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Supplementary Material Available: ORTEP structures of [Ni(NS_3^{iPr})Me](BPh_4) and tables of crystallographic data, intensity collection and structure refinement parameters, positional and thermal parameters, bond distances and angles, and calculated hydrogen atom positions for the six compounds in Table I (40 pages); calculated and observed structure factors (163 pages). Ordering information is given on any current masthead page.

Novel Visible-Light-Driven Catalytic CO_2 Fixation. Synthesis of Malonic Acid Derivatives from CO_2, α,β-Unsaturated Ester or Nitrile, and Diethylzinc Catalyzed by Aluminum Porphyrins

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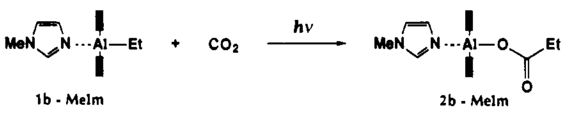
Abstract: Reaction of carbon dioxide, methacrylic esters or methacrylonitrile, and (5,10,15,20-tetraphenylporphinato)aluminum methyl or ethyl took place upon irradiation with Xenon arc light ($\lambda > 420$ nm), affording the corresponding (porphinato)aluminum malonate species under atmospheric pressure at ambient temperature. When diethylzinc was present in the above reaction systems, (porphinato)aluminum ethyl was regenerated by the exchange reaction of the malonate species with diethylzinc, and malonic acid derivatives were catalytically formed with respect to aluminum porphyrins. Detailed investigations revealed that all the elementary steps involved in the catalytic cycle were accelerated under irradiation.

Introduction

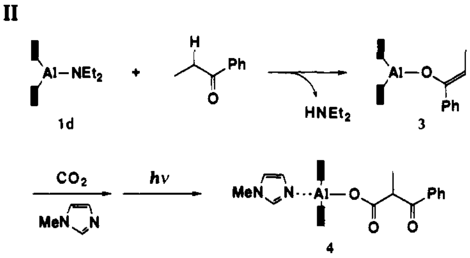
Biological photosynthesis, the fixation of carbon dioxide by green plants and some microorganisms using solar energy, is the most important chemical process running on Earth. The concentration of carbon dioxide in the atmosphere has been rapidly increasing due to the accelerating consumption of fossil fuels, and it is anticipated that the accumulation of carbon dioxide in the atmosphere should cause serious environmental problems. Artificial fixation of carbon dioxide is of much interest from these viewpoints.[1]

Carbon dioxide is the ultimate oxidation product of organic compounds and is inert under ordinary conditions. Therefore, activation of carbon dioxide is a prerequisite for developing artificial fixation of carbon dioxide. Because of the chemical inertness, only a few industrial processes have been developed using carbon dioxide as a raw material. The representative examples include production of urea, salicyclic acid, and terephthalic acid. However, recent progress in fundamental research has provided a number of potentially useful reactions of carbon dioxide:[1] electro- or photochemical reduction of carbon dioxide, reaction of carbon dioxide with unsaturated hydrocarbons catalyzed by transition-metal complexes, and biomimetic fixation of carbon dioxide. In particular, photochemical fixation of carbon dioxide is not only of great interest in relation to biological photosynthesis but also of potential importance for artificial recycling of carbon dioxide using solar energy without sacrificing fossil energy. Examples of photochemical fixation of carbon dioxide so far reported include photoreduction of carbon dioxide into formic acid,[2,3] acetic acid,[2] formate,[4] and methane.[5]

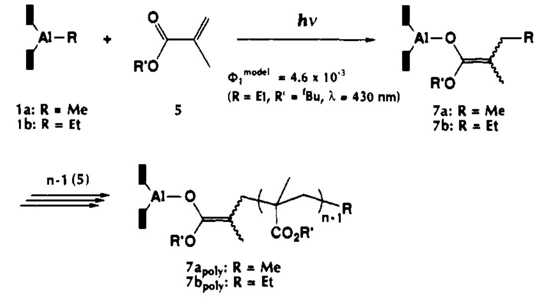
Scheme I



Scheme II



Scheme III



Photochemistry of metalloporphyrins is of interest in connection with the role of chlorophyll in photosynthesis. We have investigated the photochemistry of aluminum porphyrins **1** and found that the nucleophilicity of the axial ligands of some aluminum porphyrins can be enhanced upon irradiation with visible light.[6-10]

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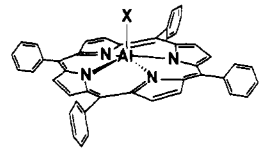

(TPP)AlX

1a: X = Me
1b: X = Et
1c: X = Cl
1d: X = NEt_2

This interesting finding has been successfully extended to the development of novel light-induced fixations of carbon dioxide with aluminum porphyrins.[11] For example, ethylaluminum porphyrin ((TPP)AlEt, **1b**) does not react with carbon dioxide by itself, while insertion of carbon dioxide into its aluminum–ethyl bond takes place in the presence of 1-methylimidazole (MeIm) under irradiation with visible light, producing the corresponding (porphinato)aluminum carboxylate (**2b**-MeIm) (Scheme I).[8] (Porphinato)aluminum enolates **3**, which are generated by the action of (porphinato)aluminum diethylamide **1d** to aromatic ketones,[12] also react with carbon dioxide in the presence of 1-methylimidazole under irradiation with visible light, affording the corresponding β-ketocarboxylate complexes (**4**) in excellent yields (Scheme II).[10] This reaction is quite interesting in relation to biological assimilation of carbon dioxide, where pyruvate is carboxylated into oxaloacetate via phosphoenolpyruvate as reactive intermediate.

Recently, we have succeeded in photochemical generation of ester enolate species **7** and $\mathbf{7}_{poly}$ by 1,4-addition of alkylaluminum porphyrin **1** (X = alkyl) to alkyl methacrylates **5** under irradiation with visible light (Scheme III).[9] In the present study, we have investigated the reaction of the ester enolate species with carbon dioxide, in order to develop a novel one-pot photosynthetic route to malonic acid derivatives directly from carbon dioxide and methacrylic esters using aluminum porphyrins as photocatalysts.

Experimental Section

Materials. 5,10,15,20-Tetraphenylporphine ($TPPH_2$) was prepared by the reaction between pyrrole and benzaldehyde in refluxing propionic acid, and recrystallized from $CHCl_3$/MeOH.[13]

Trimethylaluminum (Me_3Al), triethylaluminum (Et_3Al), diethylaluminum chloride (Et_2AlCl), and diethylzinc (Et_2Zn) were fractionally distilled under reduced pressure in a nitrogen atmosphere. *tert*-Butyl methacrylate (**5** (R′ = ^{t}Bu)) and methyl methacrylate (**5** (R′ = Me)) were distilled under reduced pressure in a nitrogen atmosphere over CaH_2. Methacrylonitrile (**6**) was distilled in a nitrogen atmosphere over P_2O_5. Benzene, benzene-d_6, *n*-octane, and tetrahydrofuran were refluxed over sodium wire and distilled in a nitrogen atmosphere. Dichloromethane, shaken successively with concentrated H_2SO_4, water, aqueous $NaHCO_3$, and water, was dried over $CaCl_2$, and distilled after refluxing over CaH_2 in a nitrogen atmosphere. Carbon dioxide was passed through a column packed with silica gel, molecular sieve 4A, and P_2O_5 prior to use.

