Supplementary Material for:

Electrochemical SERS study on a copper electrode of the insoluble organic pigment Quinacridone Quinone using Ionic Liquids (BMIMCl and TBAN) as dispersing agents

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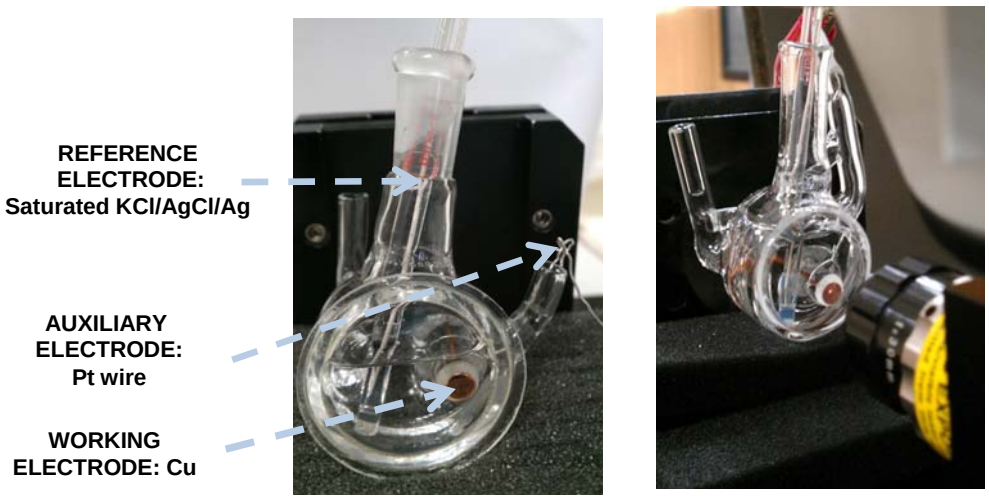

Fig. 1S. Electrochemical cell employed, two compartments, three electrodes.

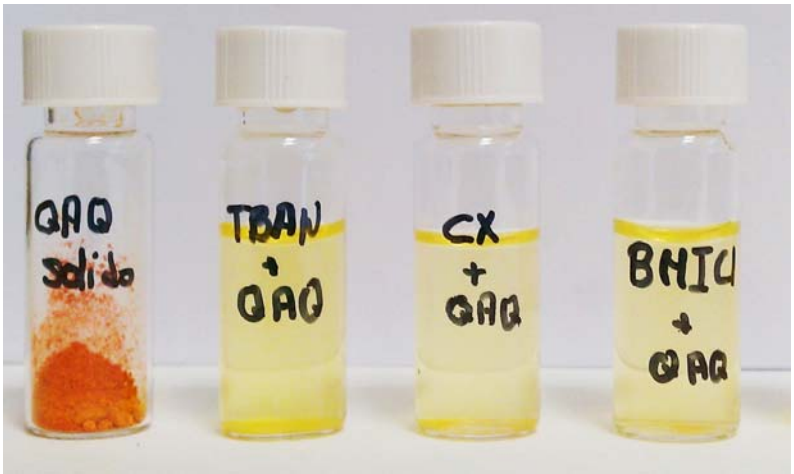

Fig. 2S. QAQ pigment in solid state and dispersed in TBAN, BMIMCl and calixarenes (CX). When dispersed, QAQ is pale yellow; only in solid state it adopts its characteristic orange color, signaling the involvement of strong molecular interactions.

Raman and SERS spectra of tetrabutylammonium nitrate (TBAN)

Figure 3S shows the Raman spectrum of solid TBAN, excited at 785 nm, and the SERS spectrum at 0.2V *vs* Ag/AgCl(KCl_{sat}). To our knowledge there is only one paper [1] reporting Raman and SERS spectra of a tetrabutylammonium salt (tetrabutylammonium perchlorate, TBAP), which presents a minor discussion of both of them, even including some mistakes (the most intense band in the Raman spectrum of solid TBAP is there assigned to "C-C skeletal", while it corresponds to $ClO4^-$, as well as the bands at 630 and 463 cm^{-1}[2]. We can assert such fact because in our case, TBAN, the by far most intense band (at 1039 cm^{-1}) in the Raman spectrum of the solid sample corresponds to the nitrate anion $NO3^-$). In order to support the assignment of the spectra we have carried out the calculation of vibrational frequencies of the cation moiety of TBAN using hybrid DFT method, B3LYB and 6-31G (d,p) as a basis set and the Gaussian 09 program[3]. A plausible assignment of the Raman bands is given in Table 1S.

