Synthesis of Two Novel Water-Soluble Iron Phthalocyanines and Their Application in Fast Chromogenic Identification of Phenolic Pollutants

Jingjing Gong · Dapeng Li · Jun Huang · Liyun Ding · Yilin Tong · Kun Li · Cong Zhang

Received: 6 October 2013/Accepted: 26 November 2013/Published online: 13 December 2013 © Springer Science+Business Media New York 2013

Abstract The novel water-soluble and sterically hindered phthalocyanine complexes, i.e. iron(III) tetra-(4-carboxyphenoxy)phthalocyanine (3) and iron(III) tetra-(8-quinolineoxy-5-sulfonicacid)phthalocyanine (4) were synthesized for fast detection of phenolic pollutants. These two FePc complexes exhibited the high catalytic activity in the chromogenic reactions of phenolic pollutants. Five phenolic substrates, including phenol, 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol and 1-naphthol could be efficiently oxidized by tert-butyl hydroperoxide in the presence of these selected FePc catalyst. UV-Vis spectroscopy and HPLC technique were used to monitor the catalyzed oxidation of phenolic substrates. Compared with catalytic methods by other reported phthalocyanines, this system has the obvious advantages of fast oxidation and high-yield conversion of phenolic substrates. Under the optimal conditions, the chromogenic process of 2-chlorophenol could be completed just within 10 min with more than 90 % of conversion. Potentially, this system is

Electronic supplementary material The online version of this article (doi:10.1007/s10562-013-1178-0) contains supplementary material, which is available to authorized users.

e-mail: hjun@whut.edu.cn

D. Li

promising for the application of fast chromogenic identification of phenolic pollutants.

Keywords Iron phthalocyanines · Chromogenic identification · Phenols · Catalysis · Oxidation

1 Introduction

Iron phthalocyanine (FePc) complexes are attractive and versatile catalysts not only for the reproduction of biological oxidation performance of natural cytochrome P-450 system [1], but also in the application of selective oxidation and bleaching treatment [2-7]. Among them, tetrasulfonated iron phthalocyanine (TSFePc) has been intensively studied and become the important representative for its wide application, low cost and accessibility at a large scale [8–12]. Essentially, the central iron atom is the active site of TSFePc catalyst, and phthalocyanine ligand can stabilize iron atom with different valences from II to IV. More importantly, the substituent groups on Pc ring, as a particular composite unit, have a great influence on some physical properties (such as SO₃H for water-solubility) and determine the catalytic activity in most cases. Despite of the good dissolution of TSFePc in aqueous solution and its satisfactory catalytic activity in most oxidation reactions, the aggregation of TSFePc monomers was inevitable and considered to be main reason of low catalytic efficiency [13–16]. Thus acetonitrile was commonly used to increase the ratio of monomers [17], however, the use of organic solvent would increase cost on TSFePC catalysis in environmental pollutant control. To overcome these problems, the design and synthesis of highly monodisperse FePc catalysts have been a promising strategy and become a challenging goal in phthalocyanine catalysis chemistry.

J. Gong · J. Huang (\boxtimes) · L. Ding · Y. Tong · K. Li · C. Zhang National Engineering Laboratory for Fiber Optic Sensing Technology, Key Laboratory of Fiber Optic Sensing Technology and Information Processing (Ministry of Education), Wuhan University of Technology, Wuhan 430070, People's Republic of China

Key Laboratory for Micro-Nano Energy Storage and Conversion Materials of Henan Province, School of Chemistry and Chemical Engineering, Institute of Surface Micro and Nano Materials, Xuchang University, Henan 461000, People's Republic of China

The introduction of sterically hindered groups onto phthalocyanine ring has proved to be an efficient method to decrease the aggregation of phthalocyanine monomers. Many literatures have described the design and synthesis of metal phthalocyanine with phenyl, quinolyl and other groups [18-23]. For example, Wöhrle's group synthesized the variously unsymmetrical zinc phthalocyanine complexes with *p*-sulfophenoxy and *p*-carboxyphenoxy substituted groups and observed the high ratio of monomer in DMF solution [24]. Iliev's group reported the synthesis of zinc tetrakis (8-quinolineoxy-5-sulfonicacid) phthalocyanine complexes [ZnPc(QnSO₃H)₄] and proposed the high catalytic effectiveness attributed to the high monomer concentration of ZnPc(QnSO₃H)₄ [25]. It was reported that the phthalocyanine complexes containing quaternized pyridyl groups also had excellent water solubility and good monodispersity [20, 21, 23]. These appropriate substituent groups not only increased the dispersion of metal phthalocyanine in water or organic solvents, but also improved the catalytic behavior.

