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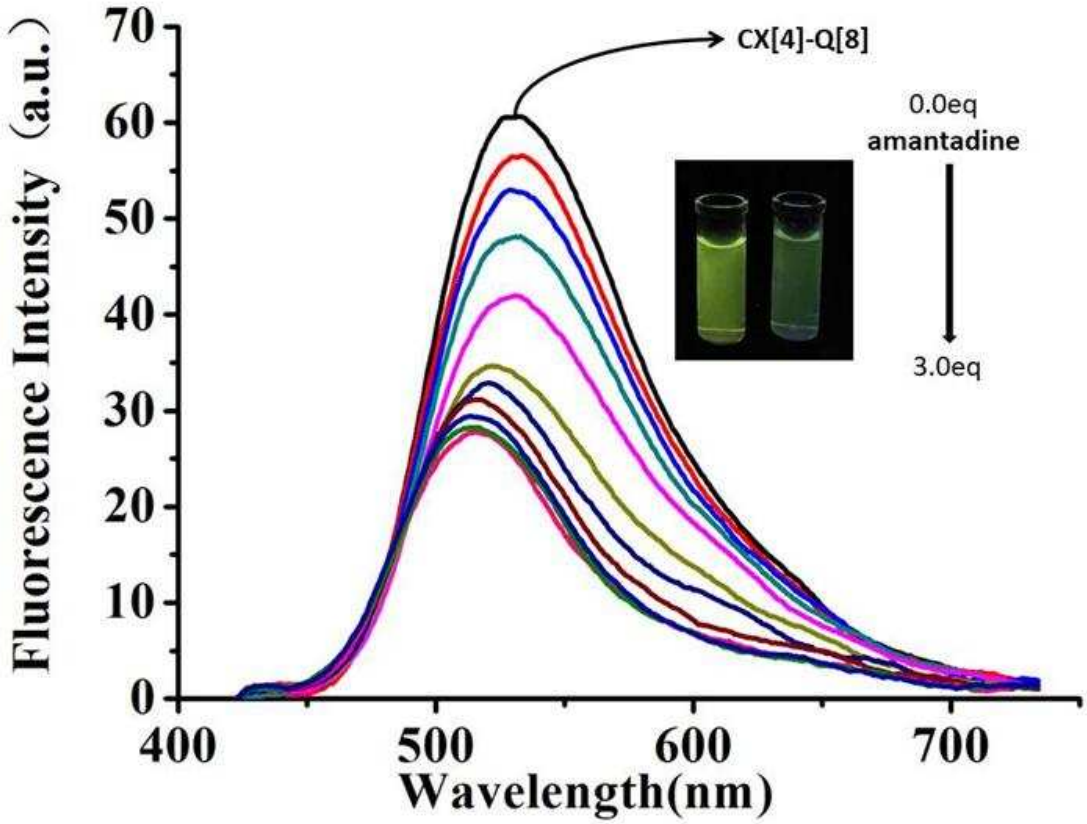
Fluorescence Intensity (a.u.)
70
60
50
40
30
20
10
0
400
500
600
700
Wavelength(nm)
CX[4]-Q[8]
0.0eq
amantadine
3.0eq

Synthesis of a functionalised calix[4]arene and its interactions with hemicucurbit[6,7]urils and cucurbit[8]uril

Jin Ming Zhu [a], Li Xia Chen [a], Kai Chen*[b], Xi Zeng*[a], Zhu Tao*[a]

[a] *Key Laboratory of Macrocyclic and Supramolecular Chemistry of Guizhou Province, Guizhou University, Guiyang 550025, China. Email:gzutao@263.net(Z. Tao); zengxi1962@163.com(X. Zeng)*

[b] *Collaborative Innovation Center of Atmospheric Environment and Equipment Technology, Jiangsu Key Laboratory of Atmospheric Environment Monitoring and Pollution Control, School of Environmental Science and Engineering, Nanjing University of Information Science & Technology, Nanjing 210044, China. Email:kaichen85@nuist.edu.cn or catqchen@163.com(K. Chen)*

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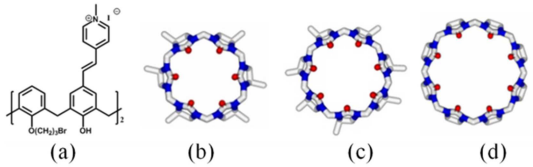
ABSTRACT

In the present work, we synthesised a functionalised calix[4]arene with 5,11-di(N-methyl-E-(4-pyridylethylene) moiety (CX[4]), and investigated interactions of it with HemiMeQ[6], HemiMeQ[7], and Q[8]) in both water and DMSO using fluorescence spectrophotometry and ^{1}H NMR spectroscopy. Titration ^{1}H NMR spectra revealed that Q[*n*]s prefers to include the N-methyl-E-(4-pyridylethylene) moiety. In particular, the interaction of CX[4] with Q[8] in water resulted in intense fluorescence emission, and this interaction system can respond to compounds such as amantadine.

