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PAPER

Cucurbit[8]uril-stabilized charge transfer complexes with diquat driven by pH: a SERS study†

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In this work, we have studied the pH-dependence of the formation of DQCB[8] complexes by surface-enhanced Raman scattering (SERS) spectroscopy. The SERS spectra suggest that at acidic pH CB[8] can form a binary complex with the dication DQ^{+2} while at higher pH ternary complexes with the radical cation dimer $(DQ^{+\bullet})_2$ and the radical cation–dication dimer $(DQ^{+\bullet}DQ^{+2})$ are formed. The pH-enhanced diquat (DQ) dimerization inside the cucurbit[8]uril cavity has not been reported until now. In addition, this study provides very valuable information regarding the use of CB[8] functionalized silver nanoparticles as SERS substrate for sensing applications.

1. Introduction

Cucurbit[*n*]uril (CB[*n*], *n* = 5–8,10) hosts are macrocycles characterized by a hydrophobic cavity surrounded by two polar carbonyl portals.¹ Due to their unusual binding properties they play a prominent role in the design of new supramolecular architectures oriented to the development of molecular devices. The strategy commonly consists of building pseudorotaxanes to design molecular necklaces, switches, shuttles and other molecular machines, also incorporating guest molecules.² In recent years, CBs and their complexes have been widely investigated because of their wide range of applications,³ from chemical sensing and catalysis⁴ to drug delivery.⁵ In all cases, it is of vital importance to control the recognition process through an external stimulus, either chemical (pH, reductants), photochemical or electrochemical.

Diquat (DQ) is a bipyridinium dicationic herbicide belonging to the viologens family (Fig. 1), which can be rapidly and reversibly reduced to the radical cation ($DQ^{+\bullet}$) and subsequently to the neutral molecule (DQ^0) in aqueous solution.⁶ Since this molecule is a good electron acceptor, it is often linked to supramolecular systems conferring them the ability to form highly stable charge-transfer (CT) complexes with a variety of π -electron donors. In particular, the viologen inclusion complexes with CBs have attracted much attention since they can be potentially used as molecular switches.² In comparison with its lower size homologues, CB[8] (Fig. 1) has the additional property of binding two aromatic molecules due to its voluminous cavity,

which makes possible the formation of homo- (2 : 1) and hetero- (1 : 1 : 1) ternary complexes stabilized by charge-transfer (CT) interactions.^{1,2} The host–guest complex formation between DQ and CB[8] at neutral pH was investigated through spectroscopic techniques (¹H NMR, UV-vis, and fluorescence), X-ray and cyclic voltammetry.⁷ Their results indicated that when DQ is present as a dication a 1 : 1 inclusion complex of $DQ^{+2}\cdot CB[8]$ is formed. However, when the electrochemically obtained radical cation arises, a binary complex of $DQ^{+\bullet}\cdot CB[8]$ is selectively formed in preference to the former due to the higher binding affinity shown by the latter.

Although it was earlier observed that some viologen UV-visible spectra are pH-dependent,⁸ little attention has been paid to the pH response of neither DQ nor its supramolecular complexes with CB[8]. In this work, we have studied the formation of DQCB[8] complexes under the influence of a chemical stimulus such as pH, through SERS spectroscopy. SERS spectroscopy has proved to be a powerful tool to provide useful information regarding not only the adsorption mechanism on the metal surface but also the host–guest binding mode.⁹ This is because changes in the vibrational spectra are correlated with the structural changes occurring in the studied molecules as a consequence of the complex formation and their interaction with the surface. Taking advantage of our previous experience on SERS studies on DQ¹⁰ we have investigated the effect of the solid–liquid interface nearby the silver colloidal metal nanoparticles (NPs) on the DQCB[8] complex formation. A laser excitation wavelength of 532 nm and Ag colloid were employed.

