Detection of the pesticide dodine using a cucurbit[10]uril-based fluorescent probe

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ABSTRACT

In this contribution, we discuss a new fluorescent probe which is capable of the selective recognition and determination of dodine (**DD**) from amongst 16 different pesticides. The system utilizes a simple guest-replacement mechanism, which allows for fluorescence turn-on. The probe is constructed from a combination of cucurbit[10]uril (Q[10]) and protonated acridine (**MeAD**), and makes use of the strong fluorescence ability of **MeAD** in aqueous solution *versus* the lack of fluorescence for the homoternary inclusion complex **MeAD**$_2$@Q[10]. Addition of pesticide **DD** to an aqueous solution of **MeAD**$_2$@Q[10] results in **MeAD** displacement and subsequent recovery of the strong fluorescence. Interestingly, similar addition of a number of other common pesticides (15 others were tested herein) failed to result in the recovery of the fluorescence. ^{1}H NMR spectroscopic studies were used to investigate the guest-replacement fluorescence turn-on mechanism.

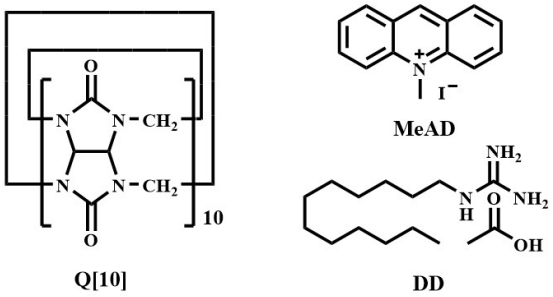
Keywords: Cucurbit[10]uril, Fluorescent probe, Inclusion complex, Pesticide.

Introduction

To make the most of agricultural land and to optimize both the quantity and quality of food accessible, there is a real need to tackle unwanted food pests. This has led to the increased use of pesticides, and as a result, there is concern over the increased harm this may pose to both the environment and to human health [1-3]. One such protective fungicide is dodine (1-dodecylguanidinium acetate, see scheme 1), which is widely used to control a variety of major mold diseases on fruit trees, vegetables, nuts, ornamental plants, and shade trees. Its *modus operandi* is that it is easily adsorbed at the surface of negatively charged microorganisms, and can penetrate their membranes, with resultant destruction of cell structure. In turn, this results in a sterilizing effect and ultimately eliminates algae [4-6]. Moreover, it has seen widespread use in a variety of other applications primarily as a disinfectant [7,8], though again this use is not without risk [9,10]. Indeed, its most obvious unpleasant feature is that it is a skin irritant both as a solid or in concentrated solutions. There is thus a real need to evolve uncomplicated, fast and sensitive analytical methods capable of identifying and quantifying distinct pesticide residues. A number of methods have been previously reported, including the use of ultra-high performance liquid chromatography, gas chromatography, mass spectrometry and fluorescent spectroscopy [11-19]. Of significance is the fluorescent spectroscopy approach given the excellent selectivity and sensitivity and ease and speed of operation it has demonstrated. That said, the ability to construct useful and effective fluorescent probes for specific pesticides still remains a real challenge.

