Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

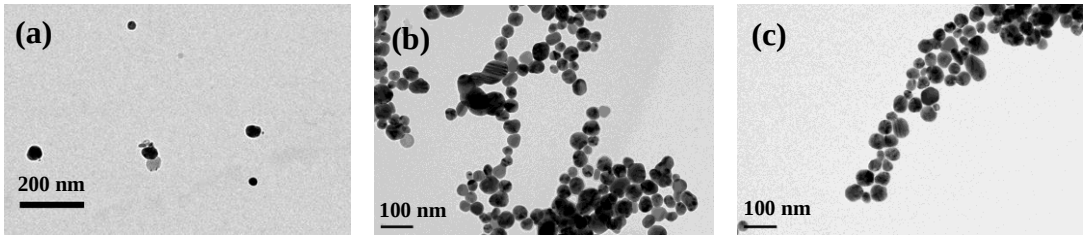
Electronic Supporting Information

Cucurbit[8]uril-stabilized charge transfer complexes with Diquat driven by pH: A SERS Study

María L. Roldán[*a], Santiago Sanchez-Cortes[a], José V. García-Ramos[a] and Concepción Domingo[*a]

Instituto de Estructura de la Materia, CSIC, Serrano 121, 28006 Madrid, Spain. Fax: +34915645557; Tel: +34 915616800; E-mail: lorena@iem.cfmac.csic.es, cdomingo@iem.cfmac.csic.es

Fig. 1. UV-visible absorption spectra at pH=2, 7 and 11 of (a) Ag colloid aggregated with 0,01M KNO_3, and the same Ag colloid solution with (b) 10^{-6}M CB[8] and (c) 10^{-5}M/10^{-6}M DQCB[8]. TEM micrographies of (a) Ag NPs, (b) Ag NPs functionalized by CB[8] and (c) Ag NPs functionalized by DQCB[8]. The λ_{SPR}=405-407 nm and the NPs size of the Ag colloid is in accord with our previous studies[1].



