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Preparations and Photosensitizing Properties of 2,7,12,17-Tetra-*n*-propylporphycenatotin(IV) Dihalide Complexes

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2,7,12,17-Tetra-*n*-propylporphycenatodihalotin(IV) complexes ([Sn(TPrPc)X_2], X = F, Cl, and Br) were synthesized and their photophysical properties were investigated. These complexes exhibit strong absorptions in the red region (600–630 nm). Strong quenching was observed during the fluorescence emission of the dibromotin(IV) complex, which is caused by an intramolecular heavy-atom effect. The complexes emit NIR phosphorescence in 1-iodopropane at room temperature and the intensity of the emission of the dibromotin(IV) complex is found to be smaller than that of the dichlorotin(IV) complex. The quantum efficiency (Φ_Δ) of generation of singlet oxygen using the dibromotin(IV) complex is the highest among the porphycenatotin(IV) complexes ($\Phi_\Delta = 0.79$). Photooxidation of 1,3-diphenylisobenzofuran catalyzed by the complexes upon irradiation with red light (over 600 nm) was studied and a rapid oxidation of the substrate was observed when using the dibromotin(IV) complex.

Singlet molecular oxygen, $^1O_2$, attracts much attention due to its variety of applications including synthetic oxidation, photodynamic therapy (PDT), and the decomposition of pollutants.[1] The most common method of $^1O_2$ generation is photosensitization. From the viewpoints of environmental chemistry and PDT, the photosensitizer should be excited by visible light rather than by UV light because such short wavelength light is very energetic and could generate toxic and persistent compounds.[2] One typical group of dyes which can be excited by long wavelength light are porphyrins and many photosensitizers have been prepared and studied.[3] $^1O_2$ is formed by energy transfer from a triplet excited species of the photosensitizer to $^3O_2$. The intersystem crossing of an excited photosensitizer is therefore an important step. To accelerate this key step, the introduction of heavy atoms into the dye is effective because the intersystem crossing is facilitated by the intramolecular heavy-atom effect.[4] Complexation with heavy metals is the most simple and effective method for inducing the heavy-atom effect, and many complexes of porphyrins have been investigated in order to develop novel photosensitizers.[3] One group of complexes containing a heavy metal atom is the tin(IV) porphyrins, which are very stable against oxidation.[5] The tin(IV) porphyrin complexes can prepare $^1O_2$ by visible light irradiation. Morgan et al. reported that such tin(IV) complexes are effective photosensitizers against tumors in animals.[6]

Porphycenes, which are structural isomers of porphyrins and first synthesized by Vogel's group,[7] display strong absorption bands in the red region due to their lower symmetry relative to porphyrins.[8] The absorption has been utilized for the development of photosensitizers which can be excited by red light.[9] Red light can deeply penetrate tissue. Nonell et al. reported that palladium(II) porphycene complex can be excited by red light (over 600 nm) and it should be very useful for the PDT of biomedical applications.[10] Although brominated porphycenes are free-base porphycenes, the absorption band exists in the deep red region and they are effective photosensitizers since intersystem crossing is facilitated by the heavy bromo atoms.[11] Recently, we reported that the dichlorotin(IV) complexes of octaethylporphyrin isomers (porphyrin, porphycene, and hemiporphycene) can generate $^1O_2$ more effectively than their free-base ligands, and the porphycene complex is the best photosensitizer among the complexes of porphyrin isomers.[12]

In this study, the 2,7,12,17-tetrapropylporphycenatotin(IV) dihalide complexes were synthesized to study the effect of axial ligands (Chart 1). 2,7,12,17-Tetrapropylporphycene can be more easily synthesized than 2,3,6,7,12,13,16,17-octaethylporphycene. The luminescence, phosphorescence, and quantum efficiency of generation of singlet oxygen by the complexes were investigated. The photooxidation of 1,3-diphenylisoben-