Phenols and their derivates (such as chlorophenols and naphtols) are common environmental pollutants generated from industrial manufacturing processes of pesticide, fungicide, chemical dye and polymer, and so on. Contamination by these phenolic chemicals is the most serious problem for their high toxicity, non-biodegradation, and heavy diffusibility in water environment [26, 27]. For their damage to natural environment and potential threat to human health, they have been listed as the priority control pollutants by US Environmental Protection Agency [28]. Therefore, the requirement for fast identification of phenolic pollutants and facile transformation of them to less harmful products has been the great research interest. Since 1965, the K₃Fe(CN)₆-based chromogenic reaction for measurement of phenolic compounds has been proved to be an efficient approach and become a standard method for the determination of phenols in water [29, 30]. Except for this standard method, the chromogenic identification of phenols based on catalytic oxidation by metal complexs has been studied [31–33]. However, the investigations on MPc catalytic chromogenic system have just been paid enough attention until recent years. In 2006, Rajendiran [34] presented that metal tetrasulfophthaloyanines (mainly, TSMnPc and TSFePc) could catalyze H₂O₂ oxidation of phenol assited with 4-aminoantipyrine (4-AAP). And our group reported that tetranitro iron(II)phthalocyanine (TNFe(II)Pc) could efficiently catalyze oxygen oxidation of phenols and chlorophenols into pink dyes of quinone imide in the presence of 4-AAP in 2011 [35]. Although these chromogenic reactions catalyzed by FePc complexes, especially by homogeneous TSFePc catalyst, showed the obvious chromogenic indication and good applicability in broad pH range, longer time was needed to achieve the completion of chromogenic reaction. Therefore, the improvement for higher catalytic efficiency of catalysts to shorten the test time of chromogenic assay is necessary. For this purpose, the FePc complexes with sterically hindered groups on Pc ring should be developed and their optimal working conditions need to be determined.

In this paper, two novel water-soluble FePc complexes, i.e. iron(III) tetra-(4-carboxyphenoxy)phthalocyanine (3) and iron(III) tetra-(8-quinolineoxy-5-sulfonicacid)phthalocyanine (4), were synthesized for the detection of phenolic pollutants. These two FePc complexes showed excellent monodispersion in aqueous solution due to the high hydrophilicity and space steric hindrance of selected groups on Pc ring. Five phenolic compounds as model pollutants could be oxidized rapidly and transformed into pink dyes in the presence of FePc (3 or 4) and tert-butyl hydroperoxide (t-BuOOH). To the best of our knowledge, this is the first report upon the high catalytic effectiveness of novel water-soluble iron phthalocyanines and their fast chromogenic response to various phenolic pollutants. The detail mechanism for the formation of dyes and the transformation of iron-oxygen active species was proposed based on the results of control experiments and current theory of MPc catalysis. Moreover, the experimental conditions (such as concentration of t-BuOOH and 4-AAP, pH and temperature) for FePc catalyzed chromogenic reaction were optimized for the purpose of fast chromogenic identification of phenolic pollutants.

2 Experimental

2.1 Materials

Phenol, 2-chlorophenol (2-CP), 4-chlorophenol (4-CP), 2,4-dichlorophenol (DCP), 1-naphthol (1-NP), and 4-aminoantipyrine were purchased from Sinopharm Chemical Reagent Co., Ltd. Dimethyl sulfoxide (DMSO) and *n*-pentanol were purified by pre-drying over BaO and distilled under reduced pressure. K_2CO_3 was dried in oven before use. Column chromatography purifications were preformed on silica gel. Na₂HPO₄–KH₂PO₄ buffer solution (0.2 M, pH 5.0), Boric acid–borax buffer solution (0.2 M, pH 11.0) were used as catalytic reaction medium. Deionized water was used in all the experiments. Methanol and acetonitrile (HPLC grade, Sinopharm Chemical Reagent Co., Ltd.) were used as elution solution.





