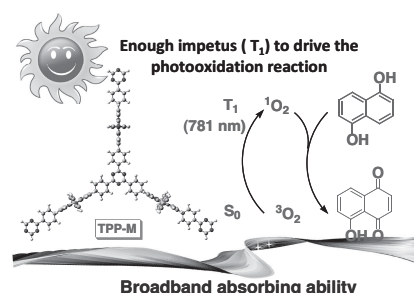


Broadband Absorbing Polyporphyrin Membrane as Singlet Oxygen Photosensitizer for Photo-oxidation

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A novel polymer membrane (**TPP-M**) with strong light harvesting ability within the entire visible-light spectrum has been prepared, in which the meso-tetrakis(4-cyanophenyl) porphyrin (**TPP-1**) as a functional unit is highly crosslinked through an aromatic nitrile trimerization reaction. The designed triazine framework controls the size of the π -conjugation and retains the excellent photophysical properties of monomeric porphyrin, such as strong absorption and high singlet oxygen quantum yield. Due to these excellent photophysical properties and low solubility in common organic solvents, polyporphyrin membranes, as efficient singlet oxygen ($^1\text{O}_2$) sensitizers, could be easily recycled and reused for the photo-oxidation of 1,5-dihydroxynaphthalene (DHN).



1. Introduction

Singlet oxygen ($^1\text{O}_2$) photosensitizers have attracted much attention due to their application in photodynamic therapy (PDT),^[1–4] photocatalysis,^[5] luminescent oxygen sensing,^[6–8] etc. The singlet oxygen photosensitizers are usually limited to monomeric compounds, such as Ru(II) polyimine complexes, Ir(III)/Pt(II) complexes, or simple organic complexes, and these conventional singlet oxygen photosensitizers suffer from some disadvantages, such as weak absorption of visible light, and more importantly, poor recyclability. More attentions need to be focused on the development of new photosensitizers to overcome the disadvantages mentioned above.

In order to overcome the challenge of recycling photosensitizer, polymers insoluble in common solvents were desired. The advanced polymeric singlet oxygen ($^1\text{O}_2$) sensitizers should also have the following properties: 1) strong absorption of visible light,^[9] preferably over the whole visible light range; 2) the first triplet excited state (T_1) energy level should be appropriately higher than that of singlet oxygen ($^1\text{O}_2$, 1270 nm), large energy gap could provide enough impetus for the triplet–triplet energy transfer (TTET) process between the photosensitizer and the dioxygen molecule (O_2);^[10] 3) efficient intersystem crossing ability to produce triplet excited state, preferably without heavy atom, such as Pt, Ir, and Ru.^[11]