In order to provide more detailed information about the complex, we have first studied the CB[8] adsorption on Ag NPs as a function of pH, which is of great importance considering their application as a metal surface functionalizing agent in chemosensing. Only one report dealing with SERS of CB[*n*]

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Fig. 1 Chemical structures of the diquat (DQ) guest and cucurbit[8]uril (CB[8]) host macrocycle.

(on a commercial solid SERS substrate) has been reported until now.¹¹ Afterwards, we investigated the influence of pH on DQ adsorption, as the herbicide itself shows a relatively high affinity toward the metal surface. Finally, we have focused on DQCB[8] complex formation and its adsorption on Ag as a function of pH. Additionally, we have followed the complexes formation in aqueous solution by UV-visible spectroscopy.

2. Experimental section

2.1 Materials

Diquat dibromide and hydroxylamine hydrochloride (employed for silver colloid fabrication) were purchased from Aldrich with analytical purity. Cucurbit[8]uril (CB[8]) was also supplied by Aldrich with *ca.* 20% of water content and acids of crystallization, which was taken into account when preparing the stock solutions. Silver nitrate and potassium nitrate were supplied by Merck with analytical purity. All the aqueous solutions were prepared using Milli-Q water. CB[8] stock solutions were prepared at a 10^{-4} M concentration gently heating at 30 °C under agitation. Stock solutions of DQ were prepared with a final concentration of 10^{-2} M. These solutions were then diluted to obtain the desired concentrations.

2.2 Raman, SERS and UV-visible measurements

SERS spectra were recorded using a Confocal Raman Microscope Renishaw Invia equipped with a Leica microscope and an electrically refrigerated CCD camera. The laser excitation line used was 532 nm (Nd:YAG laser) and the power in the sample was 0.5 mW. The spectra were obtained as an average of 3 scans of 10 s each with a spectral resolution of 2 cm^{-1} and geometry of 180° . CB[8] and DQ Raman spectra in the solid state were recorded on a microconfiguration with 10 scans of 10 s each with the same resolution. The absorption spectra of aqueous solutions of DQ and DQCB[8] complex were recorded on a UV-vis-NIR Shimadzu 3600 spectrophotometer. Aqueous solutions were placed on a $1 \times 1\text{ cm}$ path length quartz cuvette and Milli-Q water was employed for calibration.

2.3 Sample preparation

Silver NPs were prepared by reduction of silver nitrate with hydroxylamine hydrochloride at room temperature.¹² For SERS measurements, the silver colloids were first activated with an aliquot of potassium nitrate solution 0.5 M up to a final concentration of 2×10^{-2} M. Then, 10 μL of CB[8] and

10 μL of DQ at the suitable concentration were added to 1 mL of the nitrate-aggregated colloid to obtain the SERS spectra of the host-guest complex. For measurements at different pH values, NaOH 0.5 M or HNO_3 0.5 M were used for adjusting pH before the aggregating procedure.

UV-visible characterization (Fig. S1 of ESI†) of the surface plasmon resonance (SPR) of Ag-colloid at the three pH values 2, 7 and 11 shows a λ_{SPR} around 405–407 nm, according to our previous studies.¹³ The λ_{SPR} of the Ag NPs functionalized by CB[8] shows a second broad band at 602 nm for pH = 2, 612 nm for pH = 7 and 650 nm for pH = 11 in the absorption spectra due to the formation of NPs aggregates, as was expected. This band could be originated by the presence of longitudinal aggregates and shifts about 50 nm to red when pH decreases proving that different aggregation mechanisms are involved. The guest addition also produces a plasmon resonance red shift with respect to the functionalized CB[8]/Ag NPs. TEM micrographs of silver NPs together with silver NPs covered by CB[8] and DQCB[8] are also included in ESI.†

2.4 Theoretical vibrational frequencies

DFT calculations were performed using Gaussian 03¹⁴ package at the B3LYP/6-31G* level of theory for CB[8]. The molecular structure was modelled with D_{8h} symmetry and the optimized parameters were subsequently used to calculate the harmonic force field. Observed bands on the Raman and SERS spectra of CB[8] along with their assignment are given in Table 1. Additionally, SERS bands for DQ and DQCB[8] complexes are listed in Table S1 of ESI† and Table 2, respectively.