One relevant rapidly developing area is supramolecular chemistry, and in terms of fluorescent species, the encapsulation of guests by macrocyclic hosts has proved to be a useful tool. Systems based on cyclodextrins [20], calix[*n*]arenes [21], and pillar[*n*]arenes [22-28] have shown potential. We are interested in macrocyclic hosts called cucurbit[*n*]urils (Q[*n*]s) [29,30], and we note that there are only a limited number of reports concerning their use as fluorescent probes. In 2012, Xing *et al*. [31] employed a system based on Q[7] and acridine orange for the detection of paraquat in aqueous solution. Indeed, Q[7]-based systems had earlier been employed by del Pozo, Hernández and Quintana for the detection of carbendazim in oranges [32]. More recently, our group utilized a system based on a twisted Q[14] and thioflavin T for the detection of flusilazole [33]. Herein, we wish to expand on the use of Q[*n*]-based systems for the detection of pesticides, and we now report a water-soluble fluorescent probe. In this study, we have utilized the large conjugated fluorophore acridine as the guest, and to improve solubility issues, we have specially used the methyl substituted derivative 10-methylacridin-10-ium iodide (**MeAD**, Scheme 1 and Figure S1, SI). Given the rather large size of this guest, Q[10] was selected as the host of choice, and the resulting probe is designated herein as **MeAD**$_2$@Q[10]. The synthetic procedure is very simple and involves just mixing together Q[10] and **MeAD** in aqueous solution in a 1:2 stoichiometry. The utility of this **MeAD**$_2$@Q[10] probe was then investigated for the detection of 16 different pesticides possessing varying shapes and sizes. Our studies involved the 10-fold addition of the following pesticides: dinotefuran, thiamethoxam, acetamiprid, pyroquilon, dodine, metalaxyl, pyrimethanil, oxadixyl, carbaryl, ethiofencarb, pymetrozine, azaconazole, tebuconazole, triadimenol A, penconazole, flutriafol, flusilazole, triadimefon, tricyclazole and paraquat (Figure S2 in the SI). The results revealed that only dodine prompted a strong

fluorescence enhancement, whilst the other named pesticides led to observed reductions in the fluorescence albeit to differing extents. These results illustrate that the probe **MeAD**$_2$@Q[10] is capable of the selective detection of dodine, and add to the growing literature on the host-guest chemistry of cucurbit[*n*]uril for potential application in everyday life. In particular, this work reveals a new effective method for the detection of dodine.



Scheme 1. The structures of Q[10], **MeAD** and dodine.

Results and Discussion

Monitoring the formation of the homoternary inclusion complex MeAD$_2$@Q[10]

The use of ^{1}H NMR spectroscopic titration experiments in D_2O provides direct evidence for the formation of the homoternary complex produced from **MeAD** and Q[10]. As revealed in Figure 1, the proton signals associated with **MeAD** all gradually shift upfield on addition of increasing amounts of Q[10] (0.72 ppm Ha, 0.70 ppm Hb, 0.74 ppm Hc, 1.01 ppm Hd, 1.02 ppm He, and 0.50 ppm for Hf , respectively – see Table S1), which indicates that the entire **MeAD** molecule is embedded within the Q[10] cavity. It is noteworthy that these chemical shift changes show a linear dependence on the concentration of Q[10] up to 2.0 equivalents, consistent with a 1:2 stoichiometry. These observations thus imply that the Q[10] cavity is large enough to accommodate two **MeAD** molecules thereby forming the homoternary inclusion complex **MeAD**$_2$@Q[10]. Concomitantly, only a single set of signals was observed for the **MeAD** at each

Q[10] concentration, suggestive of fast exchange of the ternary complex.

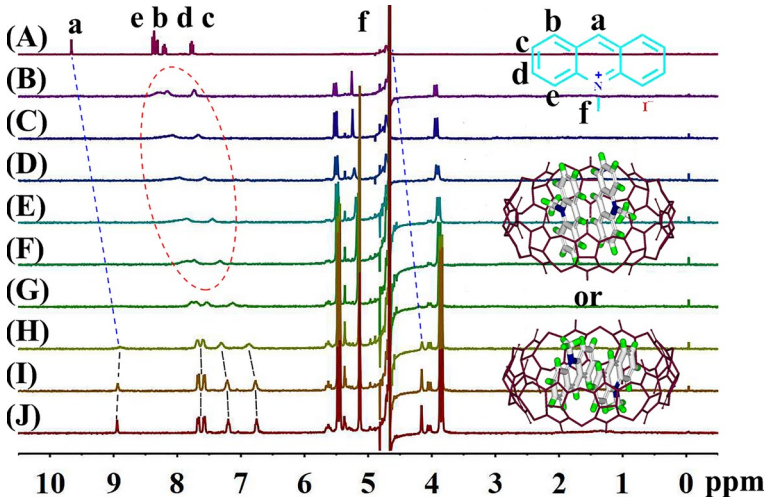


Figure 1. Interaction of **MeAD** and Q[10] (25 ℃): ^{1}H NMR spectra (400 MHz, D_2O, pD=4.0) of **G1** (5.0×10^{-4} mol·L^{-1}) in the absence of Q[10] (A), in the presence of 0.11 equiv. (B), 0.15 equiv. (C), 0.22 equiv. (D), 0.34 equiv. (E), 0.41 equiv. (F), 0.46 equiv. (G) 0.51 equiv. (H), 0.57 equiv. (I) and 0.66 equiv. of Q[10] (J).

