



One silver(I)/tetraphosphine coordination polymer showing good catalytic performance in the photodegradation of nitroaromatics in aqueous solution

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ABSTRACT

Reaction of AgNO_3 with one tetraphosphine ligand, 1,4-*N,N,N',N'*-tetra(diphenylphosphanylmethyl) benzene diamine (dpppda), gave rise to a Ag(I)/tetraphosphine coordination polymer $[\text{Ag}_4(\text{NO}_3)_4(\text{dpppda})]_n$ (**1**). Compound **1** has a one-dimensional (1D) chain structure in which the chair-like $[\text{Ag}_4(\text{NO}_3)_4]$ cores are linked by the dpppda ligands using a Z-shaped $\mu\text{-}\eta^2\text{:}\eta^2$ side-by-side mode. Compound **1** exhibited good catalytic activity towards the photodegradation of nitrobenzene (NB), paranitrophenol (PNP) and 2,4-dinitrophenol (2,4-DNP) in aqueous solution under UV light irradiation. The kinetics and the mechanism of such catalytic photodegradation reactions were also investigated. The present work provided some new insight into the design and preparation of new coordination polymers as catalyst for high-performance photodegradation of toxic and persistent organic species existed in industrial wastewaters.

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1. Introduction

In the past decades, industrial wastewaters have become one of the most serious problems related to our human environment [1]. Among them, nitroaromatics such as nitrobenzene (NB) and nitrophenol (NP) are commonly encountered, and toxic and persistent. Even at low concentrations, NB or NP may pose a high risk to the environment and human health [2–6]. General methods for treating the industrial wastewaters include ozonation, adsorption and biodegradation, which are not environmentally friendly and relatively expensive due to the fact that these methods require further treatments and may lead to the secondary pollution [7–10]. Catalytic photodegradation is a promising technique for the treatment and purification of such wastewaters as it could completely mineralize organic pollutants into harmless inorganic compounds [11–17]. Currently, semiconductor compounds such as metal oxides (e.g. TiO_2 , ZnO , WO_3 , SnO_2 , ZrO_2), metal sulfides (e.g.

CdS and ZnS) and metal or non-metal-doped composites are frequently employed as catalysts for the photodegradation reactions [18–30]. For example, Priya et al. reported that a series of nitrobenzenes could be photodegraded to less than 10% of their original concentrations within 2–3 h by using nano TiO_2 as a catalyst [18].

Apart from those semiconductors, in recent years, some metal coordination compounds such as $\{[\text{Cu}^{\text{II}}(\text{SallmCy})][\text{Cu}^{\text{I}}]_2\cdot\text{DMF}\}_n$ ($\text{SallmCy} = N,N'$ -bis-[(imidazol-4-yl)methylene]cyclohexane-1,2-diamine) [31], $[\text{Mn}_2(\text{pytpy})_{4/3}(\text{pbcppy})_2]$ ($\text{pytpy} = 4'-(4\text{-pyridyl})-4,2':6',4''\text{-terpyridine}$; $\text{pbcppy} = 4\text{-phenyl-2,6-bis}(4\text{-carboxyphenyl})\text{pyridine}$) [32], $[\text{Cu}(\text{dmbimdZ})]_n$ ($\text{dmbimdZ} = 5,6\text{-dimethylbenzimidazol-2-ylidene}$) [33] and $[\text{Ni}(\text{pytpy})_2\text{Mo}_4\text{O}_{13}]_n$ [34] have also been reported to be active in catalyzing the photodegradation of organic dyes [31–45]. For the silver-containing compounds, there have been mainly nanoparticles, simple salts and composite materials that are used as catalysts for the photodegradation reactions [46–51]. Only a very few Ag(I) coordination compounds have been utilized as catalysts for decomposing organic dyes like methylene blue (MB) [37,41,51]. This is because Ag(I) coordination compounds are usually sensitive to light and water. For instance, Wałęsa-Chorab reported that a dinuclear helical Ag(I) complex could catalyze the photodegradation of MB with up to 90% efficiency [51]. However its practicability was limited due to its long

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photoreaction time (9 h) and non-recyclability. To our knowledge, no metal coordination compounds have been employed as catalysts for the photodecomposition of nitroaromatics so far.

