reported herein. The shape-complementary difluorotoluene:4-methylindole and related base couples,[8, 14] as well as analogous arrangements of substituted phenyl groups with geometries that do not allow interstrand stacking destabilize a DNA duplex.[5] On the other hand, extended aromatic units, for example, the isocarbostyryls (1-hydroxyisoquinolines)[3, 6] or pyrene,[10] which have the potential (at least partially) to stack if they occupy opposite positions in a duplex, show equal or higher stability than natural base pairs. The importance of interstrand stacking to duplex stability has also been pointed out recently in the case of the DNA and RNA analogues p-RNA and homo-DNA.[26] A high-resolution structural analysis of a duplex that contains a dBP base pair is currently in progress.

The reported experimental results provide the basis for the simple rationale that non-hydrogen-bonding non-shape-complementary base-arrangement in a DNA duplex can attain similar or even enhanced stabilities relative to a Watson–Crick base pair only if interstrand base stacking of such opposing units is possible. This rationale may prove useful in further base design for applications in molecular biology or materials science.

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# Efficient Photooxidative Degradation of Organic Compounds in the Presence of Iron Tetrasulfophthalocyanine under Visible Light Irradiation[**]

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The degradation of organic pollutants by photocatalysis[1] and (photo-)Fenton reactions[2] has been described extensively. Meunier and co-workers reported an efficient oxidative degradation of trichlorophenol (TCP) in the presence of iron tetrasulfophthalocyanine ([Fe(PcS)]) and $\mathrm{H_2O_2}$ in the dark.[3] In this process the metal–peroxo species [Fe(OOH)(PcS)] is involved as an active oxygen intermediate. A merit of this system is that [Fe(PcS)] is a readily available biomimetic catalyst that can be fixed onto amberlite and therefore does not enter into the environment and cause additional pollution. It should, however, be noted that the solvent employed contains a large amount of acetonitrile. If water is used as the sole solvent, the conversion rate of TCP is greatly reduced.[4]

Here we report that when visible light is introduced to an aqueous system containing test compounds, [Fe(PcS)], and

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$H_2O_2$, the degradation of organic pollutants is markedly accelerated compared to the reaction carried out in the dark. The visible-light-assisted degradations of organic compounds such as salicylic acid (SA), *p*-hydroxybenzoic acid, Rhodamine B (RhB), Sulfo-Rhodamine B, Crystal Violet, Acridine Orange, and Orange II were examined in an aqueous [Fe(PcS)]/$H_2O_2$ system: All compounds could be degraded rapidly, although these processes are very slow in the dark. The investigation of RhB and SA will be described in detail (see below). The reaction under irradiation with visible light involves the photoassisted generation of $HO^\bullet$ radicals, which display very high oxidation activity, rather than an iron–peroxo species. This finding provides another approach to the effective treatment of organic pollutants in wastewaters, and also reveals a reaction mechanism different from that taking place in the dark. The latter is also useful for a better understanding of reaction mechanisms in biomimetic photochemistry.

The photodegradation of RhB under various conditions is shown in Figure 1. This compound was scarcely decomposed after 160 min of irradiation with visible light when placed alone in a solution (curve a) or together with [Fe(PcS)] (curve b), and slightly decomposed in the presence of $H_2O_2$ (curve c). When both [Fe(PcS)] and $H_2O_2$ were present, about 20 % of RhB disappeared after reaction for 160 min in the dark (curve d). In contrast, approximately 95 % of RhB was degraded under otherwise identical conditions as in (d) but under irradiation with visible light (curve e). Evidently, irradiation with visible light significantly accelerated the degradation of RhB in the presence of [Fe(PcS)] and $H_2O_2$. During the photoreaction no degradation of [Fe(PcS)] was observed by UV/Vis spectroscopy, and no free $Fe^{2+}$ or $Fe^{3+}$ ions were detected, indicating that [Fe(PcS)] is an efficient photocatalyst to degrade organic pollutants. The removal of total organic carbon (TOC) of RhB in the aqueous RhB/[Fe(PcS)]/$H_2O_2$ system was about 30 % after 8 h of reaction.[5]