Absorption and fluorescence spectroscopy of $MeAD_2$@Q[10]

In aqueous solution, **MeAD** exhibits a prominent absorption peak at 354 nm (Figure S3), and the intensity changes over the pH range 1−12. From its pKa titration curve, the pKa is estimated to be 9. We set the pH of the **MeAD** solution at ~4.0, and gradually added Q[10], whereupon the absorption peak at 354 nm was red shifted to 360 nm whilst the intensity greatly decreased. This suggested a high binding affinity between Q[10] and **MeAD**, and the mol ratio titration method (Figure 2b) revealed that the binding interaction fitted a 1 : 2 (host : guest) binding model, as observed for the ^{1}H NMR spectroscopic titration experiments.

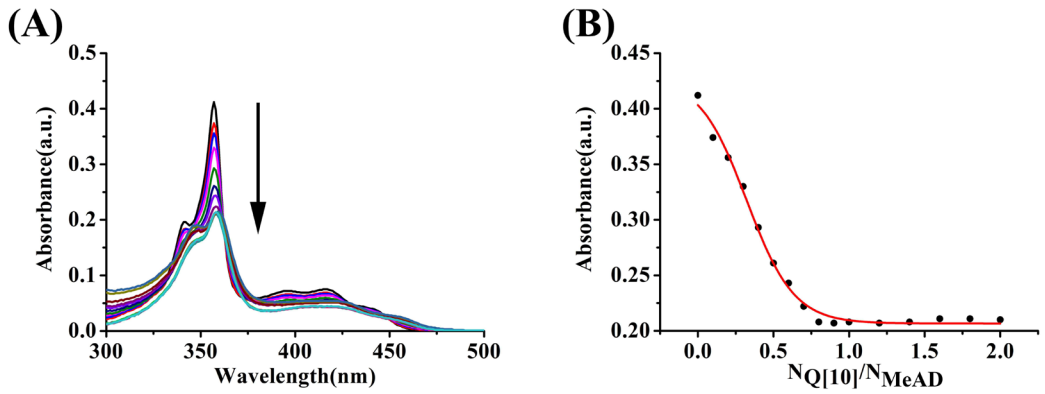


Figure 2. (Colour online) (A) Absorption of **MeAD** (2×10^{-5} mol·L^{-1}) upon addition of increasing amounts (0, 0.1, 0.2……0.9, 1.0, 1.2, 1.4……1.8, and 2.0 equiv) of Q[10] in aqueous HCl solution (pH=4.0); (B) concentration and absorbance *vs*. $N_{Q[8]}/N_{\mathbf{G2}}$ plots in aqueous HCl solution (pH=4.0).

It is known that **MeAD** possesses strong intrinsic fluorescence in aqueous solution, which is pH sensitive; the emission spectra of **MeAD** at different pH are shown in Figure S4. **MeAD** emits the strongest fluorescence at pH ~4.0 (Figure 3B), and so the following studies were conducted at pH ~4.0. The addition of Q[10] under very dilute conditions (using aqueous solutions of **MeAD** at 2.0×10^{-5} mol·L^{-1}) resulted in strong fluorescence quenching (Figure 3A) and the titration curve fitted a 1 : 1 inclusion stoichiometry (Figure 3B). This quenching behaviour is attributed to the formation of an inclusion complex. It is known that the carbonyl oxygen atoms on the Q[10] portals are good electron donors, whereas protonated **MeAD** is a strong electron acceptor. Thus in the inclusion complex, the close proximity of the Q[10] and the **MeAD** facilitates a charge transfer process, which in-turn results in the observed fluorescence quenching in the inclusion complex.

