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A host-guest complexation based fluorescent probe for the detection of paraquat and diquat herbicides in aqueous solutions

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The supramolecular interactions among thioflavin T (ThT), two herbicides, paraquat (PQ) and Diquat (DQ), and macrocyclic cucurbit[8]uril (Q[8]), were studied using spectrofluorimetry, ultraviolet-visible absorbance spectrometry, ^{1}H nuclear magnetic resonance spectroscopy, and isothermal titration calorimetry. A new method based on fluorescence quenching of the fluorescent host–guest complexes of Q[8]-ThT (the probe) upon cooperative binding with PQ or DQ to form a ternary complex, was proposed for the analytical determination of the two herbicides in aqueous solutions. Detection limits of 7.95×10^{-9} mol L^{-1} and 8.07×10^{-9} mol L^{-1} were obtained for PQ and DQ, respectively. Recoveries obtained by the proposed method in real-world examples such as river water and cabbage extracts were 104–108%. Interestingly, this method demonstrated high selectivity towards PQ and DQ in the presence of various metal ions and quaternary ammonium substances. Such a method provides a rapid, selective, sensitive and facile strategy for herbicides detection and quantification.

Introduction

The bipyidinium-derived herbicides, paraquat (PQ) and diquat (DQ) (Fig. 1), are non-selective contact herbicides that are used to control weeds and grasses. They are often present as environmental residues because of their water solubility and non-volatility. PQ and DQ have been banned in the European countries, and their use has also been strictly limited in more than 20 other countries because they are moderately hazardous. For drinking water, the United States Environmental Protection Agency has established a maximum contamination level of 20 μg L^{-1} for DQ and a goal of 3 μg L^{-1} for PQ.[1-2] The European Union has not regulated the levels of these compounds in water and instead, values of 0.1 μg L^{-1} for individual and 0.5 μg L^{-1} for total herbicides content are applied.[3] Paraquat dichloride often exists in tuberous and corm vegetables at around 5 ppm level according to the Environmental Protection Agency.[4] Traditional high-performance liquid chromatography (HPLC) is used extensively for the analysis of PQ and DQ by adding ion pair reagents to improve the separation and peak profiles in the mobile phase because of their strong cationic character.[5] Highly sensitive analytical methods have also been used for the determination of trace quantities of PQ and DQ because of low level residues in water and vegetation samples. These methods include liquid chromatography-mass spectrometry,[6] gas chromatography-tandem mass spectrometry[7] and optical immunosensing using capillary electrophoresis-ultraviolet spectroscopy.[8] Also, other rapid method, such as enzyme immunoassays, has been previously developed for the analysis of these herbicides.[9] Still, to help enforce legislated values, more sensitive, facile, and fast analytical methods are highly sought after.

Indicator-displacement assay (IDA), utilizing non-covalent interactions between a receptor (the host), indicator (the guest), and an analyte (the competitive guest), has become a popular approach for chemical sensing. In a typical IDA assay, the analyte competes with the indicator for the same binding site that is offered by the receptor. When the analyte is added to the indicator-receptor pair, the indicator is released to the environment, inducing an absorbance and/or fluorescent change.[10-11] Among many synthetic receptors, cucurbit[n]urils (Q[*n*]s) are highly symmetrical macrocyclic hosts comprised of glycoluril units linked through methylene bridges, and they possess highly polar carbonyl portals with a hydrophobic cavity. Q[*n*]s form remarkably stable complexes with a variety of guest molecules in aqueous solution through a combination of ion-dipole, hydrogen bonding, and hydrophobic interactions inside the cavity.[12-13] In recent years, fluorescence enhancement method (with IDA principle) based on Q[*n*] host–guest complexation has been used extensively for the determination of pesticides[14-15] and other compounds.[16-17] This method, by converting Q[*n*]-dye complexes into optical sensors, has recently attracted widespread attention owing to their simplicity, rapidity, sensitivity, and selectivity. For example,

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the presence of non-fluorescent or weakly fluorescent substances, such as ethambutol, sotalol, ranitidine and paraquat can be detected through IDA approach involving Q[7,8] and fluorescent indicators, such as isoquinoline alkaloid and other dyes.[18-21]

