Selective photooxidation of cyclohexene with molecular oxygen sensitized by palladium phthalocyaninesulfonate

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Abstract

Photooxidation of cyclohexene by molecular oxygen was studied in an organic aqueous solution under visible light irradiation, using the title complex PdPcS and its analogues AlPcS and ZnPcS as sensitizer. The reaction gave cyclohexene hydroperoxide as the major product, and 2-cyclohexen-1-one and 2-cyclohexen-1-ol as the minor products. However, the product yield and selectivity, as well as the catalyst stability, were all greatly dependent on the sensitizer, organic solvent, and water concentration present in the mixed solution. Among the three sensitizers examined, PdPcS was the best in terms of both photoactivity and stability. The selectivity of cyclohexene hydroperoxide as high as 99% was obtained with PdPcS in a mixed solvent of CH_3CN and H_2O (85:15, v/v). Quenching experiments with sodium azide and benzoquinone showed that singlet oxygen was involved as the main reactive species responsible for the sensitized oxidation of cyclohexene.
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1. Introduction

Alkane and alkene oxidation has been a subject of intensive research, since the reaction products such as alcohols, ketones and aldehydes are very important to fine chemical synthesis and industrial processes. The key issue in the oxidation process is the product selectivity. Traditional thermal catalytic oxidation often gives various products with a low selectivity, due to the side reactions that are hardly controlled. Comparatively, the light-initiated oxidation holds some special promise [1]. The photooxidation can occur at room temperature, and allows for selective activation of relevant molecules. As a result, unwanted thermal reactions are largely minimized, and desirable product can be produced with a high selectivity [2]. Proper design of a photochemical system may also permit utilization of solar light as a driving force and molecular oxygen as a green oxidant for the selective oxidation of organic substrates under mild conditions.

Recently, dye-sensitized oxidation of cyclohexene by molecular oxygen under visible light irradiation has been reported. For example, Maldotti et al. have found that palladium porphyrin

is an excellent sensitizer [3]. The reaction gives cyclohexene hydroperoxide as the major product with a high selectivity up to 90%, whereas cyclohexenol and cyclohexenone are only formed in a trace amount. The reaction is proved to be initiated by singlet oxygen ($^1O_2$), and the catalyst is quite stable during the photoreaction. Sehlotho and Nyokong have employed zinc phthalocyanine as the sensitizer [4]. This complex, as compared to palladium porphyrin, can utilize a larger portion of solar light. However, the sensitized reaction results in several products with a low selectivity, including cyclohexene hydroperoxide, cyclohexene oxide, cyclohexenone, cyclohexenol and *trans*-cyclohexanediol. Also the catalyst itself suffers a serious bleaching during the reaction [4]. Such undesirable degradation is also found with other phthalocyanines of iron, cobalt and manganese, during the thermally catalytic oxidation of cyclohexene [5–7].

In order to improve the efficiency of photosensitized reaction, several aspects need to be considered. First, the sensitizer should possess a high quantum yield in the production of $^1O_2$. Second, it should be robust against (photo)bleaching during the reaction. Third, it is available at a low cost, and can collect visible light as much as possible. In this regard, metal phthalocyanine (MPc) is worthy of further study. As compared to porphyrin complexes [1,3,8], MPc possesses a higher absorption coefficient toward

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visible light in the region of 600–700 nm, and also is easily synthesized. In general, the MPc complex that contains a metal ion with filled electron shells or d orbitals such as Al(III) and Zn(II) have a high quantum yield of $^1O_2$ formation, whereas the complex containing paramagnetic transitional metal ion such as Co(II) has a very low quantum yield [8]. However, an exception has been observed with palladium(II) complex of sulfonated phthalocyanine (PdPcS), the situation similar to palladium porphyrin [3]. PdPcS shows a high quantum yield in its triplet state formation (1.0) and in $^1O_2$ generation (0.86 at 606 nm) in an aqueous solution [9,10]. During the photosensitized oxidation of chlorophenols in an aqueous solution, PdPcS exhibits a superior activity and stability to its analogues, AlPcS and ZnPcS [10]. It is also known that the dye photoactivity is higher in a monomeric form than that in an aggregated form, to which solvent plays an important role [11,12]. Moreover, during the photosensitized reaction, there is always a competition of energy-transfer with electron-transfer, the latter of which would depend on the redox properties of both solvent and target substrate. An attachment of electron-attracting groups to the Pc ring such as –SO$_3$– may result in a reduced electron density, thus improving the sensitizer stability. Therefore, for a specific reaction, it is necessary to examine both the photoreactivity and stability of sensitizer in different solvents.