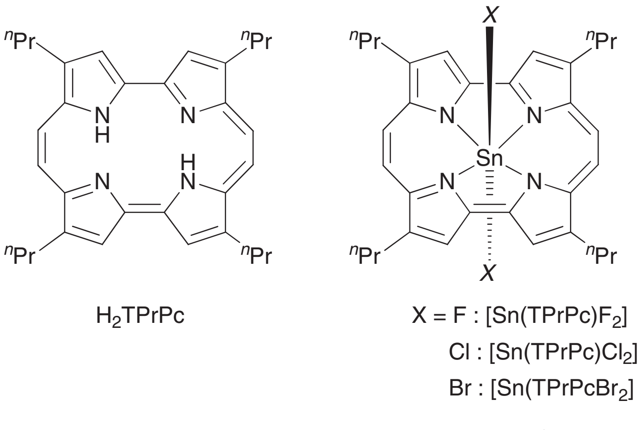

Chart 1. Structure of 2,7,12,17-tetra-*n*-propylporphycene (H_2TPrPc) and its complexes involving dihalotin(IV) ([Sn(TPrPc)X_2]).

zofuran (DPBF) by the complexes upon irradiation with red light (over 600 nm) was carried out. Rapid oxidation of the substrate was observed with the dibromotin(IV) complex caused by an intramolecular heavy-atom effect. The complex would be able to effectively utilize low energy light and thus applications of these systems for the decomposition of pollutions and PDT based on the [Sn(TPrPc)X_2] complexes are highly encouraged.

Experimental

Chemicals. For measurement of the absorption and fluorescence spectra, dichloromethane, which was obtained from DOJINDO (Japan), was used as received. 1-Iodopropane, which was obtained from TCI (Japan), was carefully purified before use for study of the phosphorescence emission. Benzene, which was obtained from WAKO (Japan), was used as received to determine the quantum yield of $^1O_2$ generation from the dyes by light irradiation. For the synthesis of the complexes, decalin was dried over sodium under nitrogen for 1 day followed by distilling under reduced pressure, then used as a solvent. 5,10,15,20-Tetraphenylporphinatozinc(II) ([Zn(tpp)]) was purchased from Sigma-Aldrich and used without further purification.

Measurements. The ^{1}H NMR spectra were obtained using a Bruker Avance 500 NMR spectrometer with CD_3CN as the solvent and TMS as the internal standard (δ 0). The MALDI-TOF mass spectra were obtained using a Bruker Autoflex II without a matrix. The elemental analyses were performed by the Service Center of Elementary Analysis of Organic Compounds affiliated with the Faculty of Sciences at Kyushu University. The UV–vis spectra were measured on a Hitachi U-3300 spectrophotometer at room temperature. The fluorescence spectra were measured using a Hitachi F-4501 fluorescence spectrophotometer at room temperature. The quantum yield of the fluorescence (Φ_{fluo}) was measured using a Hamamatsu C9920-02 Absolute PL Quantum Yield Measurement System; dichloromethane was used as the solvent and excitation was performed at 400 nm. The near infrared (NIR) emission was recorded using a HORIBA SPEX Fluolog-NIR spectrophotometer at room temperature.

Synthesis of 2,7,12,17-Tetra-*n*-propylporphycenatodichlorotin(IV) [Sn(TPrPc)Cl_2]. Under a nitrogen atmosphere, a mixture of H_2TPrPc (109 mg, 2.28×10^{-4} mol) and $SnCl_2 \cdot 2H_2O$ (555 mg, 2.46×10^{-3} mol) was refluxed in dry decalin (23 mL) for 13 h. The solution was cooled to room temperature and stirred for 20 h in air. The mixture was filtered, and the obtained green solid was washed with *n*-hexane and then extracted with dichloromethane. The solution was washed with an aqueous solution of 10% HCl and dried over anhydrous Na_2SO_4. The dry solution was filtered and evaporated, and then recrystallization of the residue from dichloromethane/*n*-hexane gave a purple powder (128 mg, 1.92×10^{-4} mol, 84.2%).

^{1}H NMR (CD_3CN, 298 K, 500 MHz): δ 1.44 (t, 12H, $J = 7.3$ Hz), 2.56 (m, 8H), 4.33 (t, 8H, $J = 7.4$ Hz), 9.82 (s, 4H), 10.60 (s, 4H). UV–vis (CH_2Cl_2): λ/nm (ε/mol^{-1} dm^3 cm^{-1}) 391 (134000), 404 (125000), 606 (54000), 625 (89000). MALDI-TOF-MS: Calcd for $[C_{32}H_{36}N_4ClSn]^+$, $m/z = 631.17$; found, 631.22. Anal. Calcd for $C_{32}H_{36}N_4Cl_2Sn$: C, 57.69; H, 5.45; N, 8.41%. Found: C, 57.58; H, 5.41; N, 8.38%.