We have been interested in the construction of coordination polymers derived from metal ions and bridging N- or P- donor ligands [52–58]. Some of them could efficiently catalyze the photodegradation of organic dyes [43,44]. These preliminary results activated us to attempt these coordination compounds to catalytically photodecompose nitroaromatics such as NB and NP in aqueous solutions. The Ag(I) complexes of polyphosphine ligands attracted our attention because the rich coordination sites of these ligands could greatly stabilize the Ag(I) ions by forming insoluble and less light- and water-sensitive coordination polymers [52–55]. Thus a tetraphosphine ligand, 1,4-*N,N',N',N'*-tetra(diphenylphosphanylmethyl)benzene diamine (dpppda) [59], was selected to react with AgNO₃ to produce a 1D coordination polymer [Ag₄(NO₃)₄(dpppda)]_n (**1**). Complex **1** was revealed to exhibit good catalytic activity towards the photodegradation of three different nitroaromatics including nitrobenzene (NB), paranitrophenol (PNP) and 2,4-dinitrophenol (2,4-DNP) in aqueous solution. This catalyst could be recycled for at least five times to maintain its high catalytic efficiency. In addition, the mechanism for the catalytic photodegradation of these nitroaromatics was also studied. Described below are the preparation, characterization and catalytic photodegradation performance of **1**.

2. Experimental

2.1. General procedures

The ligand dpppda was prepared according to literature method [59]. All organic solvents were pre-dried over activated molecular sieves and refluxed over the appropriate drying agents under argon. Other chemicals were obtained from commercial sources and used as received. Elemental analyses for C, H and N were performed on a Carlo-Erba CHNO-S microanalyzer. The IR spectrum was recorded on a Varian 1000 FT-IR spectrometer as KBr disks (4000–400 cm⁻¹). The ¹H and ³¹P{¹H} NMR spectra were recorded at ambient temperature on a Varian UNITY plus-400 spectrometer. Chemical shifts were referenced to the solvent signal in DMSO-*d*₆ (¹H). The UV–vis absorption spectra of NB, PNP and 2,4-DNP aqueous solutions were measured on a Varian Cary-50 UV–vis spectrophotometer. The solid-state optical diffuse-reflection spectra were measured on a Shimadzu UV-3150 spectrometer at room temperature in the range of 200–800 nm.

2.2. Synthesis of [Ag₄(NO₃)₄(dpppda)]_n (**1**)

To a solution of AgNO₃ (7 mg, 0.04 mmol) in MeCN (5 mL) was added a solution of dpppda (9 mg, 0.01 mmol) in MeCN (5 mL). The resulting mixture was stirred for 30 min and filtered. Diethyl ether (40 mL) was layered onto the filtrate at ambient temperature for 2 days to form yellow crystals of **1**, which were collected by filtration, washed with Et₂O and dried in vacuo. Yield: 11 mg (68% based on dpppda). Anal. Calcd for C₅₈H₅₂Ag₄N₆O₁₂P₄: C, 44.05; H, 3.29; N, 5.32%. Found: C, 44.29; H, 3.33; N, 5.26%. IR (KBr disk): 3094 (w), 2359 (m), 2341 (m), 1615 (w), 1514 (s), 1474 (m), 1455 (m), 1434 (s), 1384 (m), 1296 (s), 1212 (w), 1136 (s), 1099 (m), 996 (m), 868 (m), 798 (s), 743 (m), 692 (s) cm⁻¹. ¹H NMR (400 MHz, DMSO-*d*₆, ppm): 7.70–7.40 (m, 40H, -PPh₂), 6.85 (s, 4H, -Ph- in dpppda), 4.37 (s, 8H, -CH₂- in dpppda). ³¹P NMR (161.9 MHz, DMSO-*d*₆, ppm): 23.413 (s, 1P, -PPh₂).