1. Introduction

Supramolecular chemistry was largely established through novel works by Lehn, Cram, Pedersen, and their co-workers, who explored host-guest chemistry through noncovalent interactions of some typical hosts such as crown ethers, calixarenes, and cyclodextrins with various guests.[1-3] Cucurbit[*n*]urils (Q[*n*]s) obtained by condensing glycolurils and formaldehyde in concentrated HCl [4–8] are a type of relevant new host originally derived from Q[6] as described by Mock in 1981.[4,5] Q[*n*]s are characterised by a rigid hydrophobic cavity and two polar portals rimmed with carbonyl groups, and they serve as ideal building blocks for the construction of various supramolecular assemblies through host-guest interactions.[9–14] Research from ourselves and others revealed that the positive electro-potential outer surface of Q[*n*] can also give rise to a variety of Q[*n*]-based supramolecular assemblies.[15–21] Calix[*n*]arenes were obtained from reactions between phenols and aldehydes by Adolph von Baeyer in 1872,[22–24] and more derivatives were assigned by Zinke and Zieglerin 1944,[25,26] and were eventually termed calixarenes by Gutsche in 1978.[27] Calix[*n*]arenes are also characterised by a hydrophobic cavity constructed of phenyl rings bridged by methylene groups. Importantly, multiple reactive sites on the phenyl rings allow easily functionalisation of calix[*n*]arenes.[28–30] With the development of supramolecular chemistry, more and more supramolecular assemblies involved with multi-macrocyclic hosts or building blocks, which exhibited novel properties which are different from those of the original macrocyclic hosts, respectively.[31-38] For example, Liu and co-workers demonstrated the difference between rotaxane and pseudorotaxane with two hosts, α-CD, Q[7], and an axle guest bearing two terminal ferrocene groups.[31] Using a naphthol-modified β-cyclodextrin, they successfully constructed a novel supramolecular ternary polymer mediated by Q[8] based on the charge-transfer interaction.[33] Kögerler and co-workers first demonstrated some Q[n]/POM-based hybrid compounds, which have characteristic large channels constructed from Q[*n*] molecules and POM anions, through the outer surface interaction of cucurbit[*n*]urils.[37] Lin and co-workers first demonstrated two supramolecular architectures assembled from the supermolecular building blocks of calixarenes and cucurbiturils, which exhibited the outer surface interaction of cucurbit[*n*]urils in directing the supramolecular assemblies.[38] Thus, supramolecular interactions between cucurbit[*n*]urils and other macrocyclic host, such calix[*n*]arenas occur not only through outer surface interactions of cucurbit[*n*]urils,[21] but also through host-guest interactions between cucurbit[*n*]urils and functionalised species.

In the present work, we synthesised a functionalised calix[4]arene with 5,11-di(N-methyl-E-(4-pyridylethylene)) moieties, which could serve as guests able to interact with different Q[*n*]s (hereafter referred to as CX[4]; Fig. 1a). This functionalised calix[4]arene is almost insoluble in aqueous solution but dissolves readily in DMSO. In order to investigate the interactions of this CX[4] with cucurbit[*n*]urils, we selected two hemimethyl-substituted cucurbit[*n*]urils (HemiMeQ[*n*]s),[39] HemiMeQ[6] and HemiMeQ[7], that dissolve in both aqueous solution and DMSO, and a larger normal regular cucurbit[*n*]uril, Q[8] (Fig. 1b–d). Interactions of this CX[4] with the three selected Q[*n*]s revealed that the N-methyl-E-(4-pyridylethylene)



(a) (b) (c) (d)

Fig. 1. Structures of (a) the functionalised calix[4]arene; (b) HemiMeQ[6]; (c) HemiMeQ[7]; (d) Q[8].

moiety of CX[4] can be included in the cavity of HemiMeQ[*n*]s. Although we did not directly observe the interaction of CX[4] with Q[8] due to the poor solubility of both components in aqueous solution, the intense fluorescence emission indicated strong interaction, and more importantly, the CX[4]-Q[8] interaction system could respond to organic compounds such as amantadines.

