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Photocatalytic Behavior of Di- and Triferrocenylbenzenes on Reduction of Methyl Viologen and Photochemical Hydrogen Evolution from Methanol under Visible Light

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1,4- and 1,3-Diferrocenylbenzenes (**1a** and **1b**), 1,2,4- and 1,3,5-triferrocenylbenzenes (**1c** and **1d**) can act as photocatalysts for photochemical hydrogen evolution from methanol in the 1-methyl viologen MV^{2+}-triethanolamine-colloidal Pt-catalyst system under the irradiation with visible light. The order of the photocatalytic activities of **1** is **1d**>**1c**>**1a**>**1b**. The catalytic activities of **1** can be correlated to the $E_{1/2}$ values. **1** acts as a photocatalyst in the wavelength region of λ>440 nm, whereas it acts as a quencher for the formation of $MV^{+\cdot}$ in the wavelength region of λ<440 nm. The highest quantum yield of the formation of $MV^{+\cdot}$ catalyzed by **1**(**1d**: $Q_{MV^{+\cdot}}$=0.028, at 480 nm) was obtained in the wavelength region where the intensity of the solar light is the largest.

The photochemical evolution of hydrogen from water is of interest[1] because of the need to convert of solar energy into chemical forms. The systems containing a photocatalyst, methyl viologen (MV^{2+}), platinum catalyst, and a sacrificial reductant have been intensively investigated.[1b–f,2] The most popular photocatalysts used in these systems are tris(2,2′-bipyridine)ruthenium(II) chloride[1b–f] and several zinc porphyrin complexes.[2] No ferrocene derivative has been investigated in view of photochemical hydrogen evolution, although ferrocene is known to undergo electron transfer in its excited state when a suitable electron acceptor is present,[3] and the synthetic methods of the ferrocene derivatives have been extensively investigated.[4]

Recently, we reported the photocatalytic behavior of bis(η^5-indenyl)iron(II) on the reduction of MV^{2+} [5] and the photochemical evolution of hydrogen catalyzed by diferrocenylbenzenes in methanol solutions.[6] In this paper we wish to report the full details of the photocatalytic behavior of polyferrocenylbenzenes on the hydrogen evolution under irradiation with visible light and a mechanistic study on the excited state of polyferroenylbenzenes which participate in the reduction of methyl viologen.

Experimental

Materials. 1,4-Diferrocenylbenzene (**1a**) was synthesized from ferrocene (Aldrich Chemical Co., mp 174—176 °C) and 1,4-benzenebis(diazonium tetrafluoroborate) which was prepared by diazotization of *p*-phenylenediamine (Kanto Chemical Co., E.P.) according to the method in the literature:[7] mp 176—179 °C. The ^{1}H NMR spectra of **1a** ($CDCl_3$) δ=7.38 (4H, s, C_6H_4), 4.66 (4H, t, C_5H_4–), 4.32 (4H, t, C_5H_4–), and 4.08 (10H, s, C_5H_5) were identical with those reported.[8]

1,3-Diferrocenylbenzene (**1b**) was prepared similarly from ferrocene and 1,3-benzenebis(diazonium tetrafluoroborate) prepared by diazotization of *m*-phenylenediamine (Kanto Chemical Co., E.P.): mp 188—189 °C (lit,[7] 189—191 °C).

1,2,4-Triferrocenylbenzene (**1c**) was prepared according to the reported method[9] by cyclotrimerization of ethynylferrocene in dioxane in the presence of $Co_2(CO)_8$ as a catalyst: mp 248—250 °C (lit,[9] 246—249 °C); ^{1}H NMR ($CDCl_3$) δ=7.67 (3H, m, C_6H_3), 4.77 (2H, t, C_5H_4–), 4.38 (2H, t, C_5H_4), and 4.12—3.95 (23H, m, C_5H_5×3, 8H from C_5H_4–). These ^{1}H NMR spectral data were identical with those reported by Schlögl and Soukup.[9]

1,3,5-Triferrocenylbenzene (**1d**) was prepared by the acid (HCl)-catalyzed cyclotrimerization of acetylferrocene in the presence of triethyl orthoformate (Wako Junyaku Co., E.P.) according to the method reported by Sasaki and Pittman[10a] and Schlögl and Soukup:[10b] mp 265—265.5 °C (lit,[10] 265—266 °C); ^{1}H NMR ($CDCl_3$) δ= 7.47 (3H, s, C_6H_3), 4.76 (6H, t, C_5H_4–), 4.39 (6H, t, C_5H_4–) and 4.13 (15H, s, C_5H_5). The ^{1}H NMR data were identical with those reported.[10]

Ethynylferrocene was prepared from acetylferrocene (mp 84—86 °C) in the presence of phosphoryl chloride (Wako Junyaku Co., G.R.) and DMF (Wako Junyaku Co., G.R.) and then with sodium hydroxide under the reflux in dioxane according to the method reported by Schlögl and Steyrer[11a]: mp 53.5—55.0 °C (lit,[11] 55—56 °C).

Methyl viologen dichloride hydrate (83%)(Wako Junyaku Co., G.R.) was used as received.

Colloidal platinum catalyst was prepared from dihydrogen hexachloroplatinate(IV) hexahydrate (Wako Junyaku Co., G.R.)(0.20 g) and poly(vinyl alcohol) (Wako Junyaku Co., G.R.)(degree of polymerization=500, 0.160 g) in a methanol-water (50 cm^3, 1/1, v/v) solution according to the method reported by Toshima et al.[12]

Methanol (Wako Junyaku Co., E.P.) was purified by refluxing for 2 h in the presence of calcium hydride and then distilled.

