# Grafted Squaramide Monoamine Nanoparticles as Operative Devices for Sulfate Recognition in Pure Water

**Estefanía Delgado-Pinar,[a] Carmen Rotger,[b] Antonio Costa,[b] M. Neus Piña,[b] Hermas R. Jimenez,[c] Javier Alarcón,[c] Enrique García-España.[a]**

a) Departamento de Química Inorgánica, ICMOL, Universidad deValencia, 46980, Paterna (Valencia), Spain.

b) Departament de Química, Universitat de les Illes Balears, Valldemossa, Palma de Mallorca 07122, Spain.

c) Departamento de Química Inorgánica, Universidad de Valencia,46100 Burjasot, Valencia, Spain.

## Supplementary Materials Include:

Experimental Section. Synthetic procedures of Sq and BSq/MSq and NMR spectra.

Figure 1S.- X-ray powder diffraction pattern of MSq and BSq .

Figure 2S.- TEM image of MSq and BSq hybrid system.

Figure 3S.-Changes observed in a UV-Vis spectra of a solution of Bromocresol Green ($1.48 \times 10^{-5}$ M) before and after the addition of hybrid B-Sq at 25ºC.

Figure 4S.- UV/VIS spectra resulting from the addition of MSq to a BG solution aqueous solution at pH =3.4.

Figure 5S.- Changes in the absorption spectrum BG-MSq system upon addition of different anions. BG ($1.48 \times 10^{-5}$ M).

Table 1S.-Protonation constants of the different acids.

Figure 6S.- Actual net charge at pH 3.4 of the different anions used.

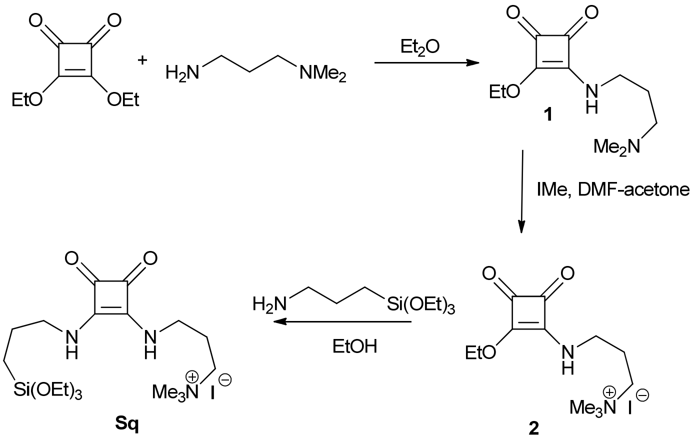
Figure 7S.- From left to right: BG solution, addition of boehmite, quaternised boehmite ($BN^+$ ) and BSq to a BG aqueous solution at pH =3.4.

## Experimental section

**Boehmite particles** were synthesized as previously reported following a two-step procedure [1].The first step was the hydrolysis of aluminium s-butoxide in an excess of water at 80 ºC under vigorous stirring. After the alkoxide addition, anexothermic reaction took place and a gel was formed almostimmediately, which was held under stirring for several hours.The second step, a peptization process, was carried out keepingthe boehmite particles in a nitric acid solution at 90±1°C for 1 week.

**Composed core–shell nanoparticles**.[2] Composed core–shell nanoparticles were obtained by a sol–gel method consisting of the hydrolysis and condensation of tetraethylorthosilicate (TEOS) in a solution of $Al(NO_3)_3.9H_2O$ in ethanol at 60 ºC. The resulting solution was refluxed and aged for 1 week. Gels were dried at 60 and 120 ºC.

