

Supplementary Material (ESI) for Chemical Communications
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Electronic Supporting Information For:

Solution SERS of an insoluble synthetic organic pigment - Quinacridone Quinone - employing Calixarenes as dispersive cavitands†

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Chemicals and reagents

Quinacridone Quinone and concentrated sulphuric acid were purchased from Aldrich with the highest purity. Hydroxylamine hydrochloride employed as reductor in the fabrication of silver colloids was also purchased from Aldrich with analytical purity. Silver nitrate and potassium nitrate, the last used as aggregating agent in the silver colloid fabrication, were supplied by Merck with analytical purity. Aqueous solutions were prepared using Milli-Q water. Calix[n]arenes (CXs) employed in this work^{*} were synthesized¹ and kindly given to us by Dr. C.Saitz (Faculty of Chemical and Pharmacological Sciences, University of Chile). The CXs were dissolved in acetone (99%) at different concentrations.

Preparation of samples

Silver colloids were prepared by reduction of silver nitrate with hydroxylamine hydrochloride at room temperature³. The colloids were previously aggregated by adding an aliquot (40 μ L) of potassium nitrate solution 0.5M up to a final concentration of 2×10^{-2} M. In the case of QAQ solved in concentrated H₂SO₄, an aliquot (10 μ L) of such solution were added to 1mL of the aggregated silver colloid.

In the experiments with CXs, an aliquot (10 μ L) of CXs solved in acetone at the concentrations required were added to 1 mL of the aggregated colloid and then different quantities (between 1.7mg and 0.03mg, depend on the sample) of the solid QAQ was added. It must be mention that no aggregation was induced after adding the CXs.

^{*} **TOHC4**: 25,26,27,28-tetrahydroxy-p-tert-butylcalix[4]arene; **DCEC4**: 25,27-dicarboetoxy-26,28-dihydroxy-p-tert-butylcalix[4]arene; **TCEC4**: 25,26,27,28-tetracarboetoxy-p-tert-butylcalix[4]arene; **TCEC8**: 49,51,53,55-tetracarboetoxy-50,52,54,56-tetrahydroxy-p-tert-butylcalix[8]arene.

Instrumentation

Raman spectrum of solid QAQ excited at 514.5 nm (argon laser) was recorded with a Renishaw Raman Microscope RM2000 equipped with a Leica microscope and an electrically refrigerated CCD camera. The laser power in the sample was 2.0 mW. The spectral resolution was set at 4 cm^{-1} . Raman spectra excited at NIR were obtained with a Bruker RFS 100/S instrument by using the line at 1064 nm provided by a Nd:YAG laser and a Ge detector cooled by liquid nitrogen. The resolution was set to 4 cm^{-1} , and 180° geometry was employed. Uv-vis spectrum of solid QAQ was recorded in a Shimadzu 3600 spectrophotometer using an integrating sphere accessory. FTIR spectrum of solid QAQ in a KBr pellet was taken with a Bruker IFS 66 instrument, using a DTGS detector. SERS spectra excited at 514.5 nm were recorded in the Renishaw system employing a macro configuration.

Computed vibrational frequencies

Calculation of vibrational frequencies were made using hybrid DFT method, B3LYB and 6-31G (d,p) as a basis set³; and considering the symmetry of the molecule as C_{2h} . When necessary the computed frequencies have been adequately scaled⁴. The most probable assignment of the principal observed IR and Raman bands is given in Table 1.

Experimental vibrational spectra

Fig. 1 shows the IR and Raman spectra of solid QAQ. The different relative intensities observed for the Raman spectra excited at two laser wavelengths, 1064 and 514.5 nm, is related to the pre-resonance situation when using the 514.5 nm line. In fact, the absorption spectrum of solid QAQ shown in Fig. 2 has a maximum centred at 434 nm. Taking profit of such pre-resonance condition, SERS spectra were also excited at 514.5 nm.