Thioflavin T (ThT) (Fig. 1) is a well-known ultrafast molecular rotor and has been chosen as an extrinsic fluorescent probe to identify amyloid fibrils.[22-24] In addition to amyloid fibrils, ThT also binds with different supramolecular assemblies, resulting in a large emission enhancement.[25-26] Association of ThT with macrocyclic hosts, such as Q[7] or Q[8], can result in a pronounced enhancement of their emission intensities.[27-28] This yields efficient fluorescent probes for the detection of target substances.[29] Q[8] (Fig. 1) can encapsulate two guest molecules simultaneously within its relatively large cavity. It is possible to develop a new spectrofluorimetric method based on cooperative ternary binding with Q[8] for the analysis of guest molecules. Therefore, a novel sensitive spectrofluorimetric method based on cooperative binding between Q[8]-ThT complexes and the analytes, herbicides, has been developed. Cooperative complexation of the fluorescent complex probe and PQ or DQ, were studied by spectrofluorimetry, ^{1}H nuclear magnetic resonance (^{1}H NMR), and isothermal titration calorimetry (ITC). The proposed method was evaluated for real-world applications, determination of PQ and DQ in river water and cabbage samples.

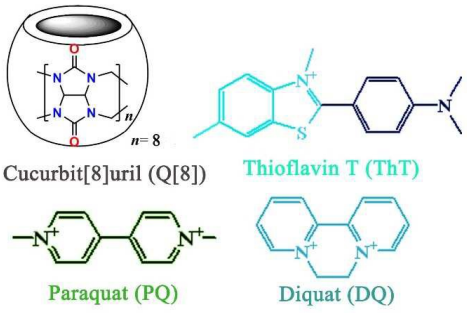

Fig. 1 Structures of Q[8], ThT, PQ and DQ.

Results and discussion

Fluorescence and ultraviolet-visible absorption studies of Q[8]-ThT and herbicides

Aqueous solutions of ThT exhibit weak fluorescence. The PQ and DQ have no or weak fluorescence. Q[8] was found to bind with ThT to form stable 1:2 or 2:2 (Q[8]-ThT) host–guest complexes in water and the complexes displayed a new emission band peaking at 570 nm and ~1000-fold emission enhancement in comparison with the guest fluorescence alone.[28] In our experiment, the effect of various Q[8] concentrations on the fluorescence intensity of Q[8]-ThT complexes was investigated. As can be seen from Fig. S1, the fluorescence intensities of the Q[8]-ThT complexes were enhanced gradually with increasing Q[8] concentration until the maximum inclusion equilibrium was reached at 4×10^{-5} mol L^{-1} Q[8] concentration. The fluorescence intensity changed only slightly when the host–guest ratio was >1. Thus, the optimal host–guest ratio was selected as 1 and the Q[8] and ThT concentrations were both 2×10^{-5} mol L^{-1}. Fluorescence quenching of the Q[8]-ThT complex was observed upon addition of PQ or DQ. The fluorescence spectra of the Q[8]-ThT complexes, in the presence of different concentrations of PQ or DQ, are shown in Fig. 2. The fluorescence spectra of the Q[8]-ThT complexes at 570 nm exhibited a progressively lower intensity with wavelength blue-shift and intensity enhancement at 490 nm emission with increased herbicide concentration. This occurrence of fluorescence quenching is likely because that parts of the ThT molecule entered the Q[8] cavities by the introduction of herbicides and the 2:2 Q[8]-ThT dimer inclusion complex is destroyed with an obvious fluorescence "turn off" at 570 nm. When the herbicide concentration was half to that of the Q[8]-ThT (2:2) complex, the fluorescence intensity became constant (Fig. 2). We therefore chose this value as a standard probe test concentration. The fluorescence quenching (ΔF) values show a good linear relationship with the PQ and DQ concentration for a specific concentration range. The linear regression equations relating fluorescence intensity (y) to PQ and DQ concentration (x) using Q[8]-ThT as probe are y = 0.48x + 2.84 (R = 0.9996) and y = 0.47x + 5.48 (R = 0.9994), respectively. Hence, Q[8]-ThT provides a promising candidate as a fluorescent probe complex for herbicide determination.