2.2 Equipment

IR spectra were recorded on a Thermo Nicolet Nexus FT-IR spectrometer with the standard KBr pellet method. ¹H NMR spectra were recorded on a Varian NMR System 600 MHz Spectrometer. Elemental analyses were performed on a Vario ELIII Elemental Analyzer. Catalytic oxidation reaction was monitored by a UV–Vis spectrophotometer (Shimadzu UV-2450) and high performance liquid chromatography (HPLC, Dalian Elite P230 series). The chromatography instrument was equipped with a C 18 reverse column (200 × 4.6 mm) and connected to a variable wavelength UV–Vis detector (set at $\lambda = 220$ nm). The mobile phase consisted of acetonitrile–methanol– water mixture (4:1:5, v/v) with a flow rate of 1.0 mL/min. The column temperature was set at 25 °C. The inject volume of each sample was 20 µL.

2.3 Preparation and Characterization of Water-Soluble Phthalocyanines

There are two steps to synthesize the novel water-soluble iron phthalocyanine complexes of **3** and **4**. Step I: the preparation of precursor (**1**) of 4-(3,4-dicyanophenoxy)benzoic acid and precursor (**2**) of 5-(3,4-dicyanophenoxy)quinoline-8-sulfonic acid. Step II: the synthesis of water-soluble iron phthalocyanine complexes of **3** and **4** via an organic reaction in refluxed *n*-pentanol with $Fe_2(SO_4)_3$ and precursor (**1** or **2**) as reactants and 1,8diazabicyclo[5.4.0]undec-7-ene (DBU) as the catalyst (Scheme 1).

2.3.1 Synthesis of Precursors (1 and 2)

Precursors (1 and 2) were prepared by reported methods [24, 25].

1: Yield: 90 %; FT-IR (KBr pellets) 3081(m), 2235(s), 1679(s), 1587(s), 1486(s), 1249(s), 852(s) cm⁻¹; ¹H NMR (600 MHz, d6-DMSO): δ 7.26 (d, 2H, 2,6-H), 7.53 (m, 1H, 6'-H), 7.91 (d, 1H, 2'-H), 8.04 (d, 2H, 3,5-H), 8.15 (d, H, 5'-H), 13.05 (s, 1H, COOH).

2: Yield: 66 %; FT-IR (KBr pellets) 3430(s), 3100(w), 2240(s), 1640(w), 1600(s), 1240(s), 1190(s), 1100(s), 1040(s) cm⁻¹; ¹H NMR (600 MHz, d6-DMSO): δ 7.37 (dd, 1H, 6-H), 7.64 (d, 1H, 6'-H), 7.80 (dd, 1H, 2-H), 7.90 (d, 1H, 2'-H), 8.05 (d, 1H, 7-H), 8.09 (d, 1H, 5'-H), 8.91 (d, 1H, 1-H), 9.43 (d, 1H, 3-H).

2.3.2 Synthesis of Water-Soluble Iron Phthalocyanines (3 and 4)

The water-soluble iron phthalocyanine complexes (**3** and **4**) were prepared via the route similar to the reported literatures [24, 25] with some modifications. For the synthesis of **3**, 2 mmol precursor **1**, 0.6 mmol Fe₂(SO₄)₃·*x*H₂O and 1 mL DBU were added into a 50 mL two-necked flask containing 15 mL dried *n*-pentanol under magnetic stirring. The mixture was heated slowly to 140 °C to completely dissolve all the organic solid under the protection of nitrogen, and subsequently the temperature was kept to reflux for 12 h. Thereafter, the mixture was cooled to room temperature and the dark green product was obtained. The *n*-pentonal was evaporated under reduced pressure and the

residue was washed with the mixed solution of water, methanol and HCl solution for several times. Finally, the resulting mixture was precipitated from DMSO and methanol to give the desired product. Yield: 55 %. IR (KBr pellet): 3425(m), 2931(m), 1714(m), 1599(s), 1473(w), 1265(w), 1238(s), 1161(m), 852(w), 557(w) cm⁻¹. UV–Vis (DMSO), λ_{max}/nm (logɛ, dm³ mol⁻¹ cm⁻¹): 333 (4.63), 571 (3.97), 629 (4.50). Anal. Calcd. for C₆₀H₃₂FeN₈O₁₂: C, 64.76; H, 2.90; N, 10.07. Found: C, 64.27; H, 2.70; N, 10.27.