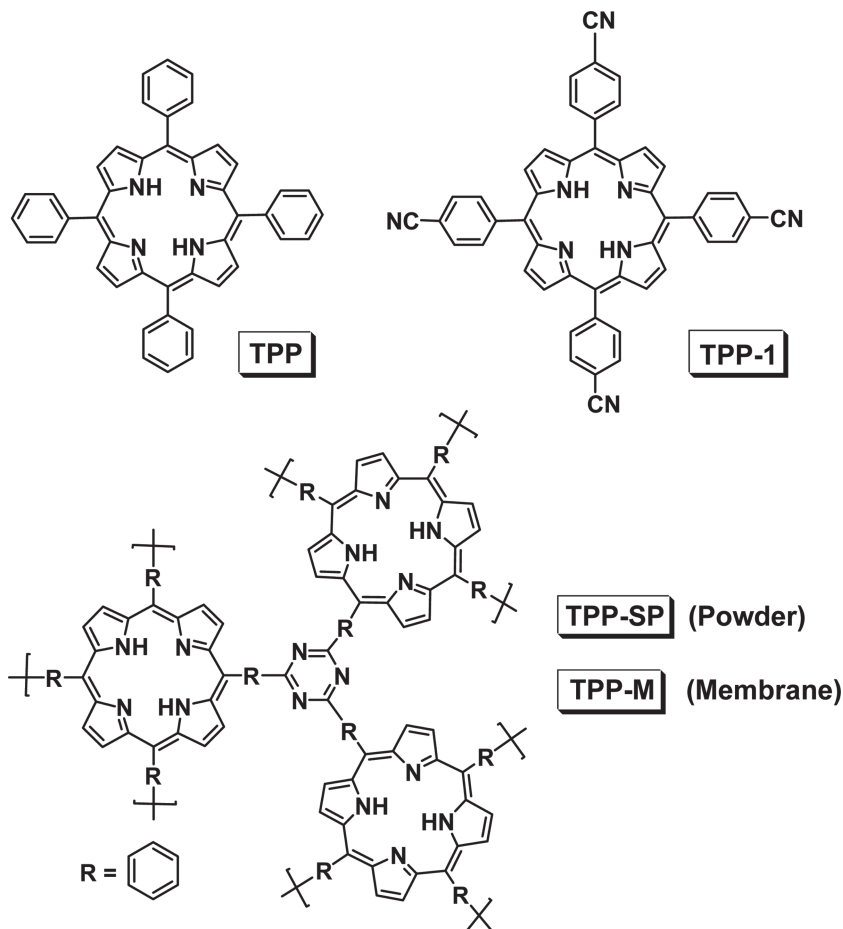
Previously, thiazo-coumarin ligands were directly cycloplatinated to obtain the ^3IL excited states (intra-ligand triplet excited state) of coumarin.^[12] The phosphorescent emission wavelength (T_1 energy level) is dependent on the size of π conjugation, rather than the intramolecular charge transfer (ICT) feature of ligands. Porphyrin has similar photophysical properties, which are also from the ^3IL excited states of porphyrin.^[13] For the tetraarylporphyrin, the aryl group is nearly perpendicular to the porphyrin core, which block the extension of π -conjugation between the porphyrin core and the aryl appendants.^[13,14] Triazine unites as crosslinkers could be incorporated into the amorphous polymers via aromatic nitrile trimerization reaction.^[13,15–19] Triazine unites are

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rigid structure and not full π conjugation with porphyrin core. Therefore, we propose that cross-linking of triazine unit could efficiently prohibit the reduction of T_1 energy level of polyporphyrin and also reduce the solubility of the singlet oxygen sensitizers in common organic solvents.

Without heavy atom, porphyrins are easy to produce the triplet excited states due to their high intersystem crossing ability. For example, the triplet quantum yield of meso-tetraphenyl porphyrin (**TPP**) is up to 0.55 in CHCl_3 , and the visible light-harvesting ability of **TPP** ($\lambda_{\text{ab}} = 419 \text{ nm}$, $\epsilon = 496\,000 \text{ M}^{-1} \text{ cm}^{-1}$)^[13] is higher than other common fluorophores, such as coumarin or fluorescein. Due to the excellent photophysical and photochemical properties of porphyrins, meso-tetrakis(4-cyanophenyl) porphyrin (**TPP-1**, the triplet quantum yield is 0.53)^[20] was selected as the starting monomer, and the polymerized porphyrin was synthesized according to the literature procedure.^[21]



Scheme 1. Molecular structures of the starting monomer **TPP-1**, **TPP-SP** (polyporphyrin powder soluble in common organic solvents), and **TPP-M** (polyporphyrin membrane with low solubility in common organic solvents). **TPP** was also shown as reference.

2. Experimental Section

2.1. General Methods

Meso-tetraphenyl porphyrin (**TPP**) and meso-tetrakis(4-cyanophenyl) porphyrin (**TPP-1**) were prepared following the reported methods.^[21] $\text{CF}_3\text{SO}_3\text{H}$ was selected to catalyze the aromatic nitrile trimerization reaction for polymerization.^[15] At a low temperature, the state of polyporphyrin was membrane (**TPP-M** low soluble in common solvents, Scheme 1), whereas polyporphyrin in powder state was obtained at 40°C (**TPP-SP** soluble in common solvents, Scheme 1).