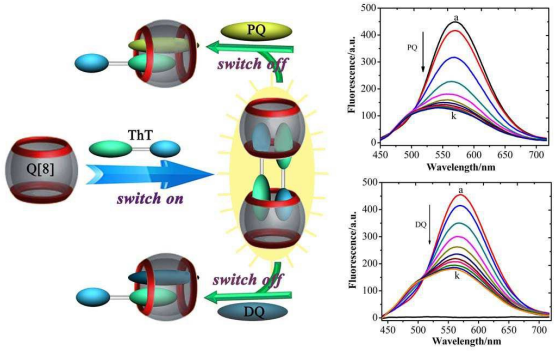

Fig. 2 Possible inclusion model of Q[8] and ThT with herbicides (left); fluorescence spectra of Q[8]-ThT (both 2×10^{-5} mol L^{-1}) with PQ and DQ (0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, and 2.0 equivalent) in aqueous solution (λ_{ex} = 406 nm, slit:10 nm/10 nm) (right).

When PQ (2×10^{-5} mol L^{-1}) was added to aqueous Q[8]-ThT (1:1) solution, the absorption signal of the Q[8]-ThT fluorescent probe decreased and underwent broadening and exhibited red shift from 414 to 433 nm with an isosbestic point at 425 nm (Fig. 3A). Similarly, when DQ was added, the absorption band of Q[8]-ThT-DQ system exhibited a red shift, with a shoulder peak at 440 nm and an isosbestic point at 425 nm as well (Fig. 3A). The fluorescent spectrum of Q[8]-ThT in the presence of PQ or DQ displayed a distinct spectral profile compared with that of the Q[8]-ThT complex alone(3B). Noticeably, a slight blue fluorescence was visible for all these samples due to the excitation wavelength at 365 nm (inset of Fig. 3B). These changes in the absorption and fluorescence spectra indicate the formation of a new inclusion complex

between Q[8] and ThT with included herbicides. We attribute the broadening and red shift in absorption to the inclusion of a π-π-stacked ThT-herbicide complex within the Q[8] cavity with a 1:1:1 (Q[8]:ThT:herbicide) stoichiometry.

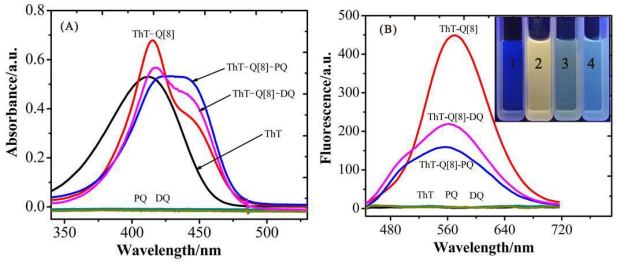

Fig. 3 Ultraviolet-visible absorption spectra (A) and fluorescence spectra (B) of ThT (2×10^{-5} mol L^{-1}), ThT-Q[8](1:1), ThT-Q[8]-PQ(1:1:1), and ThT-Q[8]-DQ(1:1:1) in aqueous solution. Inset: photograph of ThT(1), ThT-Q[8](2) in the absence and presence of PQ(3) and DQ(4) upon excitation at 365 nm with an ultraviolet lamp.

The effect of pH on the reaction of ThT-Q[8] is shown in Fig. S2. The pH-dependence of the fluorescence intensity was studied from a pH of 1.0 to 12.0. The fluorescence intensity reached a maximum value at pH of 5.0, and this intensity remained constant until pH 9.0 was reached. However, the fluorescence intensity decreased when the pH was in the range of 2.0-5.0 and 9.0-12.0. Therefore, we chose pH 7.0 aqueous solution as the experimental media. The fluorescence intensity reached a maximum value 10 min after the reagent addition and remained constant for at least 4 h. For this reason, room temperature for 10 min was selected as the standard reaction condition.