2. Results and Discussion

2.1. Design and synthesis of the functionalised calix[4]arene (CX[4])

Previous work showed that 4-sulfocalix[4]arene or 4-sulfocalix[6]arene (SC[*n*]As) can interact with Q[6] and form SC[*n*]As/Q[6]-based supramolecular assemblies.[38] Similarly, we recently demonstrated a supramolecular assembly constructed of 4-sulfocalix[4]arene and Q[7].[40] The driving force for the formation of these supramolecular assemblies is attributed to the outer surface interactions of cucurbit[*n*]urils via the positive electro-potential outer surface of cucurbit[*n*]urils.[21] Interestingly, multiple reactive sites on the phenyl rings on C[*n*]As can be used to introduce a variety of typical guest moieties, resulting in host-guest interactions of Q[*n*]s with functionalised calix[*n*]arenes. Thus, after a series of reactions, we eventually obtained a new pyridyl-modified calix[4]arene, namely 5,11-di(N-methyl-(4-pyridylethylene))-25,27-bis(3-bromopropoxy)-26,28-dihydroxy-calix[4]arene (CX[4]). Details of its synthesis are included in Supplementary Fig. S1-.S5. Analysis by ESI-MS supported the structure of CX[4], with molecular ions such as m/z = 1157.57 [CX[4] + H^+], consistent with the parent CX[4] coordinating to H^+ ions (Supplementary Fig. S6). Although pyridyl moieties were introduced into calix[4]arene, the water solubility of the modified calix[4]arene was not obviously improved. Therefore, we utilised the polar solvent DMSO in which the modified calix[4]arene, HemiMeQ[6], and HemiMeQ[7] could be dissolved.

2.2. Interaction of CX[4] with selected Q[n]s

Given the solubility of CX[4], which is easily dissolved in DMSO but almost insoluble in water, interactions of CX[4] with Q[*n*]s were mainly explored in DMSO, and interactions of CX[4] with Q[8] were investigated in water, because Q[8] is insoluble in DMSO.

2.2.1. Interaction of CX[4] with HemiMeQ[6] and HemiMeQ[7] in DMSO

In general, the pyridyl moiety and its derivatives can be encapsulated inside the cavity of Q[*n*]s (n >6) and can therefore reveal interactions between HemiMeQ[*n*]s and CX[4]. It is clearly evident from Fig. 2 that only one set of proton signals for CX[4] was observed with increasing number of equivalents of CX[4] (Fig. 2a–e), suggesting that these are averaged signals of free and bound CX[4] molecules due to a rapid exchange rate between binding and release of CX[4] on the NMR timescale. The resonances of pyridyl and methyl moieties on CX[4] lie in different magnetic environments, the pyridyl proton resonances (Hm) are shifted downfield, while the methyl proton resonances (Hn) are shifted upfield. This indicates that only the methyl group of CX[4] is contained within the cavity of HemiMeQ[6], while the other part of CX[4] remains outside the cavity.

A similar situation was observed in the interaction of HemiMeQ[7] and CX[4] (Fig. 3), again indicating a rapid exchange rate between binding and release of CX[4] on the NMR timescale. The entire N-methyl-(4-pyridylethylene)