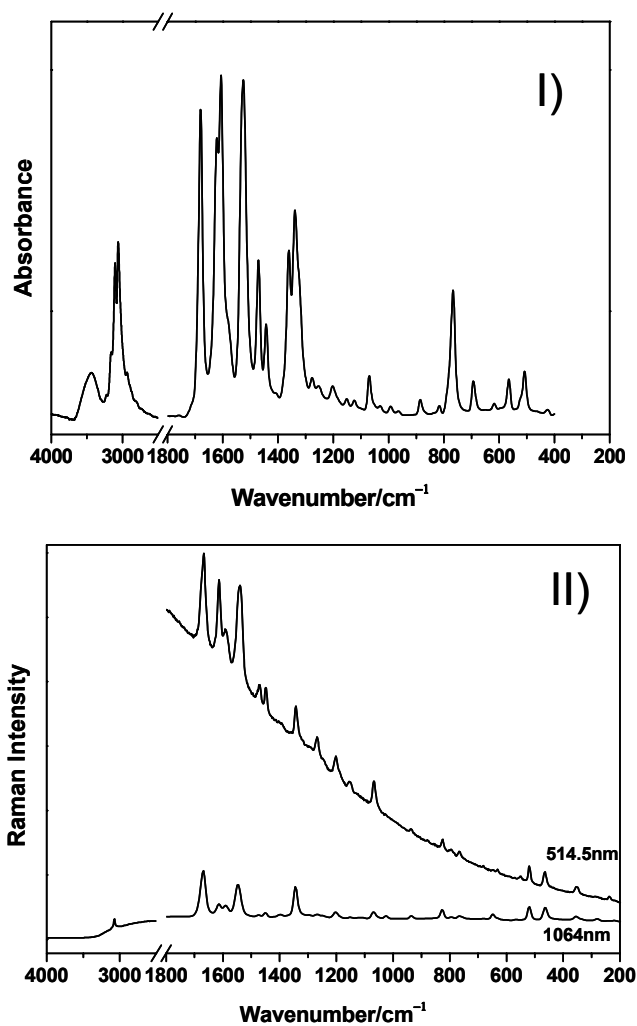


Fig. 1. I) FTIR spectrum of solid QAQ in KBr. II) Raman spectra of solid QAQ excited at the laser wavelengths indicated.

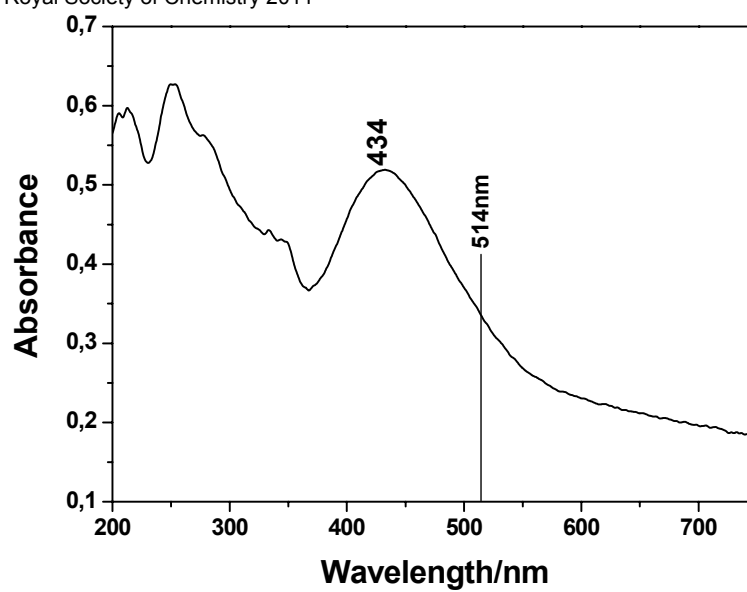


Fig. 2. UV-Vis absorption spectra of solid QAQ. Red (514.5 nm) line indicates the wavelength of the laser employed for exciting its Raman and SERS spectra.

Table 1. Experimental and calculated IR and Raman bands (cm^{-1}) of QAQ with the most probable assignment.

EXPERIMENTAL		CALCULATED ²		ASSIGNMENT
IR	Raman ($\lambda=1064\text{nm}$)	IR	Raman	
		*		
3437 b		3368		} ν (N-H)
3159 w		3223		
3104 w		3210		
3061 w		3198		
2936 w		3187		
				} ν (C-H) _{ar}
1680 s		1706		} ν_{as} (C=O) ν_s (C=O)
	1667 s		1698	
1620 s		1600		} ν (C=C)
	1613 s		1600	
1606 s		1580		
	1589 m		1589	} ν (C=N), δ ip (N-H)
	1539 s		1516	
1515 s		1505		
				} ν (C=C), δ ip(C-H) 1,2,3,4 and 5 rings
1471 m	1469 m	1459	1459	
1443 m	1448 m	1426	1431	
1360 m		1329		
1338 m	1342 m	1278	1326	} ν (C-C), δ ip (C-H) 1 and 5 rings
1253 w	1268 m		1228	
1202 w	1201 m	1176	1172	} ν (C-C), δ ip(C-H) 1 and 5 rings, δ ip (N-H)
1151 w	1150 w	1140	1139	
				} ν (C-C), δ ip (C-H) 1 and 5 rings
1070 w	1067m	1042	1031	} ν (C-C), ν (C-N), δ ip(C-H)
	824 w	**	816	} δ op (C-H) δ op (N-H)
	794 w		782	
766 m	767 w	771,6	774	} Skeletal deformation op
693 w	681 w	694	689	
618 w	631 w	625	644	} Skeletal deformation ip
565 w	548 w	576	563	
508 w	519 w	510	524	
	463 w		462	
	353 w		352	
	237 w		231,6	

ν : stretching, δ op: out of plane deformations, δ ip: in plane deformations, b=broad, vs: very strong, s: strong, m: medium, w: weak, vw: very weak. *Scale factor 0.9627 ** Scale factor 1.0028⁴

Table 2. Experimental SERS bands of QAQ in sulphuric acid and dispersed in CX, excited at 514.5 nm.

SERS QAQ in acid conditions	SERS QAQ-CX
	1616 m
	1570 m
1515 s	1519 s
1456 m	1469 m
1440 m	1447 m
1406 w	
	1365 m
1348 w	
	1300 m
1274 s	
	1241 w
	1202 w
	1153 w
1147 m	
	1123 w
	1092 m
1035 m,b	1072 sh
887 m,b	831 w
	776 w
	639 w
587 m,b	578 w
511 w	531 w
426 m,b	463 w
	390 w
	374 w
331 w	
193 s	

s: strong, m: medium, w: weak, b: broad, sh: shoulder

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