Acetonitrile (Wako Junyaku Co., G.R.) was dried overnight with molecular sieves (Wako Junyaku Co., Molecular Sieves 4A, 1/16). Calcium hydride was added and the mixture was stirred until the gas evolution ceased. This acetonitrile was refluxed for 3—4 h in the presence of anhydrous phosphorus pentaoxide and then distilled under a stream of Ar.

Dioxane (Wako Junyaku Co., Dotite Spectrosol) was used as received.

N,N-Dimethylformamide (Wako Junyaku Co., G.R.) was dried over molecular sieves (Wako Junyaku Co., 4A, 1/16) and then distilled under Ar.

Measurements. UV spectra were recorded on a Hitachi 228 UV-Vis spectrophotometer. IR spectra were obtained by use of a Hitachi 260—50 grating spectrophotometer. ^{1}H NMR spectra were taken on a Hitachi R-22 (90 MHz) spectrometer. Gas chromatography for the evolved gas was performed by use of a Shimadzu GC-5A (column: molecular sieves 13X, 30—60 mesh, 2 m; temp: 20 °C; carrier gas: Ar). The gas sample was sucked from the gas buret attached to the cell by using a syringe.

Cyclic voltammetry was carried out for **1a**, **1b**, **1c**, **1d**, ferrocene and tris(2,2′-bipyridine)ruthenium(II) chloride by using a platinum disk electrode (ϕ=2.0 mm)(reference electrode: Ag|0.1 mol dm^{-3} AgClO$_4$ in acetonitrile) in an acetonitrile–tetraethylammonium perchlorate (0.1 mol dm^{-3}) solution.

Irradiation. (a) Hydrogen Evolution. The sample solutions (methanol): 12 cm^3, **1a**: 7.8×10^{-5} mol dm^{-3}, **1b**: 1.4×10^{-4} mol dm^{-3}, **1c**: 2.2×10^{-5} mol dm^{-3}, **1d**: 2.5×10^{-5} mol dm^{-3}, [Ru(bpy)$_3$]Cl$_2$: 1.40×10^{-5} mol dm^{-3}; MV^{2+}: 4.3×10^{-2} mol dm^{-3}; TEOA: 8.9×10^{-2} mol dm^{-3}; Pt: 1.32×10^{-6} mol) were prepared under a stream of Ar in a quartz vessel (2.5×2.5×6 cm^3) equipped with a gas buret and were irradiated with a 150 W tungsten lamp attached to a slide projector for 2 h. In the cases of ferrocene and phenylferrocene the sample solutions (methanol–dioxane=9:1, v/v, 12 cm^3, ferrocene: 1.1×10^{-4} mol dm^{-3}, phenylferrocene: 9.0×10^{-4} mol dm^{-3}; MV^{2+}: 4.3×10^{-2} mol dm^{-3}; TEOA: 8.9×10^{-2} mol dm^{-3}; Pt: 1.92×10^{-6} mol) were irradiated with a 500 W Xe lamp for 10 min. Comparisons of the catalytic activities of **1** and [Ru(bpy)$_3$]Cl$_2$ were carried out by comparing the amounts of the evolved gas based on that of the blank system (without metal complex) at 30 min, when the linear correlation between the amount of the evolved hydrogen and the irradiation time was obtained (this relationship was not linear after 30 min). The volume of the evolved hydrogen gas was measured by the gas buret.

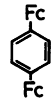
(b) Reduction of Methyl Viologen. The sample solutions containing **1**, MV^{2+}, and TEOA (**1a**: 3.4—6.8×10^{-5} mol dm^{-3}, **1b**: 0.6—1.7×10^{-4} mol dm^{-3}, **1c**: 2.3—4.6×10^{-5} mol dm^{-3}, **1d**: 2.2—5.0×10^{-5} mol dm^{-3}, phenylferrocene: 8.4×10^{-4} mol dm^{-3}; MV^{2+}: 1.29×10^{-2} mol dm^{-3}; TEOA: 6.0×10^{-2} mol dm^{-3}; methanol (for **1a** and **1b**): 5 cm^3; methanol–dioxane (9/1, v/v)(for **1c** and **1d**): 5 cm^3) were prepared under a stream of Ar in a quartz cell (1 cm×1 cm) equipped with a stopcock and were irradiated with monochromatic light (light source: Osram HBO 200 W, monochromator: Shimadzu-Bausch & Lomb grating monochromator, dispersion: 7.4 nm mm^{-1}; slit width: 1.5 mm). The quantitative analysis was carried out by measuring the absorbance at 603 nm (molar absorption coefficient of MV†: 13800 mol^{-1} dm^3 cm^{-1})[13] which is characteristic of MV†.