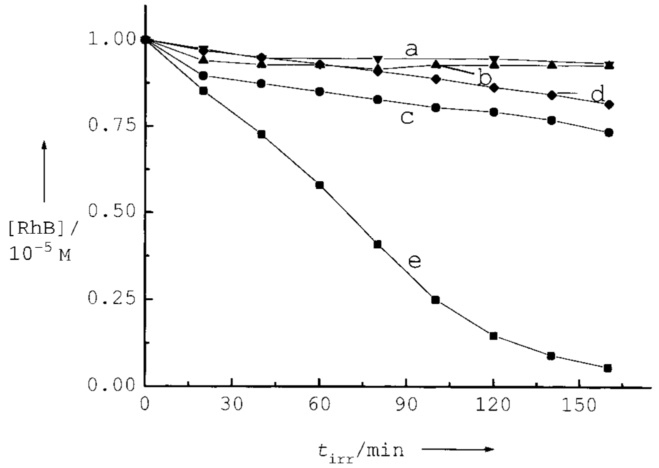


Figure 1. Degradation of RhB (10 μM) under different conditions. a) A solution containing only RhB under irradiation with visible light; b) a solution of RhB and [Fe(PcS)] (40 μM) under irradiation with visible light; c) a solution of RhB and $H_2O_2$ (1 mM) under irradiation with visible light; d) RhB in the presence of [Fe(PcS)] and $H_2O_2$ in the dark; e) RhB in the presence of [Fe(PcS)] and $H_2O_2$ under irradiation with visible light.

The ESR technique was used to gain insight into the nature of the short-lived radicals formed during the photodegradation. The spectra for the RhB/[Fe(PcS)]/$H_2O_2$ system under irradiation with visible light ($\lambda > 470$ nm) are shown in Figure 2. No signals of significant intensity were observed when the experiments were run in the dark. This is in good agreement with the results reported by Meunier et al., in which no formation of $HO^\bullet$ radicals is involved.[3] However, when the system was irradiated with visible light, signals for DMPO–$^\bullet$OH adducts (DMPO = 5,5-dimethyl-1-pyrroline-N-oxide) with a 1:2:2:1 quartet pattern appeared.[6, 7] Moreover, these signals were enhanced by further irradiation and then remained unchanged after 4 min. These results provide evidence that irradiation with visible light can greatly enhance the generation of $HO^\bullet$ radicals, and hence accelerate the degradation of the organic pollutant owing to the high oxidation potential of $HO^\bullet$ radicals ($E = +2.80$ V).[8, 9] We also carried out ESR experiments with the aqueous SA/[Fe(PcS)]/$H_2O_2$ system. Although SA has no absorption in the range of visible light, the degradation of SA can be significantly accelerated under irradiation with visible light. The ESR results are similar to those for the RhB system; namely, reactions in the dark gave no ESR signals for DMPO–$^\bullet$OH, while irradiation with visible light enhanced the intensity of the four characteristic peaks for DMPO–$^\bullet$OH.

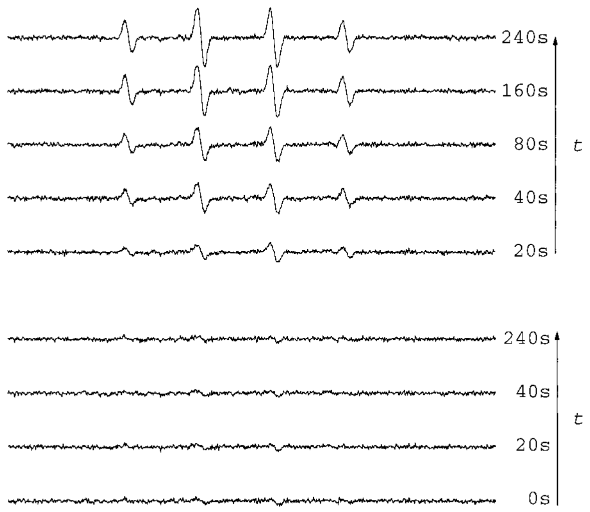
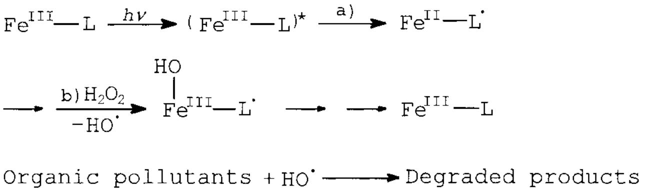


Figure 2. Changes in the ESR spectra of solutions containing RhB (0.1 mM), [Fe(PcS)] (0.2 mM), and $H_2O_2$ (0.05 M), measured both in the dark (below) and under irradiation with visible light (above). The 1:2:2:1 quartet is due to the DMPO–$^\bullet$OH adducts formed.

