



Sensitive and visual detection of p-phenylenediamine by using dialdehyde cellulose membrane as a solid matrix

Shengli Zhang^{*}, Bofang Liu, Daiyan Hu, Silue Zhang, Yanbo Pei, Zhengjun Gong^{**}

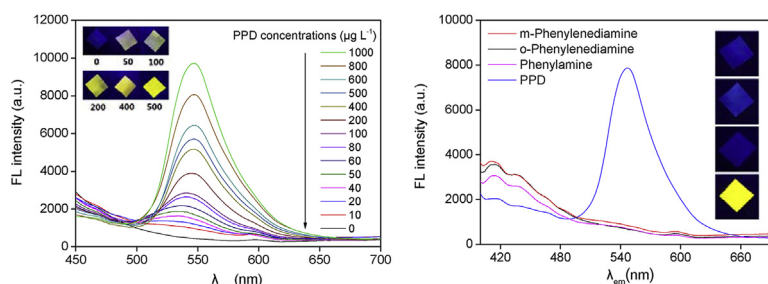
Faculty of Geosciences and Environmental Engineering, Southwest Jiaotong University, 610031, Chengdu, Sichuan, China



HIGHLIGHTS

- A novel method was developed for the sensitive and visual detection of PPD.
- DCM as a solid matrix played a vital role in the enrichment of PPD.
- The proposed method gave two linear ranges at 0.01–0.1 and 0.1–1 mg L⁻¹, respectively.
- The detection limit of PPD was calculated to be 5.35 µg L⁻¹.
- Detection mechanism was involved in two-step Schiff base reaction and AIE effect.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 5 July 2020

Received in revised form

22 September 2020

Accepted 24 September 2020

Available online 28 September 2020

Keywords:

Solid surface fluorescence

Dialdehyde cellulose membrane

p-Phenylenediamine

Salicylaldehyde

Hair dye

ABSTRACT

A novel method was developed for the sensitive and visual detection of p-phenylenediamine (PPD) via immobilizing the target specie PPD on dialdehyde cellulose membrane (DCM) followed by the reaction with salicylaldehyde. The obtained solid fluorescent membrane (S-PPD-DCM) emitted yellow fluorescence under 365 nm UV light. DCM was not only used as a solid matrix but also played a vital role in the enrichment of PPD. Experimental variables influencing the fluorescence signal were investigated and optimized. Under the optimum conditions, a detection limit of 5.35 µg L⁻¹ was obtained and two linear ranges were observed at 10–100 and 100–1000 µg L⁻¹, respectively. Moreover, the fluorescence of the resultant membrane can still be visualized by naked eye when PPD concentration was 50 µg L⁻¹. The detection of PPD was hardly affected by the coexistence of 1 mg L⁻¹ of o-phenylenediamine, m-phenylenediamine or phenylamine, exhibiting good selectivity. The developed method involved in a two-step Schiff base reaction and enhanced the fluorescence emission via blocking nonradiative intramolecular rotation decay of the excited molecules. It was applied to determine the PPD in spiked hair dye with satisfactory results.

© 2020 Elsevier B.V. All rights reserved.

1. Introduction

p-Phenylenediamine (PPD) is an important intermediate which

has been applied in aramid plastics, textile and hair dye industries [1,2]. However, it can cause a number of allergic reactions and is mutagenic [3,4]. Therefore, it is necessary to develop a simple and sensitive method for the detection of PPD.

So far, several analytical techniques, including UV spectrophotometry [5], fluorescence spectroscopy [6,7], gas chromatography (GC) [8], high-performance liquid chromatography (HPLC) [9], gas chromatography–mass spectrometry (GC-MS) [10],

^{*} Corresponding author.

^{**} Corresponding author.

E-mail addresses: zhang222@home.swjtu.edu.cn (S. Zhang), gzj@home.swjtu.edu.cn (Z. Gong).

electrochemical analysis [11,12], and capillary isotachophoresis [13], have been adopted for detecting PPD. Among them, fluorimetric methods have the advantages like rapid speed, high sensitivity, simple manipulation and low-cost [14]. Especially, solid-surface fluorescence (SSF) unites the enrichment of target species on a solid matrix with its direct fluorescence measurement, which can improve the sensitivity and selectivity of the determination compared with the conventional liquid fluorescence [15]. In addition, the method is more environmental-friendly, as the waste does not contain any reagent, which remains on the solid phase [16]. In recent years, SSF has been applied for the determination of polycyclic aromatic hydrocarbons [17], pesticides [18], nitroaromatic explosives [19], antibiotics [20], inorganic gases [21], anions [22] and metal ions [23,24]. However, to the best of our knowledge, no related studies have been conducted to detect PPD via SSF method.

During the application of SSF, solid matrix plays a key role. The reported matrix materials include C18 silica gel [25], nylon membrane [26], PVC membrane [27], glucose gel [28], cellulose-based materials [23,29] and so on. Among them, cellulose membrane not only has the advantages of natural cellulose like renewability, nontoxicity, biodegradability, biocompatibility and low price but also has the attractive features such as good transparency, high mechanical strength and low fluorescence background [30,31]. It can be used as a promising matrix for solid-surface fluorescence analysis [32].

In the present study, sensitive and visual detection of p-phenylenediamine (PPD) was achieved via immobilizing target specie PPD on dialdehyde cellulose membrane (DCM) and being followed by the reaction with salicylaldehyde. The obtained solid fluorescent membrane (S-PPD-DCM) can emit strong yellow fluorescence. DCM was not only used as a solid matrix but also played a vital role in the enrichment of PPD. The experiment variables affecting the fluorescence signal of S-PPD-DCM were studied and optimized. Meanwhile, the selectivity and potential application of the proposed method were evaluated. The related mechanism was discussed.

2. Experimental

2.1. Materials

Cotton pulp cellulose was supplied by Bailu Chemical Fiber Group Ltd., China. 40 wt% aqueous solution of tetrabutylammonium hydroxide (TBAH) was purchased from Shanghai Meryer Chemical Technology Co. Ltd., China. p-Phenylenediamine ($\geq 99.5\%$), o-phenylenediamine ($\geq 99.0\%$), m-phenylenediamine ($\geq 99.5\%$), phenylamine ($\geq 99.5\%$), salicylaldehyde, dimethylsulfoxide (DMSO), sodium periodate (NaIO_4) and alcohol were provided by Chengdu Kelong Chemical Reagent Co., China. All reagents were of analytical grade and used without further purification.

2.2. Preparation of dialdehyde cellulose membrane

Dialdehyde cellulose membrane (DCM) was prepared as our previous work [33,34]. In a typical procedure, cotton pulp (2.5 g) was dissolved in DMSO (37.5 g) and TBAH aqueous solution (10 g, 40 wt%) under stirring condition at room temperature. Then cellulose solution was defoamed and poured into a film mold of poly(tetrafluoroethylene) to obtain cellulose membrane (CM) with ca. 0.3 mm thickness. After that, 2 g of CM was immersed in a NaIO_4 solution of 1 g L^{-1} and oxidized for 6 h at 25°C in dark. The resulting CM was washed with ultra-pure water and labeled as dialdehyde cellulose membrane (DCM).

2.3. Detection of PPD

The detection of PPD was performed based on a two-step Schiff-base reaction. The prepared DCM was immersed in a PPD solution and was agitated for different time (0.5 min–6 h) at given temperature ($4\text{--}55^\circ\text{C}$). The desired pH (3–11) was adjusted by using 0.1 mol L^{-1} NaOH and 0.1 mol L^{-1} HCl. And then the PPD-immobilized DCM (PPD-DCM) was immersed into a salicylaldehyde solution of different concentrations (0.01–1 wt%). After stirring for 10 min at 25°C , the resultant membranes were washed and dried at 50°C in an oven to obtain solid fluorescence membranes (S-PPD-DCM). Their fluorescence spectra were recorded at 370 nm excitation. All the experiments were replicated at least three times.

2.4. Characterization

The fluorescence spectra of the resultant samples were measured by Hitachi F-7000 Fluorescence Spectrophotometer equipped with a solid sample holder. Excitation wavelength was fixed at 370 nm. Slit width was 5.0 nm for both excitation and emission. Scanning rate was 1200 nm min^{-1} , and scanning range was from 200 to 700 nm.

The surface functional groups of the DCM, PPD-DCM and S-PPD-DCM were determined by a FTIR spectroscope (Nicolet 6700, Thermo Fisher Scientific, America). The data in the range of $4000\text{--}400 \text{ cm}^{-1}$ were recorded at the resolution of 4 cm^{-1} . Their surface element compositions were obtained by XPS on an Escalab 250Xi X-ray electron spectrometer (Thermo Fisher Scientific, USA) with an Al K α source. The physical morphologies of the DCM, PPD-DCM and S-PPD-DCM were observed on a JSM7800F PRIME (JEOL Com., Japan) electron microscope. The samples were coated with a gold film to improve their conductivity and the quality of the SEM image.