Actinometry. Actinometry was carried out for 313, 355, 400, 440, 480, 500, 546, and 580 nm light by using potassium trioxalatoferrate(III) according to the method in the literature.[14]

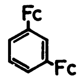
Effect of Additives on the Yield of MV†. (i) To the sample solutions (methanol–dioxane(9:1, v/v) 5 cm^3) containing MV^{2+}(1.29×10^{-2} mol dm^{-3}) and TEOA (6×10^{-2} mol dm^{-3}) was added *trans*-1,3-pentadiene (1.2—5×10^{-4} mol dm^{-3}). The solutions were irradiated with 313 nm light for 3 min and the ratios of the yield of MV† were calculated. (ii) To the methanol–dioxane(9:1, v/v) solutions containing MV^{2+}(1.29×10^{-2} mol dm^{-3}) and TEOA (6×10^{-2} mol dm^{-3}) was added **1d** (2.5—5×10^{-4} mol dm^{-3}). The solutions were irradiated with 313 nm light for 3 min and $Q_{MV^{\dagger}}$ values were calculated. (iii) The sample solutions containing **1d**, MV^{2+}, TEOA, and azulene (**1d**: 4.36×10^{-4} mol dm^{-3}, MV^{2+}: 1.29×10^{-2} mol dm^{-3}, TEOA: 6×10^{-2} mol dm^{-3}, azulene: 2.1—8.4×10^{-3} mol dm^{-3}) were irradiated with 480 nm light for 3 min.

Results and Discussion

For the ferrocene derivatives in which several ferrocenyl groups attached to benzene rings can interact with each other through the π-electron system of the benzene ring, the following two important properties of the photocatalyst are expected: (i) a higher light harvesting ability and (ii) a higher electron-donating ability than ferrocene. We thus prepared four ferrocene derivatives of this kind; 1,4-diferrocenylbenzene (**1a**), 1,3-diferrocenylbenzene (**1b**), 1,2,4-triferrocenylbenzene (**1c**), and 1,3,5-triferrocenylbenzene (**1d**), as illustrated below.



(1a)



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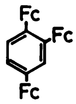

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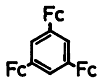

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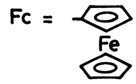


The electronic absorption spectra of **1a—1d** and those of ferrocene are shown in Fig. 1. These absorption spectra show that **1a—1d** have 10 fold as high light harvesting abilities as that of ferrocene in the wavelength region of 280—500 nm and they have slopes of absorption even at 600 nm. For the utilization of visible or solar light, **1a—1d** are better than ferrocene itself.

Photochemical Hydrogen Evolution Catalyzed by Di- and Triferrocenylbenzenes. The irradiation of the system consisting of **1** (2.2—14×10^{-5} mol dm^{-3}), MV^{2+} (4.30×10^{-2} mol dm^{-3}), triethanolamine (TEOA)(8.9×10^{-2} mol dm^{-3}), colloidal Pt-catalyst (1.32×10^{-6} mol), and methanol (12 cm^3) with a 150 W tungsten lamp for 2 h gave hydrogen gas. The results of the photochemical evolution of hydrogen for **1**-MV^{2+}–TEOA-Pt-MeOH system and for [Ru(bpy)$_3$]Cl$_2$-MV^{2+}–TEOA-Pt-MeOH system are shown in Fig. 2 and Table 1.

As seen from Fig. 2, **1a**, **1c**, and **1d** show rather high activities for the evolution of hydrogen compared to [Ru(bpy)$_3$]Cl$_2$, while **1b**, ferrocene, and phenylferrocene show low activity.

The comparisons of the photocatalytic activities of **1** were done by comparing the amount of the evolved hydrogen after the irradiation of 30 min, where a linear correlation between the amount of the evolved

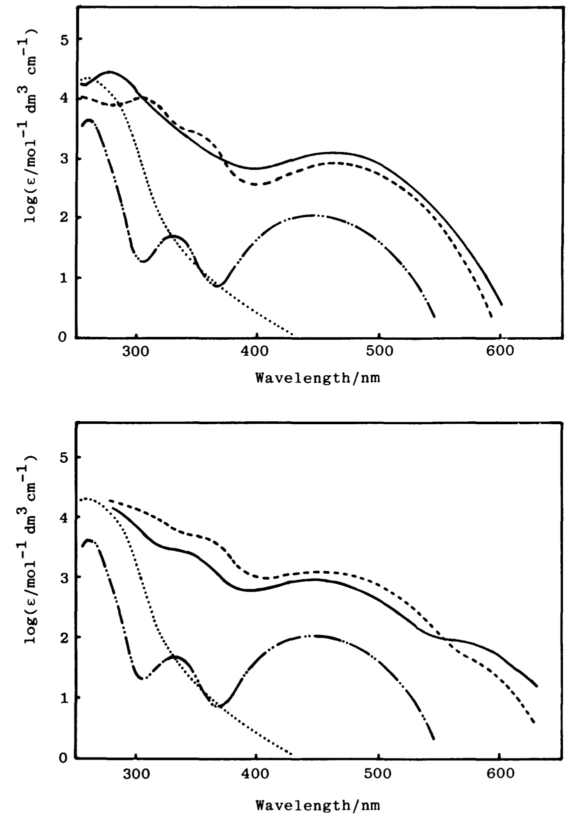


Fig. 1. Absorption spectra of 1,4-diferrocenylbenzene (**1a**) (above, ----), 1,3-diferrocenylbenzene(**1b**)(above, ——), 1,2,4-triferrocenylbenzene(**1c**)(below, ----), 1,3,5-triferrocenylbenzene(**1d**) (below, ——), ferrocene-(—-—-—), and methyl viologen(······) in methanol solutions.

hydrogen and the irradiation time is obtained (Table 1). In the third and fourth column of Table 1 are shown the fraction of light absorbed by the complex at 440 and 480 nm.

