 1685 cm^{-1} (NCOO); ^{1}H-NMR (CDCl$_3$) δ 1.42 (s, 2CH$_3$), 1.62 (m, 4CH$_2$), 2.02 (s, CH$_3$CO), 3.40 (m, N(CH$_2$)$_2$); MS (*m/e*) 228 (rel. int., 2, M$^+$ + 1), 126 (100), 98 (19), 43 (21).

1,1-Dimethyl-2-oxopropyl-N,N-(oxydiethyl)carbamate. IR (neat) 1726 cm^{-1} (C=O), 1700 cm^{-1} (NCOO); ^{1}H-NMR (CDCl$_3$) δ 1.40 (s, 2CH$_3$), 2.03 (s, CH$_3$CO), 3.46 (m, N(CH$_2$)), 3.55 (m, 2CH$_2$); MS (*m/e*) 216 (rel. int., 1, M$^+$ + 1), 114 (100), 43 (28).

1,1-Dimethyl-2-oxopropyl-N,N-dimethylcarbamate. IR (neat) 1720 cm^{-1} (C=O), 1690 cm^{-1} (NCOO); ^{1}H-

NMR (CDCl$_3$) δ 1.61 (t, 2CH$_3$), 1.46 (s, 2CH$_3$), 2.14 (s, CH$_3$CO), 3.31 (q, 2CH$_2$), MS (*m/e*), 202 (M$^+$ + 1).

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Syntheses of 5-Pentadecyl-10,15,20-Triphenylporphyrin, and Its Zn(II) and Mn(III) Complexes

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Solar energy storage systems, which mimic the plant photosynthesis system, are studied extensively[1,2]. We are in-
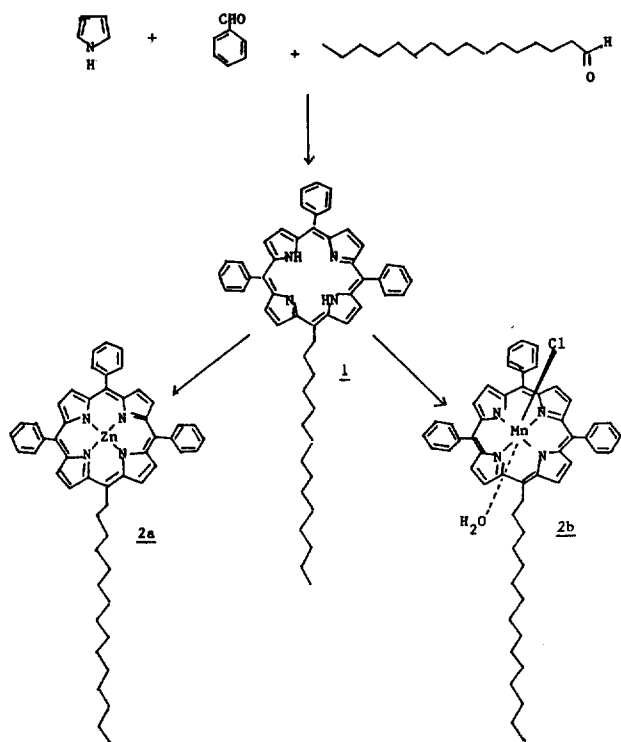
Figure 1. Synthetic scheme of 5-pentadecyl-10,15,20-triphenyl-porphyrin Zn and Mn(III) complex.

terested particularly in the vesicle[3,4] or microemulsion[5] system to retard or prevent the back reaction of redox reaction of artificial photosynthesis. In order to anchor a sensitizr and/or an electron donor into the vesicle or microemulsion, a sensitizer and/or an electron donor with a long hydrocarbon chain for the study of solar energy storage needs to be synthesized. Although several unsymmetric substituted tetra-phenylporphyrins have been synthesized[6-9], a few mono-al-kyloxy(long hydrocarbon chain)-triphenylporphyrins have been synthesized[9,10]. Here we report the syntheses of 5-pentadecyl-10,15,20-triphenylporphyrin(1) and its Zn(II) (2a) and Mn(III) chloride(2b) complexes (see Figure 1). The synthesis of manganes porphyrin is meaningful in solar energy storage system because it has long been known that Mn is required for O_2 evolution in the O_2-evolving complex of photosystem II[11].