Apart from the Raman bands due to $NO3^-$ in our case or to $ClO4^-$ in the referenced paper on TBAP[1], spectrum of solid TBAN agrees with the one of TBAP, both corresponding to the tetrabutylammonium cation. Only such moiety gives SERS spectra, the one given is Fig. 3Sb completely agreeing with the previously reported during Ag electrodeposition at 0.2V[1].

A sketch of the relative orientation of the cation moiety of TBA to Cu electrode is given in the right part of Fig. 3S, based on the vibrational assignment and the surface selection rules of the SERS effect [4].

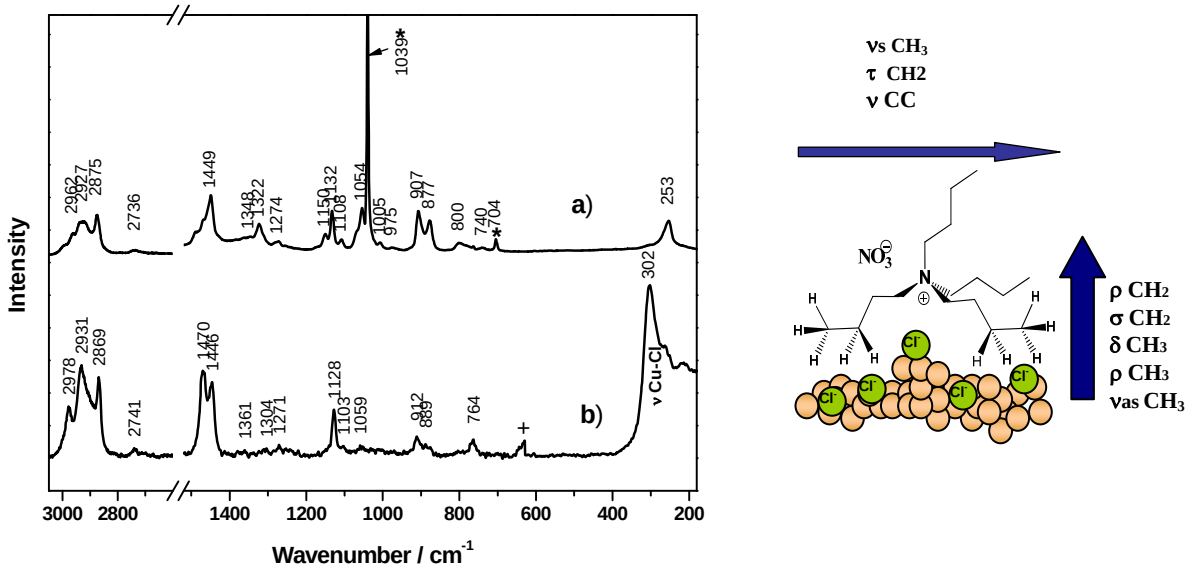

Figure 3S. *Left part*: a) Raman spectrum (ν_{exc}= 785 nm) of TBAN in solid state and b) SERS spectrum (ν_{exc}= 633nm) of TBAN on Cu electrode at 0.2V potential value. (*:$NO3^-$ bands. +: artifact). *Right part*: Outline of the TBAN molecule relative orientation to the Cu electrode where Cl^- is adsorbed. The arrows intend to indicate the TBAN vibrational modes with predominant components perpendicular or paralell to the Cu surface which, according to the surface selection rules, are enhanced or not in the SERS spectrum.

EXPERIMENTAL	CALCULATED	ASSIGNMENT
Raman (785nm)	Raman	
2989(w)	3092	ν CH_3
2962(w)	3079	ν CH_2
2927(w)	3063	
2875(w)	3014	
2736(w)	2991	
1488(w)		
1467(w)	1539	δ CH_3
1455(m)	1531	δ CH_3, σ CH_2
1449(w)	1524	σ CH_2
1322(w)	1355	τ CH_2
1274(w)	1303	
1170(w)	1183	ρ CH_3
1150(w)	1160	ρ CH_3, ν C-C
1132(m)	1148	
1108(w)	1141	
1065(w)	1075	ν C-C
1054(m)	1059	ν C-C, ν C-N
1039(s)		NO_3^-
1005(w)	1021	ν C-C
907(m)	930	ρ CH_3, ρ CH_2 , ν C-N
877(m)	915	ρ CH_3, ν C-C
800(w)	847	ρ CH_3, ρ CH_2 , ν C-N
763(w)	768	
740(w)	739	ρ CH_2
704(w)		NO_3^-
253(m)	201	δ C-C-C

Table 1S. Experimental and calculated Raman bands (cm^{-1}) of the cation moiety of tetrabutylammonium nitrate (TBAN) with the most probable vibrational assignment. Symbols: s: strong, m: medium, w: weak, ν: stretching, δ: deformation, σ: scissoring, τ: twisting, ρ: rocking.

References

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