2.2. Synthesis of TPP-M Insoluble in Common Solvents

2.5 mL of $\text{CF}_3\text{SO}_3\text{H}$ was added dropwise to **TPP-1** (50 mg, 0.07 mmol) at -10°C under nitrogen in about 3 min. The mixture became viscous green solution. After stirred for 1.5 h, the mixture was poured into a flat glass dish and allowed to spread into a thin layer. With temperature treatment of 100°C for about 20 min, a soft coating film was successfully formed. The material was then quenched in cold water and washed with diluted Na_2CO_3 solution for several hours to remove the excess $\text{CF}_3\text{SO}_3\text{H}$. After extraction with CH_2Cl_2 , toluene, and $\text{MeOH}/\text{H}_2\text{O}$ (volume ratio 1:1) in a Soxhlet extractor for 24 h, the product was dried in vacuum oven at 100°C overnight. The yield was about 90%.

2.3. Synthesis of TPP-SP Soluble in Common Solvents

Under nitrogen, **TPP-1** (100 mg, 0.14 mmol) was dissolved in 20 mL of CH_2Cl_2 . To the stirred solution, 1.5 mL of $\text{CF}_3\text{SO}_3\text{H}$ was added dropwise via a syringe in about 3 min, and then the solution was heated to 40°C overnight. Diluted Na_2CO_3 solution was added to adjust the pH to 7. The organic phase was washed with water, and then dried under vacuum. A purple solid was obtained; the yield was about 91%.

2.4. Photo-oxidation Details

Photooxidation was carried out according to a modified literature method.^[5] A CH_2Cl_2 /methanol (9:1, v/v) mixed solvent containing DHN ($1.0 \times 10^{-4} \text{ M}$) and a sensitizer was put into a two-neck round-bottom flask (20 mL). For the homogeneous reaction, the molar ratio of porphyrin (**TPP**, **TPP-1**, **TPP-SP**) to DHN was ca. 1:100. For the heterogeneous reaction, the molar ratio of porphyrin (**TPP-M**) to DHN was ca. 1:2. The solution was then irradiated using a 35 W xenon lamp (20 mW cm^{-2}) through a cutoff filter (0.72 M NaNO_2 solution, which is transmittal for light with wavelength $> 385 \text{ nm}$). UV-vis absorption spectra were recorded

at intervals of 2–5 min. The DHN consumption was monitored by a decrease in the absorption at 301 nm, and the concentration of DHN was calculated by using its molar absorption coefficient ($\epsilon = 7664 \text{ M}^{-1} \text{ cm}^{-1}$). On the other hand, the Juglone production was monitored by an increase in the absorption at 427 nm. The concentration of Juglone was calculated by using its molar extinction coefficient ($\epsilon = 3811 \text{ M}^{-1} \text{ cm}^{-1}$), and the yield of Juglone was obtained by dividing the absorption of Juglone with the initial concentration of DHN. The photostability experiments were carried out using the same method except without the substrate DHN (for the sensitizers) or without sensitizers (for DHN).

2.5. Singlet Oxygen Quantum Yields.^[1]

The $^1\text{O}_2$ quantum yields (Φ_Δ) of the porphyrin complexes were calculated with meso-tetraphenyl porphyrin (TPP) at standard ($\Phi_\Delta = 0.62$ in dichloromethane).^[22] Air-saturated dichloromethane was obtained by bubbling air into dichloromethane for 15 min. The concentration of the $^1\text{O}_2$ scavenger 1,3-diphenylisobenzofuran (DPBF) was adjusted so that its absorbance is at around 1.0 in air-saturated dichloromethane. Then, the photosensitizer was added to cuvette and photosensitizer's absorbance was adjusted around 0.2–0.3. The cuvette was irradiated with monochromatic light at the peak absorption wavelength for 10 s. Absorbance was measured for several times after each irradiation. The slopes of absorbance maxima of DPBF at 414 nm versus time graph for each photosensitizer were calculated. Singlet oxygen quantum yield (Φ_Δ) was calculated according to the Equation 1.