2.3. Single-crystal X-ray structure determination

One single crystal of **1** suitable for X-ray analysis was obtained directly from the above preparation. All measurements were made on a Rigaku Mercury CCD X-ray diffractometer by using graphite monochromated Mo *K*α (λ = 0.71073 Å) radiation. The single crystal was mounted at the top of a glass fiber with grease in a stream of gaseous nitrogen at 223 K. The program CrystalClear (Rigaku and MSC, ver 1.3, 2001) was used for the refinement of cell parameters and the reduction of collected data, while absorption corrections (multi-scan) were applied. The reflection data were also corrected for Lorentz and polarization effects. The crystal structure of **1** was solved by direct methods and refined on *F*² by full-matrix least-squares techniques with SHELXTL-97 program [60,61]. All non-hydrogen atoms were refined anisotropically, while all H atoms were placed in geometrically idealized positions. The crystal data for **1** was summarized as follows: C₂₉H₂₅O₆N₃Ag₂P₂, *M*_r = 789.20, 0.32 × 0.12 × 0.08 mm, triclinic, space group *P*₁, *a* = 10.649(2) Å, *b* = 12.367(3) Å, *c* = 12.424(3) Å, α = 95.00(3)°, β = 98.78(3)°, γ = 107.19(3)°, *V* = 1529.7(5) Å³, *Z* = 2, *D*_c = 1.714 g·cm⁻³, *F*(0 0 0) = 784 and μ = 1.431 mm⁻¹, 6844 reflections collected, 6844 unique (*R*_{int} = 0.0942). *R*₁ = 0.0940, *wR*₂ = 0.2952 and *S* = 1.012.

2.4. Evaluation of the photocatalytic activity

The catalytic photodegradation was carried out in aqueous solution containing the photocatalyst **1** and nitroaromatics (NB, PNP or 2,4-DNP). The solutions of NB, PNP and 2,4-DNP were prepared by stirring the mixture containing each compound and water for 2 h. The water phases were separated and diluted to 5 × 10⁻⁴ M for each nitroaromatic (measured by UV spectrophotometer). 20 mg (0.013 mmol) of **1** was carefully grinded and added into 30 mL (0.015 mmol) of each of the above solutions in a 50 mL quartz tube. A BET measurement showed the catalyst **1** used as a powder in the degradation has the BET surface area of 0.57 m²/g, suggesting that its pore volume **1** is small. Each nitroaromatic could easily achieve the sorption/desorption equilibrium by stirring the above mixture in the dark after 0.5 h (Fig. S1). The resulting suspension was then irradiated by a high pressure Hg lamp (400 W, 365 nm) with no light filter. The lamp and each sample were put in a water bath while the temperature was kept at lower than 35 °C to avoid any temperature effect. The distance between them was adjusted to maintain the light-power density being 30 mW/cm². At regular time intervals, 1 mL solution was aspirated, filtered and then diluted to 10 mL by water to measure the residual concentration of the sample by UV spectrophotometer.

2.5. Collection of CO₂ evolved from the photodegradation reaction

As shown in Fig. S2, a 2 mL sample cup containing saturated Ba(OH)₂ solution was hung in the reaction tube over the solution containing **1** and NB (30 mL, 5 × 10⁻⁴ M). The reaction tube was then filled with pure O₂ and stuffed up by a rubber stopper with an iron wire (Φ 0.5 mm). Upon UV light irradiation, the clear Ba(OH)₂ solution gradually became muddy and formed white BaCO₃ precipitate at the surface, which was stirred by the iron wire every 15 min to facilitate the reaction between CO₂ and Ba(OH)₂. After the irradiation, acetic acid was injected into the reaction solution to convert any CO₃²⁻ into CO₂. The BaCO₃ precipitates were finally filtered, washed by water, dried in vacuum at 45 °C and weighed to calculate the yield of CO₂.

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