The synthesis of **4** was similar to that of **3**, except that the precursor **2** was used instead of **1**. The prepared crude product of **4** was purified by flash column with the solution of CH₃OH and CH₂Cl₂ (v/v, 1:3) as the eluent. Yield: 12 %. IR (KBr pellet): 3431(m), 3093(w), 1722(s), 1602(m), 1384(m), 1259(w), 1200(m), 1040(s), 818(w), 638(m), 596(w) cm⁻¹. UV–Vis (DMSO), λ_{max} /nm (loge, dm³ mol⁻¹ cm⁻¹): 283 (4.62), 601 (3.94), 654 (4.53). Anal. Calcd. for C₆₈H₃₆FeN₁₂O₁₆S₄: C, 55.89; H, 2.48; N, 11.50. Found: C, 55.51; H, 2.18; N, 11.79.

2.4 Catalytic Oxidation Experiment

The typical catalytic oxidation of phenolic substrates with 4-AAP by water-soluble iron phthalocyanine of 3 or 4 was carried out in aqueous solution at room temperature using tert-butyl hydroperoxide (t-BuOOH) as the oxidant. A 30 mL of deionized water, 10 mL of 4-AAP aqueous solution (1.0 \times 10⁻³ mol/L), 5 mL of phenolic solution $(1.0 \times 10^{-3} \text{ mol/L})$, and 5 mL of water-soluble iron phthalocyanine stock solution $(1.0 \times 10^{-4} \text{ mol/L}, \text{ dis-}$ solving 3 or 4 completely with the addition of proper NaOH aqueous solution) were sequentially added into a 50 mL glass beaker. The catalytic reaction was initiated by addition of 5 µL t-BuOOH solution following by continuous magnetic stirring at 25 °C. A portion of reaction solution was collected at regular intervals and immediately followed with the detection by a UV-Vis spectrophotometer. HPLC was used to monitor the reaction process and identify the productions in 2-CP system. The 2-CP and 4-AAP were determined by spiking using standards via comparison of retention times in HPLC profile.

3 Results and Discussion

3.1 Chromogenic Reaction of Five Phenolic Substrates Catalyzed by **3** and **4**

It has been reported that phenol and its various derivatives could be efficiently oxidized by *t*-BuOOH in the presence of water-soluble iron phthalocyanine catalyst [2, 9, 10, 13, 14], so we selected five kinds of phenolic substrates to

investigate the catalytic effectiveness of as prepared catalyst 3 and 4. Fig. 1a, b shows the time-dependent UV-Vis absorption spectra of oxidation of phenol and 2-CP, respectively, assisted with 4-AAP and the formation process of dyes in the presence of **3** and *t*-BuOOH. Obviously, the absorbance peaks at 508 nm were observed for the formation of conjugated products of antipyriloquinoneiminium dyes, meanwhile, the color of solution changed much rapidly from pale green to dark pink (see Video data). When the catalytic reaction lasted for 10 min, the absorbance intensity of dyes did not increase any more, which meant the completion of catalytic oxidation. Different from TSFePc which has the Q bands of dimeric and monmeric forms, only an intend monomer peak in Q band of **3** was observed, which illuminated that the bulky phenyl substituent groups on Pc ring prevent $\pi - \pi$ interactions between macrocycles of FePc complexes. Moreover, it is notable that the intensity of Q band of 3 at 634 nm disappeared when the absorbance of formed dyes achieved to maximum. According to Nyokong's investigation on liquid phase oxidation of cyclohexane with peroxide catalyzed by FePc complexes, absorbance peaks of FePc in Q band could decrease gradually when peroxide was mixed with FePc [15]. For our catalytic system, the disappearance of Q band of **3** probably resulted from the decomposition of the phthalocyanine ring, which was a result of the attack of the phthalocyanine ring by the BuO[•] radical. It is noted that the homogeneous catalytic oxidation of DCP, 4-CP and 1-NP could be completed just within 10 min in the presence of 3and t-BuOOH (full UV-Vis spectra not shown). The catalytic oxidation rate for these five substrates follows the trend: DCP > 2-CP > phenol > 4-CP > 1-NP (Fig. 1c). Interestingly, we found the situation of catalytic oxidation of same phenolic substrates with t-BuOOH in the presence of 4 was similar to that of 3 (Fig. 1d, e), except for longer reaction time. (Fig. 1f) Based on the increase rate in dye absorbance, we believe that catalyst 3 shows higher catalytic activity than 4 under current conditions. The detailed reasons for activity difference of catalyst 3 and 4 would be discussed later.