Response mechanism of fluorescent probe in sensing herbicides

In the ^{1}H NMR studies, the -CH_3 (a) and -$N(CH_3)_2$ (b) protons of the respective benzothiazole and dimethylaminophenyl moieties of ThT showed an upfield shift by ~0.6 ppm and ~0.7 ppm with a clear splitting pattern, and N^+CH_3 (c) protons of the thiazole also exhibited an upfield shift of ~1.1 ppm, upon mixing ThT with 1.0 equivalent Q[8] in D_2O (Fig.4). Accordingly, the methylene proton resonances of Q[8] showed a quartet splitting pattern upon complexation, which is often observed when the Q[8] hosts asymmetrical guests. All of these changes indicate that Q[8] likely encapsulated two ThT molecules with opposing orientations to form a 2:2 (Q[8]-ThT) inclusion complex at high Q[8] concentrations.[28] When PQ underwent complexation with Q[8], the H_d and H_e protons of PQ showed an upfield shift with 1.0 equivalent of Q[8], which suggests that the bipyridyl moiety was encapsulated within the Q[8] cavity (Fig. 4).

With the addition of PQ to a Q[8]-ThT complex, the protons of -CH_3 (a) and N^+CH_3 (c) protons of the benzothiazole moiety exhibited an upfield and the -$N(CH_3)_2$ (b) protons show a downfield shift compared with those of free ThT. The H_d and H_e protons of PQ also showed an upfield shift compared with those of free PQ. These results demonstrate that the benzothiazole moiety of ThT and the bipyridyl moiety of PQ are likely incorporated within Q[8] cavities via π-π stacking between ThT and PQ in a Q[8] cavity with 1:1:1 (Q[8]:ThT:PQ) stoichiometry (Fig. 4). The Q[8]-ThT-DQ ternary complexations exhibited similar behaviors to the Q[8]-ThT-PQ system (Fig. 3S for the ^{1}H NMR spectra). Additionally, 2D Diffusion-Ordered NMR spectroscopy (DOSY) experiments provided further evidence for the formation of these two ternary complexes (Fig. 4S).

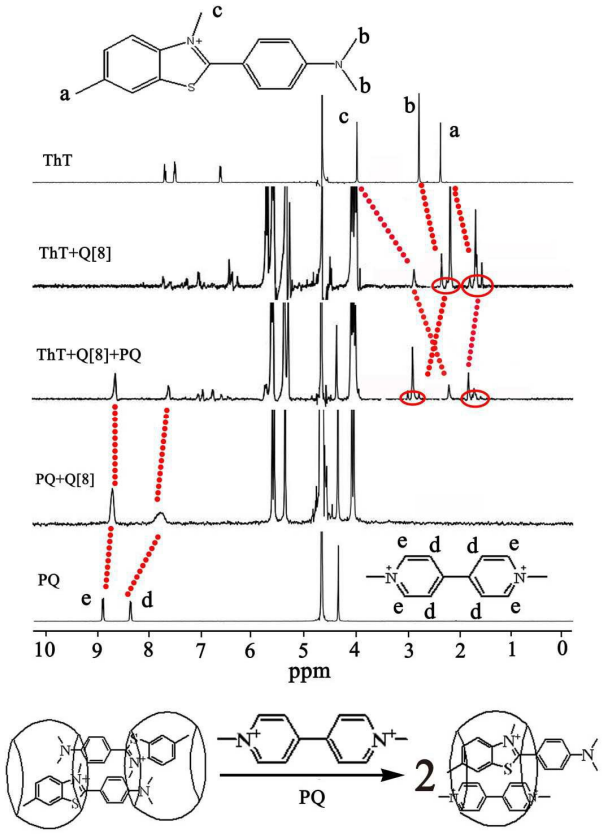

Fig. 4 ^{1}H NMR spectra (400 MHz, D_2O) of ThT and PQ in the absence and presence of 1 equivalent of Q[8].

ITC (Fig. 5) measurements of the complexation between Q[8], ThT and the herbicides indicated that the association constants of the Q[8]-ThT, Q[8]-PQ, and Q[8]-DQ complexes were $(1.37 \pm 0.12)\times10^6$ L mol^{-1}, $(8.11 \pm 0.23)\times10^5$ L mol^{-1}, and $(7.84\pm0.38)\times10^5$ L mol^{-1}, respectively. Therefore, the interaction between Q[8] and ThT with the tested herbicides was a cooperative binding process. Both the herbicides and ThT molecules attempted to occupy the Q[8] cavity, which reduced the fluorescence intensity of Q[8]-ThT due to the formation of a new ternary inclusion complex between Q[8],ThT and each of the herbicides.