**Synthesis of the organic molecule(Sq)**



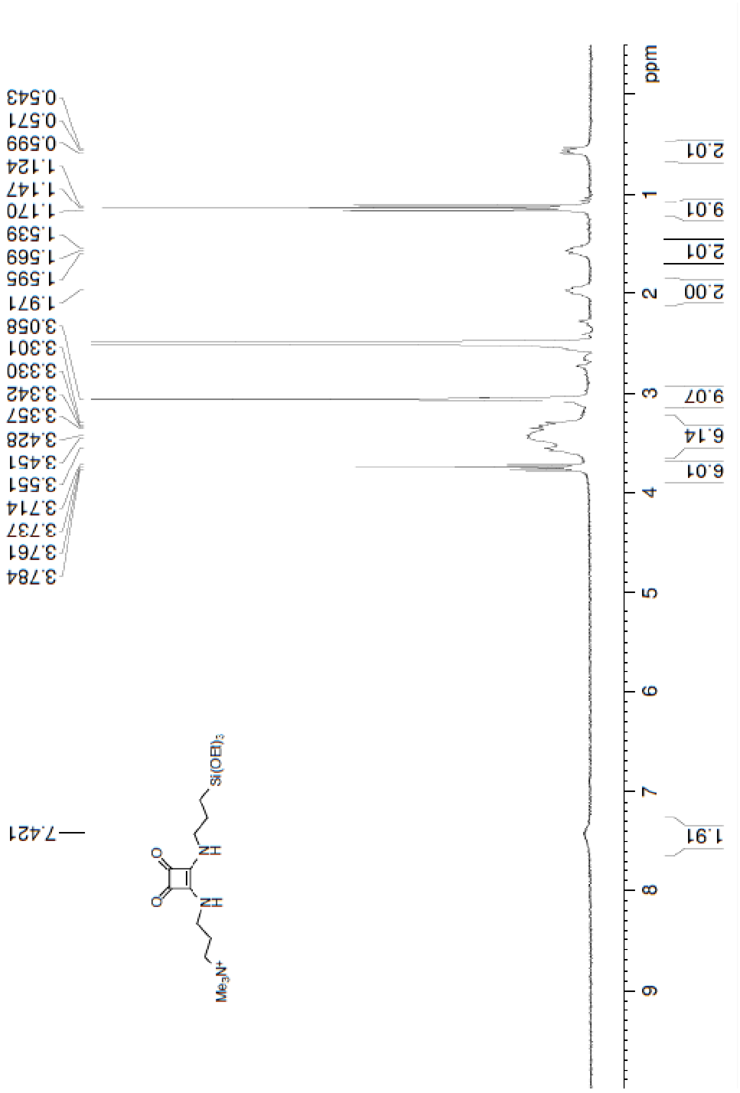
**Scheme 1**

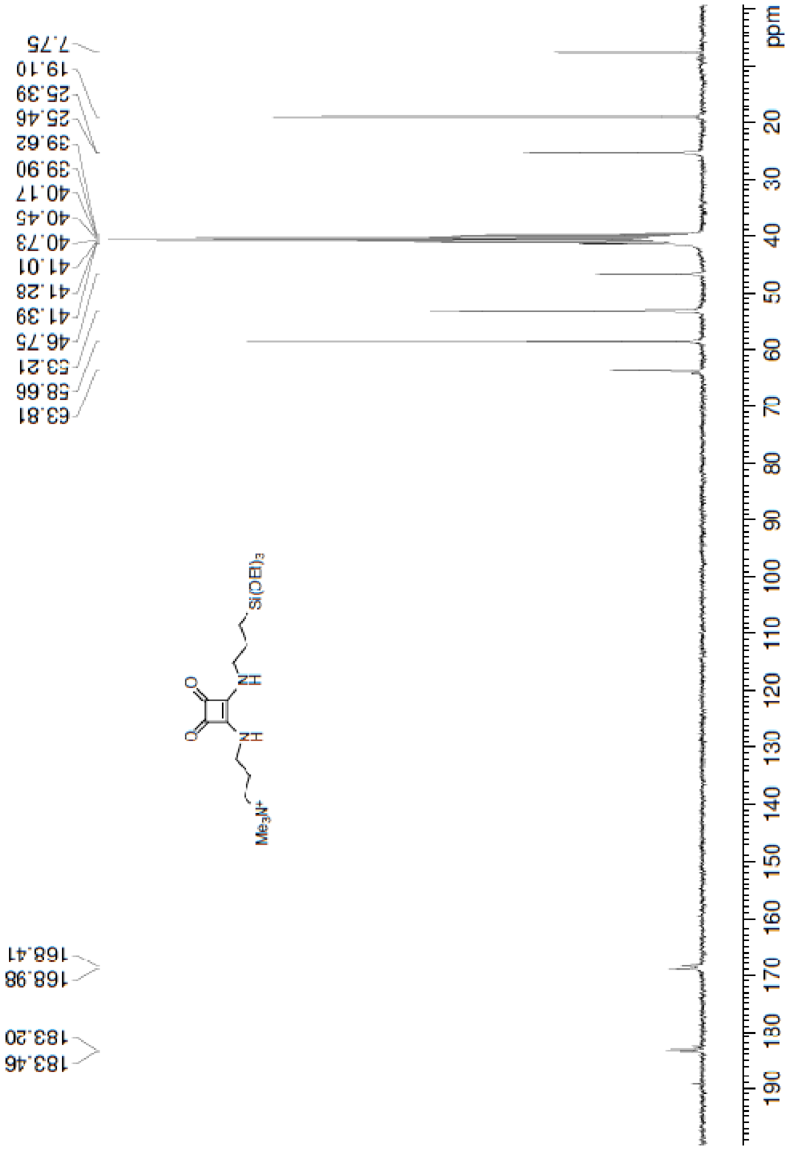
The organic squaramide portion of the particle was synthesized according to Scheme 1 fromdiethyl squarate.