3. Results and discussion

3.1 Raman and SERS spectra of CB[8]

The poor solubility of CB[8]¹⁵ in water prevents its study in aqueous solution by Raman spectroscopy, which sensitivity does not allow us to detect trace amounts. Therefore, the Raman spectrum of an aqueous solution of CB[8] in the solubility limit (10^{-4} M) gives no signal at all, as can be seen in Fig. 2. The Raman spectrum of the solid CB[8] along with its SERS spectra at pH = 2, 7 and 11 are also included in Fig. 2. Four bands of the spectra of the solid at 1758 cm^{-1} , 1380 cm^{-1} , 1228 cm^{-1} and 656 cm^{-1} show a strong intensity decrease in the SERS spectra. This fact indicates that, according to the surface selection rules,^{16,17} CB[8] is adsorbed onto the metal surface by its C=O portals with a perpendicular orientation since

Table 1 Experimental and calculated Raman and SERS ($\lambda_{\text{exc}} = 532 \text{ nm}$) bands (cm^{-1}) for the CB[8] host and their assignment

Experimental ^a				Calculated	
Raman solid	SERS			B3LYP/6-31G*	Assignment ^b
	pH = 2	pH = 7	pH = 11		
3000 s				3003	$\nu_{\text{as}}(\text{CH}_2)$
2962 vs				2925	$\nu_{\text{as}}(\text{CH})$
2941 vs	2940 vs	2941 vs	2942 vs	2911	$\nu_{\text{s}}(\text{CH}_2)$
2900 sh	2905 sh	2909 sh	2910 sh	2986	$\nu_{\text{s}}(\text{CH})$
1758 s				1711	$\nu_{\text{s}}(\text{C=O})$
1734 s				1690	$\nu_{\text{as}}(\text{C=O})$
1426 s	1427s	1427 s	1427 s	1427	sciss(CH ₂)
	1404 sh	1403 sh	1405 sh	1386	$\omega(\text{CH}_2) + \delta(\text{CH})$
1380 s	1380 w	1380 w	1382 w	1362	$\delta(\text{CH}_2) + \gamma(\text{CH})$
	1320 m	1323 m	1322 m	1329	$\nu(\text{C-N}) + \nu(\text{C-C}) + \delta(\text{CH})$
1284 m	1282 m	1283 m	1283 m	1280	$\nu_{\text{s}}(\text{C-N}) + \delta(\text{CH}_2)$
1228 m		1235 vw	1228 vw	1234	$\nu(\text{C-N}) + \rho(\text{CH}_2) + \gamma(\text{CH})$
1190 m	1191 m	1193 m	1193 m	1203	$\nu(\text{C-N}) + \delta(\text{CH})$
1138 w	1136 vw	1136 vw	1143 vw	1157	$\nu(\text{HC-CH}) + \delta(\text{CH})$
			1113 vw	1127	$\nu(\text{C-N}) + t_{\text{w}}(\text{CH}_2)$
1045 m	1044 m	1044 m	1044 m	1082	$\nu(\text{C-N}) + \rho(\text{CH}_2) + \gamma(\text{CH})$
	1012 vw	1013 vw	1016 vw	994	$\nu(\text{HC-CH}) + \delta(\text{CH}_2)$
976 w	984 vw	997 vw		984	$\rho(\text{CH}_2) + \nu(\text{C-N})$
			978 vw	961	$\nu(\text{HC-CH}) + \delta(\text{CH}) + \tau(\text{HC-CH})$
906 m	905 m	907 m	905 m	910	$\rho(\text{CH}_2)$
835 vs	833 s	835 s	833 s	819	γR_5
753 m	751 m	751 m	751 m	754	γR_5
656 m				652	$\delta_{\text{ring}} + \delta(\text{C=O})$
		476 sh		440	δ_{ring}
440 vs	441 s	441 s	441 s	423	δ_{ring}
370 w		373 vw	371 vw	373	γR_8
338 w	338 vw	333 vw	334 vw	333	γR_8
278 w				282	γR_8