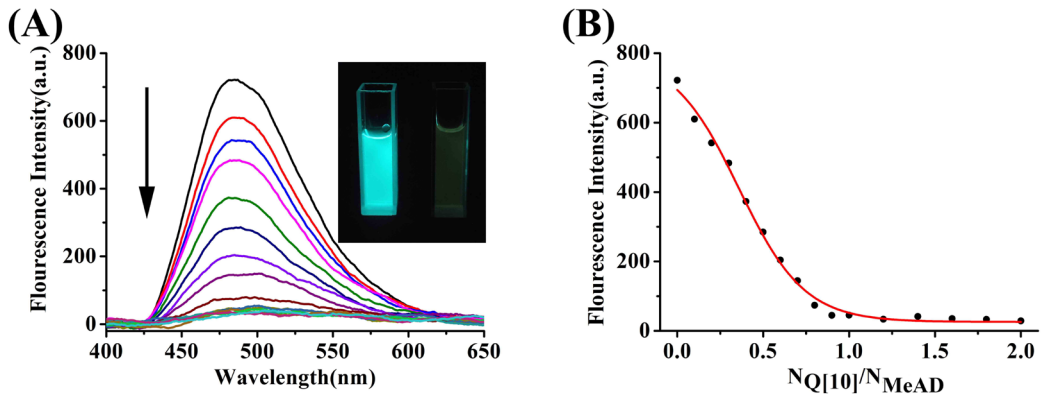


Figure 3. (Colour online) (A) Fluorescence absorption of **MeAD** (2×10^{-5} mol·L^{-1}) upon addition of increasing amounts (0, 0.1, 0.2……0.9, 1.0, 1.2, 1.4……1.8, and 2.0 equiv) of Q[10] in an aqueous HCl solution (pH=4.0); (B) concentration and fluorescence *vs*. $N_{Q[10]}/N_{\mathbf{MeAD}}$ plots in an aqueous HCl solution (pH=4.0).

The fluorescence regeneration of MeAD$_2$@Q[10] by DD

The strong fluorescence response discussed above allows for its implementation under analyte displacement conditions. Thus to ascertain whether the ternary inclusion complex **MeAD**$_2$@Q[10] has the potential to be utilized as a sensor for pesticides, a number of fluorescence detection experiments were performed. Sixteen common pesticides (Figure S2) were each employed. Notably, following addition of increasing amounts of **DD** to the aqueous solution of **MeAD**$_2$@Q[10], the fluorescence emission of **MeAD** recovered, whereas there was no pronounced fluorescence enhancement when any of the other 15 pesticides were employed. These results suggest that the ternary complex **MeAD**$_2$@Q[10] can be utilized as a fluorescent probe for the determination of the pesticide **DD** in aqueous solution.