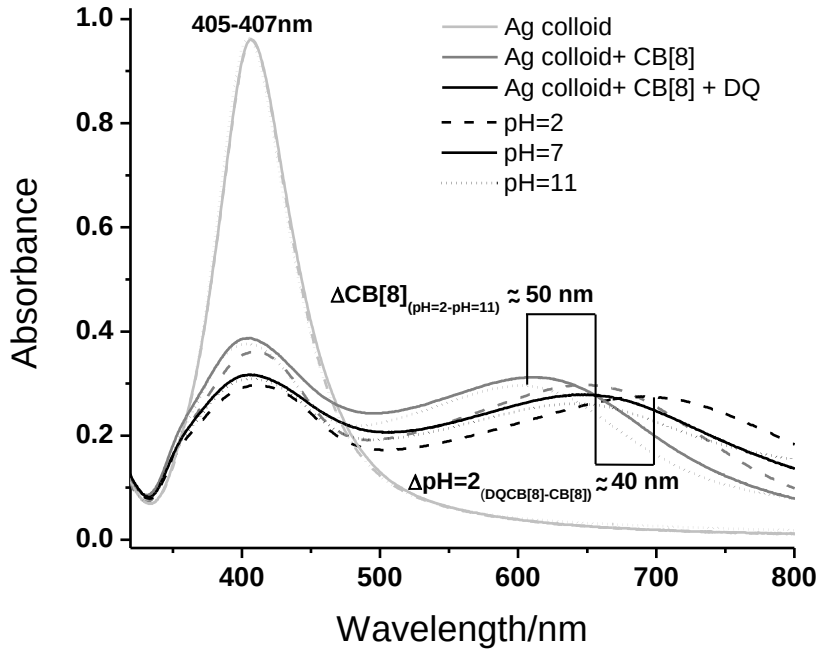
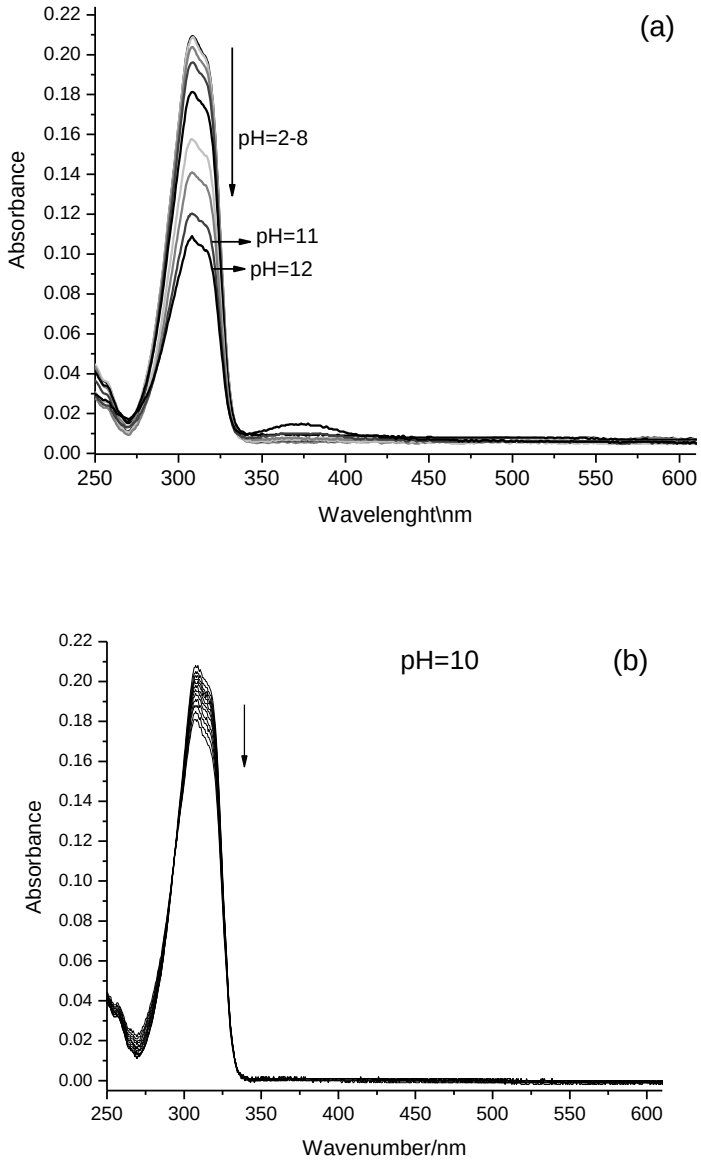
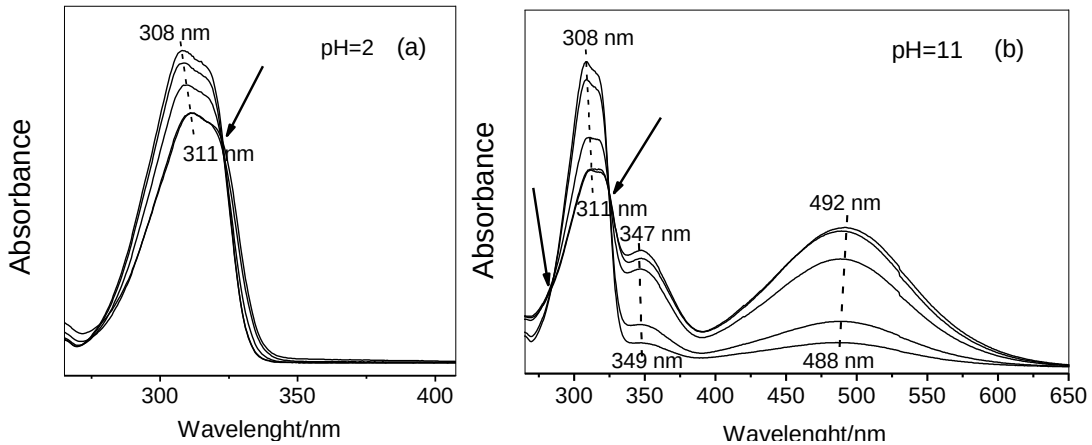


Fig. 2. (a) UV-visible absorption spectra of DQ at 10^{-5}M concentration in aqueous solution (a) at different pHs 30 minutes after pH was adjusted and (b) at pH=10 for repeated intervals during 12 hours.