(5,10,15,20-Tetraphenylporphinato)aluminum methyl ((TPP)AlMe, **1a**)[14] was prepared by the reaction of $TPPH_2$ (0.615 g, 1 mmol) and Me_3Al (0.12 mL, 1.25 mmol) in benzene or dichloromethane (50 mL) at room temperature under nitrogen.[7,8] After 2 h, the reaction mixture was evaporated to dryness to remove excess Me_3Al. (5,10,15,20-Tetraphenylporphinato)aluminum ethyl ((TPP)AlEt, **1b**)[15] was prepared in a similar way by the reaction of $TPPH_2$ (1 mmol) and Et_3Al (0.14 mL, 1 mmol).[8] (5,10,15,20-Tetraphenylporphinato)aluminum chloride ((TPP)AlCl, **1c**) was similarly prepared by the reaction of $TPPH_2$ (1 mmol) and Et_2AlCl (0.15 mL, 1.1 mmol).[16] (5,10,15,20-Tetraphenylporphinato)aluminum 2-methyl-2-*n*-propylpropanedioate mono-*tert*-butyl ester (**8b** (R′ = ^{t}Bu))[17] was prepared by the reaction of (TPP)AlMe (**1a**) with 2 equiv of 2-methyl-2-*n*-propylpropanedioic acid mono-*tert*-butyl ester (**10b** (R′ = ^{t}Bu)) in benzene at room temperature for 12 h under nitrogen, followed by evaporation to dryness under reduced pressure with heating to remove excess carboxylic acid (Scheme V).[18] For the preparation of $\mathbf{7a}_{poly}$ (R′ = ^{t}Bu),[19] *tert*-butyl methacrylate (**5** (R′ = ^{t}Bu)) (0.08 mL, 0.5 mmol) was added to a benzene-d_6 solution (5 mL) of (TPP)AlMe (**1a**) (0.1 mmol) under nitrogen, and the mixture was illuminated at 30 °C for 1 week with a 300-W Xenon arc lamp through a glass filter to cut out light with the wavelength shorter than 420 nm (Scheme III).[9]

Procedures. Reaction of CO_2, *tert*-Butyl Methacrylate (5 (R′ = ^{t}Bu)), and (TPP)AlMe (1a) (Scheme IV). Into a 100-mL round-bottom flask equipped with a three-way stopcock, containing a benzene solution (50 mL) of **1a** (1 mmol) and a Teflon-coated stirring bar under dry nitrogen, was added **5** (R′ = ^{t}Bu) (0.81 mL, 5 mmol) by means of a hypodermic syringe, followed by bubbling carbon dioxide under atmospheric pressure for 1 min. The flask was put in a water bath thermostated at 30 °C, and exposed to a 300-W Xenon arc light for 3 h from the distance of 30 cm through a glass filter to cut out light with the wavelength shorter than 420 nm and another filter to cut out heat. An aliquot of the reaction mixture (~0.5 mL) was taken out by a syringe in a nitrogen atmosphere and evaporated under reduced pressure, and then the residue was subjected to ^1H NMR analysis. The reaction mixture was poured into MeOH/aqueous HCl (5%) (30 mL), to which aqueous HCl (1 N) was further added after stirring for 10 min, followed by extraction with ether. The ether extracts combined were shaken with aqueous $NaHCO_3$, and then the water extracts were combined, washed with ether, and slightly acidified with concentrated aqueous HCl. The organic phase separated was extracted with ether, and the ether extracts combined were washed with saturated aqueous NaCl, dried over $MgSO_4$, and evaporated under reduced pressure at room temperature to leave a colorless liquid (0.085 g), which was identified to be 2-ethyl-2-methylpropanedioic acid mono-*tert*-butyl ester (**10a** (R′ = ^{t}Bu))[20] (42% yield). To an aliquot of **10a** (R′ = ^{t}Bu) dissolved in benzene/MeOH (7/2 in v/v) was added a large excess of (trimethylsilyl)diazomethane ($(CH_3)_3SiCHN_2$; 10% in hexane, Tokyo Kasei),[21] and the mixture was stirred for 30 min at room temperature, followed by evaporation under reduced pressure at room temperature to leave 2-ethyl-2-methylpropanedioic acid *tert*-butyl methyl ester (**12a** (R′ = ^{t}Bu)).[22]

Reaction of CO_2, *tert*-Butyl Methacrylate (5 (R′ = ^{t}Bu)), and (TPP)AlEt (1b) (Scheme IV). Into a 10-mL round-bottom flask equipped with a three-way stopcock, containing a benzene-d_6 solution (1 mL) of a mixture of **1b** (0.03 mmol) and **5** (R′ = ^{t}Bu) (0.15 mmol), and a stirring bar under dry nitrogen, was bubbled carbon dioxide under atmospheric pressure for 0.5 min, and the mixture was illuminated similarly to the above at 35 °C for 67 h.

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(14) ^1H NMR for **1a** (C_6D_6): δ 9.35 (s, pyrrole β), 8.28 (d, phenyl ortho), 7.70 (m, phenyl meta, para), −5.79 (s, CH_3).

(15) ^1H NMR for **1b** (C_6D_6): δ 9.34 (s, pyrrole β), 8.30 (d, phenyl ortho), 7.68 (m, phenyl meta, para), −2.57 (t, $CH_2C\mathit{H}_3$), −5.36 (q, $C\mathit{H}_2CH_3$). UV–vis (benzene, under N_2): 375, 438 (Soret), 570 nm.

(16) (a) Aida, T.; Inoue, S. *Macromolecules* **1981**, *14*, 1166. (b) Sugimoto, H.; Aida, T.; Inoue, S. *Macromolecules* **1990**, *23*, 2869.

(17) ^1H NMR for **8b** (R′ = ^{t}Bu) (C_6D_6): δ 9.36 (s, pyrrole β), 8.50 (br, phenyl ortho), 7.71 (m, phenyl meta, para), 0.57 (s, $C(CH_3)_3$), 0.47, (t, $C\mathit{H}_3CH_2CH_2$), 0.3 and −0.2 (m, $CH_3CH_2C\mathit{H}_2$), 0.1 and −0.45 (m, $CH_3C\mathit{H}_2CH_2$), −0.16 (s, CH_3CCO). UV–vis (benzene, under N_2): 416 (Soret), 547, 635 nm.

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(19) ^1H NMR for $\mathbf{7a}_{poly}$ (R′ = ^{t}Bu) (C_6D_6): δ 9.35 (s, pyrrole β), 8.45 (br, phenyl ortho), 7.71 (br s, phenyl meta, para), 1.64 (s, $CO_2C(CH_3)_3$), −0.33 (s, $=COC(CH_3)_3$), −1.06 and −1.11 (s, $=CCH_3$). The average number of repeating units (*n*) of $\mathbf{7a}_{poly}$ (R′ = ^{t}Bu), as estimated from the relative intensity of the signals at δ 1.64 and −0.33 ppm, was 4. UV–vis (benzene, under N_2): 416 (Soret), 547, 634 nm.

(20) ^1H NMR for **10a** (R′ = ^{t}Bu) ($CDCl_3$): δ 1.90 (q, $C\mathit{H}_2CH_3$), 1.47 (s, $C(CH_3)_3$), 1.40 (s, CH_3CCO), 0.91 (t, $CH_2C\mathit{H}_3$). ^{13}C NMR ($CDCl_3$): δ 178.3 (CO_2H), 171.9 ($\mathit{C}O_2C(CH_3)_3$), 82.1 ($\mathit{C}(CH_3)_3$), 54.7 ($\mathit{C}CO$), 29.2 ($\mathit{C}H_3CCO$), 27.8 ($C(\mathit{C}H_3)_3$), 19.7 ($\mathit{C}H_2CH_3$), 8.8 ($CH_2\mathit{C}H_3$).

(21) Hashimoto, N.; Aoyama, T.; Shioiri, T. *Chem. Pharm. Bull.* **1981**, *30*, 1921.

(22) ^1H NMR for **12a** (R′ = ^{t}Bu) (in $CDCl_3$): δ 3.70 (s, OCH_3), 1.86 (q, $C\mathit{H}_2CH_3$), 1.43 ($C(CH_3)_3$), 1.34 (s, CH_3CCO), 0.86 (t, $CH_2C\mathit{H}_3$). ^{13}C NMR ($CDCl_3$): δ 173.4 ($\mathit{C}O_2CH_3$), 171.5 ($\mathit{C}O_2C(CH_3)_3$), 81.3 ($\mathit{C}(CH_3)_3$), 54.8 ($\mathit{C}CO$), 52.2 (OCH_3), 29.0 ($\mathit{C}H_3CCO$), 27.8 ($C(\mathit{C}H_3)_3$), 19.3 ($CH_3\mathit{C}H_2$), 8.8 ($\mathit{C}H_3CH_2$).