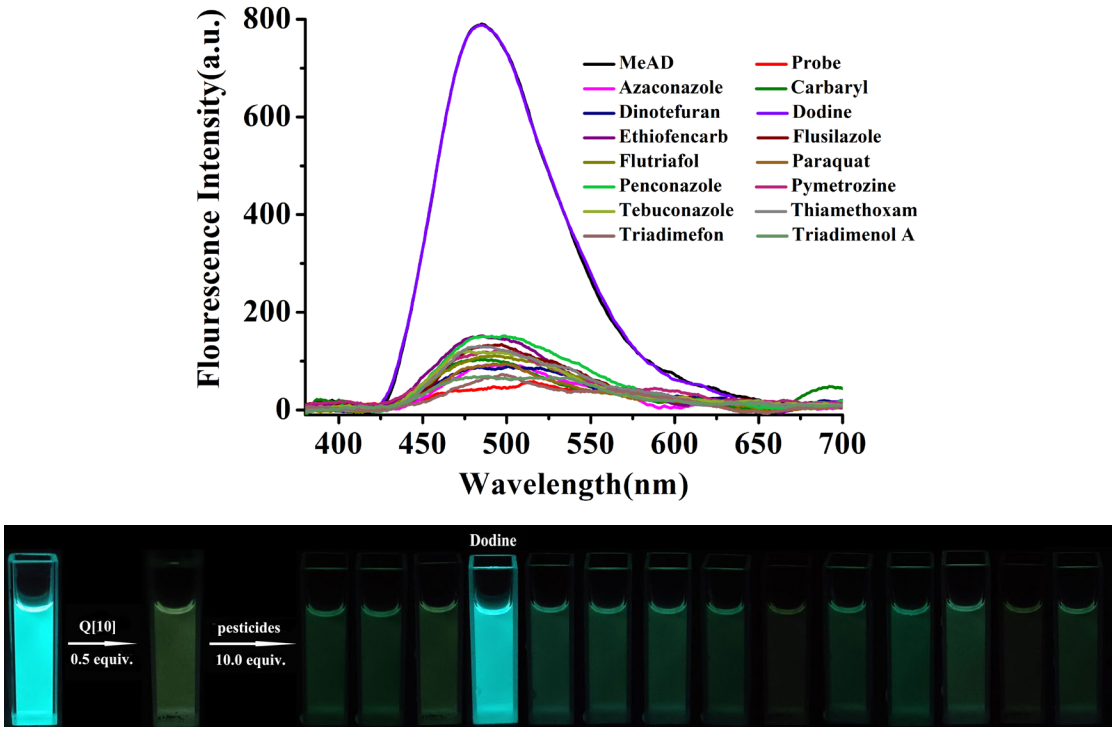


Figure 4. (top) The effect of 16 pesticides (10 equiv. of host-guest complex) on the relative fluorescence response (λmaxem=485 nm) of **MeAD**$_2$@Q[10] (2.0×10^{-5} mol·L^{-1}) (2:1); (bottom) Photographs of **MeAD**$_2$@Q[10] systems containing 10 equiv. of host-guest complex and different 16 pesticides under exposure to UV light (365 nm).

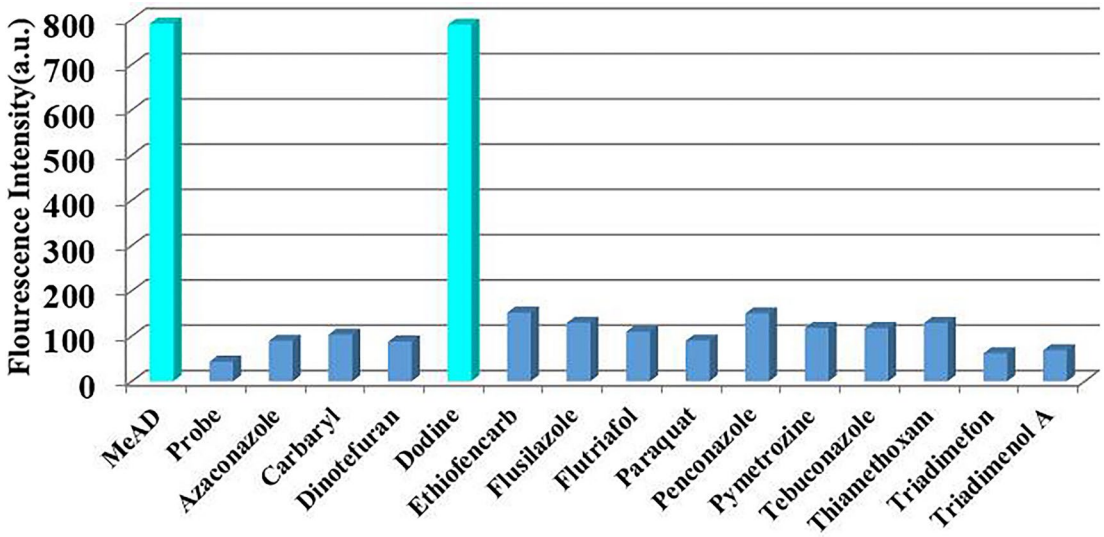


Figure 5. The effect of 16 pesticides (10 equiv. of host-guest complex) on the relative fluorescence intensity (λem=485 nm) of **MeAD**$_2$@Q[10] (2.0×10^{-5} mol·L^{-1}) (2:1).