3. Results and discussion

3.1. Effect of salicylaldehyde concentration

The Membranes obtained at different conditions exhibited good transparency as presented in Fig. 1a. Under 365 nm UV light, the S-PPD-DCM emitted yellow fluorescence. By contrast, no fluorescence was observed for the DCM, DCM + S and PPD-DCM. Their fluorescence spectra were determined as displayed in Fig. 1b. It can be found from Fig. 1b that an emission peak appeared at 545 nm for the S-PPD-DCM. This phenomenon suggested that the salicylaldehyde played a key role in the fluorescence emission except PPD. Hence, the effect of salicylaldehyde concentration (C_s) on fluorescence intensity was first investigated before optimizing the enrichment conditions. From the result shown in Fig. 2a, it was clear that the emission intensity of the S-PPD-DCM samples rapidly increased and then tended to a balance with the increase of salicylaldehyde concentration. The reason was that the amino groups of the immobilized PPD were consumed continuously because of the Schiff base reaction between PPD and salicylaldehyde. In subsequent experiments, the concentration of salicylaldehyde was fixed at 0.5 wt%.

3.2. 2 optimization of enrichment conditions

Other important parameters in the present work included solution pH, PPD concentration (C_{PPD}), reaction time (t) and reaction temperature (T) in the process of PPD enrichment. They were optimized for improving the sensitivity of the proposed method.

Fig. 2b showed the influence of solution pH. It was evident that the fluorescence intensity gradually increased at first and then

decreased with raising the pH from 3 to 9. It was attributed that the amino groups of PPD were protonated at strong acid condition, impeding the amine–aldehyde condensation reaction. The self-condensation of aldehyde groups could happen at too high basicity, which was not conducive to the introduction of PPD. After that, a new fluorescence emission peak appeared at 450 nm with the further increase of solution pH (Fig. S1). To give an explanation for the new peak, the DCM was directly immersed in a salicylaldehyde solution at pH ca. 10. The resultant membrane also exhibited a fluorescence emission peak at about 450 nm (Fig. S2). The reason is that salicylaldehyde is a weak acid ($pK_a = 8.37$) and was deprotonated at higher pH. And the deprotonated salicylaldehyde displayed a strong fluorescence at about 500 nm. The interaction between DCM and deprotonated salicylaldehyde can cause the blue-shift of its maximum emission wavelength. Hence, the new fluorescence emission peak appearing at 450 nm in Fig. S1 was related to the undeprotonated salicylaldehyde. Finally, the optimal pH value was 8 which corresponded to the natural pH of PPD solution.

Reaction time was an important factor in the formation of PPD-DCM. Therefore, its effect on the fluorescence intensity was investigated while maintaining other experimental conditions constant. The obtained result was illustrated in Fig. 2c. It was obvious that the fluorescence intensity of the prepared S-PPD-DCM quickly increased within the initial 15 min, and the increment became gradually slow afterward. No maximum value was found in the experimental range. In follow-up experiments, 60 min was chosen as the optimum reaction time.

Considering that the concentration of target specie had a direct effect on fluorescence intensity, PPD concentration was varied in the range of 0–1000 $\mu\text{g L}^{-1}$ as shown in Fig. 3a and b. It was clear that the fluorescence intensity of the S-PPD-DCM gave a gradual increase with increasing the PPD concentration. The same trend can be found from the inset of Fig. 3a that the fluorescence emission of the membranes became more and more bright under 365 nm UV light. This was ascribed that more PPD was immobilized on the DCM. When PPD concentration was as low as 50 $\mu\text{g L}^{-1}$, the yellow fluorescence of the resultant membrane can still be visualized by

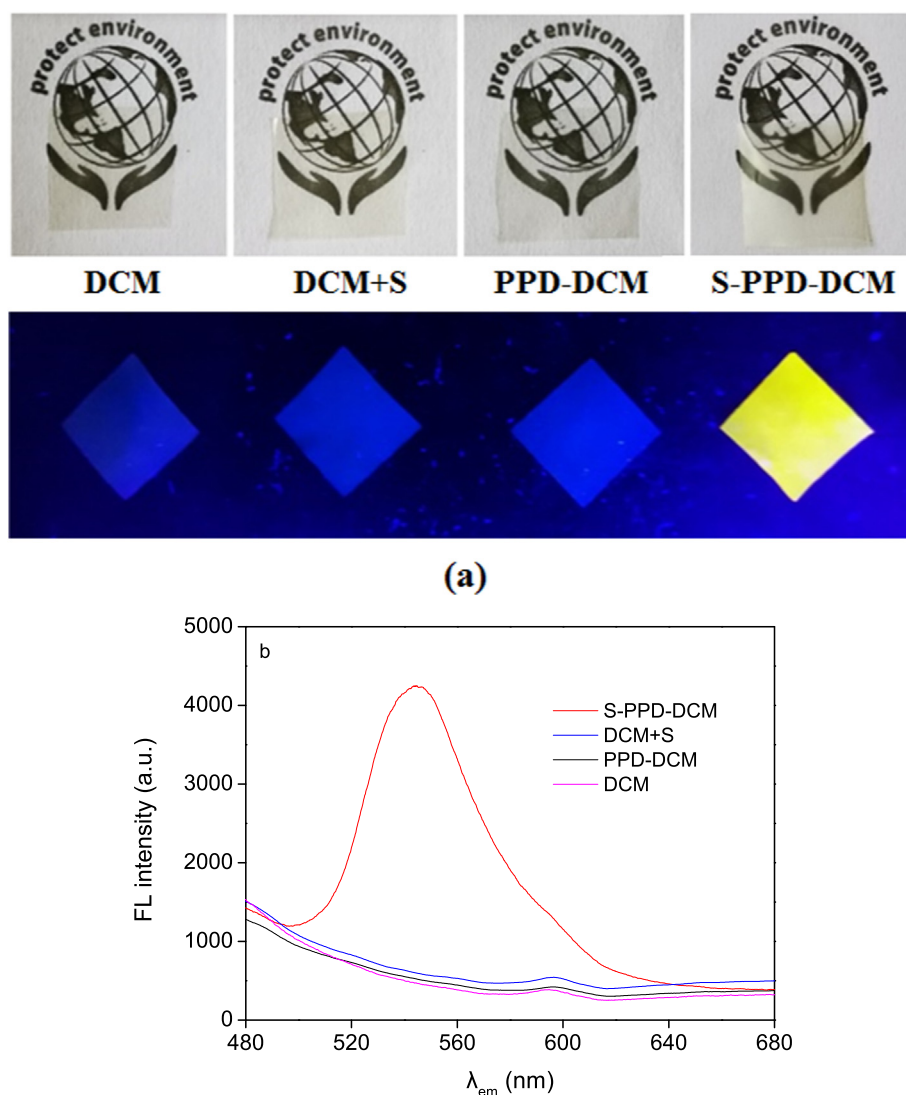


Fig. 1. (a) The colors of the DCM, DCM + S, PPD-DCM and S-PPD-DCM under visible light (top) and 365 nm UV light (bottom); (b) Fluorescence emission spectra ($\lambda_{ex} = 370$ nm) of the DCM, DCM + S, PPD-DCM and S-PPD-DCM ($C_S = 0.5$ wt%, $C_{PPD} = 250$ $\mu\text{g L}^{-1}$, pH = 8, $t = 60$ min, $T = 25$ $^{\circ}\text{C}$). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