$$\Phi(\text{sen}) = \Phi(\text{ref}) \times \frac{k(\text{sen})}{k(\text{ref})} \times \frac{F(\text{ref})}{F(\text{sen})} \times \frac{\text{PF}(\text{ref})}{\text{PF}(\text{sen})} \quad (1)$$

Where “sen” and “ref” designate the porphyrine sensitizers and “TPP,” respectively. k is the slope of difference in change in absorbance of DPBF (414 nm) with the irradiation time, F is the absorption correction factor, which is given by $F = 1 - 10^{-\text{OD}}$ (OD at the irradiation wavelength), and PF is absorbed photonic flux.

3. Results and Discussion

3.1. Structural Characterizations and Surface Properties

The structures of polyporphyrin (TPP-SP and TPP-M) were characterized by Fourier transform IR (FTIR) and ^{13}C cross-polarization magic-angle-spinning (CP-MAS) NMR spectroscopy. Compared with the starting monomer (TPP-1) (Figure S2, Supporting Information), there is no carbon nitrile band at around 2230 cm^{-1} in the FTIR spectrum of TPP-M. Instead, two strong bands at 1690 and 1250 cm^{-1} appear (Figure S6, Supporting Information), which represent the aromatic C–N stretching and “breathing” modes in the triazine unit, respectively.^[15,19] Furthermore, ^{13}C CP-MAS NMR spectroscopy confirms the presence of sp^2 carbon of the triazine ring at around 173 ppm

(Figure S8, Supporting Information), and nitrile groups at around 110 ppm could not be found.^[15,18] These results indicate that the cross-linking reaction of TPP-M is catalyzed efficiently by $\text{CF}_3\text{SO}_3\text{H}$. Similarly, two strong bands at 1680 and 1260 cm^{-1} are observed in the FTIR spectrum of TPP-SP (Figure S7, Supporting Information), which indicates the presence of triazine units.^[15,18] In the ^{13}C CP-MAS NMR spectrum of TPP-SP, the peak at 173 ppm from triazine units also supports the FTIR spectroscopy results.

The SEM results show that TPP-M was a compact membrane (Figure S10, Supporting Information) with a smooth surface. X-ray powder diffraction measurement indicates that TPP-M is amorphous (Figure S12, Supporting Information).

3.2. UV-Vis Absorption/Emission Spectra of the Monomer and the Polyporphyrin

TPP-1 with cyano group shows absorption at 419 nm, which is close to that of TPP, while the molar extinction coefficient of TPP-1 ($\epsilon = 421\,000 \text{ M}^{-1} \text{ cm}^{-1}$ at 419 nm) is slightly lower than that of TPP ($\epsilon = 498\,000 \text{ M}^{-1} \text{ cm}^{-1}$ at 419 nm). After cross-linking of triazine units, the photo-physical properties of porphyrin units are retained in polyporphyrin. For example, Soret band of TPP-SP is at 419 nm, and Q bands of TPP-SP are at 516, 550, and 590 nm, respectively (Figure 1a). These absorption wavelengths are in excellent agreement with that of TPP-1. After TPP-1 was polymerized, the molar extinction coefficient of TPP-SP soluble in solution is up to $410\,000 \text{ M}^{-1} \text{ cm}^{-1}$ at 419 nm, which is close to that of TPP-1 ($\epsilon = 421\,000 \text{ M}^{-1} \text{ cm}^{-1}$ at 419 nm) (Figure 1a). The UV-vis absorption of TPP-M was also studied. It is hard to identify the Soret band of TPP-M at around 420 nm, the reason would be the absorption is too strong to be detected. The absorption of TPP-M at 525, 560, 597, and 655 nm could be assigned to the Q bands (Figure 1b). These significant light-harvesting abilities over the whole visible light range are beneficial for potential photocatalysis application.