Reaction of CO_2, Methyl Methacrylate (5 (R′ = Me)), and (TPP)-AlMe (1a) (Scheme IV). The reaction was carried out by using 2 mmol (0.21 mL) of **5** (R′ = Me) under otherwise the same conditions as for the reaction with *tert*-butyl methacrylate.

Reaction of CO_2, Methacrylonitrile (6), and (TPP)AlMe (1a) (Scheme IV). The reaction was carried out by using 2 mmol (0.16 mL) of **6** under otherwise the same conditions as for the reaction with *tert*-butyl methacrylate. A colorless liquid, identified to be 2-cyano-2-methylbutanoic acid (**11a**),[23] was isolated in 53% yield. **11a** was treated with a large excess of $(CH_3)_3SiCHN_2$/MeOH, giving 2-cyano-3-methylbutanoic acid methyl ester (**13a**).[24]

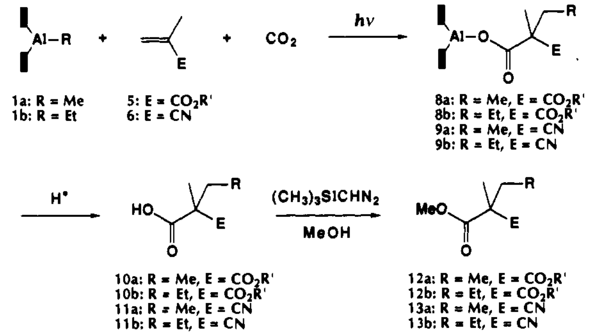
Reaction of CO_2, *tert*-Butyl Methacrylate (5 (R′ = ^{t}Bu)), and Diethylzinc Catalyzed by (TPP)AlEt (1b) (Scheme VIII). Into a 50-mL round-bottom flask equipped with a three-way stopcock, containing a benzene solution (19.5 mL) of **5** (R′ = ^{t}Bu) (0.16 mL, 1 mmol), *n*-octane (0.08 mL, 0.5 mmol; a standard for GC), and a stirring bar, was bubbled carbon dioxide for 1 min under atmospheric pressure, and then a benzene solution (0.5 mL) of **1b** (0.01 mmol) and diethylzinc (0.10 mL, 1 mmol) were added successively. A balloon (ca. 3000 mL) filled with dry carbon dioxide (ca. 1 atm) and a rubber septum were fitted through the three-way stopcock, and the reaction mixture was exposed to a 300-W Xenon arc light (λ > 420 nm) at 30 °C. An aliquot of the reaction mixture, periodically taken out by a syringe through the rubber septum, was poured into MeOH, and subjected to GC analysis to determine the conversion of **5** (R′ = ^{t}Bu). After **5** (R′ = ^{t}Bu) was almost consumed, the reaction mixture was poured into MeOH, to which concentrated aqueous HCl and naphthalene (0.0641 g, 0.5 mmol; a standard for GC) were then added. After stirring for 10 min, aqueous HCl (1 N) was again added to the solution, the mixture was shaken with ether, and the ether extracts combined were dried over $MgSO_4$. An aliquot of the ether solution was evaporated under reduced pressure at room temperature to leave a green-purple liquid, which was dissolved in benzene/MeOH (7/2 in v/v), treated with a large excess of trimethylsilyldiazomethane, and subjected to GC analysis. The residual ether solution was shaken with aqueous $NaHCO_3$, and the water extracts combined were washed with ether, and slightly acidified with concentrated aqueous HCl. The organic phase separated was extracted with ether, and the ether extracts combined were washed with saturated aqueous NaCl, dried over $MgSO_4$, and evaporated under reduced pressure at room temperature. The nonvolatile residue was subjected to bulb-to-bulb distillation (160 °C (1 mmHg)) to give **10b** (R′ = ^{t}Bu)[25] as a colorless liquid.

Reaction of CO_2, Methyl Methacrylate (5 (R′ = Me)), and Diethylzinc Catalyzed by (TPP)AlEt (1b) (Scheme VIII). The reaction was carried out by using 1 mmol (0.11 mL) of **5** (R′ = Me) under otherwise the same conditions as for the reaction with *tert*-butyl methacrylate, and **10b** (R′ = Me)[26] was obtained, which was methylated with $(CH_3)_3SiCHN_2$/MeOH to give **12b** (R′ = Me)[27] in 93% yield.

Reaction of CO_2, Methacrylonitrile (6), and Diethylzinc Catalyzed by (TPP)AlEt (1b). The reaction was carried out by using 1 mmol (0.079 mL) of **6** under otherwise the same conditions as for the reaction with *tert*-butyl methacrylate, and **11b**[28] was obtained, which was treated with $(CH_3)_3SiCHN_2$/MeOH to give **13b**[29] in 53% yield.

Reaction of CO_2 with $\mathbf{7a}_{\text{poly}}$ (R′ = ^{t}Bu) (Scheme VII). To a dry NMR tube (Φ = 5 mm) purged with nitrogen was introduced a benzene-d_6 solution (0.6 mL) of $\mathbf{7a}_{\text{poly}}$ (R′ = ^{t}Bu, *n* = 4)[19] (0.006 mmol) by a hypodermic syringe in a nitrogen stream. After the solution was frozen in a liquid nitrogen bath, a slight excess of carbon dioxide was introduced, and the tube was sealed. The sealed tube was wrapped in aluminum foil and put in a water bath thermostated at 30 °C for the first 1.5 h, and then exposed to a 300-W Xenon arc light (λ > 420 nm).

Scheme IV



Reaction of (TPP)AlCl (1c) with Diethylzinc (Scheme IX). To a dry NMR tube (Φ = 5 mm) purged with nitrogen were successively introduced benzene-d_6 solutions of **1c** (0.025 mmol, 0.5 mL) and diethylzinc (0.125 mmol, 0.125 mL) by hypodermic syringes in a nitrogen stream. Then, the tube was sealed and wrapped in aluminum foil, and the content was allowed to stand at 30 °C in the dark for 1 h before ^1H NMR analysis.

Reaction of Malonate Complex 8b (R′ = ^{t}Bu) with Diethylzinc (Scheme X). To a dry NMR tube (Φ = 5 mm) containing a benzene-d_6 solution (0.5 mL) of **8b** (R′ = ^{t}Bu) (0.005 mmol) under nitrogen was added a benzene-d_6 solution (0.1 mL) of diethylzinc (0.1 mmol) by a syringe in a nitrogen stream. The NMR tube was sealed and wrapped in aluminum foil, and the content was allowed to stand in the dark in a water bath thermostated at 30 °C for 20 h before ^1H NMR analysis. Then, the tube was exposed to a 300-W Xenon arc light (λ > 420 nm) at 30 °C for 20 min before the next ^1H NMR analysis.

Determination of Quantum Yields. General Procedures. The reactions were carried out in quartz cells (10 cm² × 1 cm), which were exposed to a 300-W Xenon arc light (ILC Technology Model LX-300F) placed apart from the cells by 25 cm, where the light was monochromatized with a band-pass filter (λ = 420 or 430 nm, bandwidth 10 nm) attached to a glass filter to cut out light with the wavelength shorter than 330 nm and a Pyrex round cell (optical path length 1 cm) filled with water to cut out heat. The light intensity transmitted through the cell (*I*) was constantly monitored by an optical power meter (Anritsu Model ML96B optical power meter) directly attached to the back side of the cell. As a reference, the transmitted light intensity through the solvent alone (I_{ref}) was similarly monitored, and the number of photons absorbed by aluminum porphyrins was calculated from the integrated value of $I_{\text{ref}} - I$ with time, the detection area of the power meter, and the energy of one photon.