3.2 Catalytic Process Monitoring by HPLC

Based on the analysis of UV–Vis absorbance spectra of chromogenic reactions, we concluded that the production of dye resulted from a fast oxidative coupling between phenolic substrate and 4-AAP, and thus HPLC chromatogram was a suitable method to observe the transformation process of these two kinds of substrate to dyes. The catalytic oxidation system of 2-CP was selected for its fast chromogenic identification. Fig. S1a and b of supplementary data presents HPLC chromatograms corresponding to chromogenic reactions catalyzed by **3** and **4**, respectively. Fig. 1 The time-dependent UV-Vis absorption spectra of dye formation process in the presence of 3 and t-BuOOH for a phenol system and b 2-CP system. c The comparison of dye formation process for five phenolic substrates with 3 as the catalyst. ($\lambda_{abs} = 508 \text{ nm}$); The time-dependent UV-Vis absorption spectra of dye formation process in the presence of 4 and t-BuOOH for d phenol system and e 2-CP system. f The comparison of dye formation process for five phenolic substrates with 4 as the catalyst. ($\lambda_{abs} = 508 \text{ nm}$) Reaction conditions: phenolic substrates $(1.0 \times 10^{-4} \text{ M})$, 4-AAP (2.0 \times 10⁻⁴ M). catalyst 3 and 4 (1.0 \times 10⁻⁵ M) and t-BuOOH (5.0 µL)



Obviously, the chromatographic peaks of 2-CP and 4-AAP disappeared completely at 10 min, which meant the completion of their oxidative coupling reaction (see Fig. S1a in supplementary data). Besides, there was only one strong peak of dyes along with some very weak peaks (retention time: 4.23 and 6.94 min) in the chromatographic profile of 10 min. The chemical components corresponding to these peaks could not be determined through the comparison of their retention times with that of standards such as p-benzoquinone and chloro-p-benzoquinones [35]. However, we could not find the peak of 3, the possible reason was that the phthalocyanine complex was not eluted from the chromagraphic column for its low polarity. Moreover, similar chromatographic results could be obtained for 4 catalyzed 2-CP system just except the longer reaction time of 30 min was needed. According to the relationship of yield = conversion \times selectivity/100, the yield of dyes could be determined as 93 and 95 % for **3** and **4** catalyzed 2-CP system, respectively. It is notable that **3** (or **4**) catalyzed chromogenic reactions could be developed to become an analytical method for their excellent advantages of fast reaction and high yield of dyes.

3.3 Proposed Mechanism of Catalytic Oxidation Reaction

It is important to understand the mechanism of catalytic oxidation reaction and determine the role of active species in chromogenic process for the practical application of catalytic technology. Therefore, some control experiments were designed and performed. Firstly, we found that both FePc catalyst and *t*-BuOOH were essential to fast



formation of dyes for the dyes could hardly be formed without one of them (curve d and e in Fig. 2). Secondly, the continuous nitrogen-bubbling operation was carried out to testify the role of dissolve oxygen for the chromogenic system exposed to air. Surprisingly, the oxygen was also beneficial to the formation of dyes, especially in the second-half stage of chromogenic reaction (curve a versus curve c). Though the dyes could not be formed rapidly just in oxygen saturated solution (curve e), the dioxygen should play a crucial role of oxidant in the dye formation process. Thirdly, to testify the effect of *t*-BuOOH in homogeneous catalytic oxidation, tert-butyl alcohol (TBA, a scavenger for hydroxyl radical) was used to testify the generation of OH[•] radicals from the homolytic cleavage of O-O bond of t-BuOOH. Indeed, the introduction of TBA showed no detectable influence on the formation process of dyes compared with typical catalysis (curve a versus curve f), illuminating that the OH^{•-}would not be the main active species participating in the generation of dyes. Moreover, the typical catalytic reaction could also proceed efficiently in the dark (curve b), which indicates that the chromogenic reaction was not dependent on light irradiation and very beneficial for practical measurement of phenolic pollutants.