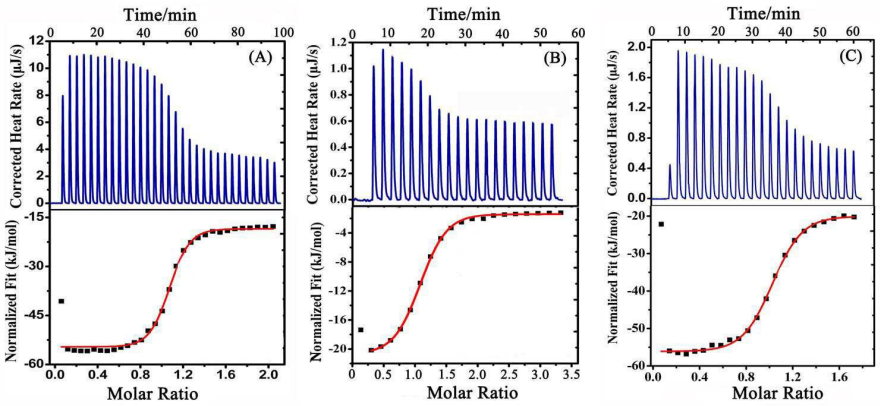

Fig. 5 Microcalorimetric titration of Q[8] with ThT(A), Q[8] with PQ (B), and Q[8] with DQ (C) in aqueous solution at 25 °C.

Quantification of herbicides and sensitivity

Under the optimal experimental conditions described above, we found a linear correlation (y = 0.48x + 2.84, R = 0.9996 and y = 0.47x + 5.48, R = 0.9994) between the fluorescence intensity and concentration of PQ and DQ from 0 to 8 μM (Fig. 5S). The detection limit of PQ and DQ was 7.95×10^{-9} mol L^{-1} and 8.07×10^{-9} mol L^{-1}, which is lower than the maximum regulatory level of 0.5 mg kg^{-1} allowed for water and 5 mg kg^{-1} allowed for vegetables.[30] The detection limit of this method is comparable with that of other methods described in analytical literature as shown in Table 1. Although the sensitivity of the proposed method is equal to or lower than that of other methods, this method still provides a simple, rapid and economic alternative to other methods since it avoids the use of expensive equipment. The precision of the method was determined by analysing 10 replicate samples of PQ and DQ and the relative error was found to be <5%. Therefore, a Q[8]-ThT fluorescent probe can detect PQ and DQ quantitatively by fluorescence spectroscopy.

Table 1. Methods for determination of PQ and DQ in different matrices

Sample	Detection technique	PQ/LOD（ng mL^{-1}）	DQ/LOD（ng mL^{-1}）
Water	SPE-HPLC[5]	0.10	0.12
Drinking water	Micellar electrokinetic chromatography[31]	0.4	2.2
Tap water	Capillary electrophoresis[32]	48	64
tea	UHPLC-ESI-MS/MS[33]	1.5	5.0
	This method	2.1	2.8

Effect of interfering substances

Due to their widespread usage in agricultural field, PQ and DQ may be present as residues in plants and surface waters.[34-35]To verify the selectivity of the proposed method, the influence of other species, such as various cations and anions, on the analytical signal of the Q[8]-ThT complex during analysis of these herbicides was established. In all cases, the maximum accepted concentration of the interference caused a relative error of <5% in the analytical signal (Table 1S and Table 2S). No interference was observed from commonly present cationic and anonic species such as metal ions (Na^+, K^+, Mg^{2+}, Cu^{2+}, Ca^{2+}, Fe^{3+}) and anions (NO_3^-, SO_4^{2-}, $H_2PO_4^-$) (Table 1S). In particular, quaternary ammonium compounds difenzoquat (DF) did not interfere with PQ and DQ determination, and paraquat and diquat did not also interference with each other at 2×10^{-7} mol L^{-1} concentration(Table 2S). This indicates good selectivity of the analytical application of the fluorescent probe