(i) For the Reaction of (TPP)AlEt (1b) and *tert*-Butyl Methacrylate (5 (R′ = ^{t}Bu)) (Scheme III). Into a benzene-d_6 solution (5 mL) of **1b** (0.2 mmol) was added **5** (R′ = ^{t}Bu) (0.32 mL, 2 mmol) in the dark under dry nitrogen, and the reaction mixture was irradiated with a monochromatized light at 430 nm for 15 h at room temperature.

(ii) For the Reaction of CO_2 and (5,10,15,20-Tetraphenylporphinato)aluminum Enolate $\mathbf{7a}_{\text{poly}}$ (R′ = ^{t}Bu) (Scheme VII). Into a benzene-d_6 solution (4 mL) of $\mathbf{7a}_{\text{poly}}$ (R′ = ^{t}Bu, *n* = 4)[19] (0.08 mmol) was bubbled dry carbon dioxide for 30 s in the dark. A balloon (ca. 3000 mL) filled with dry carbon dioxide (ca. 1 atm) was attached to the three-way stopcock, and the reaction mixture was irradiated with a monochromatized light at 420 nm for 8 h at room temperature. The quantum yield was determined on the basis of the yield of $\mathbf{8a}_{\text{poly}}$ (R′ = ^{t}Bu) thus formed (41.6%) by subtracting the yield in the dark reaction under the identical conditions (33.3%).

(iii) For the Reaction of (5,10,15,20-Tetraphenylporphinato)aluminum Malonate 8b (R′ = ^{t}Bu) and Diethylzinc (Scheme X). Into a benzene-d_6 (5 mL) solution of **8b** (R′ = ^{t}Bu) (0.1 mmol) was added diethylzinc (0.10 mL, 1 mmol), and the reaction mixture was irradiated with a monochromatized light at 420 nm for 1.5 h at room temperature.

(iv) For the Reaction of CO_2, Methyl Methacrylate (5 (R′ = Me)), and Diethylzinc Catalyzed by (TPP)AlEt (1b) (Scheme VIII). Into benzene (5 mL) saturated with carbon dioxide were added successively **5** (R′ = Me) (0.1 mL, 1 mmol), diethylzinc (0.10 mL, 1 mmol), and a benzene solution (2 mL) of **1b** (0.05 mmol) under carbon dioxide atmosphere. A balloon (ca. 3000 mL) filled with dry carbon dioxide (ca. 1 atm) was fitted through a three-way stopcock, and the reaction mixture

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(23) ^1H NMR for **11a** ($CDCl_3$): δ 7.34 (br, CO_2H), 2.05 and 1.90 (q, $CH_3C\mathit{H}_2$), 1.63 (s, CH_3CCO), 1.13 (s, $C\mathit{H}_3CH_2$).

(24) ^1H NMR for **13a** ($CDCl_3$): δ 3.85 (s, OCH_3), 2.03 and 1.87 (q, $CH_3C\mathit{H}_2$), 1.60 (s, CH_3CCO), 1.13 (t, $C\mathit{H}_3CH_2$). ^{13}C NMR ($CDCl_3$): δ 170.0 (CO_2), 119.9 (CN), 53.4 (OCH_3), 44.6 ($\mathit{C}CO$), 31.7 ($\mathit{C}H_3CCO$), 23.0 ($CH_3\mathit{C}H_2$), 9.7 ($\mathit{C}H_3CH_2$).

(25) Anal. Calcd for **10b** (R′ = ^{t}Bu) ($C_{11}H_{20}O_4$): C, 61.07; H, 9.33. Found: C, 60.74; H, 9.15. ^1H NMR ($CDCl_3$): δ 1.82 (m, $CH_3CH_2C\mathit{H}_2$), 1.46 (s, $C(CH_3)_3$), 1.41 (s, CH_3CCO), 1.30 (m, $CH_3C\mathit{H}_2CH_2$), 0.93 (t, $C\mathit{H}_3CH_2CH_2$). ^{13}C NMR ($CDCl_3$): δ 177.8 (CO_2H), 172.5 ($\mathit{C}O_2C(CH_3)_3$), 82.4 ($\mathit{C}(CH_3)_3$), 54.2 ($\mathit{C}CO$), 38.4 ($CH_3CH_2\mathit{C}H_2$), 27.9 ($C(\mathit{C}H_3)_3$), 20.5 ($\mathit{C}H_3CCO$), 18.0 ($CH_3\mathit{C}H_2CH_2$), 14.4 ($\mathit{C}H_3CH_2CH_2$).

(26) ^1H NMR for **10b** (R′ = Me) ($CDCl_3$): δ 3.75 (s, OCH_3), 1.87 (m, $CH_3CH_2C\mathit{H}_2$), 1.45 (s, CH_3CCO), 1.20 (m, $CH_3C\mathit{H}_2CH_2$), 0.94 (t, $C\mathit{H}_3CH_2CH_2$).

(27) ^1H NMR for **12b** (R′ = Me) ($CDCl_3$): δ 3.71 (s, OCH_3), 1.84 (m, $CH_3CH_2C\mathit{H}_2$), 1.41 (s, CH_3CCO), 1.24 (m, $CH_3C\mathit{H}_2CH_2$), 0.93 (t, $C\mathit{H}_3CH_2CH_2$). ^{13}C NMR ($CDCl_3$): δ 173.0 ($\mathit{C}O_2CH_3$), 53.8 ($\mathit{C}CO$), 52.5 (OCH_3), 38.0 ($CH_3CH_2\mathit{C}H_2$), 20.1 ($\mathit{C}H_3CCO$), 17.8 ($CH_3\mathit{C}H_2CH_2$), 14.4 ($\mathit{C}H_3CH_2CH_2$).

(28) ^1H NMR for **11b** ($CDCl_3$): δ 1.95 and 1.78 (m, $CH_3CH_2C\mathit{H}_2$), 1.65 (s, CH_3CCO), 1.55 (m, $CH_3C\mathit{H}_2CH_2$), 1.00 (t, $C\mathit{H}_3CH_2CH_2$).

(29) Anal. Calcd for **13b** ($C_8H_{13}NO_2$): C, 61.91; H, 8.44; N, 9.03. Found: C, 61.84; H, 8.41; N, 9.18. ^1H NMR ($CDCl_3$) δ 3.84 (s, OCH_3), 1.95 and 1.78 (m, $CH_3CH_2C\mathit{H}_2$), 1.70–1.35 (m, $CH_3C\mathit{H}_2CH_2$), 1.61 (s, CH_3CCO), 0.99 (s, $C\mathit{H}_3CH_2CH_2$). ^{13}C NMR ($CDCl_3$): δ 170.2 (CO_2), 120.1 (CN), 53.5 ($\mathit{C}CO$), 44.0 (OCH_3), 40.5 ($CH_3CH_2\mathit{C}H_2$), 23.6 ($\mathit{C}H_3CCO$), 18.9 ($CH_3\mathit{C}H_2CH_2$), 13.8 ($\mathit{C}H_3CH_2CH_2$).

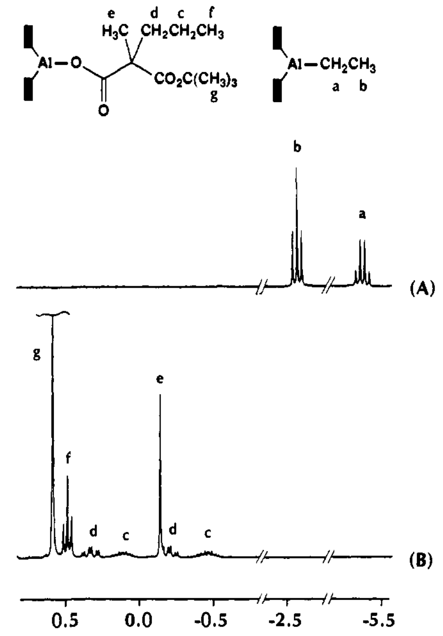
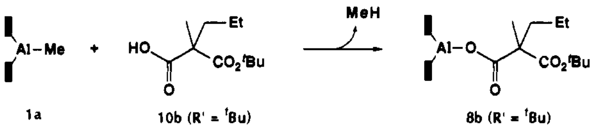


Figure 1. ^1H NMR spectra in benzene-d_6 of the reaction mixture of (TPP)AlEt (**1b**), *tert*-butyl methacrylate (**5** (R′ = ^{t}Bu)), and carbon dioxide under atmospheric pressure at 35 °C, $[\mathbf{1b}]_0 = 3.0 \times 10^{-2}$ M, $[\mathbf{5}$ (R′ = ^{t}Bu)$]_0 = 1.5 \times 10^{-1}$ M (A) before and (B) after irradiation for 67 h with visible light ($\lambda > 420$ nm).