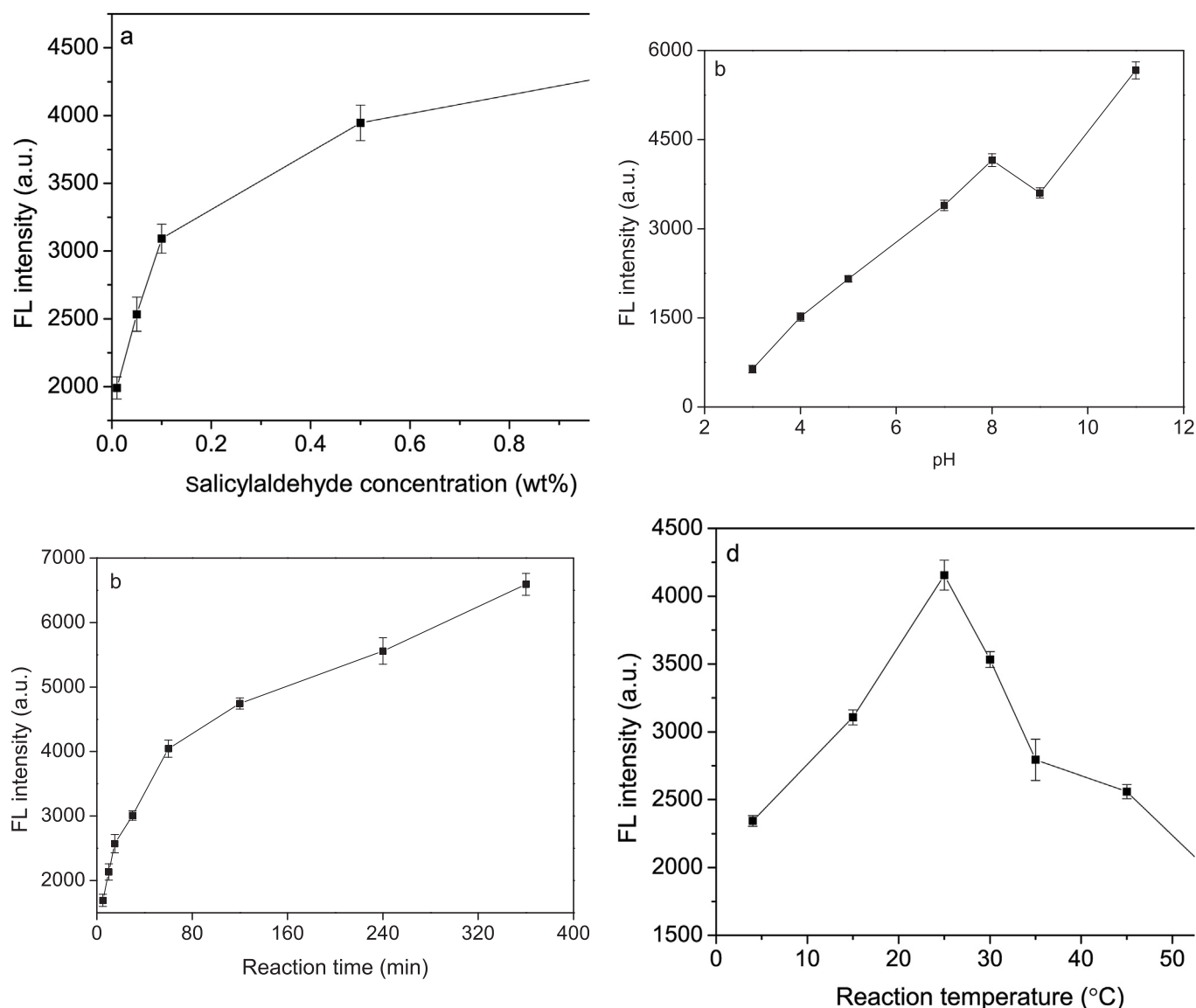


Fig. 2. Influence of salicylaldehyde concentration (a) and enrichment conditions including solution pH (b), reaction time (c), reaction temperature (d) on the fluorescence intensity of the resultant samples. A salicylaldehyde concentrations from 0.01 to 1 wt% ($C_{PPD} = 250 \mu\text{g L}^{-1}$, pH = 8, $t = 60 \text{ min}$, $T = 25^\circ\text{C}$); Solution pH from 3 to 11 ($C_S = 0.5 \text{ wt\%}$, $C_{PPD} = 250 \mu\text{g L}^{-1}$, $t = 60 \text{ min}$, $T = 25^\circ\text{C}$); Reaction time from 0.5 min to 6 h ($C_S = 0.5 \text{ wt\%}$, $C_{PPD} = 250 \mu\text{g L}^{-1}$, pH = 8, $T = 25^\circ\text{C}$); Reaction temperature from 4 to 55°C ($C_S = 0.5 \text{ wt\%}$, $C_{PPD} = 250 \mu\text{g L}^{-1}$, pH = 8, $t = 60 \text{ min}$).

naked eye.

Finally, the effect of reaction temperature was optimized as presented in Fig. 2d. With varying the temperature from 4 to 55°C , the fluorescence intensity increased initially and then decreased. 25°C was confirmed to be the optimal reaction temperature. It was due to the fact that the molecular motion was slow at a low temperature, reducing the chemical reaction activity of PPD. At a high temperature, the molecular motion became vigorous, but part of the PPD was oxidized, which decreased the available PPD content.

3.3. Analytical performance

3.3.1. Linear response range and precision

Based on the fluorescence intensity (F) obtained at different PPD concentrations, the sensitivity of the developed method was evaluated. As shown in Fig. 3b, two good linear relationship with regression equations of $F = 19.4986C + 361.8076$ ($R^2 = 0.9865$) and

$F = 7.5982C + 1445.8924$ ($R^2 = 0.9970$) can be observed in the range of 10–100 and 100–1000 $\mu\text{g L}^{-1}$, respectively. The detection limit according to $3\sigma/s$, where σ represented the standard deviation from 12 replicate blank responses and s was the slope of the calibration curve ($n = 5$), was calculated to be $5.35 \mu\text{g L}^{-1}$. The relative standard deviation (RSD) for the determination of 250 and $500 \mu\text{g L}^{-1}$ of PPD was 2.04% and 2.73% ($n = 5$), respectively.

Compared with other fluorescence methods reported in the literature, the detection limit of the present method was superior to those obtained by most of the liquid fluorescence methods for PPD analysis (Table 1). Moreover, the SSF method was simpler and more environmental-friendly. It was not involved in the synthesis of new fluorescent probes, which can minimize the amount of reagents and organic solvents. In addition, the analyte PPD was retained on the solid matrix and measured directly, thus reducing the generation of hazardous waste during the analysis process.

In order to further demonstrate the advantage of SSF analysis in

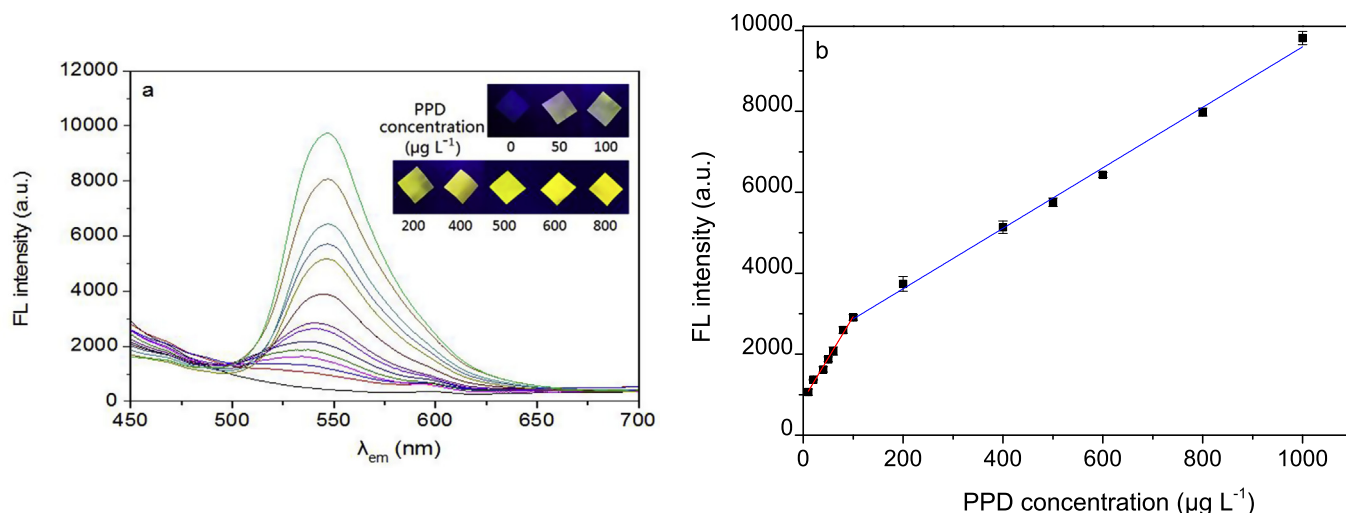


Fig. 3. (a) Effects of different PPD concentrations on the fluorescence emission spectra of S-PPD-DCM (the inset shows the colors of part of the prepared S-PPD-DCM under 365 nm UV light). (b) The linear relationship between the fluorescence intensity and PPD concentration. The PPD concentrations (from top to bottom) were: 1000, 800, 600, 500, 400, 200, 100, 80, 60, 50, 40, 20, 10, 0 $\mu\text{g L}^{-1}$; $C_s = 0.5 \text{ wt\%}$, $\text{pH} = 8$, $t = 60 \text{ min}$, $T = 25^\circ\text{C}$. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Table 1

Comparison of the developed method for the determination of PPD with previously reported fluorescence methods.

Methods	Linear range ($\mu\text{g L}^{-1}$)	LOD ($\mu\text{g L}^{-1}$)	Refs
Liquid fluorescence	3240–43200	3240	[2]
Liquid fluorescence	2.16–162	0.756	[6]
Liquid fluorescence	10.8–108	6.05	[7]
Liquid fluorescence	1080–75600	9.68	[35]
Liquid fluorescence	54,000–1080,000	9639	[36]
Solid surface fluorescence (SSF)	10–100	5.35	This work

Table 2

Surface composition (atom fraction, %) of the samples obtained at different stages from XPS survey spectra.