In this work, we have examined PdPcS as a sensitizer for cyclohexene oxidation under visible light irradiation. The effect of organic solvent and water content in the mixed solvent was studied, in terms of the product yield and selectivity, and the catalyst stability. The reactions were also performed with AlPcS and ZnPcS as the sensitizer. The results showed that PdPcS was excellent both in photoactivity and stability for the sensitized oxidation of cyclohexene in a mixed of CH$_3$CN–water. The reaction gave cyclohexene hydroperoxide as the major product, with a selectivity as high as 99%.

2. Experimental

2.1. Materials

Cyclohexene was purchased from Fisher. Cyclohexene oxide and 2-cyclohexen-1-ol were purchased from J&K Co. Ltd., and 2-cyclohexen-1-one from Wujiang Shenhong Chemical Co. Ltd. Dimethylformamide (DMF), acetonitrile, dioxane, dichloromethane, isopropyl alcohol, triphenylphosphine (PPh$_3$), sodium iodide and benzoquinone were purchased from Shanghai Chemicals. The sensitizers, PdPcS, AlPcS and ZnPcS, were synthesized and purified as previously described [10,13], using 1,2-dicyanobenzene and metal chloride (molar ratio = 4:1) as starting materials, and fume sulfuric acid as a sulfonation reagent. All the chemicals were used as received. Deionized and doubly distilled water was throughout used in this study.

2.2. Photoreaction

All the experiments were carried out in a Pyrex glass-made reactor (50 mL), thermostated at 20 °C. The reaction solution containing necessary components (cyclohexene, solvent, cata-

lyst, and *n*-decane as an internal standard) was first stirred in the dark for half an hour. Then the solution was irradiated by a Halogen lamp (500 W), which had been on for 30 min at least. At given intervals of irradiation, small aliquots were withdrawn and analyzed as described below.

2.3. Analysis

The reaction products were determined by a similar method as described by Maldotti et al. [14]. GC analysis was performed on a KeChuang gas chromatograph, equipped with an FID detector and a cross-linked capillary column (SE-54). Since allylic hydroperoxide is thermally unstable, and suffers decomposition into 2-cyclohexn-1-one and 2-cyclohexen-1-ol, the peroxide was separately analyzed by a standard spectrophotometric method [15]. For ketone and alcohol analysis, the sample should be pretreated with an excess amount of PPh$_3$ so that cyclohexene hydroperoxide was completely converted into 2-cyclohexen-1-ol. Control experiment confirmed that PPh$_3$ was not able to reduce 2-cyclohexen-1-one into the corresponding alcohol. Thus, the concentration of 2-cyclohexen-1-one in the un-treated solution could be directly determined by GC analysis. The concentration of 2-cyclohexen-1-ol in the un-treated solution was calculated by the GC-determined 2-cyclohexen-1-ol, subtracted by cyclohexene hydroperoxide concentration determined above by the spectral method.

Both the products of ketone and alcohol, formed from cyclohexene oxidation, were confirmed by GC/MS on an Agilent 6890/5973 GC/MS, equipped with DB-17 scientific column. The product yield was calculated by moles of the products formed divided by moles of the initial cyclohexene used. The product selectivity was calculated by moles of the specific product divided by total moles of the products formed. The yield of photocatalyst bleaching was estimated by the dye Q-band, monitored on an Agilent 8453 UV–vis spectrometer. All the data were expressed as percentage in the text.