Scheme V



was exposed to a monochromatized light ($\lambda = 430$ nm) for 75 min. The quantum yield was obtained on the basis of the yield of the diester **12b** (R′ = Me) after workup with concentrated aqueous HCl/MeOH followed by $(CH_3)_3SiCHN_2$/MeOH.

Measurements. ^1H and ^{13}C NMR spectra were measured with a JEOL Type GSX-270 spectrometer, where the chemical shifts were determined with respect to tetramethylsilane (δ 0.00 ppm) in chloroform-*d*, or benzene (δ 7.40 ppm) in benzene-d_6 for ^1H NMR, and with respect to the center signal of chloroform-*d* (δ 77.1 ppm) for ^{13}C NMR in chloroform-*d*. Absorption spectra were recorded on a JASCO Model Ubest-50 spectrophotometer. Gas chromatographic analyses were performed on an Ohkura gas chromatograph, model 103, equipped with a RASCOT stainless capillary column (OV-101, 0.25 mm × 25 m), or a Shimadzu gas chromatograph, model GC-14A, equipped with a Shimadzu fused silica capillary column (CBP20-M25-025, 0.2 mm × 25 m).

Results and Discussion

Photosynthesis of Malonic Acid Derivatives. Reaction of carbon dioxide, methacrylic esters, and (porphinato)aluminum alkyls took place upon irradiation with visible light, giving the corresponding malonate complexes (**8**) under mild conditions (Scheme IV). An example is shown by the reaction of carbon dioxide, *tert*-butyl methacrylate (**5** (R′ = ^{t}Bu)), and (5,10,15,20-tetraphenylporphinato)aluminum ethyl ((TPP)AlEt, **1b**) in benzene-d_6 at 35 °C under atmospheric pressure, which proceeded upon irradiation with Xenon arc light ($\lambda > 420$ nm) to give **8b** (R′ = ^{t}Bu). The ^1H NMR spectrum of the reaction mixture before irradiation showed a set of two signals at upfield region (a, δ −5.36 (2 H, q); b, δ −2.57 (3 H, t)) due to the ethyl group bound to the aluminum atom of **1b**[15] (Figure 1A). After irradiation for 67 h, the signals a and b disappeared, while a new set of signals c (δ −0.45 (m) and 0.1 (m)), d (−0.2 (m) and 0.3 (m)), e (−0.16 (s)), f (0.47 (t)), and g (0.57 (s)) appeared at upfield region (Figure 1B), which were assigned to **8b** (R′ = ^{t}Bu) by comparison with the signals of the authentic sample[18] prepared by the reaction between (TPP)AlMe (**1a**) and 2-methyl-2-*n*-propylpropanedioic acid mono-*tert*-butyl ester (**10b** (R′ = ^{t}Bu)) (Scheme V). Similarly, the reaction of carbon dioxide, (TPP)AlMe (**1a**), and **5** (R′ = ^{t}Bu) under irradiation with visible light at 30 °C for 3 h afforded the corresponding aluminum malonate species (**8a** (R′ = ^{t}Bu)) as observed by ^1H NMR.[30] When the reaction mixture thus obtained was treated with MeOH/aqueous HCl, 2-ethyl-2-methylpropanedioic acid mono-*tert*-butyl ester (**10a** (R′ = ^{t}Bu))[20] was obtained in 42% isolated yield.

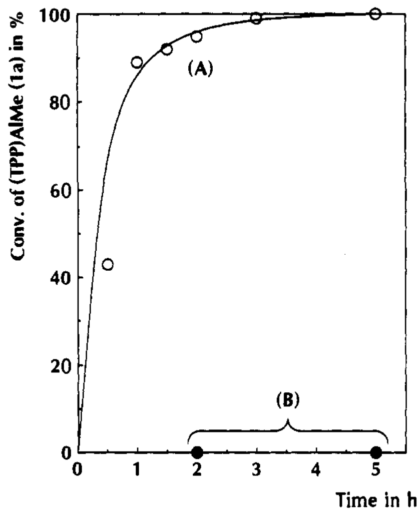
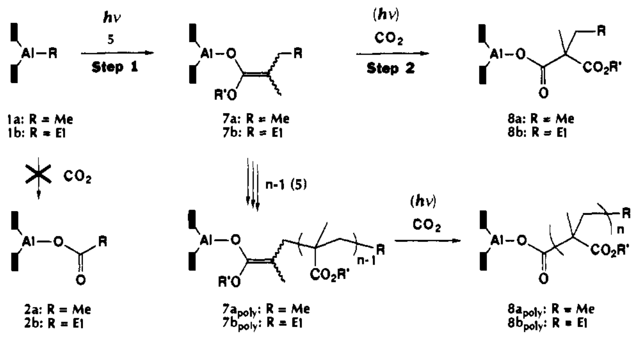


Figure 2. Reactions of carbon dioxide, (TPP)AlMe (**1a**), and *tert*-butyl methacrylate (**5** (R′ = ^{t}Bu)) in benzene-d_6 at room temperature in an NMR tube (Φ = 5 mm), $[\mathbf{1a}]_0 = 1.7 \times 10^{-2}$ M, $[\mathbf{5}$ (R′ = ^{t}*Bu*)$]_0 = 5.0 \times 10^{-2}$ M, $P(CO_2)_0$ = 1 atm, (A) under irradiation ($\lambda > 420$ nm) and (B) in the dark. Time versus conversion relationship as determined from the relative intensity of the ^1H NMR signals at δ −5.79 (**1a**, CH_3) and 0.56 (**8a** (R′ = ^{t}Bu), $OC(CH_3)_3$).

Scheme VI



It is of particular interest to note that the irradiation with visible light is quite essential to the above reaction. A typical example is shown by the time course of the reaction of carbon dioxide, *tert*-butyl methacrylate (**5** (R′ = ^{t}Bu)), and (TPP)AlMe (**1a**) at room temperature in benzene-d_6 under atmospheric pressure, where the reaction proceeded under irradiation with visible light to attain the complete consumption of **1a** after 3 h (Figure 2A). On the other hand, **1a** remained unreacted in the dark, and no signals corresponding to **8a** (R′ = ^{t}Bu)[30] were detected even after 5 h (Figure 2B).

The formation of the malonate species **8** (R′ = ^{t}Bu) from carbon dioxide, *tert*-butyl methacrylate (**5** (R′ = ^{t}Bu)), and (TPP)AlMe or (TPP)AlEt **1** (Scheme VI) is considered to occur via the two elementary reactions: generation of aluminum enolate **7** (R′ = ^{t}Bu) by 1,4-addition of the aluminum–alkyl bond of **1** to **5** (R′ = ^{t}Bu) (step 1), and subsequent addition of **7** (R′ = ^{t}Bu) to carbon dioxide (step 2). If the reaction of **1** with carbon dioxide takes place, (5,10,15,20-tetraphenylporphinato)aluminum carboxylate **2** should be formed. However, no signals assignable to **2**[31] were

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(30) ^1H NMR for **8a** (R′ = ^{t}Bu) (C_6D_6): δ 9.34 (s, pyrrole β), 8.48 (br, phenyl ortho), 7.73 (m, phenyl meta, para), 0.56 (s, $C(CH_3)_3$), 0.42 and −0.29 (q, CH_3CH_2), −0.19 (s, CH_3CCO), −0.39 (t, CH_3CH_2).