Samples	C	N	O
DCM	61.0 ± 1.3	0.7 ± 0.1	38.3 ± 1.2
PPD-DCM	61.8 ± 1.5	1.5 ± 0.2	36.7 ± 1.3
S-PPD-DCM	64.8 ± 1.3	1.4 ± 0.2	33.8 ± 1.4

this study, contrast experiments were designed to investigate the performance of liquid fluorescence for the detect of PPD. According to the optimum conditions used in SSF analysis and the stoichiometric relationship between PPD and salicylaldehyde, the fluorescence spectra of the liquid system were determined by varying salicylaldehyde concentrations from 0.25 to 10,000 mg L^{-1} with 250 $\mu\text{g L}^{-1}$ PPD or PPD concentrations from 0.05 to 1000 mg L^{-1} with 0.5 wt% salicylaldehyde. The results were shown in Fig. S3. From Fig. S3, it was evident that the fluorescence spectra of the liquid system presented an irregular shape when changing the concentration of PPD or salicylaldehyde. Furthermore, their fluorescence intensity was very low. The reason was attributed that the formed fluorophores had aggregation-induced emission (AIE) characteristics. When they were well dispersed in the solution, their intramolecular vibration and rotation were not restricted. As a result, their fluorescence was self-quenched. Meanwhile, the excess reactants could interfere with the weak fluorescent signal.

3.3.2. Selectivity

To assess the selectivity of the developed method, other aromatic

amines including phenylamine, o-phenylenediamine and m-phenylenediamine were investigated as a substitute of PPD. Their concentrations were fixed at 1 mg L^{-1} and the collected fluorescence spectra were shown in Fig. 4a. Notably, there was no fluorescence emission peak observed for the above amines. By contrast, the fluorescence intensity of the prepared S-PPD-DCM was above 9000 when the PPD concentration was 1 mg L^{-1} , indicating the proposed method had superior selectivity. This was further confirmed from the insert of Fig. 4a. It was clear that no yellow fluorescence was observed for the phenylamine, o-phenylenediamine and m-phenylenediamine. In addition, the PPD detection was also performed in the coexistence of 1 mg L^{-1} phenylamine, o-phenylenediamine or m-phenylenediamine. According to the results presented in Fig. 4b, the existence of other aromatic amines only had a very small effect on the fluorescence intensity of the S-PPD-DCM. The calculated relative errors of 250 $\mu\text{g L}^{-1}$ PPD were 0%, 1.69% and 7.61% when the coexisting aromatic amines were phenylamine, o-phenylenediamine and m-phenylenediamine, respectively. Therefore, the proposed method had good selectivity for the detection of PPD.

3.3.3. Detection of PPD in hair dye

Hair dye was used as a representative sample for evaluating the potential application of the developed method. The detailed procedure was as follows: Hair dye cream (100 mg) was added into 20.0 mL of ethanol, and the mixture was stirred for 10 min at room temperature. And then 1.0 mL of the supernatant was diluted to 100 mL with ethanol and stored at 4 $^\circ\text{C}$ for further use.

In spiked recovery experiments, moderate volumes of PPD standard solution were spiked into a certain volume of stored sample. Afterward, the developed method was applied to the

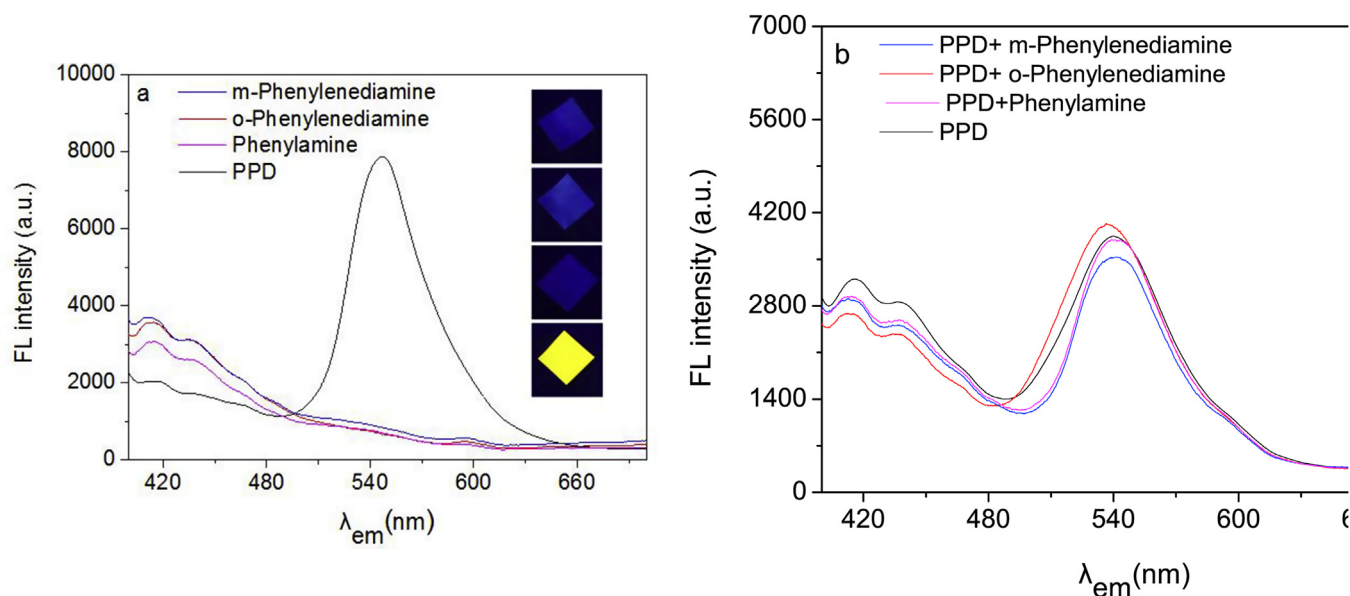


Fig. 4. (a) Fluorescence emission spectra of the samples prepared in 1 mg L^{-1} of phenylamine, o-phenylenediamine, m-phenylenediamine and PPD solution, respectively (the insert shows their colors under 365 nm UV light). The preparation conditions were: $C_S = 0.5 \text{ wt\%}$, $\text{pH} = 8$, $t = 60 \text{ min}$, $T = 25^\circ \text{C}$. (b) Fluorescence emission spectra of the samples prepared in the coexistence of different aromatic amines and PPD ($C_S = 0.5 \text{ wt\%}$, $C_{PPD} = 250 \mu\text{g L}^{-1}$, aromatic amine concentration 1 mg L^{-1} , $\text{pH} = 8$, $t = 60 \text{ min}$, $T = 25^\circ \text{C}$). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

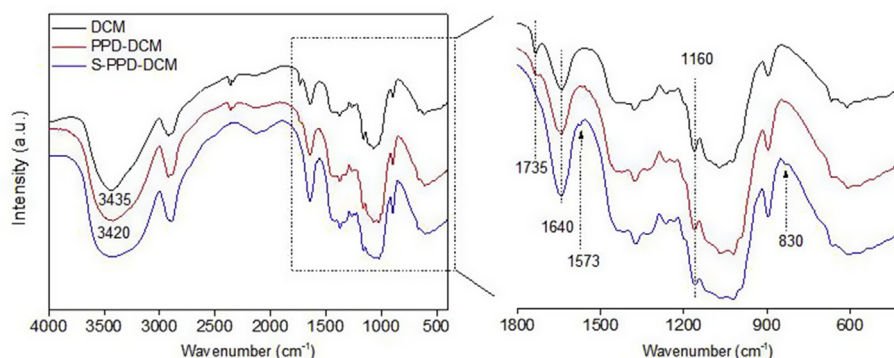


Fig. 5. FTIR spectra of the DCM, PPD-DCM and S-PPD-DCM.

determination of PPD in real sample solutions and the spiked samples under the optimum conditions. The calculated recoveries were 94.7% and 98.1% when the added amount of PPD was 300 and $500 \mu\text{g L}^{-1}$, respectively. Their RSD of three parallel experiments was calculated to be 2.97% and 3.87%, respectively. Considering that no any pretreatment was used in the whole process, the proposed method had good precision and recovery.