The data given in Table 1 show that (i) **1a** produces hydrogen about a half the amount of the case of

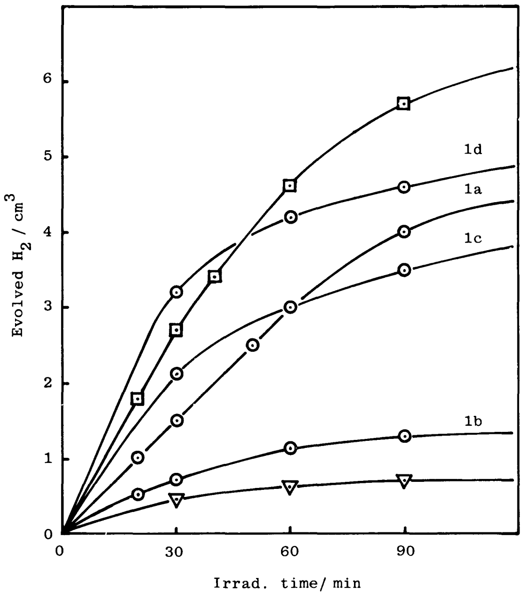


Fig. 2. Hydrogen evolution catalyzed by di- and triferrocenylbenzenes under the irradiation with a tungsten lamp (150 W).
(—⊙—): Ferrocenylbenzenes(**1a**—**d**), (—▣—): [Ru(bpy)$_3$]Cl$_2$, (—▽—): Blank(MV^{2+}–TEOA–Pt catalyst system).

Table 1. Hydrogen Evolution Catalyzed by Di- and Triferrocenylbenzenes under the Irradiation with Visible Light[a]

	[Complex] × 10^{-5} / mol dm^{-3}	H$_2$[b] × 10^{-5} / mol/30 min	Fraction of light absorbed by complex[c]		Turnover number[d]	$E_{1/2}$[e] / V
			440 nm	480 nm		
1a	7.8	4.35 (47)	27.4 (48)	24.6 (58)	47	0.025(1), 0.110(1)
1b	14.0	0.84 (9)	75.0(131)	53.3(131)	5	0.070(2)
1c	2.2	6.13 (66)	13.6 (24)	11.9 (28)	232	0.017(1), 0.133(2)
1d	2.5	10.74(115)	12.4 (22)	8.7 (21)	358	0.025(3)
Fc-H[f]	11.0	0 (0)	6.1 (11)	5.4 (13)	0	0.070(1)
Fc-Ph[f]	90.0	0 (0)	63.6(111)	56.3(133)	0	—
[Ru(bpy)$_3$]Cl$_2$	1.4	9.33(100)	57.1(100)	42.2(100)	555	0.906

a) [MV^{2+}]: 4.3 × 10^{-2} mol dm^{-3}, [TEOA]: 8.9 × 10^{-2} mol dm^{-3}, Pt: 1.32 × 10^{-6} mol, Solvent: methanol, 12 cm^3, Light source: 150 W tungsten lamp, Irradiation time: 30 min. b) The amount of evolved hydrogen gas was based on that of blank experiment. The values in parentheses are percentage of the amount of hydrogen based on that obtained in the case of [Ru(bpy)$_3$]Cl$_2$. c) Fraction of light absorbed by metal complex in 2.5 cm cell ($F = (1-10^{-(2.5)\varepsilon c}) \times 100$). The values in parentheses are percentage of the F value based on that obtained in the case of [Ru(bpy)$_3$]Cl$_2$. d) Turnover number $= \dfrac{\text{Amount of evolved hydrogen(mol)}}{\text{Amount of metal complex used(mol)}}$. e) $E_{1/2} = \frac{1}{2}(E_p^a + E_p^c)$, where E_p^a and E_p^c are anodic and cathodic peak potentials against Ag|0.1 mol dm^{-3} AgClO$_4$ in acetonitrile. The values in parentheses are the charge numbers of electrode reaction. f) The amount of evolved hydrogen gas was based on that of blank obtained in the same set of experiments which were carried out under the irradiation with a 500 W Xe lamp for 10 min. Fc- represents (C$_5$H$_5$)Fe(C$_5$H$_4$-).

$[Ru(bpy)_3]Cl_2$ with light absorption of about 50% of $[Ru(bpy)_3]Cl_2$(48% at 440 nm, 58% at 480 nm), (ii) **1c** produces hydrogen 66% of the case of $[Ru(bpy)_3]Cl_2$ with light absorption of 24—28% of that of $[Ru(bpy)_3]Cl_2$, (iii) **1d** produces hydrogen 115% of the case of $[Ru(bpy)_3]Cl_2$ with light absorption of 21—22% of $[Ru(bpy)_3]Cl_2$, (iv) **1b** produces hydrogen 9% of the case of $[Ru(bpy)_3]Cl_2$ with 31% higher light absorption than $[Ru(bpy)_3]Cl_2$, and (v) ferrocene and phenylferrocene do not show any positive effect on the production of hydrogen.