Table I. Photosynthesis of Malonic Acid Derivatives **10** and **11**. Reaction of Carbon Dioxide, Unsaturated Esters **5** or a Nitrile (**6**), and (TPP)AlX **1**[a]

	(TPP)AlX 1		CH_2=C(Me)E 5 and 6		yield of products				
					(TPP)Al–malonate[b]			malonic acid[c]	
run	X	compd	E	compd	concn, M	compd	%	compd	%
1	CH_3	**1a**	$CO_2C(CH_3)_3$	**5** (R′ = ^{t}Bu)	0.10	**8a** (R′ = ^{t}Bu)	83	**10a** (R′ = ^{t}Bu)	42
2[d]	CH_3CH_2	**1b**	$CO_2C(CH_3)_3$	**5** (R′ = ^{t}Bu)	0.15	**8b** (R′ = ^{t}Bu)	67	**10b** (R′ = ^{t}Bu)	
3	CH_3	**1a**	CO_2CH_3	**5** (R′ = Me)	0.04	**8a** (R′ = Me)	66	**10a** (R′ = Me)	
4	CH_3	**1a**	CN	**6**	0.04	**9a**		**11a**	53

[a] $[\mathbf{1}]_0 = 2.0 \times 10^{-2}$ M, $P(CO_2)_0 = 1$ atm, in benzene under irradiation with a Xenon arc lamp ($\lambda > 420$ nm) at 30 °C for 3 h. [b] ^{1}H NMR analysis. [c] Isolated yield after acid hydrolysis of **8** or **9**. [d] $[\mathbf{1b}]_0 = 3.0 \times 10^{-2}$ M, in benzene-d_6 under irradiation at 35 °C for 67 h.

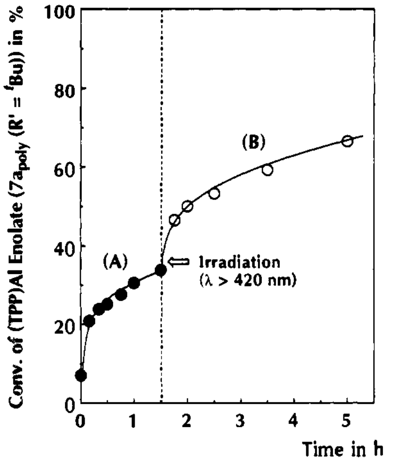
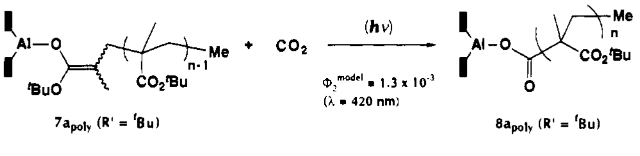


Figure 3. Reactions of carbon dioxide and (porphinato)aluminum enolate $\mathbf{7a}_{poly}$ (R′ = ^{t}Bu, n = 4) in benzene-d_6 at 30 °C in an NMR tube (Φ = 5 mm), $[\mathbf{7a}_{poly}$ (R′ = ^{t}Bu, n = 4)$]_0 = 1.0 \times 10^{-2}$ M, (A) in the dark for 1.5 h and (B) followed by irradiation ($\lambda > 420$ nm). Time versus conversion relationship as determined from the relative intensity of the ^{1}H NMR signals at δ −0.33 ($\mathbf{7a}_{poly}$ (R′ = ^{t}Bu), $OC(CH_3)_3$) and 0.6 ($\mathbf{8a}_{poly}$ (R′ = ^{t}Bu), $OC(CH_3)_3$).

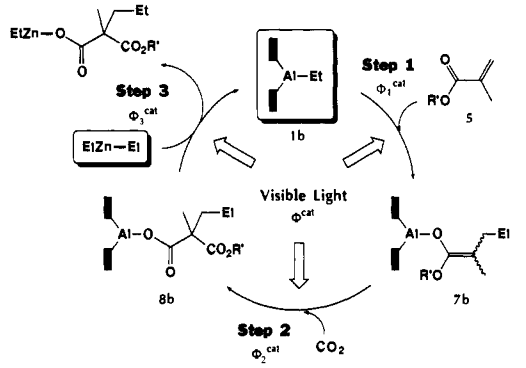
detected by ^{1}H NMR. If **7** (R′ = ^{t}Bu) reacts with **5** (R′ = ^{t}Bu) much more preferably to carbon dioxide, the polymeric products $\mathbf{7}_{poly}$ (R′ = ^{t}Bu) or $\mathbf{8}_{poly}$ (R′ = ^{t}Bu) should be formed. However, $\mathbf{7a}_{poly}$ (R′ = ^{t}Bu) was not present in the reaction mixture of carbon dioxide, **5** (R′ = ^{t}Bu), and **1a**, as evidenced by the absence of the characteristic singlet signal due to the *tert*-butyl group of the terminal enolate unit, which should be observable at δ −0.3 ppm. On the other hand, the polymer $\mathbf{8a}_{poly}$ (R′ = ^{t}Bu) provides a characteristic singlet signal at δ 0.6 ppm due to the *tert*-butyl group of the terminal carboxylate unit, which however is possibly overlapped with the corresponding signal of the aluminum malonate species **8a** (R′ = ^{t}Bu).[30] Since the intensity of the signal at δ 0.6 (9 H) relative to those of the CH_3CH_2– group of **8a** (R′ = ^{t}Bu) (δ −0.39, 3 H) and pyrrole β protons of the porphyrin moiety (δ 9.34, 8 H) was 9:2.5:8, the yield of the polymeric product $\mathbf{8a}_{poly}$ (R′ = ^{t}Bu) was calculated to be 17%, and that of **8a** (R′ = ^{t}Bu) was accordingly 83% (run 1 in Table I).

We have already reported that the irradiation with visible light is essential to the first step: 1,4-addition of (5,10,15,20-tetraphenylporphinato)aluminum alkyl **1** onto alkyl methacrylate **5** to generate the enolate species **7**.[9] An ensuing interest is whether the effect of irradiation is observable in the second step: reaction of **7** with carbon dioxide to form the malonate complex **8**. For this purpose, the polymer of *tert*-butyl methacrylate $\mathbf{7a}_{poly}$ (R′ = ^{t}Bu, n = 4),[19] prepared according to Scheme III,[9] was used as the aluminum enolate complex, since the enolate species **7** (R′ = Me, ^{t}Bu) were unable to isolate. Into a benzene-d_6 solution of $\mathbf{7a}_{poly}$ (R′ = ^{t}Bu) was introduced carbon dioxide in a slight excess with respect to $\mathbf{7a}_{poly}$ (R′ = ^{t}Bu), and the mixture was kept at 30 °C in the dark (Figure 3A). ^{1}H NMR spectrum of the reaction mixture showed a singlet signal at δ 0.6 ppm characteristic of the *tert*-butyl group at the terminal malonate unit of the polymer $\mathbf{8a}_{poly}$ (R′ = ^{t}Bu), which grew with time at the expense of $\mathbf{7a}_{poly}$ (R′ = ^{t}Bu) to attain 35% conversion in 1.5 h. When this reaction mixture was exposed to a Xenon arc light ($\lambda > 420$ nm), the reaction was slightly but definitely accelerated as shown in Figure 3B. Therefore, it can be concluded that the aluminum enolate complex $\mathbf{7a}_{poly}$ (R′ = ^{t}Bu) has a reactivity toward carbon dioxide even in the dark (Scheme VII), but the reactivity can be enhanced upon irradiation with visible light.

Scheme VII



Scheme VIII[a,b]



[a] $\Phi^{cat} = 1.7 \times 10^{-2}$ (R′ = Me, λ = 430 nm). [b] Steps 1 and 3, 100% photonic pathways; step 2, photonic + nonphotonic (major) pathway.

Methyl methacrylate (**5** (R′ = Me)) was also found to react with (TPP)AlMe (**1a**) and carbon dioxide under irradiation with visible light, giving the corresponding malonate species (**8a** (R′ = Me))[32] in 66% yield after 3 h (run 3 in Table I). Similarly, α-cyano carboxylic acid **11a**[23] was obtained in 53% isolated yield when methacrylonitrile (**6**) was used in place of methacrylic ester (run 4).