^a vs: very strong; s: strong; m: medium; w: weak, vw: very weak; sh: shoulder. ^b ν , stretching; δ , in plane deformation; γ , out of plane deformation; sciss: scissoring; ρ , rocking; t_{w} , twisting; ω : wagging; τ , torsion; R_5 : five-membered ring; R_8 : eight-membered ring; s: symmetric, a: antisymmetric. Frequencies were scaled by a factor of 0.9613 and 1.0007 for high and low frequency values, respectively.¹⁹

bands at 1758 cm^{-1} and 656 cm^{-1} are related to the stretching and deformation modes of the carbonyl portal groups and bands at 1380 cm^{-1} and 1228 cm^{-1} are attributed to $\nu(\text{C-H})$ and $\nu(\text{C-N})$ vibrations parallel to the Ag surface. These results are in agreement with those previously reported.¹¹ The proposed assignment of observed Raman and SERS bands is given in Table 1, based on our theoretical calculations at the B3LYP/6-31G* level of theory. SERS spectra at different pH values show that a pH increase results in slight shifts of some bands of the spectra. The close similarity of the Raman of the solid sample and SERS spectra of colloidal suspension is a consequence of the high rigidity of the macrocycle ring, which does not seem to undergo significant structural changes upon adsorption on the metal surface. The band shifts observed in acidic media can be associated with a certain protonation of the macrocycle portals given that the pK_{a} of the related CB[6] was reported to be 3.02.¹⁸ Likewise, slight changes at alkaline media in comparison with the solid, such as a band at 1193 cm^{-1} attributed to $\nu(\text{C-N}) + \delta(\text{CH})$, can be related to the inclusion in the cavity of Na^+ ions.

3.2 Raman, SERS and electronic spectra of DQ

The Raman and SERS spectra of DQ at different pH values are included in Fig. 3. The observed bands in the SERS spectra of DQ at different pH values are listed in Table S1 of ESI†. The interaction mechanism of DQ with a silver colloidal surface was previously well established by our group.¹⁰

According to such study, the remarkable change in the spectral profile resulting from DQ absorption on Ag NPs is due to the ionic pair formation with Br^- ions attached to the surface. These bromide ions came from stock solutions of DQ since the dication is present as a dibromide salt. The interaction is so strong that the DQ spectra and, therefore the molecular structure closely resembles the radical cation $\text{DQ}^{+\bullet}$. In the present study, the most relevant changes in the spectral profile were found under alkaline conditions. The SERS spectrum at $\text{pH} = 11$ shows a noticeable intensity enhancement of some bands in the spectral region of the marker bands associated with the electronic delocalization within rings, such as 1631 cm^{-1} , 1611 cm^{-1} and 1546 cm^{-1} , and those bands related to the aromatic rings planarity, such as 1318 cm^{-1} and 1291 cm^{-1} . A similar behaviour was earlier observed as a result of shortening the laser excitation wavelength and was attributed to other redox species, apart from the dicationic one, which can be arranged on multilayers.¹⁰ Additionally, the UV-visible spectra of a 10^{-4} M DQ solution in the absence of a CB[8] solution were measured at different pH values. The characteristic absorption band for DQ at 308 nm undergoes a decrease of the absorption intensity between $\text{pH} = 7$ and 12, 30 minutes after the host and guest were in contact (see Fig. S2 of ESI†). The monitoring of the same DQ solution at $\text{pH} = 10$ at repeated time intervals during 12 hours (Fig. S2 of ESI†) also shows a sequential intensity decrease of λ_{max} for higher contact time.