**Synthesis of 3-((3,4-dioxo-2-((3-(triethoxysilyl)propyl)amino)cyclobut-1-en-1-yl)amino)-N,N,N-trimethylpropan-1-aminium iodide. (Sq)**

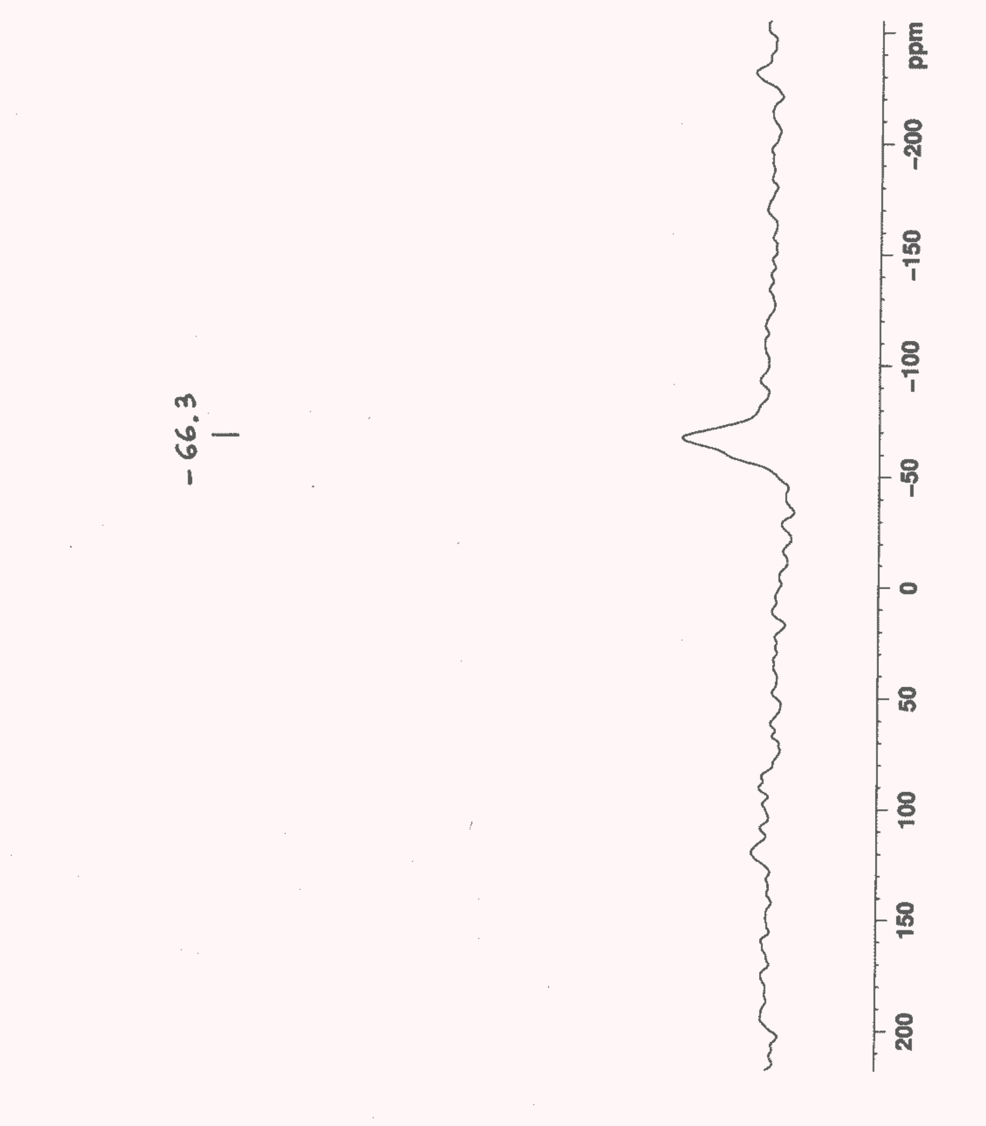
500 mg (1.35 mmol) of squaramide-ester**2** were dissolved in ethanol (75 mL). To this solution, 296 mg (1.4 mmol) of 3-(triethoxysilyl)propan-1-amine in ethanol (2 mL) were added. The reaction was left to stand for 12 h at room temperature. Then, the solvent was removed; the residue washed with n-pentane (3 x10 ml) and dried affording 611 mg (1.12 mmol) of **Sq** as a white solid. Yield 82 %. $\nu_{max}$ (KBr)/cm$^{-1}$: 3445, 2974, 1804, and1597; $\delta_H$ (300 Mhz; DMSO-$d_6$) 7.42 (br 2× NH), 3.74 (q, $J$ = 7.2 Hz, 6H), 3.55(m, 2H), 3.42 (m,4H), 3.05 (s, 9H), 1.97 (m, 2H), 1.57 (m, 2 H), 1.15 (t, $J$ = 7.1 Hz, 9H); 0.57 (m, 2H);$\delta_C$ (75 Mhz; DMSO-$d_6$) 183.46, 183.20, 168.98, 168.41, 63.81, 58.66, 53.21, 46.75, 41.39, 25.46, 25.39, 19,10, 7.75 ppm; m/z HRMS-ESI (+) 416.2599[M– I]$^+$, $C_{12}H_{21}N_2O_3$ requires 416.2594.

**The anchoring of the sensor** to the surface of the nanoparticles has been achieved by direct condensation of the OH groups located all around the surface of the boehmite particles,and the hydrolysable alkyl groups bonded to the silicon atom attached to the squaramide moiety. **Sq** (0.232g, 0.5 mmol) was dissolved in the minimum quantity of water and added dropwise to an ethanolic suspension of boehmite nanoparticles (1 g) placed in a round bottom flask. After 1 day stirring at rt, the obtained white solid wasseparated by centrifugation. Then, the solid was repeatedly washed with ethanol, and a mixture of ethanol:water (60:30) being collected in everystep by centrifugation. From elemental analysis 0.5048 mmol.g$^{-1}$ of **Sq** was determined. The same synthetic route was followed in the modification of core-shell nanoparticles. In this case and due to the amorphous behavior of silica shell, the quantity of **Sq** molecules attached to the nanoparticles decreases until 0.1595 mmol.g$^{-1}$.