For the mechanism of catalytic oxidation by water-soluble iron phthalocyanine complexes combined with peroxide, more intensive investigations were focused on the TSFePc/t-BuOOH and TSFePc/H₂O₂ systems and the well known mechanism of active iron-oxygen species was proposed by Meunier and Sorokin [2, 9, 10, 13–16]. Very recently, the molecular structure of iron(IV) oxo phthalocyanine complex of $[(Pc^{t}Bu_{4})Fe^{IV}=O(Cl)]^{+}$ was determined via the low temperature UV-Vis and cryospray MS technology by Sorokin's group, which further testified the reliability of proposed hypothesis of iron-oxygen species [36]. For the catalytic oxidation of various phenols by 3 (or 4) in our system, the catalysis processes could also be explained by their proposed mechanism (Scheme 2). In the first step, when t-BuOOH was added into the reaction solution, the initial product of PcFe^{III}-OO'Bu peroxo complex was formed. Alternatively, the O-O bond in PcFe^{III}–OO'Bu complex could undergo the homolytic or heterolytic cleavage to produce iron(IV) or iron(V) oxygen species, respectively. Since iron(V) oxidation state is less accessible in phthalocyanine complex, and thus the $PcFe^{IV}=O$ could be the main active species with t-BuO[•] as the concomitant product [13]. Otherwise, the formation of t-BuO[•] radical could provoke side reactions for the decomposition of the phthalocyanine complex during substrates oxidation process [15]. In the second step, the coordination of iron(IV) site with the two substrates of phenol and 4-AAP proceeded. The electrons could be abstracted from O atom of phenol and N atom of 4-AAP and the corresponding radicals (Antipyrine-NH[•] for 4-AAP and *p*-quinoid for 2-CP) could be generated rapidly. In the third step, these active radicals could undergo an oxidative coupling reaction with dioxygen as oxidant and the pink dyes of quinone imide were produced. Meanwhile, the high active PcFe^{IV}=O complex would transform into the anionic form of PcFe^{III}–O⁻ and then PcFe^{III}–OH resulted from the combination of PcFe^{III}–O⁻ with H⁺.

For the higher sterically hinder effect of quinolyl group on Pc ring, it was well understood that the catalytic activity of **4** was lower than that of **3** for the difficulty in the approach of substrates to iron atom of PcFe^{IV}=O (coordination process) and the consequent disassociation from the iron site. Therefore, the phenyl substituent group on Pc ring was sufficient for the purpose of improving the homogeneous catalytic activity of FePc complexes.

3.4 Effect of the Concentration of t-BuOOH and 4-AAP on Dye Formation

For fast and accurate measurement of various phenolic pollutants, the production of dyes from the transformation of phenolic compounds should achieve to their maximum as much as possible. It is known that the concentration of oxidant shows great influence on oxidation reaction rate and yield of products [16, 34]. Therefore, we selected different concentrations of *t*-BuOOH to investigate reaction rates and final production of dyes. Figure 3 shows the

Scheme 2 Proposed mechanism for the transformation of chlorophenols to dyes catalyzed by the system of 3 (or 4) and *t*-BuOOH



(oxidative coupling reaction)



Fig. 3 Effect of peroxide oxidant on the absorbance of dyes formed in the presence of 3 (a) and 4 (b). ($\lambda_{abs} = 508 \text{ nm}$) Reaction conditions: 2-CP ($1.0 \times 10^{-4} \text{ M}$), 4-AAP ($2.0 \times 10^{-4} \text{ M}$), catalyst 3 and 4 ($1.0 \times 10^{-5} \text{ M}$)

absorbance profiles of dye formation process with t-BuOOH dosage of 5 and 10 µL, respectively. It could be seen clearly that the initial rate of dye formation with 10 µL t-BuOOH was higher than that with 5 µL t-BuOOH, while more dyes were formed at the end of catalytic reaction by 3 with less t-BuOOH (Fig. 3a). Interestingly, the concentration of *t*-BuOOH on dye formation process by 3 was similar to that by 4 (Fig. 3b). These phenomenons could be interpreted as follows: more active iron-oxygen species would be formed when double dosage of t-BuOOH was used, which could accelerate the axial coordination of substrates with these active species and result in more formation of dyes at initial reaction stage, but excess t-BuOOH could also provoke side reactions for slow degradation of quinoneimine dyes [37]. Moreover, when H_2O_2 was used instead of t-BuOOH, the production of dyes decreased obviously (Fig. 3). For the electronegativity of peroxide group (-OOH) of t-BuOOH is higher than that of H₂O₂, t-BuOOH has better combination effect with iron center of phthalocyanine complexes.

The concentration ratio of 4-AAP versus phenolic substrates was also an important experimental parameter for the production of dyes. The concentration ratio of 4-AAP versus 2-CP was set as 1, 2 and 3 for **3** or **4** catalyzed chromogenic system. From the comparison of absorbance-time profiles in Fig. 4a (catalysis by **3**), we found that the dye absorbance intensities with the 4-AAP concentration of 2.0×10^{-4} M were a little greater than that of 3.0×10^{-4} M, while less production of dyes was formed when the concentration of 4-AAP is decreased to 1.0×10^{-4} M. For **4** catalyzed chromogenic reactions, similar situation was found (Fig. 4b). Therefore, double 4-AAP versus 2-CP was beneficial for maximum production of dyes under selected conditions, which could also be verified by HPLC results.