Table 2 Experimental SERS ($\lambda_{\text{exc}} = 532 \text{ nm}$) bands (cm^{-1}) observed for DQCB[8] host–guest complexes and their proposed assignment

SERS ^a pH = 2	SERRS pH = 7	SERRS pH = 11	Principal contribution	Assignment ^b
		3203 vw	G	$\nu(\text{CH})$
		3170 vw	G	$\nu(\text{CH})$
2939 vs	2933 vs	2932 w	H	$\nu_s(\text{CH}_2)$
2909 sh	2904 sh	2908 sh	H	$\nu_s(\text{CH})$
	1647 m	1646 m	G	$\nu_{\text{ring}} 8a + \delta(\text{CH}_2)$
1616 s	1614 s	1616 m	G	$\nu_{\text{ring}} 8a + \delta(\text{CH}_2)$
1583 s	1583 s	1583 m	G	$\nu_{\text{ring}} + \nu(\text{C}=\text{N}) + \delta(\text{CH}_2)$
	1560 s	1560 vs	G	$\nu_{\text{ring}} + \nu(\text{C}=\text{N}) + \delta(\text{CH}_2)$
1531 m	1531 m	1533 sh	G	$\nu_{\text{ring}} + \delta(\text{CH}) + \delta(\text{CH}_2)$
	1519 m	1519 m	G	$\nu_{\text{ring}} + \delta(\text{CH}) + \delta(\text{CH}_2)$
1458 vw	1480 w	1480 m	G	$\delta(\text{CH}_2)$
1428 s	1428 m		H	sciss(CH_2)
		1434 m	G	$\delta(\text{CH}_2) + \delta(\text{CH})$
1405 sh			H	$\omega(\text{CH}_2) + \delta(\text{CH})$
1383 m	1387 w		H	$\delta(\text{CH}_2) + \gamma(\text{CH})$
		1384 m	G	$\nu_{\text{ring}} + \delta(\text{CH}) + t_w(\text{CH}_2)$
	1377 m	1353 m	G	$\nu(\text{C}-\text{C})_{\text{ir}}$
1321 s	1321 vs	1321 s	H/G	$\nu(\text{C}-\text{N}) + \nu(\text{C}-\text{C}) + \delta(\text{CH}); \nu(\text{C}-\text{C})_{\text{ir}}$
1286 m	1282 m		H/G	$\nu_s(\text{C}-\text{N}) + \delta(\text{CH}_2); \nu_{\text{ring}} + \delta(\text{CH}) + t_w(\text{CH}_2)$
		1261 m	G	$\nu_{\text{ring}} + \delta(\text{CH}) + t_w(\text{CH}_2)$
	1235 m	1235 m	G	$\omega(\text{CH}_2)$
1193 s	1193 m		H/G	$\delta(\text{C}-\text{H}) + \nu(\text{C}-\text{N}); \nu(\text{H}_2\text{C}-\text{N}) + \delta(\text{CH})$
1180 vw	1174 sh	1175 m	G	$\nu_{\text{ring}} + \delta(\text{CH})$
		1165 sh	G	$\nu_{\text{ring}} + \delta(\text{CH})$
	1148 sh	1154 sh	G	$\nu_{\text{ring}} + \delta(\text{CH})$
1077 sh	1079 sh		G	$\delta_{\text{ring}} + \delta(\text{CH})$
1070 m	1069 m	1067 w	G	$\delta_{\text{ring}} + \delta(\text{CH})$
1044 m	1042 m	1042 w	H	$\nu(\text{C}-\text{N}) + \rho(\text{CH}_2) + \gamma(\text{CH})$
1011 w		1014 vw	H	$\nu(\text{HC}-\text{CH}) + \delta(\text{CH}_2)$
998 w	1002 w	985 vw	H/G	$\rho(\text{CH}_2) + \nu(\text{C}-\text{N}); \nu(\text{H}_2\text{C}-\text{CH}_2) + \gamma(\text{CH})$
906 m	907 m	906 w	H	$\rho(\text{CH}_2)$
835 s	835 s	833 w	H	γR_5
818 sh		820 sh	H	γR_5
804 w	807 sh	808 w	H/G	$\delta_{\text{ring}} + \gamma(\text{CH}); \delta_{\text{ring}} + \gamma(\text{CH})$
		777 w	G	δ_{ring}
751 m	751 m	747 w	H	γR_5
736 m	736 m	732 w	G	δ_{ring}
		702 w	G	$\tau_{\text{ring}} + \gamma(\text{CH})$
		648 vw	H	$\delta_{\text{ring}} + \delta(\text{C}=\text{O})$
		614 vw	G	$\delta_{\text{ring}} + \tau(\text{H}_2\text{C}-\text{CH}_2)$
552 w	552 m	554 vw	G	$\delta_{\text{ring}} + \gamma(\text{CH})$
539 w	540 sh	545 w	G	$\delta_{\text{ring}} + \gamma(\text{CH})$
		484 w	G	$\tau(\text{C}-\text{C})_{\text{ir}}$
456 vw	455 sh	462 sh	H	δ_{ring}
441 s	441 s	441 w	H	δ_{ring}
		424 sh	H	δ_{ring}
		411 w	G	τ_{ring}
373 w	371 vw	376 w	H	γR_8
		363 sh	H	γR_8
		309 vw	G	$\tau_{\text{ring}} + \tau(\text{H}_2\text{C}-\text{CH}_2)$
276 w	277 w	278 w	H	γR_8