Analytical application

The applicability of the developed fluorescent probe was evaluated by determining the concentration of PQ or DQ residues in river water or cabbage samples. Solid-phase extraction method was used to prepare samples of PQ and DQ from water and cabbage described in Experimental Section. The standard addition method was used for PQ and DQ determination. HPLC was used to compare the validity between the proposed and existing methods. No background interference (i.e., blank reagent and cabbage samples) was introduced by the proposed method. The results are presented in Tables 3S and 4S. The recovery yields were 104–108% with a relative standard deviation (RSD) < 5% in river water

and in the cabbage extracts. The concentrations of PQ or DQ determined using the proposed fluorescent probe were consistent with those obtained by HPLC. The developed method therefore shows satisfactory reproducibility, with an RSD value lower than 5% (n = 3), which confirms that this method can be applied with sufficient precision for PQ or DQ residue analysis in real samples at low concentrations.

Conclusions

The herbicides PQ and DQ exhibit little or no fluorescence in aqueous solution, which makes their determination by direct fluorescence measurement methods difficult. We have developed a new sensitive fluorescent probe for quantitative detection of PQ and DQ, based upon cooperative binding between fluorescent Q[8]-ThT complexes and these herbicides to form weak-fluorescence ternary complexes. The proposed sensing mechanism was confirmed by ^{1}H and DOSY NMR, ITC, and fluorescence spectra. We have also demonstrated that the method can be applied for the practical determination of these herbicides in river water and cabbage extracts. Overall, this method is rapid, economic, and facile; and it meets regulatory requirements for assays of PQ and DQ.

Experimental

Materials

Q[8] was synthesized according to a slightly modified literature procedure[36] and characterized by ^{1}H NMR. ThT, PQ, and DQ were obtained from Sigma-Aldrich (Shanghai, China). All reagents were of analytical-reagent grade and used as received. Doubly distilled water was used.

Absorption and fluorescence spectra measurement

Absorption and fluorescence spectra of the host–guest complexes were recorded on an Agilent-8453 spectrophotometer (Agilent-8453, California, America) and a Varian photofluorescent spectrometer (Varian, California, America) at 25 ℃. Stock solutions of Q[8] were prepared with a concentration of 1×10^{-4} mol L^{-1}. Meanwhile, stock solutions of ThT, PQ and DQ (all 1×10^{-3} mol L^{-1}) were prepared in water. All working solutions were prepared by diluting the stock solution to the required concentration.

Aqueous solutions of Q[8] and ThT (2.00×10^{-5} mol L^{-1} of Q[8]-ThT (1:1) complexes) were prepared for characterization via absorption and fluorescence spectroscopy. For the fluorescence spectra, samples of these solutions were combined to form solutions with herbicide:Q[8]-ThT ratios of 0, 0.2:1, 0.4:1, 1:1, and 2:1, respectively. The photomultiplier gain was medium, with a 10 nm emission and excitation bandwidths. The maximum excitation and emission wavelengths ($\lambda_{ex}/\lambda_{em}$) were 406 nm/570 nm for the Q[8]-ThT complex with the herbicide. For the absorption spectra, aqueous solutions of PQ (2×10^{-5} mol L^{-1}) or DQ (2×10^{-5} mol L^{-1}) were added to an aqueous Q[8]-ThT (1:1) solution, and the absorbance intensity was monitored at 200–600 nm at room temperature. For each experiment, three replicate measurements were taken.

^{1}H NMR measurements

To analyze the host–guest complexation of ThT-Q[8] and PQ and DQ, 6.0×10^{-5} mol L^{-1} ThT-Q[8] (1:1) in 0.6 mL D_2O with 1 equivalent of PQ and DQ, and the corresponding ^{1}H NMR spectra were recorded at 25 ℃ using a Varian Inova-400 spectrometer (San Francisco, California, America).

ITC measurements

A thermostated and fully computer-operated ITC(TA, America) instrument was used for the microcalorimetric experiments. All microcalorimetric titrations were performed in aqueous solution at atmospheric pressure and 298.15 K. Each solution was degassed and thermostated using a ThermoVac accessory prior to the titration experiment.