3. Results and discussion

3.1. Photooxidation of cyclohexene and reaction mechanism

The photocatalyst PdPcS is highly soluble in water, but cyclohexene is hardly dissolved. Because of that, all the reactions were performed in an organic aqueous solvent. Fig. 1 shows the product distribution of cyclohexene oxidation in an aerated solution of CH$_3$CN/H$_2$O under visible light irradiation in the presence of PdPcS. The major product was cyclohexene hydroperoxide (99%), with a trace amount of 2-cyclohexen-1-one and 2-cyclohexen-1-ol. Although the product yield was low (about 14% at 8 h), the yield continuously increased with irradiation time. It is highly possible that nearly all of cyclohexene can be completely convert to hydroperoxide at a sufficiently long irradiation time under the present conditions. Control experiments showed that the products were negligible either in the dark or under irradiation without catalyst. This indicates that PdPcS is not able to function as a thermal catalyst. PdPcS is only the light-
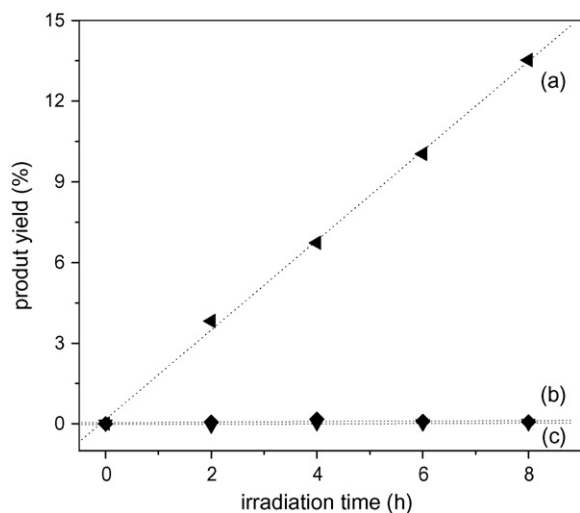
Fig. 1. Variation of the product concentration with irradiation time recorded during the photosensitized oxidation of cyclohexene in $CH_3CN:H_2O$ (85:15, v/v). (a) cyclohexene hydroperoxide, (b) 2-cyclohexen-1-one, and (c) 2-cyclohexen-1-ol. Initial concentration of cyclohexene was 9.86 mM, and PdPcS was 22 µM.

absorbing species that initiate the observed cyclohexene oxidation in an aerated solution.

In the literature, two types of primary pathways are proposed for the sensitized reaction by phthalocyanine [8]. One is the energy-transfer from an electronically excited complex to ground molecular oxygen, producing $^1O_2$. Another is the electron-transfer from the excited complex to molecular oxygen or reacting substrates, generating radicals such as superoxide radicals $(O_2^{\bullet-})$. In order to elucidate the mechanism involved, sodium azide and benzoquinone were used here as $^1O_2$ and $O_2^{\bullet-}$ scavengers, respectively (Fig. 2). The formation of cyclohexene hydroperoxide was almost completely inhibited in the presence of sodium azide, whereas the reaction rate was only slightly decreased on addition of benzoquinone. In a nitrogen-bubbling solution, almost no products were found by GC analysis. How-
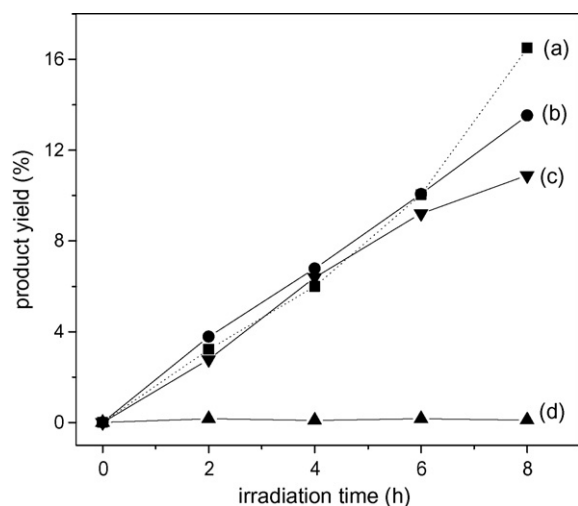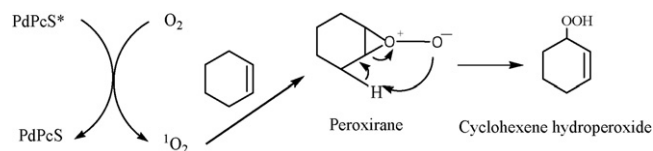

Fig. 2. Formation of cyclohexene hydroperoxide from cyclohexene oxidation in different aerated solutions of (a) CH_3CN/H_2O (70:30), (b) CH_3CN/H_2O (85:15), and (c) CH_3CN/H_2O (85:15) + benzoquinone (0.46 mM), and (d) CH_3CN/H_2O (70:30) + NaN$_3$ (0.01 M). Other conditions were the same as in Fig. 1.