Photocatalytic Carbon Dioxide Fixation. The above interesting findings prompted us to examine the possibility of catalytic photocarboxylation of α,β-unsaturated esters and nitriles in the presence of an organometallic compound. If the (porphinato)aluminum malonate **8** and an organometallic compound (MR) exchange ligands, alkylaluminum porphyrin **1** is expected to be regenerated (Scheme VIII). In this case, the organometallic compound is required to have no potential reactivities toward carbon dioxide and the unsaturated compounds. Therefore, an organozinc compound was selected for this purpose.

Into a benzene solution of *tert*-butyl methacrylate (**5** (R′ = ^{t}Bu); 100 equiv) was bubbled carbon dioxide, benzene solutions of (TPP)AlEt (**1b**; 1 equiv) and diethylzinc (100 equiv) were successively added, and then the reaction mixture was irradiated at

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(31) ^{1}H NMR for **2a** (C_6D_6): δ 9.36 (s, pyrrole β), 8.30 (d, phenyl ortho), 7.67 (m, phenyl meta, para), −0.44 (s, CH_3).

(32) ^{1}H NMR for **8a** (R′ = Me) (C_6D_6): δ 9.33 (s, pyrrole β), 8.44 (br, phenyl ortho), 7.71 (m, phenyl meta, para), 2.45 (s, OCH_3), −0.24 (s, CH_3CCO), −0.41 (t, CH_3CH_2), −0.45 (m, CH_3CH_2).

Table II. Photocatalytic Synthesis of Malonic Acid Derivatives **12** and **13**. Reaction of Carbon Dioxide, Unsaturated Esters **5** or a Nitrile (**6**), and Diethylzinc (Et_2Zn) Catalyzed by (TPP)AlX **1**[a]

	(TPP)AlX **1**[b]		CH_2=C(Me)E **5** and **6**						yield of
run	X	compd	E	compd	concn, M	Et_2Zn concn, M	time, h	convn of **5** and **6**[c], %	**12** and **13**[d] (=turnover no.), %
1	CH_2CH_3	**1b**	$CO_2C(CH_3)_3$	**5** (R' = ^{t}Bu)	0.25	0.28	50		43
2	CH_2CH_3	**1b**	$CO_2C(CH_3)_3$	**5** (R' = ^{t}Bu)	0.10	0.10	20	100	58
3	CH_2CH_3	**1b**	$CO_2C(CH_3)_3$	**5** (R' = ^{t}Bu)	0.05	0.05	20	>93	72
4[e]	CH_2CH_3	**1b**	$CO_2C(CH_3)_3$	**5** (R' = ^{t}Bu)	0.05	0.05	16	>94	56
5[f]	CH_2CH_3	**1b**	$CO_2C(CH_3)_3$	**5** (R' = ^{t}Bu)	0.10	0.11	456	100	0[g]
6	CH_2CH_3	**1b**	$CO_2C(CH_3)_3$	**5** (R' = ^{t}Bu)	0.05	0.05	18	86	27
7[h]	Cl	**1c**	$CO_2C(CH_3)_3$	**5** (R' = ^{t}Bu)	0.05	0.05	18	47	17
8	CH_2CH_3	**1b**	CO_2CH_3	**5** (R' = Me)	0.05	0.05	23	100	93
9	CH_2CH_3	**1b**	CN	**6**	0.05	0.05	23		53

[a] $P(CO_2)$ = 1 atm, in benzene under irradiation with a 300-W Xenon arc lamp (λ > 420 nm) at 30 °C. [b] 0.01 equiv with respect to $[\mathbf{5}]_0$ or $[\mathbf{6}]_0$. [c] GC analysis. [d] GC analysis after treating the reaction mixture with MeOH/aqueous HCl followed by $(CH_3)_3SiCHN_2$. [e] In dichloromethane. [f] In the dark. [g] Polymeric product was obtained. [h] In tetrahydrofuran.

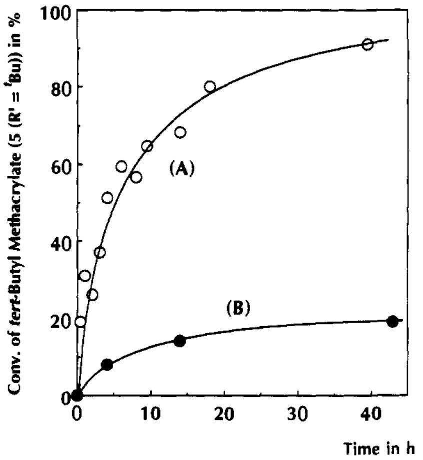


Figure 4. Reactions of carbon dioxide, *tert*-butyl methacrylate (**5** (R' = ^{t}Bu)), and Et_2Zn in the presence of (TPP)AlEt (**1b**) in benzene under atmospheric pressure at 30 °C, $[\mathbf{5}\ (R' = {}^tBu)]_0 = 1.0 \times 10^{-1}$ M, $[Et_2Zn]_0 = 1.0 \times 10^{-1}$ M, $[\mathbf{1b}]_0 = 1.0 \times 10^{-3}$ M, (A) under irradiation (λ > 420 nm) and (B) in the dark. Time versus conversion relationship as determined by GC analyses.

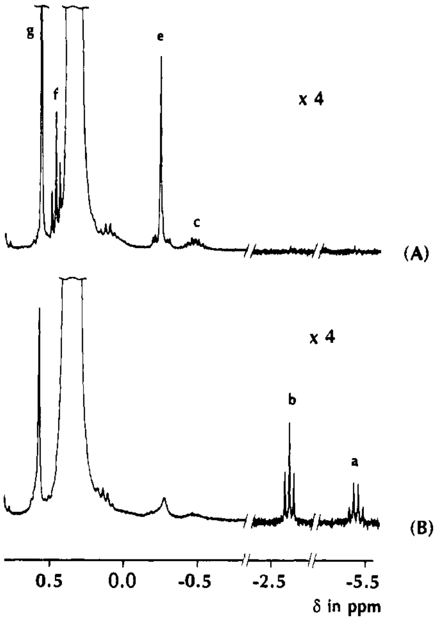
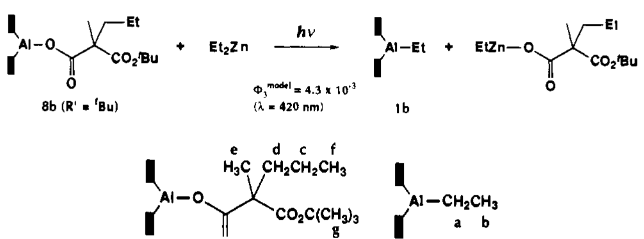


Figure 5. ^1H NMR profiles in benzene-d_6 of the reaction mixture of aluminum malonate species **8b** (R' = ^{t}Bu) and Et_2Zn at 30 °C (A) after 20 h in the dark and (B) after an additional 20 min under irradiation with visible light (λ > 420 nm).

Scheme IX

Scheme X



30 °C under atmospheric pressure. After 20 h, the reaction mixture was treated with MeOH/aqueous HCl followed by $(CH_3)_3SiCHN_2$/MeOH to give 2-methyl-2-*n*-propylpropanedioic acid *tert*-butyl methyl ester (**12b** (R' = ^{t}Bu))[33] in 72% yield, which corresponds to the turnover number of 72 (run 3 in Table II). This catalytic reaction also requires irradiation with visible light. Under irradiation, **5** (R' = ^{t}Bu) was consumed almost completely within 40 h (Figure 4A), while in the dark only 18% of **5** (R' = ^{t}Bu) was consumed in 43 h (Figure 4B). Although the complete consumption of **5** (R' = ^{t}Bu) was attainable in the dark when the reaction was prolonged (456 h), only polymeric products were formed, but **12b** (R' = ^{t}Bu) was not obtained (run 5). It should be further noted that neither the consumption of **5** (R' = ^{t}Bu) nor the formation of **12b** (R' = ^{t}Bu) took place when (TPP)AlEt (**1b**) was absent in the above reaction system.