3.3.4. Detection mechanism of PPD

FTIR spectrum can give some information about the functional groups on a sample. Therefore, the FTIR spectra of the DCM, PPD-DCM and S-PPD-DCM were recorded as shown in Fig. 5. Meanwhile, an enlarged range from 1800 to 400 cm^{-1} was also presented. In the DCM spectrum, a characteristic peak corresponding to the C=O stretching vibration appeared at 1735 cm^{-1} . The strong adsorption at 3435 cm^{-1} was due to the O–H stretching vibration. The bands in the range of $3000\text{--}2800 \text{ cm}^{-1}$ represented the C–H stretching vibration in methyl or methylene. The peak at 1642 cm^{-1} was associated with the absorbed water, and the bands ranging from 1450 to 1200 cm^{-1} were attributed to the C–H and O–H deformation vibrations. The band at 1160 cm^{-1} belonged to the

stretching vibrations of glycosidic linkages while the sharp peak at 895 cm^{-1} corresponded to the ring stretching of glucose. The strong absorption between 1100 and 900 cm^{-1} was ascribed to the C–OH deformation vibration and/or C–O stretching vibration in cellulose.

After the enrichment of PPD, the peak at 1735 cm^{-1} showed a weak intensity, suggesting that a chemical reaction had happened between the dialdehyde groups of DCM and PPD. The peak at 1642 cm^{-1} became stronger, which was related to the C=N formation, indicating that a Schiff base reaction was involved. Meanwhile, the adsorption locating at 3435 cm^{-1} gave a red shift to 3420 cm^{-1} and became broader, which was attributed to the overlapping of N–H and O–H stretching vibrations. The C–H stretching vibration at $3000\text{--}2800 \text{ cm}^{-1}$ and the adsorption at $1600\text{--}1400 \text{ cm}^{-1}$ became stronger because of the introduction of benzene rings. In the FTIR spectrum of the S-PPD-DCM, most of the peaks/bands became stronger because of the introduction of salicylaldehyde. The stronger peak at 1642 cm^{-1} indicated that the formation of S-PPD-DCM was involved in another Schiff base reaction. The broader adsorption at 3420 cm^{-1} was ascribed to the overlapping of phenolic hydroxyl. In addition, two new peaks can be clearly observed at 1573 and 830 cm^{-1} , respectively. The former

was assigned to the skeleton vibration in benzene rings, and the latter was due to para-substituted benzene derivatives. These results confirmed that a two-step Schiff base reaction had happened during the preparation of S-PPD-DCM.

XPS can provide a more accurate analysis of chemical reactions occurring in the PPD detection process. Hence, the surface chemical composition of the DCM, PPD-DCM and S-PPD-DCM were investigated by an XPS study. Their survey spectra and atom concentrations were shown in Fig. S4a and Table 2, respectively. After PPD enrichment, the N atom concentration of the PPD-DCM increased from 0.7% to 1.5% while O atom concentration gave a decrease, verifying the introduction of PPD. As the PPD-DCM reacted with salicylaldehyde, it was anticipated that the N atom concentration presented a slightly decrease.

The high resolution XPS spectra of the C1s and N1s were displayed in Figs. S4b–c. They were decomposed into subcomponents by using software XPS-Peak 4.1. From Fig. S4b, it was clear that the C1s spectra of the samples can be fitted into four components. The peaks, centered near 284.7 eV and 285.2 eV, were assigned to C–C and C–N bonds, respectively. The bands, centered at approximately 286.5 eV and 288.0 eV, were attributed to the C–O and C=O bonds, respectively. Their trend accorded with the proposed mechanism of two-step Schiff base reaction. After PPD enrichment, it can be found that the N1s spectrum (Fig. S4c) of the PPD-DCM was deconvoluted into two peaks centered at ca. 399.5 eV ($-\text{N}=\text{}$) and 400.0 eV ($-\text{NH}-/-\text{NH}_2$) [37]. As the salicylaldehyde was introduced to the PPD-DCM, the $-\text{N}=\text{}$ peak increased and shifted slightly from 399.4 eV to 399.6 eV. These confirmed the formation of Schiff base in detecting PPD.

The SEM images of the DCM, PPD-DCM and S-PPD-DCM were exhibited in Fig. S5. No obvious change was observed from the surface morphologies of three samples, suggesting that the PPD and salicylaldehyde were not simply deposited on the membrane surface.

On the basis of the above results, it was proposed that the detection mechanism of PPD was involved in a two-step Schiff base reaction (see Fig. 6 for the schematic illustration of the detection process of PPD) and the aggregation-induced emission (AIE) effect. Firstly, the target specie was immobilized on the cellulose membrane via a Schiff base reaction between PPD and DCM. Afterward, When the obtained PPD-DCM was immersed into the salicylaldehyde solution, the other Schiff base reaction happened between the

primary amines of PPD and the aldehyde groups of salicylaldehyde. At the same time, the “solid” state blocked the nonradiative intramolecular rotation decay of the excited molecules, enhancing the fluorescence emission.

In order to verify that the fluorescence “turn-on” mechanism was related to an AIE effect, the following experiments were carried out. A series of mixed solutions of 0.5 wt% salicylaldehyde and different PPD concentrations (0, 250, 500, 1000 and 10,000 $\mu\text{g L}^{-1}$) were prepared. Then they were filled in five plastic tubes, respectively. Afterward, dumping the solution, the unwashed plastic tubes were dried at 50 °C in an oven. Their images under visible light and 365 nm UV light were presented in Fig. 7. It was evident from Fig. 7a that the mixed solution of salicylaldehyde and PPD only had a very weak fluorescence even if the PPD concentration was increased to 1000 $\mu\text{g L}^{-1}$. When the PPD concentration reached 10,000 $\mu\text{g L}^{-1}$, a enhanced yellow fluorescence was observed while some yellow precipitate was formed. By contrast, the residue in all the plastic tubes can emit strong yellow fluorescence as shown in Fig. 7b. These further confirmed that the yellow fluorescence of S-PPD-DCM was involved in an AIE effect.

4. Conclusions

A novel SSF method was developed for the detection of PPD. The target specie PPD was immobilized on dialdehyde cellulose membrane followed the reaction with salicylaldehyde. The resultant membrane S-PPD-DCM emitted yellow fluorescence under 365 nm UV light, which can be used for the qualitative and quantitative analysis of PPD. Experimental variables affecting the fluorescence intensity were investigated and optimized. Under the optimum conditions, a detection limit of 5.35 $\mu\text{g L}^{-1}$ was obtained and two linear ranges were observed at 10–100 and 100–1000 $\mu\text{g L}^{-1}$, respectively. When PPD concentration was as low as 50 $\mu\text{g L}^{-1}$, the yellow fluorescence of the membrane can still be visualized by naked eye. Moreover, the detection of PPD was hardly affected in the coexistence of 1 mg L^{-1} of o-phenylenediamine, m-phenylenediamine or phenylamine, exhibiting good selectivity. It was the first time that SSF analysis was employed to the determination of PPD. The developed method was satisfactorily used to determine the PPD in the spiked hair dye with recovery rate more than 94% and RSD of three parallel experiments less than 5%. The FTIR and

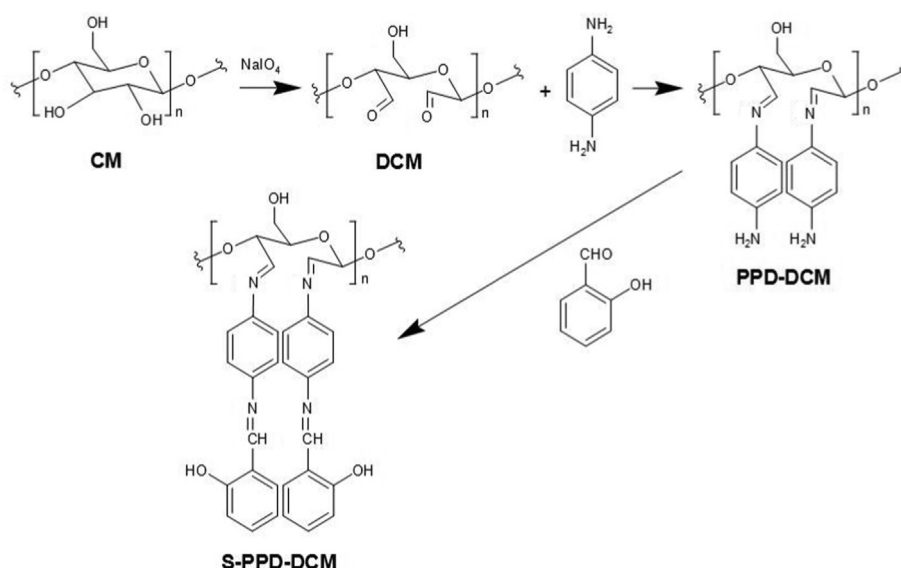


Fig. 6. The schematic illustration for the enrichment and SSF detection of PPD on cellulose membrane.



Fig. 7. (a) The colors of the mixed solution containing 0.5 wt% salicylaldehyde and different concentrations of PPD under visible light (top) and 365 nm UV light (bottom). The PPD concentrations were: 0, 250, 500, 1000, 10,000 $\mu\text{g L}^{-1}$ (b) The colors of the residue in the plastic tubes under visible light (top) and 365 nm UV light (bottom). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

XPS results confirmed that the PPD detection was involved in a two-step Schiff base reaction. At the same time, the “solid” state blocked the nonradiative intramolecular rotation decay of the excited molecules, enhancing the fluorescence emission.