Scheme 1. Proposed mechanism for the photosensitized oxidation of cyclohexene by PdPcS.

ever, in an oxygen-bubbling solution, the product yield was increased as two times as that only in an aerated solution. It suggests that $^1O_2$ is involved in the observed oxidation of cyclohexene, sensitized by PdPcS in an aerated solution. The 'ene' reaction between $^1O_2$ and cyclohexene [16,17] results in the formation of cyclohexene hydroperoxide as the major product. The product selectivity was calculated to be 99%, which gives a strong support for the reaction mechanism as presented by Scheme 1.

In the ZnPc-sensitized cyclohexene photooxidation in dioxane [4], which involves both $^1O_2$ and unspecified radicals, the selectivity of major product (2-cyclohexen-1-one) is only about 60%. Cyclohexene oxide as the main product from some thermal oxidations of cyclohexene [6] and as the minor product from the photosensitized oxidation of cyclohexene [4,14] was not found in the present system. It is reported that cyclohexene oxide is formed via the addition of peroxy radicals $(ROO^\bullet)$ to cyclohexene, followed by a homolytic decomposition [18]. In a traditional enzyme-like catalytic oxidation of cyclohexene, where organic peroxide was used as the oxidant and FePc or CoPc as the catalyst [6], the selectivity toward major product (2-cyclohexen-1-one or 2-cyclohexen-1-ol) is low (61–72%). Moreover, all the reported catalysts (ZnPc, FePc, CoPc and MnPc) suffer serious bleaching during the (photo)oxidation process of cyclohexene [5–7]. In this study, PdPcS was quite stable. After 8 h of photoreaction, the Q band at 652 nm was only decreased by 4.8%. In this regard, PdPcS is an excellent photocatalyst for the sensitized oxidation of cyclohexene to cyclohexene hydroperoxide with a high selectivity. If alcohol product is desirable, the hydroperoxide could be easily transferred into 2-cyclohexen-1-ol by iodide reduction [9]. In a previous study [19], Brown and coworker showed that cyclohexene could react rapidly with palladium acetate in acidic solution to yield benzene. For this concern, we checked this possibility in the present system. The experiment was performed using palladium chloride $(2 \times 10^{-5}\,M)$ in a mixed solvent of CH_3CN and H_2O (85:15, v/v), the conditions similar to those used in the sensitized reaction. After 8 h, no reaction products of cyclohexene oxidation were found either in the dark or under visible light irradiation. This can be ascribed to the fact that the catalyst loading used for this study is too low to initiate the catalytic process. Therefore, the observed oxidation of cyclohexene in the presence of PdPcS under visible light irradiation is only due to the photocatalytic event.

3.2. Effect of solvent and comparison with other sensitizers

The solvent has great influence on both the cyclohexene oxidation and the catalyst stability. Table 1 summarizes the data

Table 1
Photosensitized oxidation of cyclohexene and the product distributions in different solvents[a]

Solvent	Photocatalyst	Product yield (%)	Bleaching (%)[b]	Product selectivity (%)		
				Hydroxide	cyclohexenol	cyclohexenone
CH$_3$CN/H$_2$O	PdPcS	13.67	4.8	99.0	0.5	0.5
	AlPcS	4.97	10.5	98.7	1.3	Trace
	ZnPcS	3.04	99.4	95.7	4.3	Trace
Dioxane/H$_2$O	PdPcS	2.74	5.5	83.9	12.4	3.5
	AlPcS	2.14	6.7	79.0	16.8	4.2
	ZnPcS	4.68	98.6	77.1	19.9	3.0
DMF/H$_2$O	PdPcS	19.59	80.4	78.4	16.7	4.2
	AlPcS	10.62	97.4	80.0	20.0	–
	ZnPcS	6.64	99.1	65.1	34.9	–

[a] The data was obtained at 8 h. The initial concentration of cyclohexene was 9.86 mM, and catalyst at 22 μM. CH$_3$CN or dioxane:H$_2$O = 85:15, but DMF:H$_2$O = 98:2.
[b] Photocatalyst bleaching percentage.