^a vs: very strong; s: strong; m: medium; w: weak, vw: very weak; sh: shoulder. ^b ν , stretching; δ , in plane deformation; γ , out of plane deformation; sciss, scissoring; ρ , rocking; t_w , twisting; ω , wagging; τ , torsion; ir: inter-ring; R_5 : five-membered ring; R_8 : eight-membered ring; s: symmetric, a: antisymmetric. H: host; G: guest.

3.3 Raman, SERS and electronic spectra of DQCB[8]

The formation of a host–guest complex between the herbicide and the macrocycle CB[8] in aqueous solution at acidic and alkaline pH was confirmed by isosbestic points observed with increasing host concentration (Fig. S3 of ESI†). Also, the stoichiometries of the formed complexes under both conditions were investigated by means of Job's plot analysis (Fig. S4 of ESI†). Interestingly, these data reveal that at acidic pH a 1 : 1 complex can be formed whereas ternary 2 : 1 complexes can be

observed at alkaline pH. Therefore, the stoichiometry of DQCB[8] complexes in aqueous solution depends on the selected pH. Taking this into account, DQCB[8] complex adsorption on the metal surface was also studied by varying pH, as is displayed in Fig. 4. A proposed assignment of the observed bands in the SERS spectra of DQCB[8] at different pH values is given in Table 2. Two different spectrochemical behaviours were observed for the host–guest complex according to pH ranges. Under acidic conditions (pH = 2–5), the spectral region of DQ marker bands in the SERS spectra of the complex

Fig. 2 Raman spectra of CB[8] (a) solid and (b) 10^{-4} M aqueous solution; and SERS spectra of 10^{-6} M solution of CB[8] on Ag colloid at (c) pH = 2, (d) pH = 7 and (e) pH = 11. $\lambda_{\text{exc}} = 532$ nm.

Fig. 3 Raman spectra of DQ (a) solid and (b) 0.5 M aqueous solution; and SERS spectra of 10^{-5} M solution of DQ on Ag colloid at (c) pH = 2, (d) pH = 7 and (e) pH = 11. $\lambda_{\text{exc}} = 532$ nm.