The plot of fluorescence intensity *vs* the $N_{DD}/N_{MeAD2@Q[10]}$ ratio is shown in Figure 6A. It is clear that a gradual increase in the **DD** concentration affords a steep increase in the fluorescence and then a leveling off. Figure 6B reveals that the fluorescence enhancement (ΔI) increases linearly with **DD** concentration, and with the linear regression equation ΔI = 470.41C+17.658 (R = 0.9923, C denotes the **DD** concentration). The detection limit (DL) for **DD** was determined to be 1.405×10^{-7} mol·L^{-1}, and the way in which the fluorescence intensity varies suggests it is suitable for the quantification of **DD** and can be used for detection of residual **DD**.

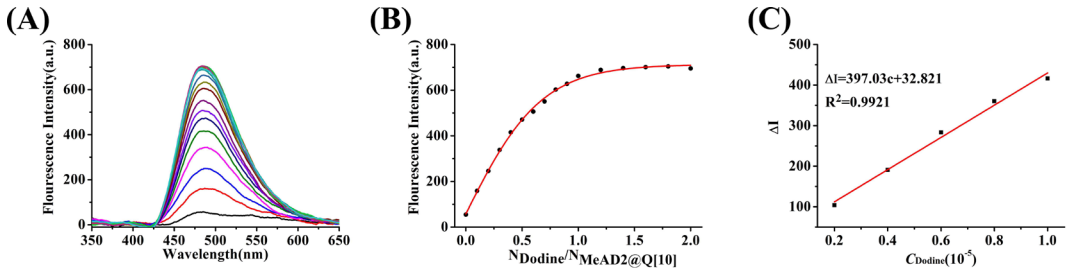


Figure 6. (A) Titration fluorescence spectra of **MeAD**$_2$@Q[10] (2.0×10^{-5} mol·L^{-1}) (2:1) with dodine; (B) Plots of $N_{Dodine}/N_{MeAD2@Q[10]}$; (C) Non-linear fitting curves for changes in the fluorescence intensity of the inclusion complex in the presence of different concentrations of dodine.

Investigating the response mechanism of the fluorescent probe

In order to better understand the response mechanism of this fluorescent probe, we conducted ^{1}H NMR titration experiments using **DD** and the homoternary complex **MeAD**$_2$@Q[10]. As shown in Figure 6, on addition of **DD** (for the 2D COSY spectrum of **DD** in Figure S5) to an aqueous solution of **MeAD**$_2$@Q[10], the proton signals associated with **DD** shift to higher field *versus* free **DD**. As this is happening, the **MeAD** proton signals of the inclusion complex shift to lower field. This can be rationalized by the displacement of two molecules of **MeAD** from the Q[10]

cavity by a molecule of **DD** *i.e.* two **MeAD** molecules were pushed out of the Q[10] cavity by a **DD** molecule. This results in the formation of a 1:1 binary inclusion complex with one **DD** molecule located inside the Q[10] cavity. The driving force for this displacement process is probably the higher binding affinity of **DD** toward Q[10] *versus* **MeAD**. The remaining 13 common pesticides were unable to displace the **MeAD** molecules from the cavity.

To summarize, encapsulation of **MeAD** into the large Q[10] cavity results in a homoternary inclusion complex **MeAD**$_2$@Q[10], and the resulting charge-transfer between the Q[10] and **MeAD** promotes fluorescence quenching. The release of the **MeAD** from the Q[10] cavity allows for fluorescence emission recovery, which overall can be viewed as a fluorescence "turn-on" process. The nature of the fluorescence response means that this probe is highly sensitive to the addition of competitive guests, and can therefore be used as a recognition tool for pesticide residues.