For the RhB/[Fe(PcS)]/$H_2O_2$ system, we also examined the degradation of RhB with a monochromatic light source ($\lambda = 640$ nm, $\Delta\lambda_{1/2} = 10$ nm, no light absorption for RhB) basically corresponding to the maximum absorption wavelength of [Fe(PcS)] ($\lambda_{max} = 636$ nm). Upon excitation of [Fe(PcS)] by monochromatic light, RhB can also be photodegraded rapidly with a quantum yield of $\phi_{640} = 0.0038$.[10] In addition, we carried out the photodegradation of RhB in the presence of [Fe(PcS)] and $H_2O_2$ under a nitrogen atmosphere. In the present system the effect of oxygen on the degradation of organic pollutants is minor: Almost the same degradation rate of RhB was observed as that under aerated conditions.

We propose a mechanism, based on the above results, for the photodegradation of organic pollutants in aqueous solutions of [Fe$^{III}$(PcS)] and $H_2O_2$ (Scheme 1). In this system [Fe$^{III}$(PcS)] exists mainly in the form of the aqua complex.[4] Upon irradiation with visible light, the excitation of [Fe$^{III}$(PcS)] can cause an intramolecular electron transfer from the ligand (L) to Fe$^{III}$, leading to reduction of Fe$^{III}$ to Fe$^{II}$ (step a).[11] The reduced Fe$^{II}$ complex immediately reacts with $H_2O_2$ to produce HO$^•$ (step b).[11d] According to the proposed mechanism, the degradation of organic compounds in the [Fe(PcS)]/$H_2O_2$ system under irradiation with visible light can be well explained without involving high-valence iron–oxo or iron–peroxo complexes.[3, 12]



Scheme 1. A possible machanism for the photooxidation of organic pollutants in the aqueous [Fe(PcS)]/$H_2O_2$ system under irradiation with visible light. See text for details.

### Experimental Section

General procedure for the photooxidation reaction: A 500-W halogen lamp was positioned inside a cylindrical Pyrex vessel surrounded by a circulating water jacket (Pyrex) to cool the lamp. The jacket was wrapped with a piece of black paper containing a small window. A cutoff filter was placed on the window (diameter 3 cm) to remove wavelengths less than 470 nm and to ensure irradiation with visible light only. The center distance between the reaction vessel and the light source was 10 cm. A typical reaction mixture for irradiation contained the following initial concentrations: RhB (10 μM) or SA (0.1 mM), [Fe(PcS)] (40 μM), and $H_2O_2$ (1 mM). Deionized and doubly distilled water was used throughout this study. The aqueous solution was adjusted to pH 3 with diluted solutions of NaOH or $HClO_4$. At the given irradiation time intervals, a sample (3 mL) were taken out and analyzed by UV/Vis spectroscopy with a lambda Bio 20 spectrophotometer (Perkin-Elmer). The ESR spectra were measured on a Bruker EPR 300E spectrometer.

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# Branched Star-Type Polysilyllithium Compounds: The Effects of β-Silyl Substitution and of Complexation on Their Molecular Structure[**]

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*Dedicated to Professor Hideki Sakurai*
*on the occasion of his 70th birthday*

In contrast to the wealth of information on organolithium reagents,[1] relatively little is known about the analogous silyllithium compounds, despite their important role in silicon chemistry.[2] Furthermore, only a limited number of silyl metal reagents have been characterized by X-ray crystallography.[2, 3] Of special interest are branched “hypersilyl” anions such as $[(Me_3Si)_3Si]^-$, which were often used for the synthesis of novel compounds,[2] for example, by us for the synthesis of stable silenes.[4] The $[(Me_3Si)_3Si]^-$ ion was first prepared in

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