of product yield and selectivity, as well as the percentage of the bleached catalyst, determined in three different solvents. For a comparison, other two analogues, AlPcS and ZnPcS, were also examined under similar conditions. Among the solvents studied, CH$_3$CN/H$_2$O appeared to be the best in terms of both the product yield and the catalyst stability. In DMF/H$_2$O, although the product yield of cyclohexene oxidation was relatively high, all the catalysts suffered a fast decomposition into some colorless fragments. However, all the reactions still gave hydroperoxide as the major product, with a selectivity higher than 65%. The result clearly showed that as compared to AlPcS and ZnPcS, PdPcS was the best in terms of both the photoactivity and stability. The product selectivity toward cyclohexene hydroperoxide formation was nearly 100% in CH$_3$CN/H$_2$O (85:15, v/v).

The change in solvent can result in the following changes. First, the catalyst used in this work is sulfonated phthalocyanine, which is highly soluble but has a great tendency to form aggregates in the aqueous solution [11]. Such dye aggregation normally has a detrimental impact on the production of ^{1}O$_2$, due to self-annihilation of the excited state [20–23]. Although a large amount of organic solvent was present, the dye aggregation was still evident, the degree of which following the order of DMF/H$_2$O < CH$_3$CN/H$_2$O < dioxane/H$_2$O, as demonstrated in Fig. 3. This was in agreement with the product yield of cyclohexene oxidation, which was lower in dioxane/H$_2$O than that in CH$_3$CN/H$_2$O (Table 1) (note that the catalyst stability was similar in both the solvents). Second, the catalyst (photo)stability is greatly affected by the solvent. The catalyst bleaching would result in the decrease in the rate of ^{1}O$_2$ generation, and thus the decrease in the rate of cyclohexene oxidation. However, the product yield was enhanced, especially in DMF/H$_2$O (Table 1). It implies that cyclohexene oxidation also occurs through a radical mechanism. The radicals or intermediates, once produced from the electron-transfer between the excited dye and solvent (or molecular oxygen and cyclohexene), may directly participate into the process of cyclohexene oxidation. Such involvement of both ^{1}O$_2$ and radicals in the cyclohexene oxidation has been reported with ZnPc as a sensitizer in dioxane [4]. The radical-mediated reaction seems to yield 2-cyclohexen-1-

ol, and consequently the product selectivity toward cyclohexene hydroperoxide is decreased (Table 1). The solvent effect on ^{1}O$_2$ life time [20] and its reaction rate constant [16] is also possible, but it is negligible, as compared to the solvent effect on the ^{1}O$_2$ generation and on the catalyst stability discussed above.

The central metal ion in the phthalocyanine is known to have a great influence on the photophysical and chemical properties of the complex [8]. The quantum yield of ^{1}O$_2$ generation, as determined in DMF, follows the order of AlPcS < ZnPcS < PdPcS [8,10,20–23]. This explains the results of the product yield which is much higher with PdPcS than that with AlPcS (Table 1). The low product yield obtained with ZnPcS is obviously due to the catalyst poor stability during the sensitized reaction [21,23].

3.3. Effect of water content

The result above shows that PdPcS is an excellent catalyst in CH$_3$CN/H$_2$O. Then, it is necessary to examine if there is an opti-
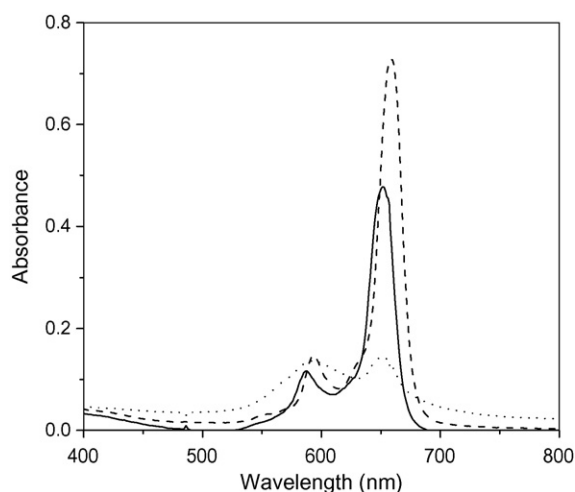

Fig. 3. Absorption spectra of PdPcS (22 μM) in different solvents of CH$_3$CN/H$_2$O (solid), dioxane/H$_2$O (dotted), and DMF/H$_2$O (dashed). Organic solvent:H$_2$O = 85:15.