resembles the Raman spectra of DQ solid and 0.5 M solution. This is proved by bands located at 1616 cm^{-1} , 1583 cm^{-1} , 1531 cm^{-1} and 1321 cm^{-1} , as is shown in Fig. 5. Moreover, since the SERS spectra of DQ adsorbed on the metal surface strongly differs from the SERS spectrum for the complex at pH = 2, it can be deduced that DQ is encapsulated within CB[8] avoiding their direct interaction with the Ag NPs. Bands appearing below 1300 cm^{-1} are principally due to the macrocycle molecular vibrations (see Fig. 2). The analysis of the SERS spectra reveals that vibrational modes which involve the aromatic ring and the aliphatic chain of 1077 cm^{-1} (1079 cm^{-1}) and 998 cm^{-1} (1002 cm^{-1}) bands corresponding to $\delta_{\text{ring}} + \beta(\text{CH})$, and $\nu(\text{H}_2\text{C}-\text{CH}_2)$ are shifted, in comparison with that of DQ in the absence of CB[8]. Slight shifts in CB[8] spectra are in agreement with results from an X-ray study⁷ which shows that the guest can be included in

Fig. 4 SERS and SERRS spectra of DQCB[8] solution of 10^{-5} M/ 10^{-6} M concentration on Ag colloid at (a) pH = 2, (b) pH = 5, (c) pH = 6, (d) pH = 7, (e) pH = 9, (f) pH = 11 and (g) pH = 12. Spectra (e)–(g) were scaled to fit into the graph. $\lambda_{\text{exc}} = 532$ nm.

Fig. 5 Raman spectra of (a) 0.5 M aqueous solution of DQ and SERS spectra on Ag colloid of (b) DQ 10^{-5} M at pH = 2, (c) DQCB[8] 10^{-5} M/ 10^{-6} M at pH = 2, (d) DQ 10^{-5} M at pH = 11 and (e) DQCB[8] 10^{-5} M/ 10^{-6} M at pH = 11 in the region of the marker bands. $\lambda_{\text{exc}} = 532$ nm.

CB[8] without any significant distortion of the macrocycle. On the other hand, for $\text{pH} \geq 6$ the spectral profile changes drastically. For a better understanding of the processes

occurring at alkaline pH the absorption spectra of a 10^{-4} M solution of DQ in the presence of 10^{-5} M CB[8] solution were measured by varying pH, as can be shown in Fig. 6. The data show that while λ_{max} at 308 nm decreases for all the pH range measured, two new bands located at 347 nm and 495 nm arise at pH = 9, whose intensities increase with raising pH. This fact is accompanied by a concomitant color change of the colorless solution to red. Moreover, these bands undergo a blue shift from 488 nm to 492 nm as the concentration of CB[8] host is increased (Fig. S3 of ESI[†]). These new bands were previously observed for the reduction of the dication with several reductants (cysteine, dithionite, mercaptoethanol, *etc.*) at alkaline pH^{20,22} and were assigned to the radical cation species.²² The temporal evolution of the same concentration of DQCB[8] solution at pH = 10 is shown in Fig. 6. Here, the two characteristic bands for the radical cation also appear and reach the maximum absorption 80 minutes after the reactants were in contact. Then, these bands diminish until two new bands can be clearly distinguished at 280 nm and 372 nm. The yellow color of the solution at this point probably can be associated with the appearance of the totally reduced form of DQ.^{20–23} Surprisingly, it seems that redox species of DQ can be formed under alkaline conditions. In the absence of CB[8], higher concentrations of DQ and higher pH conditions (pH = 11 and 12) are required

for the process to occur (see discussion on Fig. S5 of ESI[†]). Conversely, CB[8] addition could prompt the reaction in such a way that CT bands can be observed at pH two units lower than without CB[8].

Furthermore, under alkaline conditions a resonant effect between the laser excitation wavelength at 532 nm and the absorption band observed at 495 nm in solution leads to SERRS (surface-enhanced resonance Raman scattering) spectra for DQCB[8] (see Fig. 6). In Fig. 3 remarkable SERS enhancements and band shifts occur in the whole spectra, particularly in the marker band region. Bands related to the ring π -delocalization at 1616 cm^{-1} and 1583 cm^{-1} are greatly enhanced as well as new strong bands at 1646 cm^{-1} , 1560 cm^{-1} and 1519 cm^{-1} experience an intensity increase as pH increases. Also, new bands around 1321 cm^{-1} can be observed. Variations in the marker bands region at alkaline pH can be observed in detail in Fig. 5. Taking in mind the results obtained from the UV-visible spectra of the complex at alkaline pH, we propose that those pronounced changes observed in the SERRS spectra are due to the dimer formation of $(\text{DQ}^{\bullet+})_2$ and $(\text{DQ}^{\bullet+}\text{DQ}^{+2})$ like species within the CB[8] cavity. These face-to-face dimers are stabilized by CT interactions inside the cavity overcoming the steric repulsion effect from the lateral aliphatic chain and giving rise to the intense red color of the solution. This is an important finding regarding the application of CB[8] as a