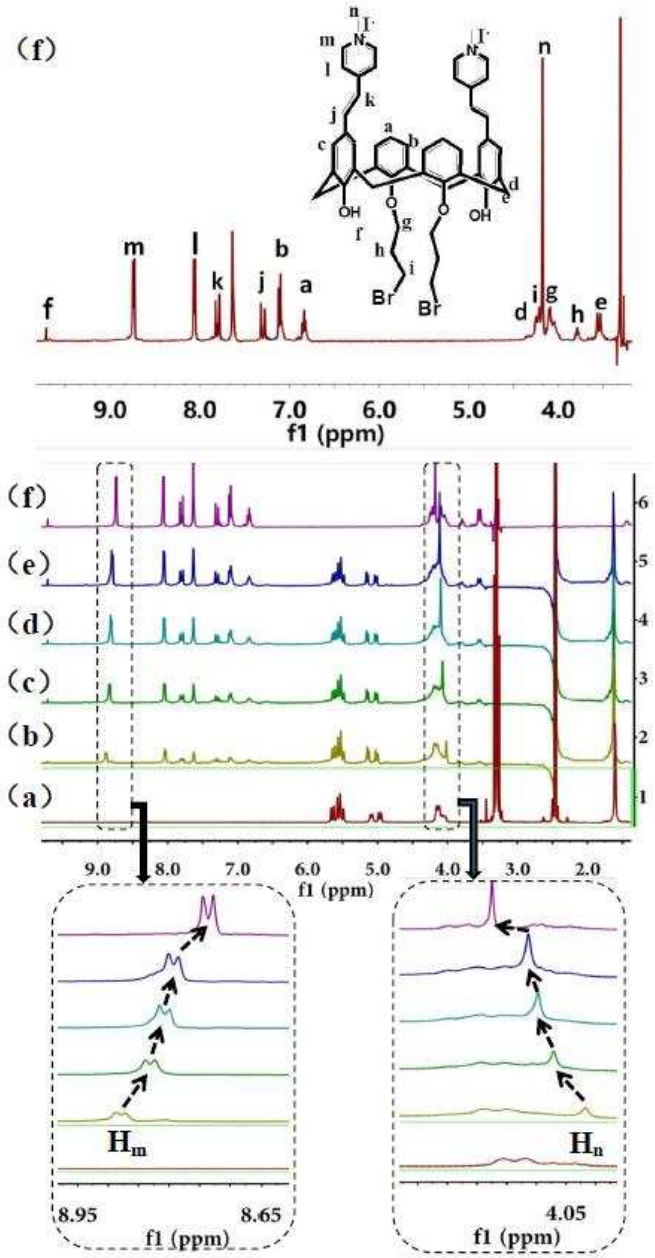


Fig. 2. Titration ^{1}H NMR spectra (500 MHz, $DMSO_{d6}$) of HemiMeQ[6] in the presence of 0 (a), 0.25 (b), 0.50 (c), 0.75 (d), and 1.00 (e) equivalents of CX[4], and (f) ^{1}H NMR spectrum of neat CX[4] at 25°C.

moiety of CX[4] appeared to experience an upfield shift, suggesting that HemiMeQ[7] can include the whole N-methyl-(4-pyridylethylene) moiety due to its larger cavity than that of HemiMeQ[6].

Furthermore, CX[4] exhibited fluorescence at 513 nm, whereas its interaction with HemiMeQ[6] and HemiMeQ[7] yielded almost the same fluorescence spectra, with only a slight decrease in emission intensity (Supplementary Fig. S7). From the change in fluorescence intensity, we inferred that the inclusion complex was mainly formed with 1:1 stoichiometry. The binding constants (K) of CX[4] with HemiMeQ[6] and HemiMeQ[7] were estimated as to be 2.85×10^6 and 7.60×10^6 $L\cdot mol^{-1}$, respectively.[41]

2.2.2. Interaction of CX[4] with HemiMeQ[6], HemiMeQ[7] and Q[8] in water

Although interaction of CX[4] with the three selected Q[*n*]s, namely HemiMeQ[6], HemiMeQ[7], and Q[8], were not