The soluble porphyrin (TPP and TPP-1) and polyporphyrin (TPP-SP) show intensive red emission in the range

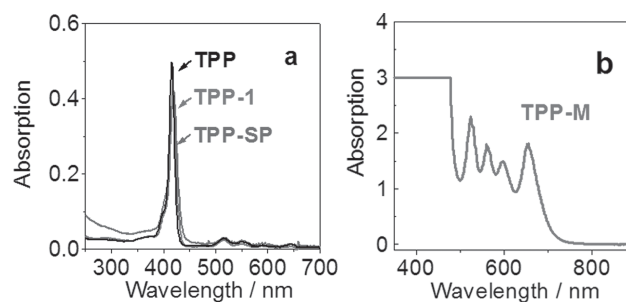


Figure 1. UV-vis absorption of a) TPP, TPP-1, and TPP-SP with equal molar ratio of TPP-1. $c = 1.0 \times 10^{-6} \text{ M}$ in CH_2Cl_2 , 20°C . b) TPP-M in the solid state.

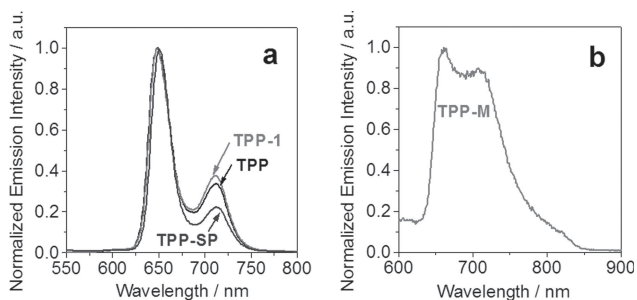


Figure 2. The normalized emission of a) **TPP**, **TPP-1**, and **TPP-SP** with equal molar ratio of **TPP-1**, $\lambda_{\text{ex}} = 419 \text{ nm}$, $c = 1.0 \times 10^{-6} \text{ M}$ in CH_2Cl_2 , $20 \text{ }^\circ\text{C}$. b) **TPP-M** in the solid state, $\lambda_{\text{ex}} = 419 \text{ nm}$.

of 620–750 nm (Figure 2a). The similar emission profile of these porphyrin complexes indicate that polymerization have little influence on the photophysical properties of polyporphyrin, and there is little electronic communication between porphyrin monomers even connected with triazine units. Compared to **TPP-SP** in CH_2Cl_2 , the maximum emission wavelength of **TPP-M** in solid state is at 660 nm, about 10 nm red-shifted (Figure 2b). It would be due to the strong absorption of **TPP-M** at 655 nm (Figure 1b), which reduces the emission intensity at around 650 nm. For the porphyrin, the singlet excited state energy level is close to that of triplet excited state, so the heavy-atom-free intersystem crossing process is efficient. The similar emission of **TPP-1** and **TPP-M** implies that the energy levels of triplet excited states are not reduced after polymerization, which is also proved by the theoretical calculation. Thus, to keep the strong impetus in TTET process, there is still a large energy gap between the T_1 states of photosensitizers (**TPP-M**) and acceptors ($^3\text{O}_2$).

3.3. Theoretical Calculations

Previously we studied monomeric porphyrin, as well as their Pt porphyrin complexes.^[13] Here, we carried out theoretical calculations to reveal the geometry and photophysical properties of polyporphyrin complexes.