Synthesis of 2,7,12,17-Tetra-*n*-propylporphycenatodifluorotin(IV) [Sn(TPrPc)F_2]. A solution of [Sn(TPrPc)Cl_2] (57 mg, 8.56×10^{-5} mol) in dichloromethane (30 mL) was stirred with an aqueous solution of 1 mol dm^{-3} KF (30 mL) at room temperature for 4 h. The two solvent layers were then separated and the dichloromethane layer was dried over anhydrous Na_2SO_4. The dried solution was evaporated and recrystallization of the residue from dichloromethane/*n*-hexane gave a purple powder (49 mg, 7.70×10^{-5} mol, 90%).

^{1}H NMR (CD_3CN, 298 K, 500 MHz): δ 1.45 (t, 12H, $J = 7.3$ Hz), 2.55 (m, 8H), 4.32 (t, 8H, $J = 7.5$ Hz), 9.58 (s, 4H), 10.35 (s, 4H). UV–vis (CH_2Cl_2): λ/nm (ε/mol^{-1} dm^3 cm^{-1}) 388 (165000), 607 (68000), 620 (103000). MALDI-TOF-MS: Calcd for $[C_{32}H_{36}N_4FSn]^+$, $m/z = 615.19$; found, 615.36. Anal. Calcd for $C_{32}H_{36}N_4F_2Sn$: C, 60.68; H, 5.73; N, 8.85%. Found: C, 60.50; H, 5.77; N, 8.84%.

Synthesis of 2,7,12,17-Tetra-*n*-propylporphycenatodibromotin(IV) [Sn(TPrPc)Br_2]. Under a nitrogen atmosphere, a mixture of H_2TPrPc (15.7 mg, 2.36×10^{-5} mol) and $SnBr_2$ (147 mg, 5.28×10^{-4} mol) was refluxed in dry decalin (1 mL) for 4.5 h. After the solution was cooled to room temperature, the mixture was filtered, and the obtained green solid was washed with *n*-hexane and then extracted with dichloromethane. The solution was washed with an aqueous solution of 2 mol dm^{-3} NaBr and dried over anhydrous Na_2SO_4. The dry solution was filtered and evaporated, and then recrystallization of the residue from dichloromethane/*n*-hexane gave a purple powder (13.9 mg, 1.83×10^{-5} mol, 55.8%).

^{1}H NMR (CD_3CN, 298 K, 500 MHz): δ 1.41 (t, 12H, $J = 7.3$ Hz), 2.54 (m, 8H), 4.34 (t, 8H, $J = 7.6$ Hz), 9.95 (s, 4H), 10.69 (s, 4H). UV–vis (CH_2Cl_2): λ/nm (ε/mol^{-1} dm^3 cm^{-1}) 393 (125000), 404 (114000), 609 (49400), 627 (78100). MALDI-TOF-MS: Calcd for $[C_{32}H_{36}N_4BrSn]^+$, $m/z = 675.11$; found, 674.96. Anal. Calcd for $C_{32}H_{36}N_4Br_2Sn$: C, 50.89; H, 4.80; N, 7.42%. Found: C, 51.04; H, 4.59; N, 7.37%.

Determination of the Quantum Yield of Singlet Oxygen Generation. For the singlet oxygen phosphorescence measurements, an air-saturated benzene solution containing the sample in a quartz cell (optical path length: 10 mm) was excited at 560 nm using a HORIBA SPEX Fluolog-NIR spectrophotometer at room temperature. Each Φ_Δ was determined from the slope of the plot at an intensity at 1270 nm versus the concentrations of the samples based on [Zn(tpp)] as the standard ($\Phi_\Delta = 0.73$).[13]

Photooxidation of 1,3-Diphenylisobenzofuran (DPBF). The photooxidation was carried out in a quartz cell (1 cm × 1 cm) at room temperature. A benzene solution (2 mL) containing a photosensitizer (6.0×10^{-9} mol dm^{-3}) and DPBF (4.0×10^{-5} mol dm^{-3}) was irradiated with a 200-W tungsten lamp through a cut-off filter (SIGMA KOKI SCF-50S-60R; light shorter than 600 nm is cut). The decreasing DPBF was monitored by measuring the absorbance at 415 nm ($\varepsilon = 23300$ mol^{-1} dm^3 cm^{-1}).[14]