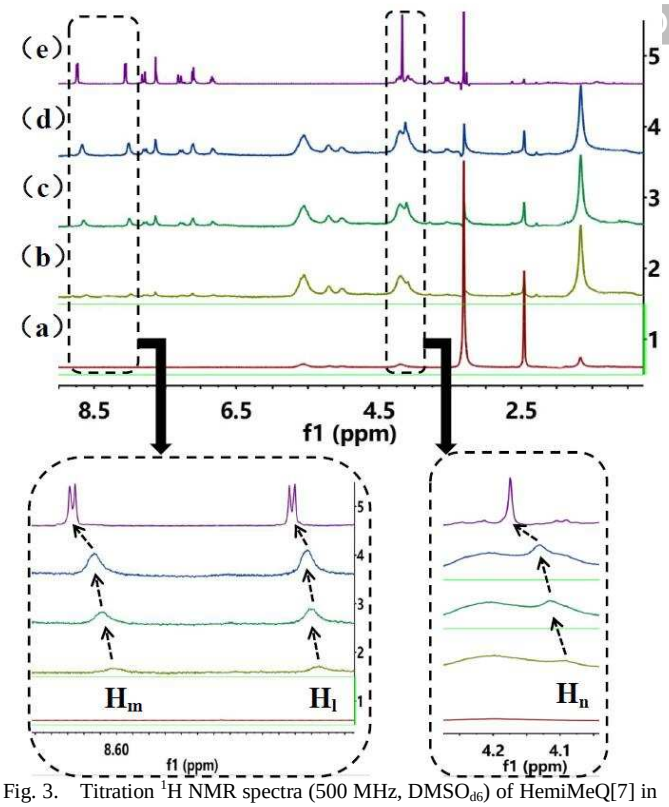


Fig. 3. Titration ^{1}H NMR spectra (500 MHz, $DMSO_{d6}$) of HemiMeQ[7] in the presence of 0 (a), 0.30 (b), 0.70 (c), and 1.00 (d) equivalents of CX[4], and (e) ^{1}H NMR spectrum of neat CX[4] at 25°C.

directly observed by ^{1}H NMR spectra due to poor solubility of related species in neutral water, their fluorescence spectra provide useful interaction information. In particular, interaction between CX[4] with Q[8] was apparent (Fig. 4) because the fluorescence intensity increased upon the addition of Q[8], and the emission wavelength hypsochromically shifted from 503 to 530 nm. An approximately 3-fold enhancement in fluorescence was observed upon the addition of 1 equivalent of Q[8], accompanied by a colour change from cyan to yellow (Supplementary Fig. S8). From the change in fluorescence intensity, we inferred that the interaction product was mainly formed with 1:1 stoichiometry (inset in Fig. 4). The interaction constant (K) for the CX[4]-Q[8] complex was estimated to be 1.22×10^7 mol/L according to the literature.[41]

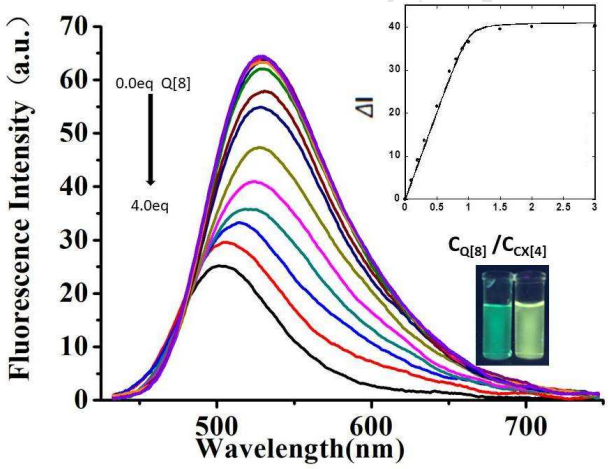


Fig. 4. Fluorescence spectra (λ_{ex} = 503 nm) of CX[4] (1×10^{-5}M) in the presence of 0 (a), 0.10 (b), 0.20 (c), 0.30 (d), 0.40 (e), 0.50 (f), 0.60 (g), 0.70 (h), 0.80 (i), 0.90 (j), 1.00 (k), 1.50 (l), 2.00 (m), 3.00 (n) and 4.00 (0) equivalents of Q[8].

However, interaction of CX[4] with HemiMeQ[6] and HemiMeQ[7] yielded a slight decrease in fluorescence intensity, with a small blue shift for both systems (Supplementary Fig. S9). From the change in fluorescence intensity, we also inferred that the inclusion complex was mainly formed with 1:1 stoichiometry. The binding constants (K) of CX[4] with HemiMeQ[6] and HemiMeQ[7] were estimated to be 4.81×10^7 and 7.60×10^6 L·mol^{-1}, respectively.[41]