First, the geometry of the porphyrin complexes were optimized (Figure 3). For **TPP-1**, the dihedral angle of the 4-cyanophenyl group and porphyrin core is 66.8° . For the polyporphyrin, the triazine unit is almost perpendicular to the porphyrin core, the dihedral angle of the two unites is 89.8° , which is larger than that of **TPP-1**. Such perpendicular geometry is probably due to the significant steric hindrance of the triazine units, which completely rules out the π -conjugation. The triplet excited states of polyporphyrin were

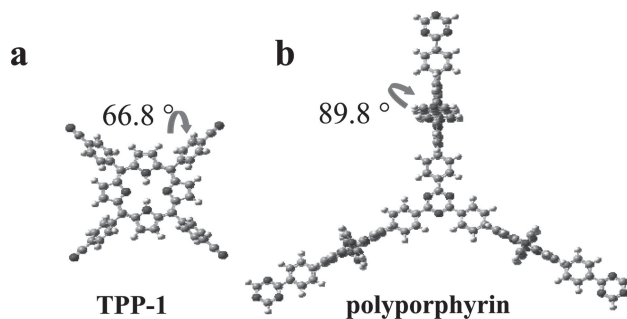


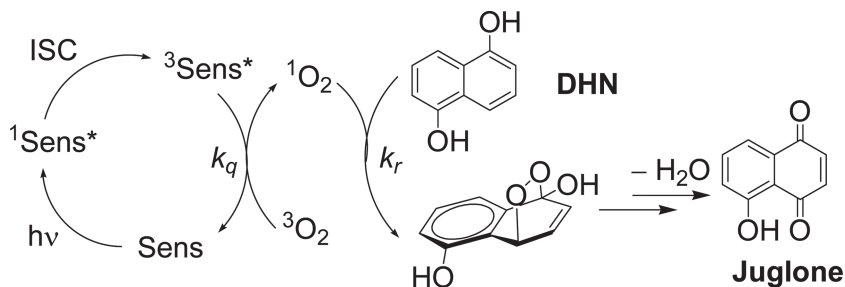
Figure 3. Optimized molecular structures of **TPP-1** and the hypothesized fragment of polyporphyrin (**TPP-SP** and **TPP-M**) which are presented to illustrate the distortion between the porphyrin core and the aryl group. Calculated at Hartree-Fock/3–21G level with Gaussian 09 W.

also studied with the TDDFT calculation based on the optimized ground state geometry, which was performed at B3LYP/6–31G level with Gaussian 09W. The calculated $S_0 \rightarrow T_1$ energy gap is 1.59 eV (781 nm), which is close to the phosphorescent emission of **TPP** (650–750 nm).^[13] The triplet excited state energy level of polyporphyrin is higher than that of $^1\text{O}_2$, so there is enough impetus to drive the photosensitizing of the singlet oxygen ($^1\text{O}_2$).

3.4. Application of Porphyrin Complexes for Photo-oxidation of 1,5-dihydroxynaphthalene (DHN)

Recently, cyclometalated Ir(III) complexes were used as a singlet oxygen photosensitizers for photo-oxidation of 1,5-dihydroxynaphthalene (DHN) (Scheme 2).^[5] However, these complexes show very weak visible-light absorption.^[5] Furthermore, polymer singlet oxygen sensitizers without heavy atom could be recyclable and cost-efficient. Thus, porphyrin as monomer was selected to construct polymer singlet oxygen sensitizers for these purposes. Here, we studied the application of the polyporphyrin (**TPP-M** and **TPP-SP**) as singlet oxygen sensitizer in the photo-oxidation of DHN.

The mechanism for the photo-oxidation of DHN with singlet oxygen photosensitizer was presented in Scheme 2.^[5] $^1\text{O}_2$ is produced upon photoexcitation of



Scheme 2. Mechanism for the photo-oxidation of **DHN** with singlet oxygen ($^1\text{O}_2$) photosensitizer.