Results and Discussion

Synthesis of the Dihaloporphycenatotin(IV) Complex. 2,7,12,17-Tetra-*n*-propylporphycene (H_2TPrPc) was synthesized according to a reported method.[7] The corresponding dihalotin(IV) complexes, dichlorotin(IV) complex and dibromotin(IV) complex, were prepared by treatment with $SnCl_2\cdot 2H_2O$ and $SnBr_2$ in dry decalin at 180 °C under nitrogen, respectively. However, the fluorotin(IV) complex was not obtained by the same method using SnF_2. We found that the fluorotin(IV) complex was successfully obtained by the heterogeneous reaction of the [Sn(TPrPc)Cl_2]/dichloromethane solution with an aqueous $1.0\,mol\,dm^{-3}$ KF solution. These complexes were identified from the ^{1}H NMR, MALDI-TOF mass spectra, and elemental analyses. In the ^{1}H NMR spectra, the low field shift of the aromatic signals of [Sn(TPrPc)Br_2] (9.95 and 10.69 ppm) is greater than [Sn(TPrPc)F_2] (9.58 and 10.35 ppm) in CD_3CN. The same tendency of the aromatic signals in the ^{1}H NMR spectra to shift depending on the axial ligands was observed for the porphynatodihalotin(IV) complexes.[15] It is suggested that the conjugated electron density on the porphycene ring is higher in the order of decreasing atomic number of the halogens. The axial ligands whose ionic radii are smaller could more effectively buffer the positive charge of the cationic tin(IV).

Absorption and Emission Properties of [Sn(TPrPc)X_2]. The absorption spectra of [Sn(TPrPc)X_2] are shown in Figure 1. Because of the lower symmetry of the macrocyclic structure of the porphycene, the Q bands of the tin(IV) complexes are sharper and stronger than the bands of the free-base ligands.[16] Such a narrow half-bandwidth would be advantageous for excitation by a laser. When the atomic weight of the axial ligands increased, the wavelength of the peak top of the absorption band of [Sn(TPrPc)X_2] was found to be insensitive, but is red shifted and the molar absorption coefficient (ε) slightly decreased. The chemical shift of the aromatic signals of the complexes in the ^{1}H NMR spectra suggests that the conjugated electron density on the porphycene ring should be higher in the order of decreasing atomic number of the halogens. Thus ε of [Sn(TPrPc)F_2] should be the highest among the [Sn(TPrPc)X_2] complexes. Although the value of ε of [Sn(TPrPc)Br_2] is the lowest among the [Sn(TPrPc)X_2] complexes, their values are comparable and the ε of the Q bands should be high enough to react as a photosensitizer with red light irradiation.

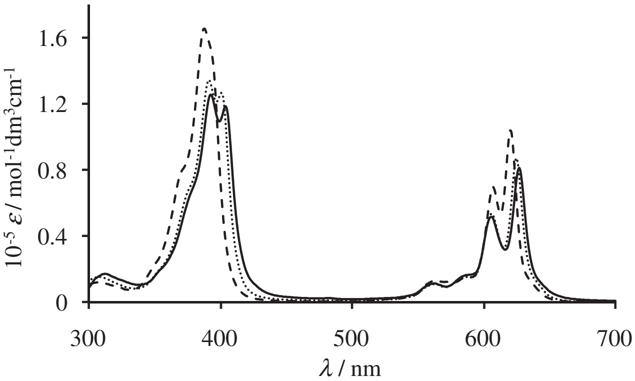

Figure 1. Absorption spectra of [Sn(TPrPc)X_2] (X = F, broken line; Cl, dotted line; Br, solid line) in dichloromethane.

A more obvious difference among the present complexes was observed during the fluorescence emission. Figure 2 shows the fluorescence spectra of the complexes. As shown in Figure 2, the fluorescence emission was best quenched with the bromide ligands. Although the quantum yields of the fluorescence emission (Φ_{fluo}) was drastically diminished by introduction of tin(IV) and bromide into the porphycene, the stokes shifts of the tin(IV) complexes were small and similar to each other (Table 1). These results suggest that the fluorescence emission is not quenched through internal conversion, but through an intersystem crossing which is facilitated by the heavy-atom effect.