2.3. Responses of the CX[4]-Q[8] system to certain organic compounds

Kim and co-workers first confirmed that the cavity of Q[8] is large enough to include two guest molecules simultaneously.[42,43] Based on the interaction of CX[4] with HemiMeQ[6] and HemiMeQ[7], the 4-pyridylethylene moiety on the CX[4] molecule is likely included in the cavity of the selected Q[n]s. Moreover, CX[4] forms a 1:1 stoichiometry host-guest interaction system with Q[8], and the fluorescence intensity of CX[4] was dramatically enhanced upon complex formation, suggesting that the two 4-pyridylethylene moieties of CX[4] could be simultaneously included in the Q[8] cavity. This inspired us to investigate the response of the CX[4]-Q[8] interaction system to certain molecules by observing a change in fluorescence intensity. Phenanthrene (G1) and molecules with a similar structure such as 1,10-phenanthroline (G2) enhanced fluorescence emission upon interaction with the CX[4]-Q[8] system. In contrast, amantadine (G3) and its derivatives (G4), and 4,7-dimethyl-1,10-phenanthroline (G5) quenched fluorescence emission upon interaction with the CX[4]-Q[8] system. For example, upon the addition of G1 to the CX[4]-Q[8] system, a further dramatic enhancement in fluorescence emission occurred, accompanied by a blue shift from 530 nm to 514 nm (Fig. 5), and similar results were obtained with G2 (Supplementary Fig. S10). Thus, fluorescence of the CX[4]-Q[8] (1:1) solution was stimulated by G1, and strong green fluorescence was observed by the naked eye under 365 nm UV irradiation (Fig. 5 inset). Further experiments revealed that G1 exhibited fluorescence quenching when it interacted with Q[8], indicating the formation of a novel π-π stacking of the 4-pyridylethylene moiety and G1 in the Q[8] cavity with 1:1:1 (Q[8]-CX[4]-G1) stoichiometry. Thus, the CX[4]-Q[8] interaction system could be used as a fluorescence probe to detect phenanthrene or compounds with similar structures.

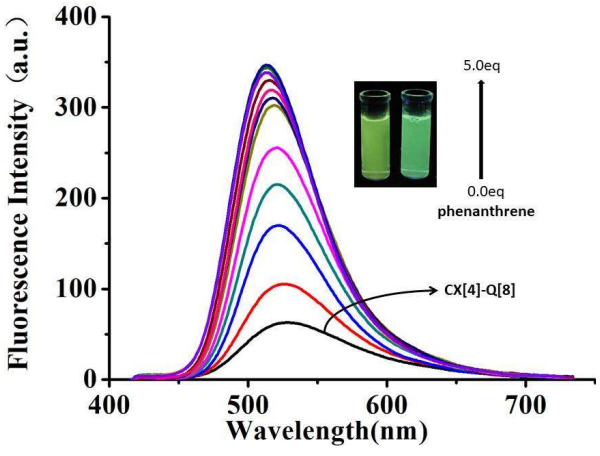


Fig. 5. Fluorescence spectra of the CX[4]-Q[8] complex upon the addition of different equivalents of phenanthrene, accompanied by a colour change from yellow to green (from 530 nm to 514 nm) in water.

In contrast, addition of G3 to the CX[4]-Q[8] system quenched the fluorescence emission and resulted in a blue shift

from 530 nm to 515 nm (Fig. 6). Thus, the fluorescence of the CX[4]-Q[8] (1:1) solution was diminished by G3, and weak fluorescence could be observed by the naked eye under 365 nm UV irradiation (Fig. 6 inset). Further experiments revealed that derivatives of G4 and G5 exhibited similar quenching behaviour (Supplementary Fig. S11 -12). We attribute the red shift in the emission spectra to the formation of a new G3-Q[8] host-guest inclusion complex that results in fluorescence quenching, and CX[4]-Q[8] interaction systems could serve as useful fluorescence probes for detecting related compounds.

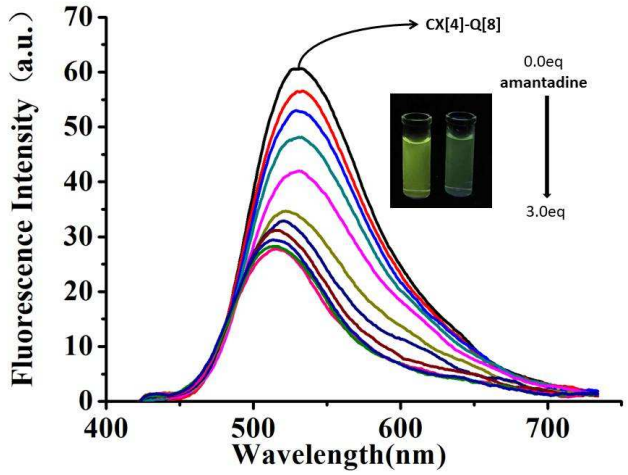


Fig. 6. Fluorescence spectra of the CX[4]-Q[8] system upon addition of different equivalents of amantadine, accompanied by a colour change from yellow to green (from 530 nm to 515 nm) in water.