CRediT authorship contribution statement

Shengli Zhang: Conceptualization, Writing - review & editing, Supervision. **Bofang Liu:** Investigation, Writing - original draft. **Daiyan Hu:** Validation, Data curation. **Silue Zhang:** Formal analysis. **Yanbo Pei:** Visualization. **Zhengjun Gong:** Writing - review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was supported by the Science and Technology Support Program of Sichuan Province (No. 2016GZ0222), National Natural Science Foundation of China (No. 21777131) and National College Students Innovation and Entrepreneurship Training Program (No. 201910613089).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.aca.2020.09.047>.

References

- [1] M. Hébert, D. Rochefort, Electrode passivation by reaction products of the electrochemical and enzymatic oxidation of p-phenylenediamine, *Electrochim. Acta* 53 (2008) 5272–5279.
- [2] K. Ngamdee, S. Martwiset, T. Tuntulani, W. Ngeontae, Selective fluorescence sensors for p-phenylenediamine using formyl boronate ester with an assistance of micelles, *Sensor. Actuator. B Chem.* 173 (2012) 682–691.
- [3] J. Farrell, C. Jenkinson, S.N. Laverne, J.L. Maggs, B.K. Park, D.J. Naisbitt, Investigation of the immunogenicity of p-phenylenediamine and Bandrowski's base in the mouse, *Toxicol. Lett.* 185 (2009) 153–159.
- [4] T.B. Zononi, F. Hudari, A. Munnia, M. Peluso, R.W. Godschalk, M.V.B. Zononi, G.J.M. den Hartog, A. Bast, S.B.M. Barros, S.S. Maria-Engler, G.J. Hageman, D.P. de Oliveira, The oxidation of p-phenylenediamine, an ingredient used for permanent hair dyeing purposes, leads to the formation of hydroxyl radicals: oxidative stress and dna damage in human immortalized keratinocytes, *Toxicol. Lett.* 239 (2015) 194–204.
- [5] H.M. Pinheiro, E. Touraud, O. Thomas, Aromatic amines from azo dye reduction: status review with emphasis on direct UV spectrophotometric detection in textile industry wastewaters, *Dyes Pigments* 61 (2004) 121–139.
- [6] L.F. Gao, X. Lin, X. Hai, X.W. Chen, J.H. Wang, Polymeric ionic liquid-based fluorescent amphiphilic block copolymer micelle for selective and sensitive detection of p-phenylenediamine, *ACS Appl. Mater. Interfaces* 10 (2018) 43049–43056.
- [7] W.J. Wang, J.M. Xia, X. Hai, M.L. Chen, J.H. Wang, A hybrid of carbon dots with 4-chloro-7-nitro-2,1,3-benzoxadiazole for selective detection of p-phenylenediamine, *Environ. Sci.: Nano* 4 (2017) 1037–1044.
- [8] H. Tokuda, Y. Kimura, S. Takano, Determination of dye intermediates in oxidative hair dyes by fused-silica capillary gas chromatography, *J. Chromatogr.* 367 (1986) 345–356.
- [9] N.A. Penner, P.N. Nesterenko, Simultaneous determination of dihydroxybenzenes, aminophenols and phenylenediamines in hair dyes by high-performance liquid chromatography on hypercross-linked polystyrene, *Analyst* 125 (2000) 1249–1254.
- [10] M. Akyüz, S. Ata, Determination of aromatic amines in hair dye and henna samples by ion-pair extraction and gas chromatography-mass spectrometry, *J. Pharmaceut. Biomed. Anal.* 47 (2008) 68–80.
- [11] J. He, J. Sunarso, J. Miao, H. Sun, J. Dai, C. Zhan, W. Zhou, Z.P. Shao, A highly sensitive perovskite oxide sensor for detection of p-phenylenediamine in hair dyes, *J. Hazard Mater.* 369 (2019) 699–706.
- [12] Y. Zhu, K. Yan, Y. Liu, J. Zhang, Photovoltammetric behavior and photoelectrochemical determination of p-phenylenediamine on CdS quantum dots and graphene hybrid film, *Anal. Chim. Acta* 884 (2015) 29–36.
- [13] S. Dong, L. Chi, Z. Yang, P. He, Q. Wang, Y. Fang, Simultaneous determination of dihydroxybenzene and phenylenediamine positional isomers using capillary zone electrophoresis coupled with amperometric detection, *J. Separ. Sci.* 32 (2009) 3232–3238.
- [14] Á. Andrade-Eiroa, M. Canle, V. Cerdá, Environmental applications of excitation-emission spectrofluorimetry: an in-depth review I, *Appl. Spectrosc. Rev.* 48 (2013) 1–49.
- [15] M.C. Talio, M. Alesso, M. Acosta, M.G. Gimena, M.O. Luconi, L.P. Fernández, Caffeine monitoring in biological fluids by solid surface fluorescence using membranes modified with nanotubes, *Clin. Chim. Acta* 425 (2013) 42–47.
- [16] A. Molina-Díaz, J.F. García-Reyes, B. Gilbert-López, Solid-phase spectroscopy from the point of view of green analytical chemistry, *Trac. Trends Anal. Chem.* 29 (2010) 654–666.
- [17] S.A. Bortolato, J.A. Arancibia, G.M. Escandar, Chemometrics-assisted fluorimetry for the rapid and selective determination of heavy polycyclic aromatic hydrocarbons in contaminated river waters and activated sludges, *Environ. Sci. Technol.* 45 (2011) 1513–1520.
- [18] G.N. Piccirilli, G.M. Escandar, A novel flow-through fluorescence optosensor for the determination of thiabendazole, *Anal. Chim. Acta* 601 (2007) 196–203.
- [19] H.R. Nie, Y. Lv, L. Yao, Y.Y. Pan, Y. Zhao, P. Li, G.N. Sun, Y.G. Ma, M. Zhang, Fluorescence detection of trace TNT by novel cross-linking electro-polymerized films both in vapor and aqueous medium, *J. Hazard Mater.* 264 (2014) 474–480.
- [20] L.M. Shen, M.L. Chen, X.W. Chen, A novel flow-through fluorescence optosensor for the sensitive determination of tetracycline, *Talanta* 85 (2011) 1285–1290.
- [21] R.N. Jia, W.G. Tian, H.T. Bai, J.M. Zhang, S. Wang, J. Zhang, Amine-responsive cellulose-based ratiometric fluorescent materials for real-time and visual detection of shrimp and crab freshness, *Nat. Commun.* 10 (2019) 795–802.
- [22] C.X. Jiao, C.G. Niu, S.Y. Huan, Q. Shen, Y. Yang, G.L. Shen, R.Q. Yu, A reversible chemosensor for nitrite based on the fluorescence quenching of a carbazole derivative, *Talanta* 64 (2004) 637–643.
- [23] H. Nawaz, W.G. Tian, J.M. Zhang, R.N. Jia, Z.Y. Chen, J. Zhang, Cellulose-based sensor containing phenanthroline for the highly-selective and rapid detection of Fe²⁺ ions with naked-eye and fluorescent dual-modes, *ACS Appl. Mater. Interfaces* 10 (2018) 2114–2121.
- [24] L.L. Bu, J.D. Peng, H.J. Peng, S.P. Liu, H. Xiao, L. Dan, Z.Y. Pan, Y. Chen, F. Chen, Y. He, Fluorescent carbon dots for sensitive detection of Cr(VI) in aqueous media and its application in test papers, *RSC Adv.* 6 (2016) 95469–95475.
- [25] G.N. Piccirilli, G.M. Escandar, F.C. Cañada, I.D. Merás, A.M. Peña, Flow-through photochemically induced fluorescence optosensor for the determination of linuron, *Talanta* 77 (2008) 852–857.
- [26] M. Alesso, M.C. Talio, L.P. Fernández, Solid surface fluorescence methodology for fast monitoring of 2,4-dichlorophenoxyacetic acid in seed samples, *Microchem. J.* 135 (2017) 60–65.
- [27] W.H. Chan, R.H. Yang, T. Mo, K.M. Wang, Lead-selective fluorescent optode membrane based on 3, 3', 5, 5'-tetramethyl-N-(9-anthrylmethyl) benzidine, *Anal. Chim. Acta* 460 (2002) 123–132.
- [28] L.M. Shen, M.L. Chen, X.W. Chen, A novel flow-through fluorescence optosensor for the sensitive determination of tetracycline, *Talanta* 85 (2011) 1285–1290.
- [29] M.C. Talio, K. Zambrano, M. Kaplan, M. Acosta, R.A. Gil, M.O. Luconi, L.P. Fernández, New solid surface fluorescence methodology for lead traces determination using rhodamine B as fluorophore and coacervation scheme: application to lead quantification in e-cigarette refill liquids, *Talanta* 143 (2015) 315–319.
- [30] D. Klemm, B. Heublein, H.P. Fink, A. Bohn, Cellulose: fascinating biopolymer and sustainable raw material, *Angew. Chem. Int. Ed.* 44 (2005) 3358–3393.
- [31] R. Li, L. Zhang, M. Xu, Novel regenerated cellulose films prepared by coagulating with water: structure and properties, *Carbohydr. Polym.* 87 (2002) 95–100.
- [32] R.N. Jia, W.G. Tian, H.T. Bai, J.M. Zhang, S. Wang, J. Zhang, Amine-responsive cellulose-based ratiometric fluorescent materials for real-time and visual detection of shrimp and crab freshness, *Nat. Commun.* 10 (2019), 795–782.
- [33] S.L. Zhang, C.C. Kai, B.F. Liu, S.L. Zhang, W. Wei, X.L. Xu, Z.W. Zhou, Preparation, characterization and antibacterial properties of cellulose membrane containing N-halamine, *Cellulose* 26 (2019) 5621–5633.
- [34] J. Cao, W. Wei, G.J. Gou, M. Jiang, Y.H. Cui, S.L. Zhang, Y. Wang, Z.W. Zhou, Cellulose films from the aqueous DMSO/TBAH-system, *Cellulose* 25 (2018) 1975–1986.
- [35] X. Cao, N. Zhao, A. Gao, H. Lv, Y. Jia, R. Wu, Y. Wu, Bisnaphthalimides self-assembly organogel formation and application in detection of p-phenylenediamine, *Mater. Sci. Eng. C* 70 (2017) 216–222.
- [36] Y.J. Zhao, K. Miao, Z. Zhu, L.J. Fan, Fluorescence quenching of a conjugated polymer by synergistic amine-carboxylic acid and π - π interactions for selective detection of aromatic amines in aqueous solution, *ACS Sens.* 2 (2017) 842–847.
- [37] W. Yu, L. Zhang, H. Wang, L. Chai, Adsorption of Cr(VI) using synthetic poly(m-phenylenediamine), *J. Hazard Mater.* 260 (2013) 789–795.