To investigate the T_1 state of these complexes, the phosphorescences of [Sn(TPrPc)Cl_2] and [Sn(TPrPc)Br_2] in the degassed 1-iodopropane were measured at room temperature. Unfortunately, [Sn(TPrPc)F_2] was not stable in 1-iodopropane, and no phosphorescence was measured. It is

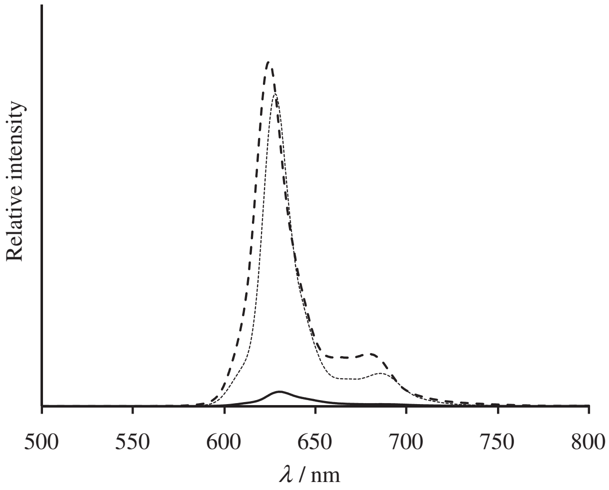

Figure 2. Fluorescence spectra of [Sn(TPrPc)X_2] (X = F, broken line; Cl, dotted line; Br, solid line) in dichloromethane. The excitation wavelength was 400 nm and absorption of the solution at 400 nm was adjusted to 0.1.

Table 1. Photophysical Data of Dihalotin(IV) Complexes

	λ_{abs}/nm ($10^{-4}\,\varepsilon$/mol^{-1} dm^3 cm^{-1}) of Q bands[a)]	λ_{fluo} /nm[a)]	Stokes shift /cm^{-1} [a)]	Φ_{fluo}[b)]	λ_{phos} /nm[c)]	Φ_{Δ}[d)]
[Sn(TPrPc)F_2]	607 (6.8), 620 (10.3)	624	103	0.139	—	0.46
[Sn(TPrPc)Cl_2]	606 (5.4), 625 (8.9)	628	76	0.106	936	0.55
[Sn(TPrPc)Br_2]	609 (4.9), 627 (7.8)	630	51	0.028	937	0.79

a) Measured in dichloromethane. b) Excitation wavelength is 400 nm. Measured in dichloromethane. c) Measured in degassed 1-iodopropane. Excitation wavelength is 630 nm. d) Measured in benzene. Excitation wavelength is 560 nm. [Zn(tpp)] is used as the standard sample.[13]

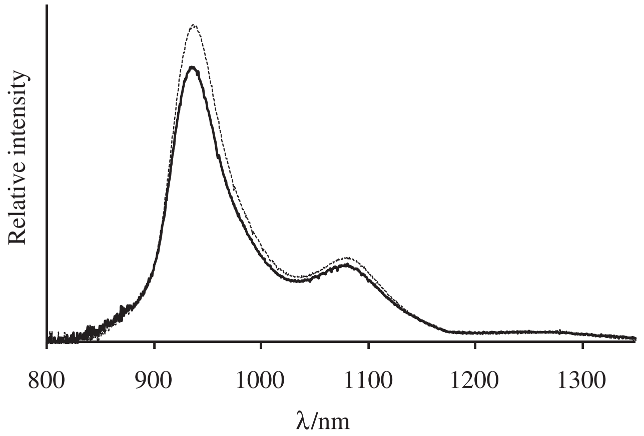

Figure 3. Phosphorescence spectra of [Sn(TPrPc)Cl_2] (dotted line) and [Sn(TPrPc)Br_2] (solid line) in 1-iodopropane. The excitation wavelength was 630 nm and absorption of the solution at 630 nm was adjusted to 0.1.

noteworthy that the complexes can emit phosphorescence in the near infrared (NIR) region at room temperature without a rare metal or noble metal; the NIR emitting complex usually contains such a precious metal ion.[17] Although the fluorescence spectra suggested that the T_1 species of [Sn(TPrPc)Br_2] should be more effectively generated via the intersystem crossing from the S_1 state than of [Sn(TPrPc)Cl_2], a rather slightly stronger intensity of the phosphorescence emission was observed from [Sn(TPrPc)Cl_2] in the NIR region as exhibited in Figure 3; the NIR light emission was readily quenched by air. These results suggest that the transition from T_1 to S_0 with the NIR light emission is not favored in [Sn(TPrPc)Br_2].