3.5 Effect of pH

Since various phenolic pollutants were water-soluble and existed in two forms of undissociated molecules and phenoxide ions, and their proportion between these two forms could be dominated by pH, therefore, their catalytic oxidation could be pH-dependent as well. According to the pKa value (8.48) of 2-CP, three buffer solutions with different pH were prepared to study the effect of pH on dye formation process, i.e. Na_2HPO_4 –NaOH buffer solution (PBS, pH 11.0), boric acid–borax buffer solution



Fig. 5 Dye formation processes in 2-CP system catalyzed by 3 (a) and 4 (b) under different pH conditions, respectively. ($\lambda_{abs} = 508 \text{ nm}$) Reaction conditions: 2-CP ($1.0 \times 10^{-4} \text{ M}$), 4-AAP ($2.0 \times 10^{-4} \text{ M}$), catalyst 3 and 4 ($1.0 \times 10^{-5} \text{ M}$), *t*-BuOOH

(5 μ L). *Filled square* in Na₂HPO₄–NaOH buffer solution, pH 11.0; *filled circle* in Na₂HPO₄–KH₂PO₄ buffer solution, pH 5.0; *filled triangle* in boric acid-borax buffer solution, pH 9.0; *inverted triangle* in deionized water

Fig. 6 Effect of temperature on the absorbance of dyes formed in the presence of 3 (a) and 4(b), respectively. $(\lambda_{abs} = 508 \text{ nm})$ Kinetic plots of dye formation at room temperature (RT) and 40 °C in the presence of 3 (c) and 4 (d), respectively. (The kinetic parameter Ln S, where $S = Abs_{\infty}/(Abs_{\infty} - Abs_{t})$ are calculated from absorbance versus reaction time). Reaction conditions: 2-CP $(1.0 \times 10^{-4} \text{ M}), 4\text{-AAP}$ $(2.0 \times 10^{-4} \text{ M})$, catalyst 3 and 4 (1.0 \times 10⁻⁵ M), *t*-BuOOH (5 µL)



(BBS, pH 9.0) and Na₂HPO₄-KH₂PO₄ buffer solution (PBS, pH 5.0). Besides, the pure deionized water solution was also used for comparison study. Figure 5a shows the effect of pH on dye formation catalyzed by 3 in 2-CP system. It is clear that the fastest formation of dyes along with the highest final production proceeded in pure deionized water (variable pH), while both acidic pH 5.0 and alkaline pH 11.0 buffer solutions were not beneficial to the satisfied chromogenic effect due to the low dye production. When faintly alkaline BBS with pH 9.0 was used, the corresponding chromogenic effect was inferior to that in deionized water (Fig. 5a). For 4 catalyzed 2-CP system, the similar reaction trend was found just except that the absorbance intensity of dyes was decreased after 10 min at pH 11.0, possibly, due to the dye degradation (Fig. 5b). In addition, to make clear the reason of fast chromogenic reaction in deionized water, pH changes was monitored and found the slight increase from 7.2 to 7.6 in 3 catalyzed 2-CP system (from 7.4 to 7.9 for 4 catalyzed 2-CP system), which illuminated that the significant contribution of molecular chlorophenols to their fast transformation into dyes.

Furthermore, the stability of water-soluble FePcs (**3** and **4**) and activity of *t*-BuOOH was also influenced by the pH of reaction solution. We found that these two water-soluble FePcs would be precipitated gradually in PBS of pH 5.0, and their poor solubility in acidic solution resulted in their

Table 1 The maximum intensity of dye absorption (Q_s) at 508 nm, the time to complete chromogenic reaction (T_s) , rate constants and correlation coefficients (R^2) for 2-CP system under different reaction temperature

Catalyst	Temperature	Qs	T _s (min)	$\begin{array}{c} k \times 10^{-2} \\ (min^{-1}) \end{array}$	R ²
3	RT	1.824	8	36.10	0.9869
3	40 °C	1.838	6	43.325	0.9900
4	RT	1.816	30	10.604	0.9679
4	40 °C	1.729	15	27.455	0.9726

low catalytic activity. In a similar way to 2-CP, for the ionization equilibrium between *t*-BuOOH molecule and t-BuOO⁻ anion, the activity of *t*-BuOOH would also be improved at the alkaline aqueous solution.