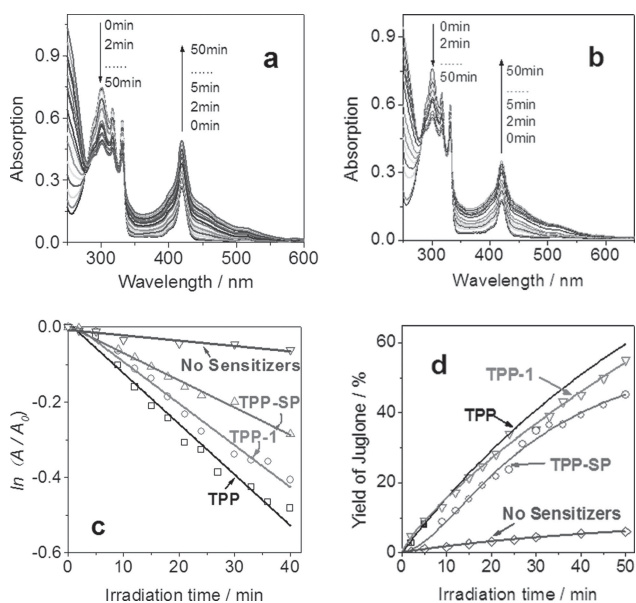


Figure 4. UV-vis absorption spectral change for the photo-oxidation of DHN (1.0×10^{-4} M) using complexes a) **TPP-1** and b) **TPP-SP** with equal molar ratio of **TPP-1** in CH_2Cl_2 /methanol (9:1, v/v) mixed solvent, [sensitizers] = 1.0×10^{-6} M, 20 °C. Light intensity: 20 mW cm^{-2} . c) Plots of $\ln(A_t/A_0)$ vs. irradiation time (t) for the photo-oxidation of DHN with **TPP**, **TPP-1** and **TPP-SP**. d) The yields of juglone against irradiation time for the photo-oxidation of DHN using complexes **TPP**, **TPP-1**, and **TPP-SP** as singlet oxygen ($^1\text{O}_2$) photosensitizers. The reaction without sensitizer was also presented.

Table 1. Photophysical and photo-oxidation of DHN-related parameters of the porphyrin complexes, measured in CH_2Cl_2 /methanol (9:1, v/v) mixed solvent, 20 °C.

Compound	$\lambda_{\text{abs}}^{\text{a)}$ [nm]	$\lambda_{\text{em}}^{\text{b)}$ [nm]	$k_{\text{obs}}^{\text{b)}$	$\Phi_{\Delta}^{\text{c)}$	Yield ^{d)} [%]
TPP-1	419(4.21), 515(0.25), 551(0.13), 590(0.09)	648, 712	11.1	0.66	55.1
TPP	419(4.98), 515(0.31), 551(0.19), 590(0.12)	649, 713	13.5	0.62	59.1
TPP-SP	419(4.10), 514(0.11), 548(0.08), 589(0.05)	651, 713	7.2	0.26	45.1
TPP-M	524, 560, 598, 655	660, 711	11.6	— ^{e)}	62.9

^{a)}Molar extinction coefficients ($10^5 \text{ M}^{-1} \text{ cm}^{-1}$) are shown in parentheses; ^{b)}Pseudo-first-order rate constant, $\ln(A_t/A_0) = -k_{\text{obs}}t$. In 10^{-3} min^{-1} ; ^{c)}Measured in CH_2Cl_2 corrected using tetraphenylporphyrin (**TPP**) ($\Phi_{\Delta} = 0.62$) as a reference; ^{d)}Yield of Juglone after irradiation 50 min photo-oxidation; ^{e)}Not available detected.

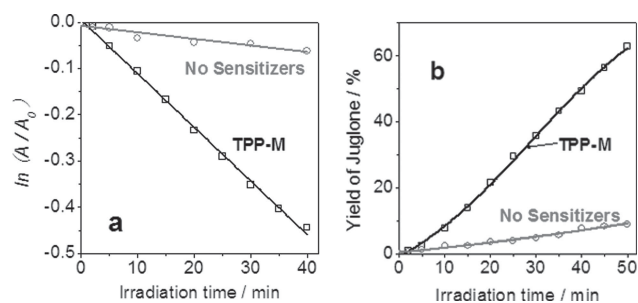


Figure 5. a) Plots of $\ln(A_t/A_0)$ vs. irradiation time (t) for the photo-oxidation of DHN (1.0×10^{-4} M) with **TPP-M** in 20 mL CH_2Cl_2 /methanol (9:1, v/v) mixed solvent, $m[\text{sensitizers}] = 7.1$ mg, 20 °C. Light intensity: 20 mW cm^{-2} . b) The yields of juglone against irradiation time for the photo-oxidation of DHN using complexes **TPP-M** as singlet oxygen ($^1\text{O}_2$) photosensitizers. The reaction without sensitizer was also presented.