The turnover number (the amount of the evolved hydrogen (mol) per the amount of the metal complex used(mol)) for **1** and $[Ru(bpy)_3]Cl_2$ at 30 min are shown in the fifth column of Table 1. The fact that the turnover numbers of **1a**—**1d** are all greater than 1 indicates that **1a**—**1d** act as a catalyst for the photochemical evolution of hydrogen. The order of the catalytic activities of **1** in terms of the amount of the evolved hydrogen is **1d**>**1c**>**1a**>**1b**. It is noteworthy that **1a**—**1d** show photocatalytic activities, whereas phenylferrocene does not have any catalytic activity. This suggests that more than one ferrocenyl group in a benzene ring is necessary for the appearance of the photocatalytic activity. In the last column in Table 1 are shown redox potentials($E_{1/2}$) of **1** and $[Ru(bpy)_3]Cl_2$ obtained by cyclic voltammetry. **1a**—**1d** show reversible waves under the experimental conditions. **1a**, **1c**, and **1d** have first oxidation potentials of 0.026, 0.025, and 0.017 V, respectively; these values are all lower than that of **1b** (0.070 V). These electrochemical properties of **1** are roughly parallel to the catalytic activity of **1**; that is, **1** with the lower oxidation potential has the higher photocatalytic activity. That the oxidation potential of **1b** was higher than that of **1a** was ascribed earlier to the inefficiency of the interaction of two ferrocenyl groups through resonance stabilization in the benzene ring.[6] However, the oxidation potential of **1d** is as low as that of **1a**, in spite of having three ferrocenyl groups at positions of benzene ring similar to those for **1b**. The relationship between the electrochemical behavior of **1** and the position of the ferrocenyl groups in the benzene ring still remains unclear and is now under investigation in our laboratory.

Photoreduction of Methyl Viologen Catalyzed by Polyferrocenylbenzenes in Methanol Solutions. In order to obtain evidence that the hydrogen evolution is initiated by the excited state of **1**, followed by an electron transfer from **1** to MV^{2+}, the modified quantum yields ($Q_{MV^{\dot{+}}}$) in terms of the amount of light absorbed by **1** were obtained at various wavelengths.

The modified quantum yield ($Q_{MV^{\dot{+}}}$)was calculated based on the amount of the cation radical ($MV^{\dot{+}}$) formed by the contribution of **1** per amount of light absorbed only by **1**, as shown in the following equation:

$$Q_{MV^{\dot{+}}} = \frac{\text{Amount of } MV^{\dot{+}} \text{ formed by the contribution of } \mathbf{1}}{\text{Amount of light absorbed by } \mathbf{1}(=I \times t)}$$

Two different cases should be considered as to the absorption of the incident light by **1** and MV^{2+}, since the $MV^{\dot{+}}$ is also formed when MV^{2+} only is excited with the light of wavelength shorter than 440 nm. In the case that most of incident light is absorbed by the system (λ<440 nm), $Q_{MV^{\dot{+}}}$ can be defined as the following equation:

$$Q_{MV^{\dot{+}}} = \frac{[MV^{\dot{+}}]_{1+MV^{2+}} - [MV^{\dot{+}}]_{MV^{2+}} \times L}{(1-L)} \times \frac{1}{I_0 t}$$

where $[MV^{\dot{+}}]_{1+MV^{2+}}$, and $[MV^{\dot{+}}]_{MV^{2+}}$, are the amounts of $MV^{\dot{+}}$(mol) in the system consisting of **1** and MV^{2+} and of MV^{2+} only; L is the fraction of light absorbed by MV^{2+} and is defined as:

$$L = \frac{(C_{MV^{2+}})(\varepsilon_{MV^{2+}})}{C_1\varepsilon_1 + (C_{MV^{2+}})(\varepsilon_{MV^{2+}})},$$

where $C_{MV^{2+}}$ and C_1 are the concentrations of MV^{2+} and **1**; $\varepsilon_{MV^{2+}}$ and ε_1 are the molar absorption coefficients of MV^{2+} and **1**; and I_0 is the amount of light quanta(mol) absorbed by the system at wavelength λ per second; t is the irradiation time.

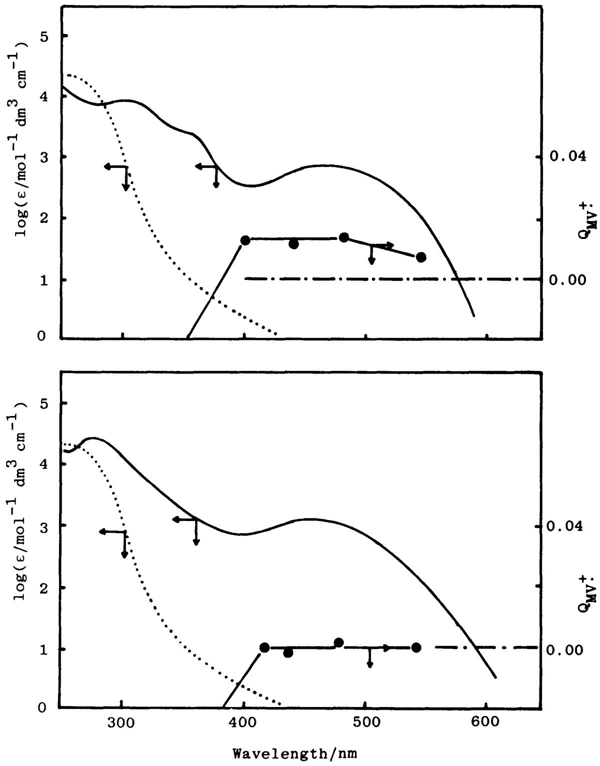


Fig. 3. Wavelength dependences of the quantum yield ($Q_{MV^{\dot{+}}}$) of photoreduction of MV^{2+} catalyzed by 1,4-diferrocenylbenzene(**1a**, above) and 1,3-diferrocenylbenzene(**1b**, below).
(—●—): $Q_{MV^{\dot{+}}}$, (——): Absorption spectra of **1**, (……): Absorption spectra of methyl viologen.