The influence of pH on the UV-visible spectra of a diluted solution of DQ in absence of CB[8] can be seen on **Fig. 2a**. A sequential decrease of DQ^{+2} characteristic absorption band at λ_{max}= 308 nm can be clearly observed. Also, at pH=11 and 12 a band located at 372 nm appears. In **Fig. 2b** no changes on the electronic spectra for DQ can be seen up to 12 hours. This fact suggests that the CT bands observed for DQCB[8] complex are a consequence of the presence of CB[8].

Fig. 3. Absorption spectra for DQ at 10^{-5}M concentration in aqueous solution with increasing concentrations of CB[8] at (a) pH=2, and (b) pH=11, 30 minutes after host and guest were in contact. Arrows indicate isosbestic points.



The DQCB[8] complex formation in aqueous solution at acidic and alkaline pH was confirmed by isosbetic points observed at 329 nm at pH=2 and at 333 nm at pH=11. Also, a second isosbestic point at 279 nm can be seen at alkaline pH, indicating that more than one type of complex can be formed at this pH. A bathocromic shift of the maximum absorption (λ_{max}) from 308 nm to 311 nm with a concomitant intensity decreasing confirmed that DQ is encapsulated by CB [8] at both acidic and alkaline pH.

Fig. 4. Host-guest ratio: Job's plot

The stoichiometry of DQCB[8] complexes at acidic and alkaline pH were investigated by Job's plot. **Fig. 4** shows Job's plots at (a) pH=2 evaluated by absorbance changes at 330 nm and (b) pH=11 evaluated by absorbance changes at 335 nm (triangle) and 272 nm (circle). It can be deduced that lowering pH binary 1:1 complexes can be formed whereas 2:1 ternary complexes can be formed when pH increase.