Generation of Singlet Oxygen and Oxidation Reaction. The quantum yields of the singlet oxygen formation (Φ_Δ) in air-saturated benzene were determined by comparing the phosphorescence of the $^1O_2$ generated by a standard compound (*meso*-tetraphenylporphinatozinc(II), [Zn(tpp)]) at 1270 nm.[13] As shown in Table 1, the value of Φ_Δ increased with increasing atomic weight of the axial ligand and the value reached ca. 0.8 when the bromide ions coordinated. Whereas the value of Φ_Δ is drastically changed, the ε value of the [Sn(TPrPc)X_2] complexes are in the same order. The ability of the photosensitizer is dependent on not only the value of Φ_Δ but also the amount of the absorbed photon. Thus [Sn(TPrPc)Br_2] should be the most effective photosensitizer among the [Sn(TPrPc)X_2] complexes. To evaluate the capacity of the complexes as a photosensitizer upon irradiation with red light over 600 nm, the photooxidation of 1,3-diphenylisobenzofuran (DPBF) was estimated using a tungsten lamp attached to a light filter.

The red light irradiation of the DPBF solution containing a catalytic amount of the photosensitizer caused obvious absorption spectral changes associated with the degradation of DPBF, which was monitored by the absorbance decrease at 415 nm (λ_{max} of DPBF).[14] The time-dependent conversion of DPBF is shown in Figure 4. As shown in Figure 4, DPBF was rapidly oxidized in the solution containing [Sn(TPrPc)Br_2]. Thus [Sn(TPrPc)Br_2] is the best photosensitizer among the [Sn(TPrPc)X_2] complexes for the photooxidation by red light irradiation.

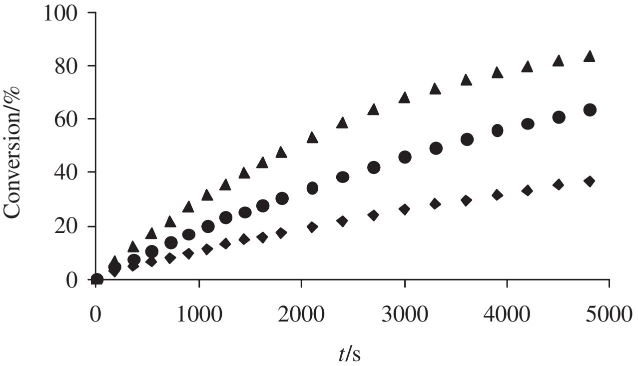

Figure 4. Photooxidation of 1,3-diphenylisobenzofuran with [Sn(TPrPc)F_2] (◆), [Sn(TPrPc)Cl_2] (●), and [Sn(TPrPc)Br_2] (▲) in benzene; [complex] = 6.0×10^{-9} mol dm^{-3}, [1,3-diphenylisobenzofuran] = 4.0×10^{-5} mol dm^{-3}.

Conclusion

The introduction of heavy atoms at the axial position of porphycenatotin(IV) complexes causes an increase in the Φ_Δ value of the porphycenatotin(IV) complex with only a slight decrease in the value of ε. The fluorescence and phosphorescence spectra suggest that the bromide ion may prevent the phosphorescence emission in the porphycenatotin(IV) system. The NIR phosphorescence emission of the porphycenatodihalotin(IV) complexes was observed in the degassed solution at room temperature. Although the complexes contain no precious metal, but base metal, they emit NIR phosphorescence around 950 nm in the degassed solution at room temperature. [Sn(TPrPc)Br_2] gives the highest value of Φ_Δ among the [Sn(TPrPc)X_2] complexes and is a very effective photosensitizer for singlet oxygen generation with red light irradiation because of its high Φ_Δ value and strong absorption over 600 nm. This work demonstrated that these photosensitizers effectively utilize a low energy light and these are suitable for applications involving the decomposition of pollutions and PDT.

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