Analytical application

Analytical parameters

To obtain the calibration curves, ~0–8.00×10^{-6} mol L^{-1} solutions of tested herbicides PQ and DQ were added to corresponding aliquots of concentrated stock solution in the presence of the Q[8]-ThT (1:1) complex (2.00×10^{-5} mol L^{-1}) in aqueous solution. According to the International Union of Pure and Applied Chemistry recommendations, a blank solution was measured ($n \geq 20$) to determine the precision and limit of detection (LOD) of the method.

Solutions of PQ and DQ (0–8 μM) and Q[8]-ThT(1:1) (2.00×10^{-5} mol L^{-1}) were prepared by adding an aliquot of concentrated solution of the tested herbicides and the Q[8]-ThT complex and diluting this mixture with water. PQ and DQ residues were not detected in the blank solutions.

Sample preparation and analysis

Cabbages were purchased from a local market, chopped up, and homogenized. A solid phase dispersion sample preparation was carried out as follows. Cabbage extract (5 g) was placed in a conical flask, and mixed with 0.1–0.4 mL of a 0.1 mol L^{-1} herbicide standard sample and 200 mL of doubly distilled water. The pH was adjusted to ~7 with 1 mol L^{-1} pH 7 ammonium phosphate buffer. The mixture was extracted by ultrasonication for 60 min and kept at room temperature for 30 min. Supernatant fluid (100 mL) was removed and concentrated to 5 mL by solvent evaporation. A WCX solid phase extraction column was activated with 2 mL of methanol and 2 mL of water. The mixture was slowly poured into the WCX solid phase extraction column (200 mg × 3 mL). After the sample was washed with 1 mL of water and 1 mL of methanol, it was eluted with 5 mL of acetonitrile containing 2 wt% formic acid. The eluent was concentrated to dryness and the residue was dissolved in 5 mL of doubly distilled water. Finally, the test sample was prepared by combining 1 mL of the cabbage extract sample and the Q[8]-ThT fluorescence probe (5 mL, 1×10^{-4} mol L^{-1} Q[8] and 500 μL 1×10^{-3} mol L^{-1} ThT) and subsequently diluting the sample to 25 mL in aqueous solution.

River water samples were filtered through a 0.45-μm membrane filter (Science Reagent Co., Ltd., Guiyang, China), collected in glass bottles that had been cleaned with hydrochloric acid, and stored in a refrigerator (Haier Group, Qingdao, China) at 4 °C.

Acknowledgements

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A host-guest complexation based fluorescent probe for the detection of paraquat and diquat herbicides in aqueous solutions

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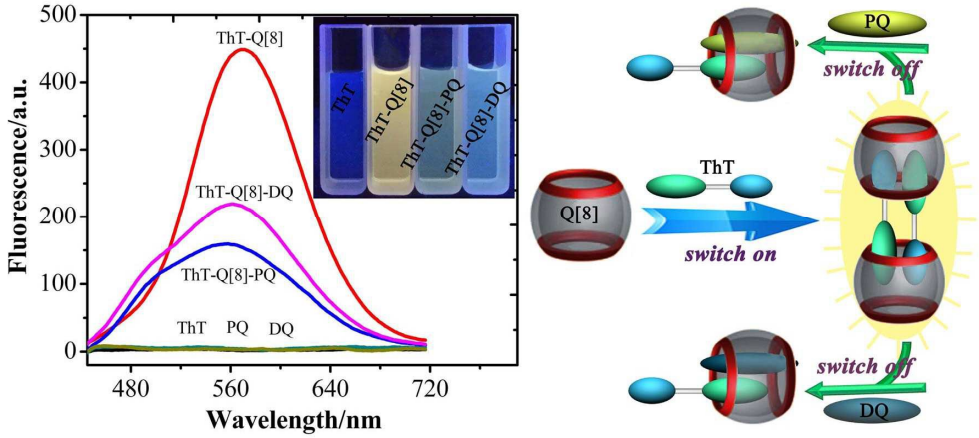

The supramolecular interaction between Thioflavin T and two herbicides, paraquat and diquat, was studied using spectrofluorimetry, ultraviolet-visible absorbance spectrometry, ^{1}H nuclear magnetic resonance spectroscopy and isothermal titration calorimetry. A new method based on fluorescence quenching of host-guest complexation was proposed for the determination of the two herbicides in river water and cabbages by cooperative binding of a fluorescent probe. The method is rapid, direct and simple.