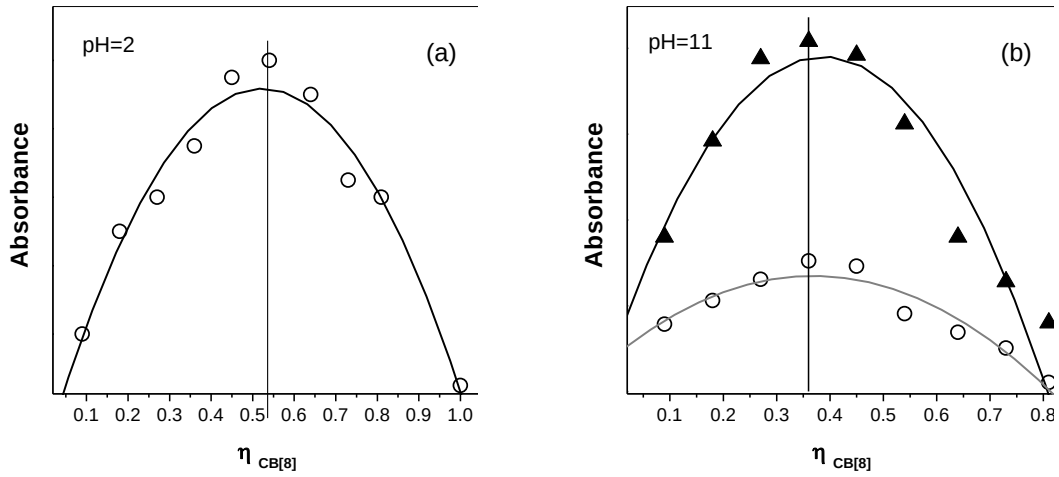
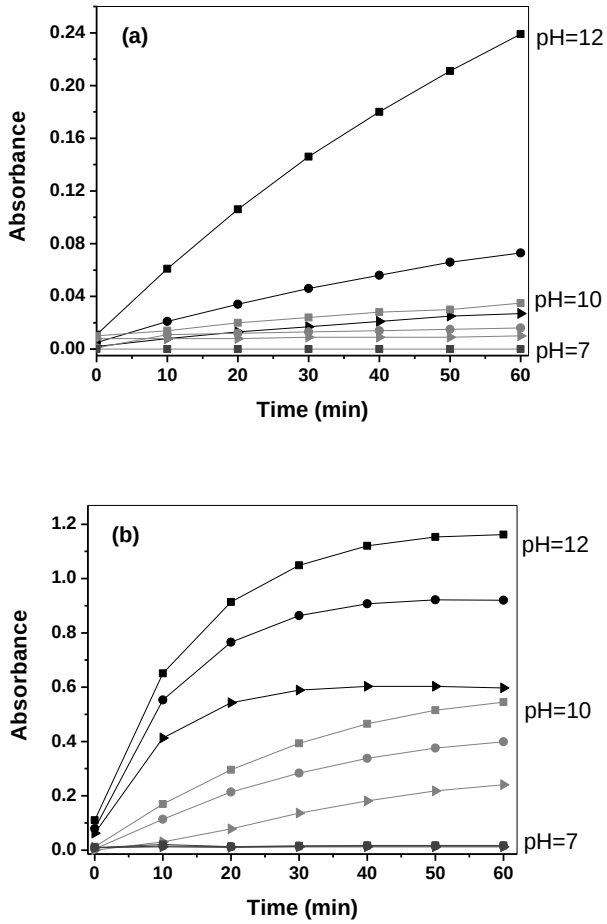
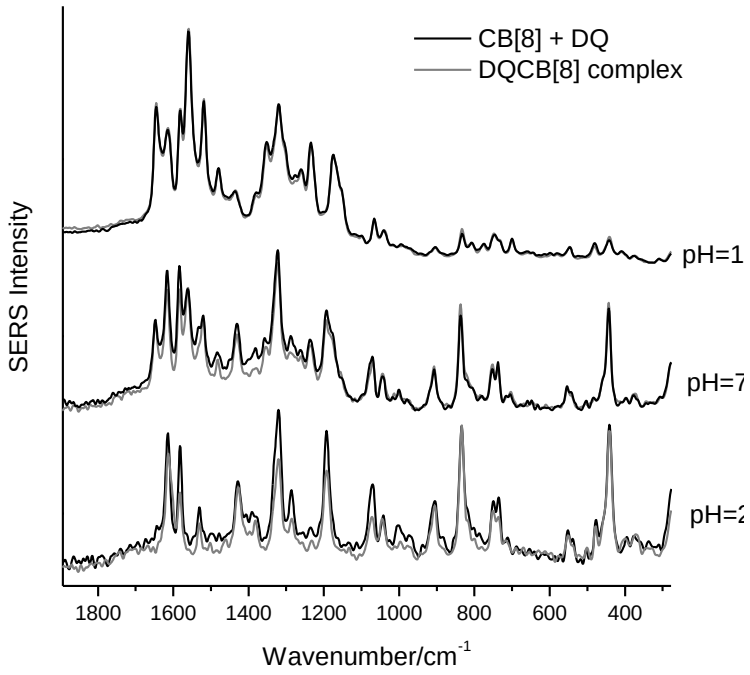


Fig. 5. Influence of DQ concentration and pH on the UV-visible absorption of DQCB[8] at a fixed concentration of CB[8] (10^{-6}M). Fig. 4 shown the absorbance at 495 nm for (a) DQ and (b) DQCB[8] at pH=7, pH=10 and pH=12 with a DQ concentration of 3.10^{-5}M (triangle), 5.10^{-5}M (circle) and 1.10^{-4}M (square).