Sensitive and Visual Detection of p-Phenylenediamine by Using Dialdehyde Cellulose Membrane as a solid Matrix

Shengli Zhang*, Bofang Liu, Daiyan Hu, Silue Zhang, Yanbo Pei, Zhengjun Gong*

Faculty of Geosciences and Environmental Engineering, Southwest Jiaotong University,

610031 Chengdu, Sichuan, China

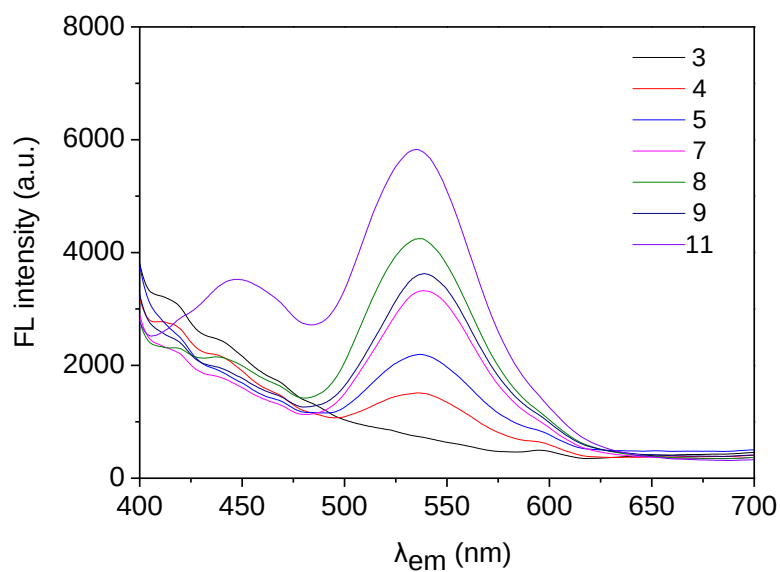


Fig. S1 Effect of solution pH in the process of PPD enrichment on the fluorescence spectra of the samples ($C_S=0.5$ wt%, $C_{PPD}= 250 \mu\text{g L}^{-1}$, $t=60$ min, $T=25$ °C).

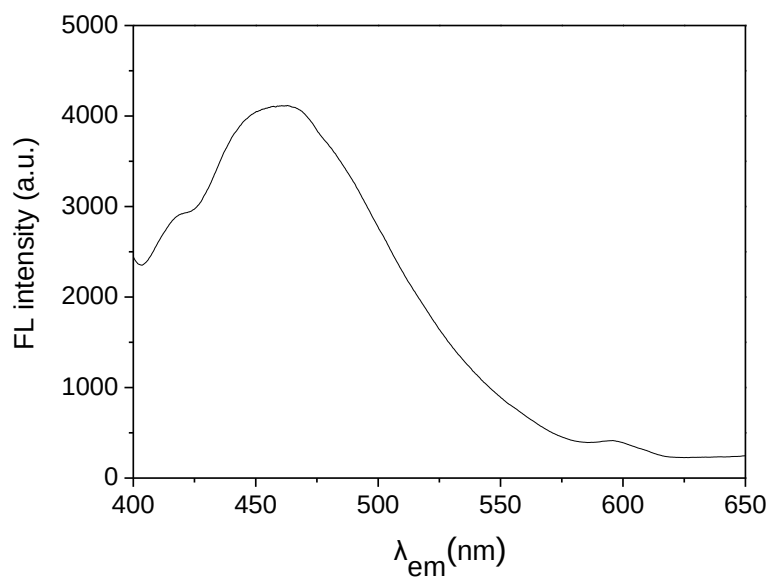


Fig. S2 Fluorescence spectrum of the DCM immersed in a 0.5 wt% salicylaldehyde solution with pH ca. 10 and then dried at 50 °C.