In the case that most of the incident light is passed through the system and the light is absorbed only by **1** (λ>440 nm), $Q_{MV^{+\cdot}}$ can be defined as the following equation:

$$Q_{MV^{+\cdot}} = \frac{[MV^{+\cdot}]_{1+MV^{2+}} - [MV^{+\cdot}]_{MV^{2+}}}{I \times t},$$

where $[MV^{+\cdot}]_{1+MV^{2+}}$, $[MV^{+\cdot}]_{MV^{2+}}$, and t are the same as defined above; I is the amount of light quanta(mol) absorbed solely by **1** per second. The amount of $MV^{+\cdot}$ is calculated for the irradiation of 10 min, when the linear relationship between the amount of formed $MV^{+\cdot}$ and the irradiation time is obtained. However, in the case of the irradiation with 313 nm light, the amount of formed $MV^{+\cdot}$ at 10 min was obtained by extrapolation of that obtained for 4 min irradiation since the irradiation after 4 min did not follow a linear relationship.

Wavelength dependences of $Q_{MV^{+\cdot}}$ for **1a**—**d** were obtained as shown in Figs. 3 and 4. These results indicate that: (i) **1a**, **1c**, and **1d** promote the formation of $MV^{+\cdot}$ in the wavelength region longer than 440 nm where only **1** absorbs light, whereas in the shorter wavelength region, where both MV^{2+} and **1** absorb light competitively, **1** inhibits the formation of $MV^{+\cdot}$; (ii) the highest $Q_{MV^{+\cdot}}$(0.028) is obtained in the **1d**-MV^{2+}-TEOA system under the irradiation with 480 nm light, so, **1d** is a suitable photocatalyst for the photochemical hydrogen evolution with solar light, whose intensity is maximum at 480 nm; and (iii) **1b** shows a small promotion effect in the wavelength region longer than 440 nm, but an inhibiting effect similar to that of **1d** was observed in the wavelength region of λ<440 nm.

The inhibiting effect of **1** on the formation of $MV^{+\cdot}$ in the wavelength region shorter than 440 nm can be accounted for by the quenching of the excited triplet state of MV^{2+}(E_T=299 kJ mol^{-1})[15] by the ground state of **1** (cf. ferrocene: E_T=179 kJ mol^{-1}).[16] In Fig. 5 are shown the Stern–Volmer plots for the effect of a typical triplet quencher, *trans*-1,3-pentadiene(E_T=248 kJ mol^{-1})[17] and **1d**, on the formation of $MV^{+\cdot}$ under the irradiation with 313 nm light. That the linear correlation in the Stern–Volmer plots was obtained in the cases of both *trans*-1,3-pentadiene and **1d** indicates that the excited triplet state of MV^{2+} is quenched by **1d** by energy transfer process and that this results in the inhibition of the formation of $MV^{+\cdot}$. Similar results were obtained in the cases of **1a**, **1b**, and **1c**. Recently, Hoffman and Jones II[18] reported that MV^{2+} forms a charge-transfer(CT) complex with TEOA in the ground state and that the excitation of this CT-complex gives $MV^{+\cdot}$(Φ=0.0018—0.010, at pH 8.7). The results shown in Fig. 5 may thus be explained by the quenching of the excited triplet state of the CT-complex,$^3(MV^{2+}\cdots TEOA)^*_{CT}$ by **1** although the absorption band which originated from the CT-complex was

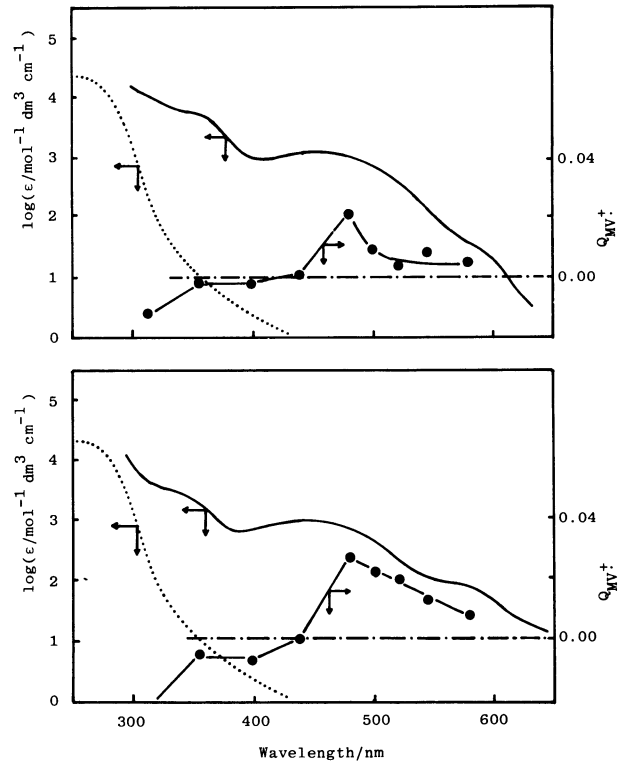


Fig. 4. Wavelength dependences of the quantum yield ($Q_{MV^{+\cdot}}$) of photoreduction of MV^{2+} catalyzed by 1,2,4-triferrocenylbenzene(**1c**, above) and 1,3,5-triferrocenylbenzene(**1d**, below).
(—●—): $Q_{MV^{+\cdot}}$, (——): Absorption spectra of **1**, (······): Absorption spectra of methyl viologen.