Methyl methacrylate (**5** (R' = Me)) and methacrylonitrile (**6**) were also catalytically photocarboxylated by the reactions with diethylzinc and carbon dioxide using (TPP)AlEt (**1b**) as catalyst, and gave the corresponding malonic acid derivatives (runs 8 and 9). In particular, **5** (R' = Me) was very selectively converted into 2-methyl-2-*n*-propylpropanedioic acid dimethyl ester (**12b** (R' = Me))[27] in excellent yield (93%; turnover number 93) (run 8). (Tetraphenylporphinato)aluminum chloride ((TPP)AlCl, **1c**) was also applicable as catalyst (runs 6 and 7), where **1c** possibly underwent an exchange reaction with diethylzinc at the initial stage to generate (TPP)AlEt (**1b**) (Scheme IX), which served as the true catalytic species. In fact, **1b** was generated in 37% yield by mixing **1c** with 5 equiv of diethylzinc in benzene-d_6 at 30 °C in the dark under nitrogen.

The catalytic reaction mentioned above is considered to proceed by the three elementary steps, as illustrated in Scheme VIII. Actually, the (porphinato)aluminum malonate species **8b** (R' = ^{t}Bu)[17] was also detected by ^1H NMR in the reaction mixture of carbon dioxide, *tert*-butyl methacrylate (**5** (R' = ^{t}Bu)), and diethylzinc using (TPP)AlEt (**1b**) as catalyst. Therefore, the third step, ligand exchange of **8b** (R' = ^{t}Bu) with diethylzinc and regeneration of **1b** (Scheme X), was investigated in detail. When

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(33) ^1H NMR for **12b** (R' = ^{t}Bu) ($CDCl_3$): δ 3.74 (s, OCH_3), 1.82 (m, $CH_3CH_2CH_2$), 1.45 (s, $C(CH_3)_3$), 1.41 (s, CH_3CCO), 1.30 (m, $CH_3CH_2CH_2$), 0.92 (t, $CH_3CH_2CH_2$).

8b (R′ = ^{t}Bu),[17] prepared by the reaction of **1a** and **10b** (R′ = ^{t}Bu) (Scheme V), and 20 equiv of diethylzinc in benzene-d_6 were stirred in the dark at 30 °C, no signals assignable to **1b** were observed by ^{1}H NMR even after 20 h, and **8b** (R′ = ^{t}Bu) remained unreacted (Figure 5A). However, when this reaction mixture was irradiated with visible light, the signals a and b characteristic of the ethyl group of **1b** appeared at the expense of **8b** (R′ = ^{t}Bu) (signals c–g) (Figure 5B). The yield of **1b** after 20-min irradiation, as determined from the intensity of the signal b at δ −2.57 (3 H) relative to that of the pyrrole β protons of the porphyrin moiety (δ 9.34, 8 H), was 13%. This means that the irradiation with visible light is also essential to the ligand exchange reaction between (porphinato)aluminum malonate **8b** (R′ = ^{t}Bu) and diethylzinc (Scheme X). It was also noted that the signals a and b once appeared gradually disappeared upon further irradiation, indicating the occurrence of a concomitant degradation of **1b**. In connection with this observation, the ethyl–aluminum bond in **1b** has been demonstrated to undergo homolytic degradation upon irradiation in benzene in the absence of any reactive electrophiles such as methacrylates.[34] Therefore, in the model exchange reaction in the absence of methacrylates (Scheme X), the photoinduced generation of **1b** competes with the degradation.

The above studies well demonstrated that the irradiation with visible light affects all the three elementary steps involved in the catalytic cycle (Scheme VIII), where the first step (step 1, addition of **1b** to **5** to form **7b**) and the third step (step 3, exchange of **8b** with diethylzinc to give zinc malonate and regenerate **1b**) are the perfect photonic steps, while the second step (step 2, addition of **7b** to carbon dioxide to form **8b**) involves the contribution of a nonphotonic pathway to a considerably large extent.

Evaluation of Quantum Efficiencies. The quantum yield of the overall catalytic reaction (Φ^{cat}) (Scheme VIII) was obtained by using methyl methacrylate (**5** (R′ = Me)) as the substrate, since the best selectivity of the reaction was achieved in run 8 (Table II). On the basis of the yield of **12b** (R′ = Me) after irradiation with a monochromatized light (λ = 430 nm) for 75 min ([**5** (R′ = Me)]$_0$/[Et$_2$Zn]$_0$/[**1b**]$_0$ = 20/20/1, [**1b**]$_0$ = 7.1 × 10^{-3} M, in benzene), Φ^{cat} was calculated to be 1.7 × 10^{-2}. For obtaining the quantum yields of the model reactions corresponding to the three elementary steps (steps 1–3 in Scheme VIII), *tert*-butyl methacrylate (**5** (R′ = ^{t}Bu)) and the corresponding intermediates (**7a**$_{poly}$ (R′ = ^{t}Bu, *n* = 4)[19] and **8b** (R′ = ^{t}Bu)) were used, since the reactions can be followed by ^{1}H NMR with ease and accuracy by the virtue of their strong OC(CH$_3$)$_3$ signals. As for the reaction of **1b** (Soret band 438 nm[15]) with **5** (R′ = ^{t}Bu) (Scheme III), the mixture ([**5** (R′ = ^{t}Bu)]$_0$/[**1b**]$_0$ = 10) was irradiated at 430 nm for 15 h, and the quantum yield (Φ_1^{model}) of 4.6 × 10^{-3} was obtained on the basis of the yield of **7b**$_{poly}$ (R′ = ^{t}Bu). As for the reaction of **7a**$_{poly}$ (R′ = ^{t}Bu, *n* = 4) (Soret band 416 nm[19]) with carbon dioxide (Scheme VII), two identical reactions were conducted respectively under irradiation at 420 nm and in the dark under atmospheric pressure of carbon dioxide for 8 h, and the quantum yield (Φ_2^{model}) of 1.3 × 10^{-3} was obtained on the basis of the yield of **8a**$_{poly}$ (R′ = ^{t}Bu) under irradiation (41.6%) by subtracting the yield in the dark (33.3%). As for the exchange reaction of **8b** (R′ = ^{t}Bu) (Soret band 416 nm[17]) with diethylzinc (Scheme X), the mixture ([Et$_2$Zn]$_0$/[**8b** (R′ = ^{t}Bu)]$_0$ = 10) was irradiated at 420 nm for 1.5 h, and the quantum yield (Φ_3^{model}) of 4.3 × 10^{-3} was obtained on the basis of the amount of **1b** observed.

The quantum yields thus observed are in the range 10^{-2}–10^{-3}. If all the elementary steps are perfectly photonic, the overall quantum efficiency (Φ^{cat}) can be ideally given by the equation $\Phi^{cat} = \Phi_1^{cat}\Phi_2^{cat}\Phi_3^{cat}$. However, this equation cannot be applied to the present case primarily because of the major contribution of the *nonphotonic* pathway to the second catalytic step. It should be also noted that the quantum yield of the model exchange reaction (Φ_3^{model}) corresponding to step 3 is estimated to be much higher than that actually observed, considering the occurrence of a competitive photoinduced degradation of **1b**.[34]

Conclusion

Although photochemical properties of metalloporphyrin complexes have been extensively studied in relation to biological photosynthesis, the focus has been placed mostly on the mechanistic elucidation of the electron-transfer processes, and no achievement has been reported to make use of metalloporphyrins as photocatalysts for chemical fixation of carbon dioxide. In the present study, we have developed a novel artificial photosynthetic reaction that utilizes carbon dioxide directly as a source of carbon, by the virtue of photoenhanced nucleophilic reactivities of aluminum porphyrin complexes. A potential synthetic utility of the present reaction has been also demonstrated by the catalytic transformation of carbon dioxide achieved by the combined use of an organozinc compound with aluminum porphyrins as photocatalysts.

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