Table 2
Effect of water concentration on the PdPcS-sensitized oxidation of cyclohexene[a]

Volume ratio (CH$_3$CN:H$_2$O)	Product yield (%)	Product selectivity (%)			Photocatalyst bleaching (%)
		Hydroxide	Cyclohexanol	Cyclohexanone	
98:2	0.9	92.0	8.0	Trace	9.6
90:10	7.1	92.3	6.0	1.7	0.8
85:15	13.7	99.0	0.5	0.5	4.8
80:20	15.2	89.6	8.4	2.0	3.8
70:30	19.1	86.5	12.4	1.0	0

[a] The reaction solution was irradiated for 8 h. Initial concentration of cyclohexene was 9.86 mM, and catalyst at 22 μM.

mal concentration of water. It was observed that with increasing the ratio of water to CH$_3$CN in the mixed solution, the product yield of cyclohexene oxidation increased correspondingly (Table 2). The spectral analysis showed that the absorption band at 652 nm, due to the disassociation of PdPcS aggregates into the corresponding monomers, also increased with water concentration present in solution (Fig. 4). This illustrates again that the monomeric species of PdPcS is the main photoactive species responsible for the cyclohexene oxidation by either ^{1}O$_2$ or radical pathway and/or both. However, the product selectivity toward cyclohexene hydroperoxide was observed to decrease with water content, at the ratio of CH$_3$CN to H$_2$O higher than 85:15 (Table 2), whereas the alcohol selectivity increased correspondingly. The reason for this is not known, but it may relate with the relative stability between the peroxirane intermediate (Scheme 1) and the electron-transfer-produced radicals as a function of solvent polarity. The radical mechanism favors the formation of 2-cyclohexen-1-ol. On the other hand, the life time of ^{1}O$_2$ is shorter in water (3 μs) than that in CH$_3$CN (77 μs), which may disfavor the formation of hydroperoxide (Scheme 1). For highly selective production of cyclohexene hydroperoxide, the mixed solvent of CH$_3$CN:H$_2$O at a volume ratio 85:15 appears to be the best. In such solvent, the equivalents of produced hydroxide per equivalents of consumed PdPcS are about 1.3×10^3, similar to that obtained with Pd–porphyrin complex [3].
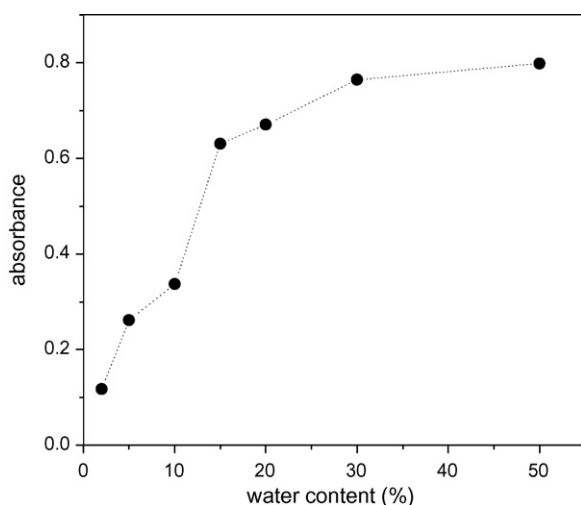
4. Conclusions

This work has shown that PdPcS is an excellent catalyst for the sensitized oxidation of cyclohexene in CH$_3$CN/H$_2$O under visible light irradiation. Since the reaction occurs via singlet oxygen, the product selectivity toward cyclohexene peroxide formation is high, and could be reached as high as 99%. However, the product yield and selectivity are greatly influenced by organic solvent and water content present in the mixed solution. In comparison, AlPcS is less efficient in the photoactivity, whereas ZnPcS suffers a fast decomposition during the photosensitized reaction. In the view of green chemistry, water as a co-solvent is a good idea. But its presence in a large amount unfortunately decreases the product selectivity. Further study for improvement of the solvent properties in a low polarity and in a high strength of minimizing the dye aggregation is needed.

Acknowledgements

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Fig. 4. Effect of water volume percentage on PdPcS absorbance at 652 nm in CH$_3$CN. Total concentration of PdPcS was fixed at 22 μM.

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