3. Conclusions

In summary, we have designed and synthesized a functionalised calix[4]arene, namely 5,11-Di(N-methyl-(4-pyridylethylene))-25,27-Bis(3-bromopropoxy)-26,28-dihydroxy calix[4]arene (CX[4]), in which the N-methyl-(4-pyridylethylene) moieties can serve as a guest and interact with cucurbit[*n*]urils. Given the solubility of CX[4], two DMSO-soluble guests, HemiMeQ[6] and HemiMeQ[7], and unsubstituted Q[8] were selected to investigate the interactions of these two types of macrocyclic compounds. The results showed that the N-methyl-(4-pyridylethylene) moieties on CX[4] can be included in the cavity of the selected cucurbit[*n*]urils. In particular, the interaction of CX[4] and Q[8] with 1:1 stoichiometry induced an enhancement in fluorescence emission from cyan to light yellow. Moreover, the CX[4]-Q[8] interaction system could respond to certain compounds by fluorescence enhancement for phenanthrene (G1) and molecules with similar structures such as 1,10-phenanthroline (G2), or fluorescence quenching for amantadine (G3), its derivatives (G4), and 4,7-dimethyl-1,10-phenanthroline (G5), thereby serving as probes for detecting these compounds.

4. Experimental Section

4.1. Materials and methods

All chemicals and solvents were used as supplied without further purification. HemiMeQ[6] and HemiMeQ[7] were synthesised according to our previous work,[39] and Q[8] was prepared according to the literature.[6,7] ^{1}H NMR spectra were recorded at 20°C on a Varian INOVA-400 spectrometer.

4.2. Synthesis and characteristics

4.2.1. 25,26,27,28-tetrahydroxycalix[4]arene

A suspension of p-tert-butyl C[4]A (6.48 g, 10 mmol), phenol (4.32 g, 46 mmol), and $AlCl_3$ (8.0 g, 66 mmol) in anhydrous toluene (60 mL) was stirred at room temperature for 2 h. After cooling, the reaction mixture was added to 100 mL of hydrochloric acid solution (0.2 mol/L), the toluene layer was separated, and solvent was evaporated in vacuo. The yellowish product was suspended in MeOH (100 mL) and refluxed for 30 min. After cooling, the resulting precipitates were filtered to afford product as a white powder: yield 2.64 g (76.6%). ^{1}H NMR ($CDCl_3$) δ 9.45 (4H, s, ± OH), 7.61 (8H, d, J = 7.8, aromatic-H), 6.75 (4H, t, aromatic-H), 4.27(s, 4H, Ar-CH_2-Ar), 3.56(s, 4H, Ar-CH_2-Ar), *m*/*z* 425.2 ($M + H^+$).

4.2.2. 25,27-Bis(3-bromopropoxy)-26,28-dihydroxy calix[4]arene

To a suspension of 25,26,27,28-tetrahydroxycalix[4]arene (2.12 g, 5.00 mmol) in MeCN (250 mL) were added 1,3-dibromopropane (20.2 g, 100 mmol) and K_2CO_3 (3.45 g, 25.0 mmol). The reaction mixture was refluxed for 48 h. The solvent and unreacted dibromopropane were then removed *in vacuo*, and the residue was quenched with 5% HCl (100 mL) and $CHCl_3$ (200 mL). The organic phase was separated, washed with water, and dried. The solvent was then distilled off, and the oily residue was subjected to column chromatography (CH_2Cl_2-petroleum ether (60-90 °C) 2:3) to give a white, pure aim compound (2.30 g, 69%): mp 288–290 °C; ^{1}H NMR ($CDCl_3$) δ 7.70 (s, 2H, OH), 7.15, 6.88 (s, 4H each, ArH), 4.27 (d, *J* = 13.0 Hz, 4H, $ArCH_2Ar$), 4.12 (t, *J* = 7.8 Hz, 4H, $OCH_2CH_2CH_2$), 4.01 (t, *J* = 8.0 Hz, 4H, $BrCH_2CH_2CH_2$), 3.35 (d, *J* = 13.0 Hz, 4H, $ArCH_2Ar$), 2.53 (m, 4H, $BrCH_2CH_2$-CH_2), 1.27 (s, 18H, CH_3), 1.02 (s, 18H, CH_3); ^{13}C NMR ($CDCl_3$) δ 150.7, 149.3, 147.4, 141.8, 132.8, 127.7, 125.5 (d), 77.1 (t),73.5, 34.0 (d), 33.6, 31.0, 31.8, 31.1, 30.3; MS, *m*/*z* 667.2 ($M + H^+$).