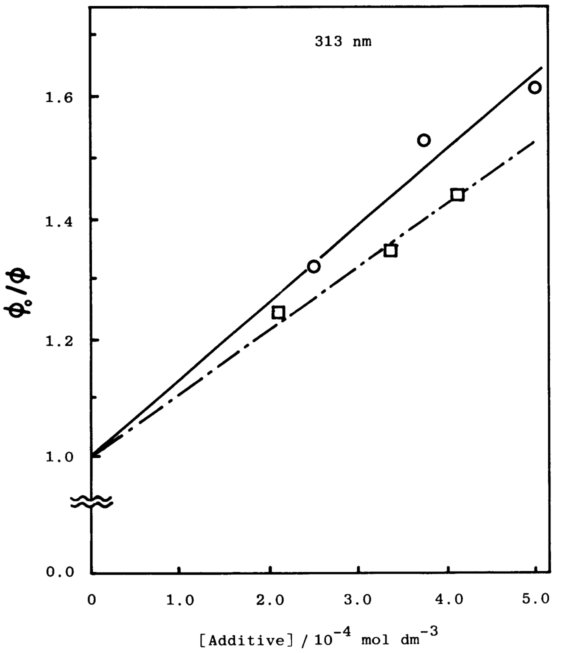


Fig. 5. Stern–Volmer plots for quenching of photoreduction of MV^{2+} under the irradiation with 313 nm light.
(—○—): MV^{2+}-TEOA-1,3-pentadiene system,
(—□—): MV^{2+}-TEOA-1,3,5-triferrocenylbenzene(**1d**) system.

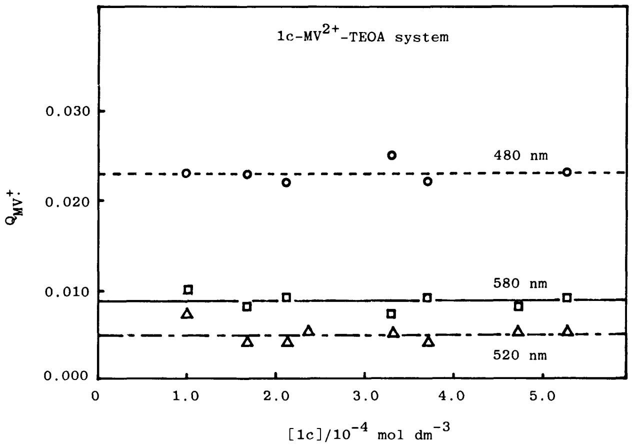


Fig. 6. Dependence of $Q_{\mathrm{MV}^{+\cdot}}$ on concentration of 1,2,4-triferrocenylbenzene(**1c**).
(—○—): Irradiation with 480 nm light, (—△—): Irradiation with 520 nm light, (—□—): Irradiation with 580 nm light.

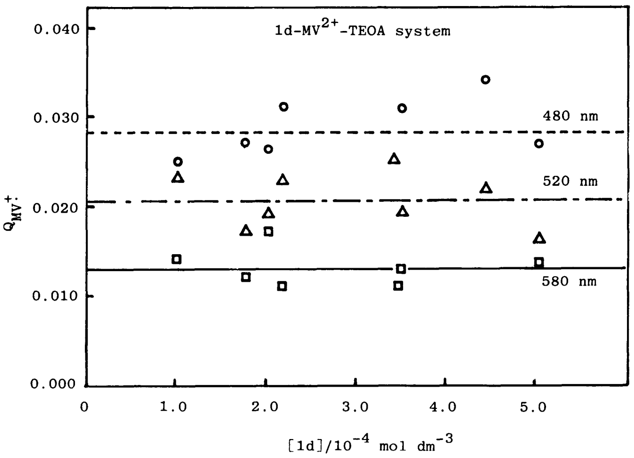


Fig. 7. Dependence of $Q_{\mathrm{MV}^{+\cdot}}$ on concentration of 1,3,5-triferrocenylbenzene(**1d**).
(—○—): Irradiation with 480 nm light, (—△—): Irradiation with 520 nm light, (—□—): Irradiation with 580 nm light.

not observed in our case.

The effects of the concentration of **1** (**1c** and **1d**) on $Q_{\mathrm{MV}^{+\cdot}}$ under the irradiation with 480, 520, and 580 nm are shown in Figs. 6 and 7. The $Q_{\mathrm{MV}^{+\cdot}}$ values are independent of the concentrations of **1**. In Fig. 8 is shown the effect of concentrations of MV^{2+} on $Q_{\mathrm{MV}^{+\cdot}}$ values. It is clear that the $Q_{\mathrm{MV}^{+\cdot}}$ values are proportional to the concentration of MV^{2+}. The results in Figs. 6—8 show that (i) the photoreduction of MV^{2+} proceeds in first order with respect to the excited state of **1** (Figs. 6 and 7) and (ii) the photoreduction is first order with respect to MV^{2+} under the irradiation with the light of wavelength longer than 440 nm.

Information on the excited state of **1** involved in the photoreduction was gained by another quenching experiment using azulene; its triplet energy level (E_{T}=163.6 kJ mol^{-1})19) is lower than ferrocene. The Stern-Volmer plots are shown in Fig. 9. The absence of any effect of added azulene on $Q_{\mathrm{MV}^{+\cdot}}$ indicates that the reduction of MV^{2+} is initiated by the excited singlet state of **1**, followed by the electron transfer from $^1(\mathbf{1})^*$ to MV^{2+} under the irradiation with light of wavelength longer than 440 nm.