3.6 Effect of Reaction Temperature

The influence of temperature on the dye formation process was investigated in 2-CP system catalyzed by **3** and **4**, respectively. Figure 6a, b presented the time-dependent absorbance profiles for dyes formed at room temperature (RT) and 40 °C, respectively. Interestingly, similar to our previous investigation on TNFe(II)Pc catalyzed chromogenic reactions [35], more dyes were produced at RT while the higher reaction rate of dye formation attributed to

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Catalyst	Substrate	Oxidation	$k \times 10^{-2} (min^{-1})$	Byproduct	Reference
TNFe(II)Pc	2-CP $(1 \times 10^{-4} \text{ M})$	Dissolved O ₂	5.338	Something unknown	[35]
3	2-CP $(1 \times 10^{-4} \text{ M})$	t-BuOOH (5 µL)	36.10	Very few	Current method
4	2-CP $(1 \times 10^{-4} \text{ M})$	t-BuOOH (5 µL)	10.604	Very few	Current method
TSFe(III)Pc	Phenol $(2 \times 10^{-3} \text{ M})$	H ₂ O ₂ (500 µL)	19.62	Not given	[34]
3	Phenol $(1 \times 10^{-4} \text{ M})$	t-BuOOH (5 µL)	32.822	Not given	Current method
4	Phenol (1 \times 10 ⁻⁴ M)	t-BuOOH (5 µL)	10.219	Not given	Current method

Table 2 Comparison of chromgenic reactions catalyzed by various iron phthalocyanine complexes

higher temperature of 40 °C. Based on the comparison of rate constants calculated from pseudo-first-order equation (Fig. 6c, d), **4** catalyzed chromogenic system was more sensitive to temperature than that of **3** for their obvious difference between 10.604 (RT) and 27.455 min⁻¹ (40 °C) (Table 1). Indeed, RT could already meet the requirement of chromogenic assay for the fast identification of phenolic pollutants.

3.7 Comparison of Several Chromgenic Systems

We summarized the features of various FePc catalyzed chromogenic reaction for detail comparison (Table 2). For the identification of 2-CP pollutant, the pseudo-first-order model was suitable for illuminating the reaction kinetic of dye formation. Therefore, the catalytic activity could follow the sequence: 3 > 4 > TNFe(II)Pc. Despite of the lower activity and yield of heterogeneous TNFe(II)Pc, it is superior to other homogeneous catalysts due to its recyclable performance and the utilization of green oxidant of oxygen. For the identification of phenolic pollutant with homogeneous catalyst of 3, 4 and TSFePc, the chromogenic reaction with catalyst 3 still had fastest reaction rate in three homogeneous catalyst systems. Besides, it is noted that only less quantity of oxidant (5 µL t-BuOOH) was used in 3 and 4 catalyzed reaction and sufficient for fast and obvious chromogenic effect. From the analytical point of view, catalyst 3 was promising for the application of identification and measurement of phenolic pollutants in the future.

4 Conclusion

In this study, two novel water-soluble FePc complexes were synthesized for the detection of phenolic pollutants and showed high catalytic activity in the selected chromogenic system of phenolic substrates. The high valent iron oxo species were possible active species in our catalytic system which resulted in the fast formation of the pink quinone imide dyes. In addition, the oxygen is also essential for the recombination of p-quinoid radical and Antipyrine-NH[•]. The chromogenic effect in our catalytic system was significantly influenced by the concentration of *t*-BuOOH and 4-AAP, pH and temperature, respectively. Compared with other MPc catalytic chromogenic system, our system has the obvious characteristics of less side reaction, fast catalytic oxidation and the chromogenic reaction was not dependent on light irradiation. In conclusion, our investigation has illustrated a potential application of fast chromogenic identification and measurement of phenolic pollutants.

Acknowledgments This work was financially supported by the National Natural Science Foundation of China (Nos. 61377092 and 51302241), the Fundamental Research Funds for the Central Universities (WUT: 2013-IV-010), the Science and Technology Key Project of Education Department of Henan Province (No. 13B430233 and No. 13A150743). We thank professor Yu Cao (College of Chemistry, Huazhong Normal University) for the help of chemical characterization and measurement. We thank MSc Shilong Zhao (School of Materials Science and Engineering, Wuhan University of Technology) for the help of purification of two novel water-soluble iron phthalocyanines.

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