Fig. 6 (left) UV-visible absorption spectra of 10^{-5} M/ 10^{-6} M aqueous solution of DQCB[8] at (a) pH = 2, (b) pH = 3, (c) pH = 5, (d) pH = 7, (e) pH = 8, (f) pH = 10, (g) pH = 11 and (h) pH = 12 after 30 minutes. Inset: absorption decrease from pH = 2 to pH = 7. (middle) Temporal evolution of the same solution of DQCB[8] at pH = 10 from $T = 0$ to $T = 24$ h. Inset: absorption variation of bands at 280 nm, 308 nm, 349 nm and 495 nm. (right) Color change of a 10^{-4} M/ 10^{-5} M DQCB[8] solution with time.

Fig. 7 Scheme of inclusion complexation of DQ inside CB[8].

chemical sensor for detecting hazardous pesticides and opens the possibility to be applied in soil remediation. The use of CB[8] to remediate polluted alkaline soils should have the advantage of selectively removing two molecules instead of one. Also, the color change provides a rapid detection method of DQ in soils reducing the detection limit that previously was achieved with a chemical reductant.²¹ The complexation process between DQ and CB[8] is represented in Fig. 7.

In order to get a better insight on the interaction mechanism of the DQ guest with the CB[8] receptor molecule, two different approaches were followed. First, an aliquot of the 10^{-6} M CB[8] solution was added to the silver NPs previously aggregated with KNO_3 0.5 M. Subsequently, an aliquot of the 10^{-5} M DQ solution was added to the mixture. Second, an aliquot of the 10^{-5} M/ 10^{-6} M DQCB[8] complex solution was added to the nitrate aggregated silver NPs. The resulting SERS spectra (Fig. S6 of ESI†) show that regardless of the pH value, the spectral profile does not show significant changes. Due to the fact that CB[n] are bifunctional agents it is expected that not only they can selectively bind a guest molecule but also they have the capability to act as a bridging ligand producing the so-called hot spots. Therefore, from the similarity among SERS spectra it can be deduced that DQ is certainly able to be included within the internal cavity of CB[8] molecules which link silver NPs, in the same way as it does in aqueous solution.

Also, it is interesting to note that the spectral changes associated with the 2 : 1 complex formation become evident at pH = 6 in the SERS spectra immediately after adding the host and the guest to the colloid, whereas for the UV-visible spectra they can be observed at pH = 9 and required a certain contact time. This fact can be explained by the great sensitivity of the SERS technique, which allows detecting only those species that are selectively bound to the surface, independently of the bulk solution. Furthermore, the metallic superficial effect seems to favor the formation of $\text{DQ}^{+\bullet}$, as was deduced from the adsorption study of DQ on Ag NPs.¹⁰

4. Conclusions

The formation of DQCB[8] complexes is highly dependent on pH. We have shown that an increase in pH induces the cation radical formation and also, the addition of CB[8] promotes their dimerization within the cavity due to the spatial restriction imposed by the host. The CB[8]/Ag NPs were successfully employed as a chemical sensor based on surface enhanced spectroscopy for detecting DQ herbicide, providing very useful structural information. The approach followed in this work could be applied as a general technique for sensing viologen herbicides and also for analyzing CB[n] complexes. Further studies exploring the influence of the excitation wavelength and the effect of the guest concentration on the formation of these complexes are currently in progress.

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