4.2.3. 5,11-Diformyl-25,27-Bis(3-bromopropoxy)-26,28-dihydroxycalix[4]arene

25,27-Bis(3-bromopropoxy)-26,28-dihydroxycalix[4]arene (3.33 g, 5.0 mmol)) was dissolved in 100 mL of dry chloroform and the solution was kept under N_2 and cooled to 0°C in an ice bath. After 15 min, Cl_2CHOCH_3 (11.38 g, 0.1 mol) and $TiCl_4$ (18.68 g, 0.1 mol) were added to the vigorously stirred solution. After 1.5h, the reaction mixture was poured into 300 mL of 1 M HCl and the solution was stirred for 2h. After the addition of 150 mL of CH_2Cl_2 to the solution, the organic phase was separated and washed twice with water, dried over Na_2SO_4, and filtered. The solvent was evaporated under reduced pressure and the mixture three compounds was obtained after purification by column chromatography (eluent: hex/EtOAc= 7:3) to give a pale yellow solid, 2.07 g, yield 57 %: δ: mp 306–309°C; ^{1}H NMR (CDCl3) δ 9.789 (s, 2H，CHO), 8.892 (s, 2H, OH), 7.637(s, 4H, ArH), 6.98 (d, J = 7.6 Hz, 4H，ArH), 6.82 (t, 2H, ArH), 4.28 (d, J = 13.2 Hz, 4H,$ArCH_2Ar$), 4.18 (t, 4H, $OCH_2CH_2CH_2Br$), 3.978 (t, 4H, $OCH_2CH_2CH_2Br$), 3.543 (d, J = 13.2 Hz, 4H, $ArCH_2Ar$), 2.56 (m, 4H, $OCH_2CH_2CH_2Br$); ^{13}CNMR ($CDCl_3$) δ 190.9, 159.2, 151.1, 132.3, 131.1, 129.7, 128.9, 128.5, 126.2, 74.0, 33.3, 31.3, 29.8; MS (FAB), *m*/*z* 745.2 ($M + Na^+$).

4.2.4. 5,11-Di(N-methyl-(4-pyridylethylene))-25,27-Bis(3-bromopropoxy)-26,28-dihydroxycalix[4]arene

5,11-Diformyl-25,27-Bis(3-bromopropoxy)-26,28-dihydroxy calix[4]arene (0.89 g, 6 mmol), N-methyl-4-methylpyridine (500 mg, 2.12 mmol), and piperidine (0.6 mL) were mixed and stirred in ethanol (20 mL) at 80°C for 8h. During the heating process, the solution changed from pale yellow to dark purple. After completion of the reaction, the mixtures were cooled to 0°C. The formed precipitate was filtered and washed with

ethanol several times to afford a purple fluffy powder of 5,11-Di(N-methyl-(4-pyridylethylene))-25,27-Bis(3-bromoprop oxy)-26,28 -dihydroxy calix[4]arene (0.368 g, 51.6 % yield). *δ*: mp 239–242 °C; ^{1}H NMR ($CDCl_3$) *δ* 9.713 (s, 2H, OH), 8.74 (d, J=10.8 Hz, 4H, C_5H_4N), 8.06 (d, J = 10.8 Hz, 4H, C_5H_4N), 7.80 (d, J = 16 Hz, 2H, CH=CH), 7.63 (s, 4H, ArH), 7.29 (d, J = 16 Hz, 2H, CH=CH), 7.11 (d, J = 8 Hz, 4H, ArH), 6.84 (t, 2H, ArH), 4.175 (s, 3H, N-CH_3), 4.270–4.028 (m, 19H, $ArCH_2Ar$, $OCH_2CH_2CH_2Br$, N-CH_3), 3.547 (d, J = 13.2 Hz, 4H, $ArCH_2Ar$); ^{13}C NMR ($CDCl_3$) *δ* 150.7, 149.3, 147.4, 141.8, 132.8, 127.7, 125.5 (d), 77.1 (t),73.5, 34.0 (d), 33.6, 31.0, 31.8, 31.1, 30.3; MS (FAB), *m*/*z* 1157.57 ($M + H^+$).

Acknowledgments

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