the aerated solution of the sensitizer. In this process, an energy transfer from the triplet excited state of a sensitizer to triplet oxygen ($^3\text{O}_2$) produces singlet oxygen ($^1\text{O}_2$). Then, the DHN can be oxidized by the $^1\text{O}_2$ and produce Juglone, which could be monitored by UV-vis spectrum. Upon irradiating the mixed solution of porphyrin complexes and DHN with a xenon lamp, the absorption of DHN at 301 nm decreased and the absorption of the product Juglone at 427 nm increased (Figure 4a,b).

In order to study the photo-oxidation effect of **TPP-M**, which has low solubility in common solutions, we compared the photo-oxidation velocities with polyporphyrin (**TPP-SP** soluble in common solutions) and the results with **TPP** (reference) and **TPP-1** (starting monomer) as singlet oxygen sensitizers by plotting the $\ln(A_t/A_0)$ - t curves (Figure 4c). The slopes (k_{obs}) of the photo-oxidation with **TPP-1** ($11.1 \times 10^{-3} \text{ min}^{-1}$) is close to that of **TPP** ($13.5 \times 10^{-3} \text{ min}^{-1}$) (Table 1). After polymerization, the polyporphyrin (**TPP-SP**) still keeps high photo-oxidation ability. The slope of **TPP-SP** could come to $7.2 \times 10^{-3} \text{ min}^{-1}$ (Table 1). The singlet oxygen quantum yield of **TPP-SP** ($\Phi_{\Delta} = 0.26$) is lower than that of **TPP-1** ($\Phi_{\Delta} = 0.66$) (Table 1), which may be due to the aggregation of the porphyrin cores.^[23] However, the yield of Juglone using **TPP-SP** (45.1%) as singlet oxygen sensitizers is close to that of **TPP-1** (55.1%), which is due to the higher visible-light-harvesting ability of **TPP-SP** (Figure 4d).

TPP-M has low solubility in common solvents, and the photo-oxidation reaction with **TPP-M** is heterogeneous reaction. Here, **TPP-M** as the singlet oxygen sensitizers was also detected (Figure 5). The slope (k_{obs}) of the photo-oxidation with **TPP-M** is $11.6 \times 10^{-3} \text{ min}^{-1}$ (Figure 5a), and the yield of Juglone is up to 62.9% (Figure 5b and Table 1). It should be noted that photo-oxidation ability of **TPP-M** (polymerization with triazine unit) are not dramatically influenced by the polymerization, and the photophysical

properties of the monomer porphyrin, such as high light-harvesting ability, is still maintained. The recyclability and reusability of **TPP-M** were also examined. **TPP-M** could be recovered from the reaction mixtures by simple filtration. There is no obvious deterioration of conversion after four times repeated experiments with the same **TPP-M** (Table S1, Supporting Information). From the UV-vis absorption spectrum analysis, **TPP-M** is very stable under irradiation (Figure S21, Supporting Information) and there is no sign of porphyrine complexes leaching into the solution (Figure S19 and S20, Supporting Information).

4. Conclusion

Under lower reaction temperature, triazine units have been introduced into the polyporphyrin for polymerization, so **TPP-M** possess a high T_1 energy level and low solubility. **TPP-M** shows high light-harvesting ability within the entire visible light spectrum. Without heavy atom, **TPP-M** was used as efficient, recyclable, and reusable singlet oxygen sensitizer for photo-oxidation of 1,5-dihydroxynaphthalene. Our results will be useful for the development of polymers as recyclable singlet oxygen photosensitizers for photo-oxidation reactions.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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