To synthesize 5-pentadecyl-10,15,20-triphenylporphyrin (1), hexadecanal(3.66g, 15.2 mmole), pyrrole(4.23 ml, 60 mmole) and benzaldehyde(4.64 ml, 46 mmole) in propionic acid(300 ml) was heated at reflux for 2 hrs. The reaction mixture was dried and eluted on neutral alumina column (70-230 mesh) with methylene chloride. The red prophyrin band was collected and dried by evaporation(0.91g). The solid mixture was developed on TLC plate(silicagel 60 G_F) to give four bands(R_f= 0.89. 0.84, 0.77, 0.69). The compounds with R_f= 0.89(yield 26 mg) and R_f= 0.84(233 mg) were not identified. The band of R_f= 0.77 was 5-pentadecyl-10, 15, 20-triphenylporphyrin(1, 343 mg, 0.46 mmole, 3%, mp 62-65°C). The visible absorption of 1 appears at 420, 515, 550, 593 and 650 nm. The ^{1}H-NMR spectrum of 1 shows peaks at (δ from TMS, CDCl$_3$) 0.88(t, 3H, CH$_3$), 1.25(s, 28H, CH$_2$), 7.6-8.4(m, 15H, phenyl), 8.7-8.9(6H, pyr-

role-β-proton), 9.3-9.5(2H, pyrrole-β-proton). The elemental analysis data of 1(C$_{53}$H$_{56}$N$_4$) is consistent with the theoretical data(Theoretical: C; 84.90, H; 7.53, N; 7.49%, Found: C; 84.73, H; 7.56, N; 7.28%). The band with R_f= 0.69 was tetraphenylporphyrin (307 mg). The porphyrin 1(100 mg, 0.13 mmole) was metallized by heating it with zinc acetate (400 mg) in acetic acid (50 ml) to boiling for 2 hrs[12,13]. The zinc porphyrin(2a) was purifid on TLC(silicagel 60 G_F, methylene chloride:cyclohexane = 1:3). The yield of zinc porphyrin(2a) was 99 mg (C$_{53}$H$_{54}$N$_4$Zn, 0.12 mmole, 94%, mp 72-75°C). The visible spectrum of 2a showed λ_{max} at 423, 551, 589 nm. The absorption band of the free base porphyrin(1) at 650 nm is absent in the absorption spectrum of the zinc porphyrin(2a). The absorption bands of 2a at 551 and 589 nm are characteristic for zinc porphyrin compounds[14]. The elemental analysis data of 2a is consistent with theoretical one(Theoretical: C; 78.36, H; 6.69, N; 6.89%, Found: C; 78.63, H; 6.68, N; 6.87%).

(5-Pentadecyl-10,15,20-triphenylporphyrinato) manganese(III) chloride(2a) was synthesized by heating the mixture of the free base porphyrin(1, 100 mg, 0.13 mmole) and manganese acetate (210 mg) in dimethylformamide (20 ml) to boiling for 30 min[15]. Reaction was followed by disappearance of visible absorption of the ligand at 650 nm. The cold NaCl solution was added to the reaction mixture. The greenish solid was filtered, washed with 20 ml of water, and dried. The solid was dissolved in 20 ml of methanol and filtered. When 6 M HCl solution was added to the filtrate, the greenish solid appeared. The solid was filtered and dried(88.2 mg, 0.11 mmole, mp. 175-179°C). The visible absorption spectrum showed λ_{max} at 374, 479, 589 and 625 nm. The elemental analysis data of 2b(C$_{53}$H$_{54}$N$_4$MnCl) is consistent with the theoretical data(Theoretical: C; 74.4, H; 6.30, N; 6.50, Found: C; 74.1, H; 6.20, N; 6.40).

We are currently studying theses compounds(2a, 2b) as sensitizers and electron donors in the vesicle system of solar energy storage system.

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