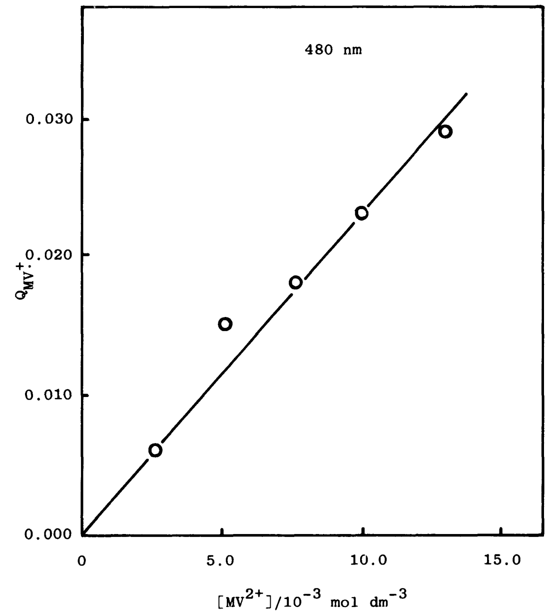


Fig. 8. Dependence of $Q_{\mathrm{MV}^{+\cdot}}$ on concentration of methyl viologen (MV^{2+}) under the irradiation with 480 nm light.

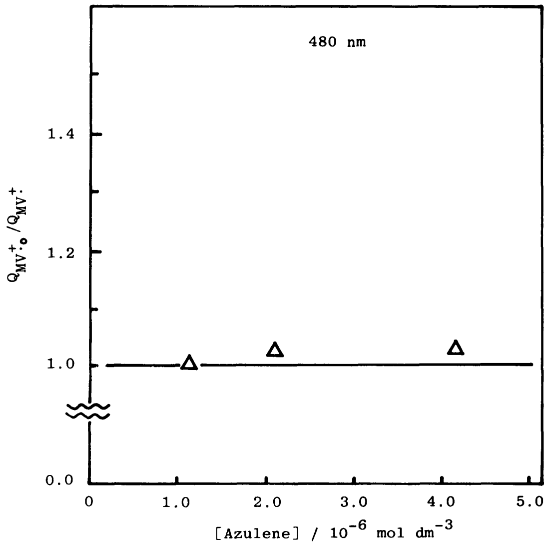
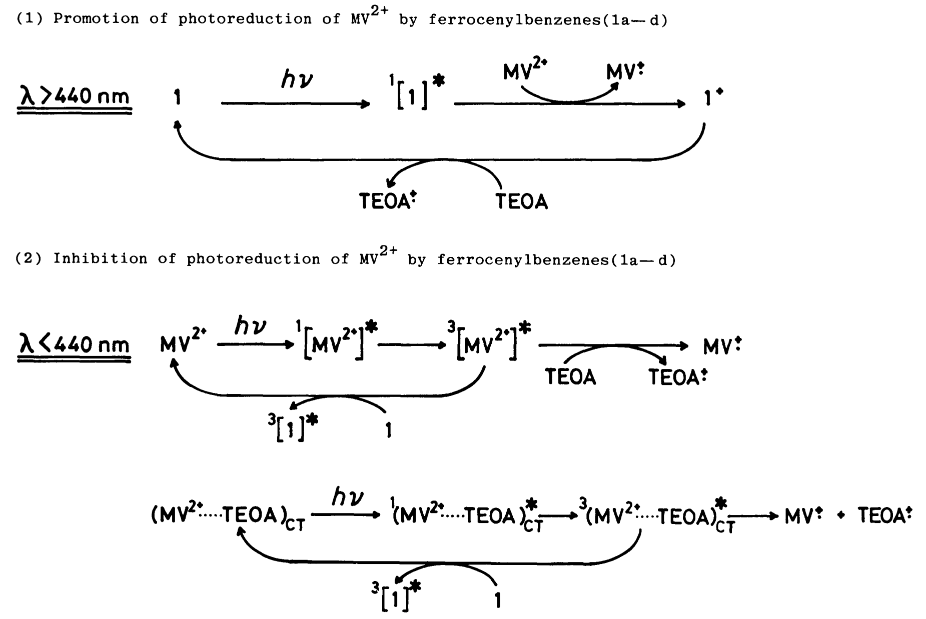


Fig. 9. Stern-Volmer plots for $Q_{\mathrm{MV}^{+\cdot}_0}/Q_{\mathrm{MV}^{+\cdot}}$ under the irradiation with 480 nm light.

The Excited State of 1 Involved in the Photoreduction of Methyl Viologen. The assignments of the absorption bands of di- and triferrocenylbenzenes have not been reported, but those of ferrocene were reported



Scheme 1.

by several workers.[20,21,22] According to Sohn[20] and Gordon,[22] the bands at 440 and 324 nm have d–d character and the bands at 265 nm has LMCT character.[22] In the cases of ferrocene and phenylferrocene the irradiation with the light of wavelength longer than 440 nm gave $Q_{MV^{+\cdot}}$ values of zero. Therefore, the excited state involved in the reduction of MV^{2+} can be considered to have some LMCT character. These red shifts of LMCT-band might be accounted for by the intramolecular interaction of ferrocenyl groups through π-electron systems.

The reaction mechanism for the photoreduction of MV^{2+} catalyzed by **1** is shown in Scheme 1.

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