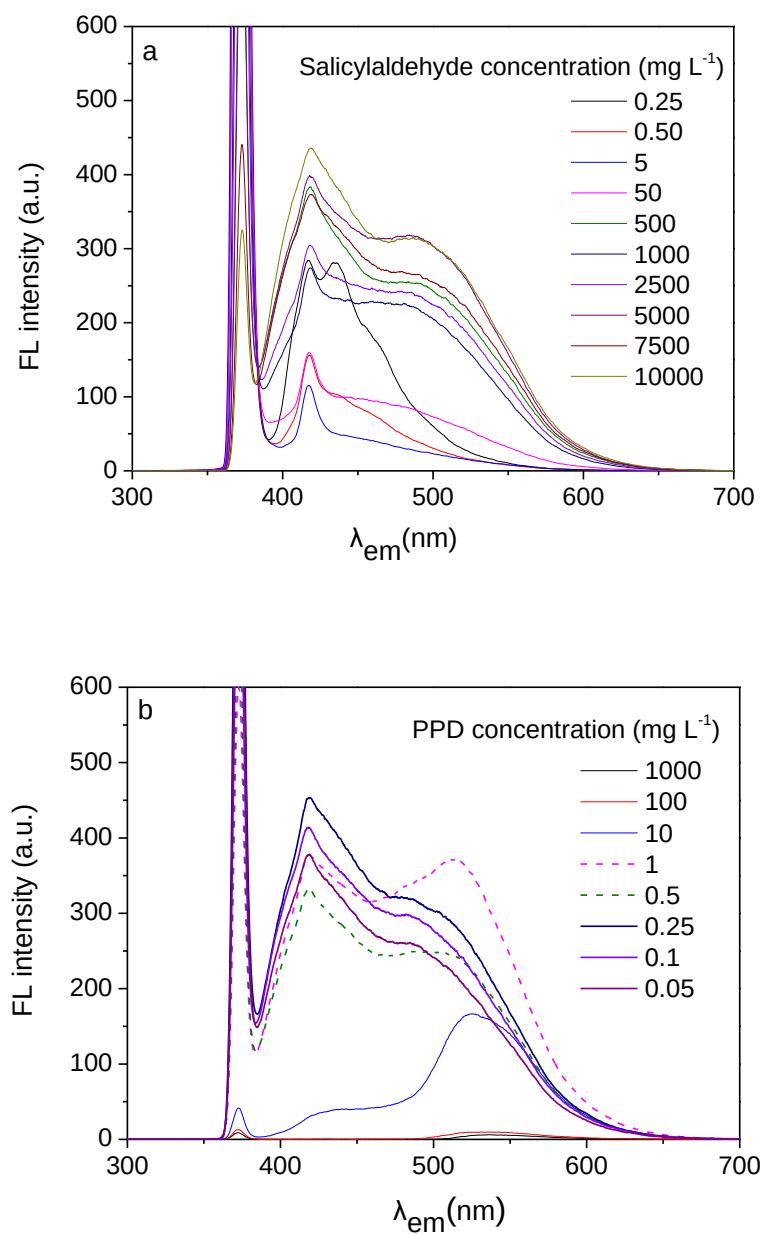
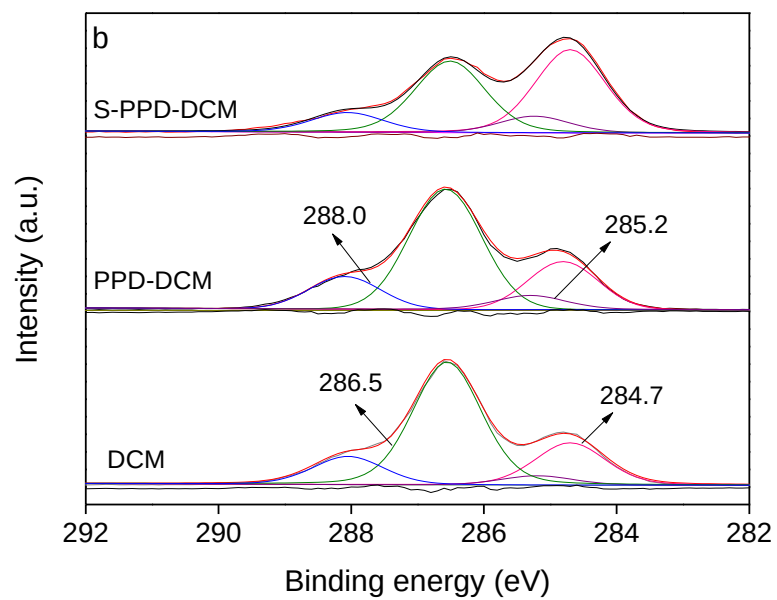
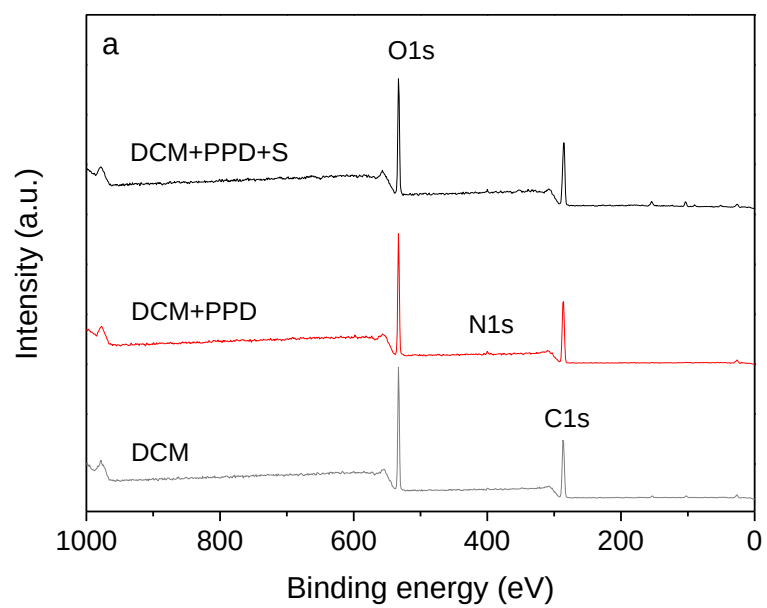


Fig. S3 Fluorescence emission spectra ($\lambda_{ex}=370$ nm) of the liquid system in the coexistence of PPD and salicylaldehyde: (a) changing PPD concentrations ($C_S=0.5$ wt%); (b) changing salicylaldehyde concentrations ($C_{PPD}= 250 \mu g L^{-1}$).



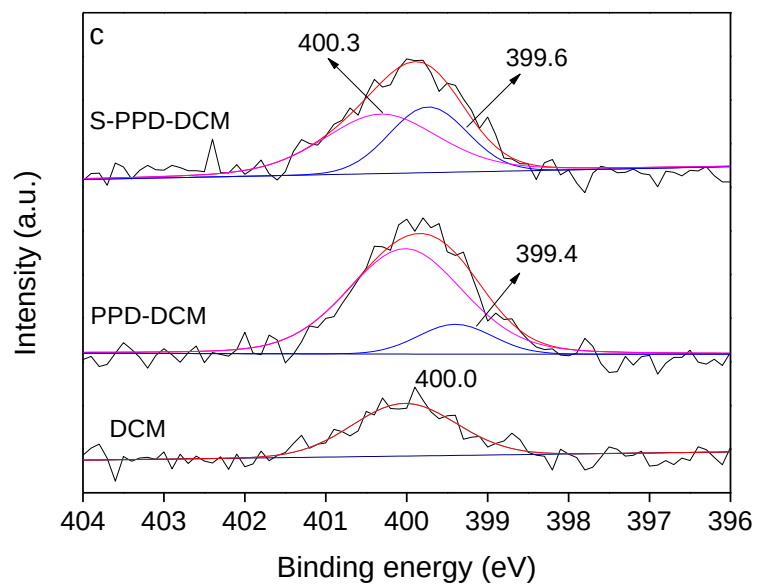


Fig. S4 (a) Survey spectra of the DCM, PPD-DCM and S-PPD-DCM. (b) High-resolution XPS spectra of C1s. (c) High-resolution XPS spectra of N1s.

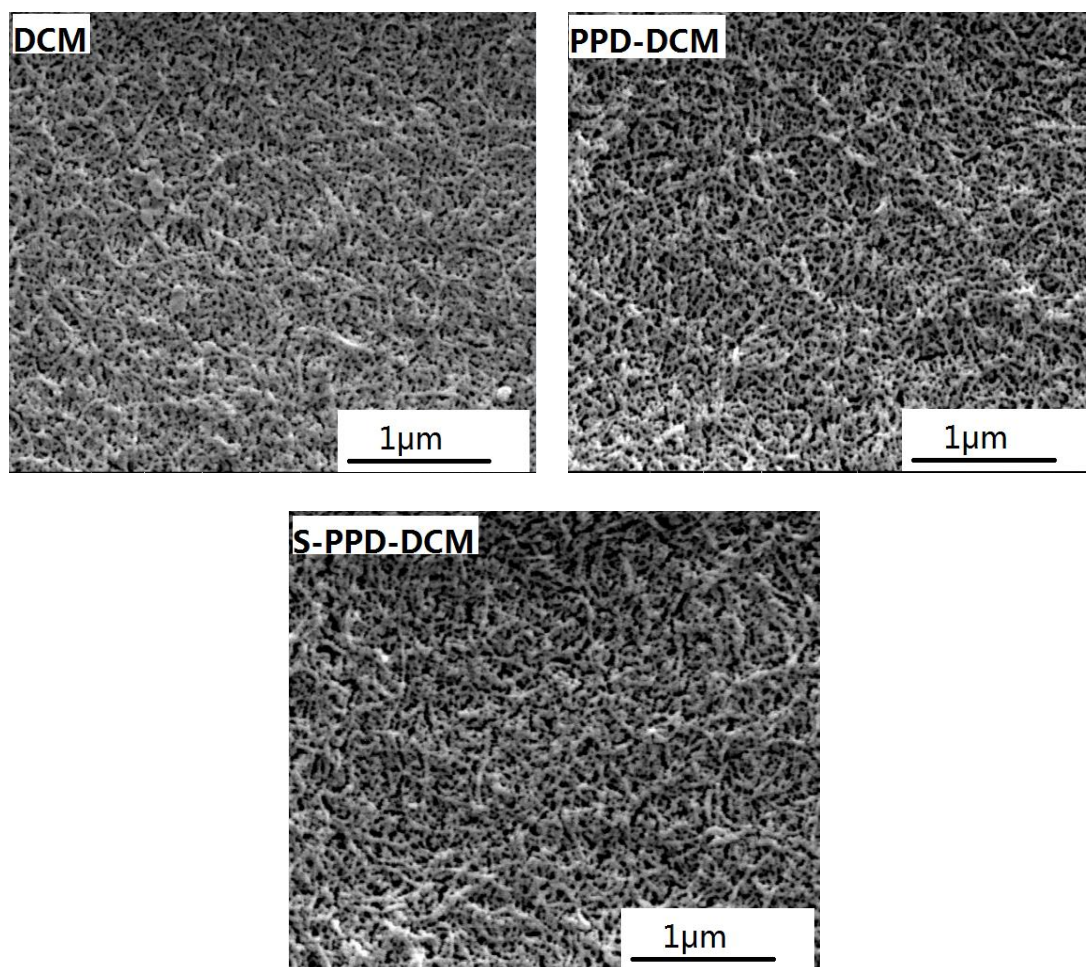


Fig. S5 SEM images of the DCM, PPD-DCM and S-PPD-DCM.