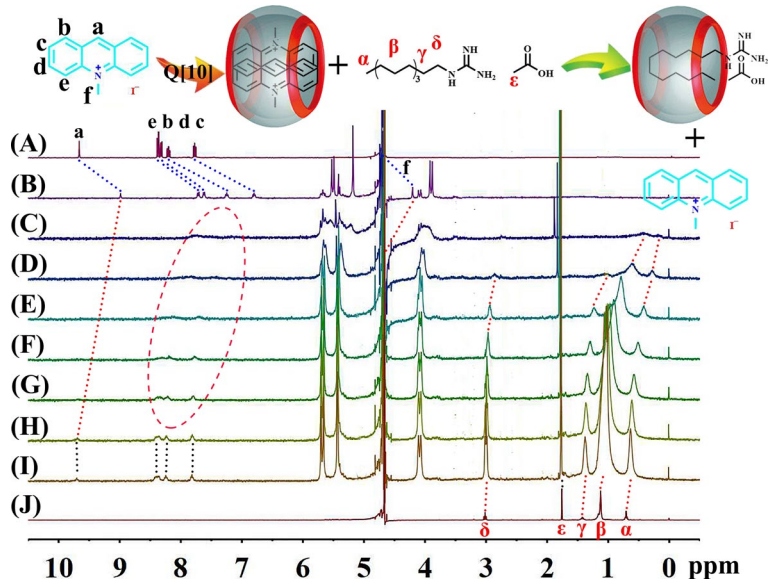


Figure 7. ^{1}H NMR titration spectra (D_2O, pD=4.0) of (A) neat **MeAD**, Q[10]@ **MeAD** (2:1, 5.0×10^{-4} mol·L^{-1}) in the presence of (B) 0.00, (C) 0.42, (D) 0.86, (E) 1.62, (F) 2.48, (G) 3.37, (H) 4.26 and (I) 5.42 equiv. of dodine, and (J) neat dodine.

Conclusions

Herein, we have investigated the binding properties of Q[10] toward the fluorescence dye **MeAD** in aqueous solution. The data presented reveals that **MeAD** can be encapsulated into the Q[10] cavity and form a homoternary inclusion complex, namely **MeAD**$_2$@Q[10]. The encapsulation of the **MeAD** into the Q[10] cavity quenches the fluorescence emission as the result of a charge-transfer process. However, following the addition of the dodine (**DD**), the **MeAD** molecules are displaced by **DD** from the Q[10] cavity, whereupon the fluorescence emission recovers. Interestingly, the addition of the other 15 pesticides screened herein fails to turn on the fluorescence in any effective way. Such observations suggest that this fluorescence probe system can be utilized to recognize the pesticide **DD** in variable concentrations. This simple strategy will help inform us to construct other fluorescent probe systems for the detection of other 'problematic' analytes.

Experimental Section

Instruments: The absorption spectra of the host−guest complexes were recorded on an Aglient 8453 spectrophotometer at ambient temperature. The fluorescence spectra were recorded on a Varian RF-540 fluorescence spectrophotometer. NMR spectroscopic data were recorded on a Bruker DPX 400 spectrometer in D_2O (pD = 4.0) at 293.15K.

Reagents and chemicals

The Q[10] was prepared in our laboratory according to the literature method [29]. All the pesticides used herein were commercially available and were used as received without further

purification. Stock standard solutions of **MeAD** and the screened pesticides (1.0×10^{-3} mol·L^{-1}) were prepared by dissolving them in doubly-distilled water. A stock solution of **MeAD** was prepared by adding doubly-distilled water to a final concentration of 1.0×10^{-3} mol·L^{-1}. The Q[10] stock solution of 1.0×10^{-4} mol·L^{-1} was prepared by dissolving Q[10] in doubly-distilled water. The stock standard solutions were stable for several weeks at ambient temperature. Standard working solutions were prepared by dilution of the stock standard solutions with doubly-distilled water prior to use. All chemicals were of analytical reagent grade, and doubly-distilled water was used throughout the procedures.

Acknowledgments

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