In **Fig. 2a** and **2b** it was observed that for 10^{-5}M DQ aqueous solution at pH=10 and during 12 hours no CT bands can be seen in the spectra. However, as can be seen at **Fig. 5a**, higher concentrations of DQ (3.10^{-5}M, 5.10^{-5}M and 1.10^{-4}M) give rise to weak CT bands in the electronic spectra. Clearly visible red color solutions are observed in a shorter time at pH=12 with higher DQ concentration (1.10^{-4}M). The addition of CB[8] to the guest leads to notably higher absolute absorbance values, in comparison with a DQ solution without CB[8] at the same concentration and pH. Results evident that, higher pH and guest concentrations provide higher dimerization of the radical cation inside CB[8] cavity. Also, the radical cation dimer within CB[8] seems to be more stable in time at pH=10 than at pH=12.

Fig. 6. SERS and SERRS spectra of DQCB[8] on Ag colloid at pH=2, 7 and 11 obtained from (a) an aliquot of the 10^{-6}M CB[8] solution plus an aliquot of the 10^{-5}M DQ solution and (b) an aliquot of the 10^{-5}M/10^{-6}M DQCB[8] complex solution.



Vibrational data analysis

Table 1. Observed bands (cm^{-1}) for the Raman and SERS (λ_{exc}=532nm) spectra of DQ guest and their assignment based on previous authors[2].

Raman[a]		**SERS**			**Assignment**[b]
Solid	Aqueous 0.5M	pH=2	pH=7	pH=11	
3085 w					ν(CH)
3059 w	3104 w				ν(CH)
2916 m	2968 vw	2939 w	2933 m	2932 m	$\nu_s(CH_2)$
1613 s	1617 s	1613 w	1614 w	1611 w	ν_{ring} 8a
1579 m	1584 m	1581 vs	1581 vs	1581 vs	ν_{ring} + ν(C=N)
1529 m	1533 m	1526 w	1533 w	1530 w	ν_{ring} + δ(CH)
1460 vw	1451 vw	1459 w	1466 w	1456 w	$\delta(CH_2)$
1431 w	1440 vw		1441 w	1443 w	δ(CH)
1393 w	1387 w	1387 w	1384 w	1382 w	ν_{ring} + δ(CH) + $t_w(CH_2)$
1326 s	1322 s	1319 m	1321 m	1318 s	$\nu(C\text{-}C)_{ir}$
1288 w	1290 w	1292 m	1289 m	1290 s	ν_{ring} + δ(CH) + $t_w(CH_2)$
1233 w	1236 w	1240 w	1239 w	1240 w	$\omega(CH_2)$
1194 m	1196 m	1186 s	1186 s	1186 m	$\nu(H_2C\text{-}N)$ + δ(CH)
1174 w		1162 sh	1168 sh	1172 sh	ν_{ring} +δ(CH)
1155 vw		1145 w	1145 w	1154 sh	ν_{ring} +δ(CH)
1073 w	1072 w	1079 m	1078 m	1078 m	δ_{ring} + δ(CH)
		1069 sh	1068 sh		δ_{ring} + δ(CH)
		1048 w	1043 w	1042 w	δ_{ring} + δ(CH)
998 w	999 w	1002 w	1002 w	1002 w	$\nu(H_2C\text{-}CH_2)$ + γ(CH)
739 w	736 w	736 w	736 w	736 w	δ_{ring}
544 w	550 w	555 vw	553 vw		δ_{ring} + γ(CH)
	538 w				γ(CH)
			481 w	481 w	δ_{ring}
450 vw	454 vw	441 w	443 w	440 w	γ(CH)
404 vw	394 vw	397 w	395 w	397 w	τ_{ring}

[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; t_w, twisting; ω, wagging; τ, torsion; ir: inter-ring; s: symmetric, a: antisymmetric.

References

1. M. V. Cañamares, J. V. Garcia-Ramos, J. D. Gomez-Varga, C. Domingo, S. Sanchez-Cortes. *Langmuir*, 2005, **21,** 8546.

2. M. R. López-Ramírez, L. Guerrini, J. V. García-Ramos and S. Sanchez-Cortes, *Vib. Spect.*, 2008, **48**, 58.