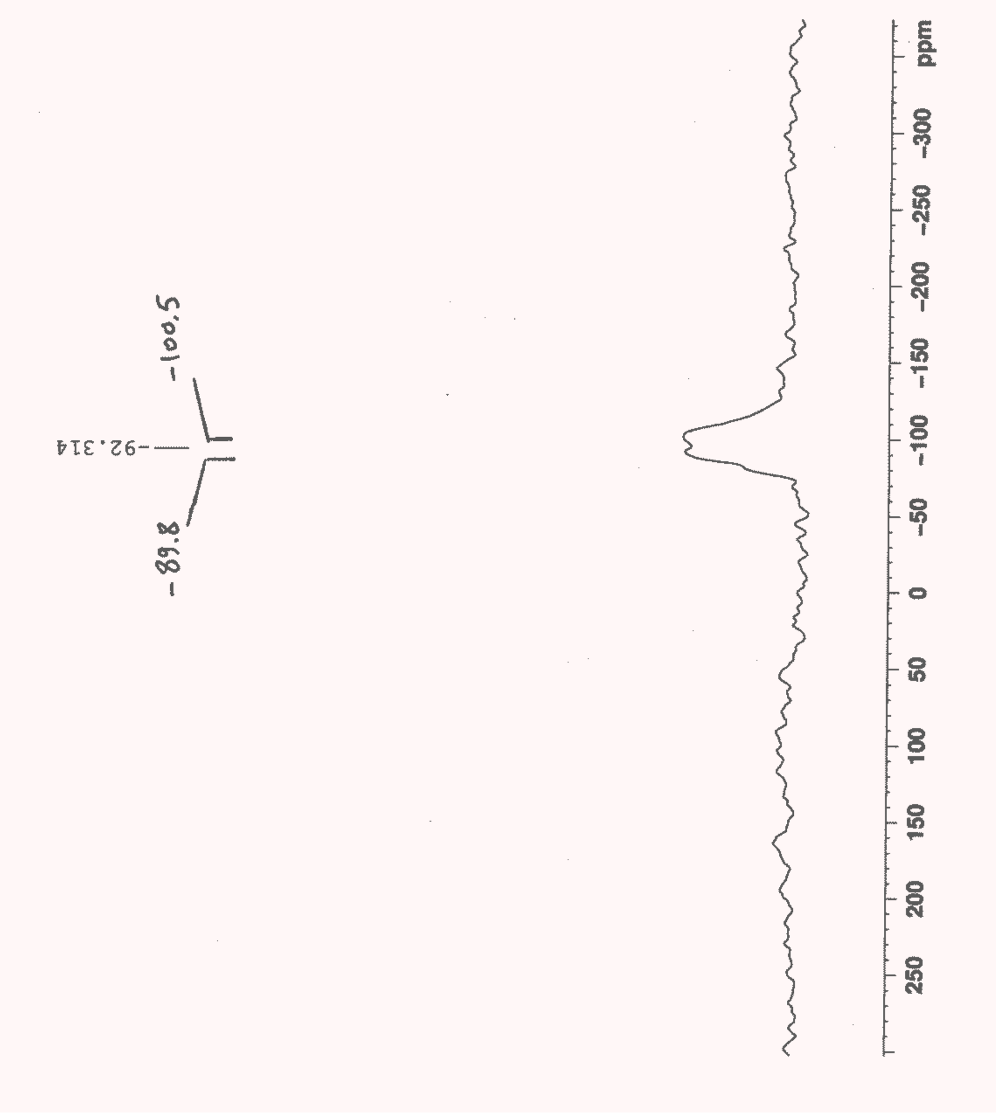

0.543
0.571
0.599
1.124
1.147
1.170
1.539
1.569
1.595
1.971
3.058
3.301
3.330
3.342
3.357
3.428
3.451
3.551
3.714
3.737
3.761
3.784
7.421
O
O
N H
N H
Si(OEt)3
Me3N+
ppm
1
2
3
4
5
6
7
8
9
2.01
9.01
2.01
2.00
9.07
6.14
6.01
1.91


7.75
19.10
25.39
25.46
39.62
39.90
40.17
40.45
40.73
41.01
41.28
41.39
46.75
53.21
58.66
63.81
168.41
168.98
183.20
183.46
Si(OEt)3
NH
O
O
NH
Me3N+
ppm
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190

$^{29}$Si NMR for BSq hybrid system



$^{29}$Si NMR for MSq hybrid system



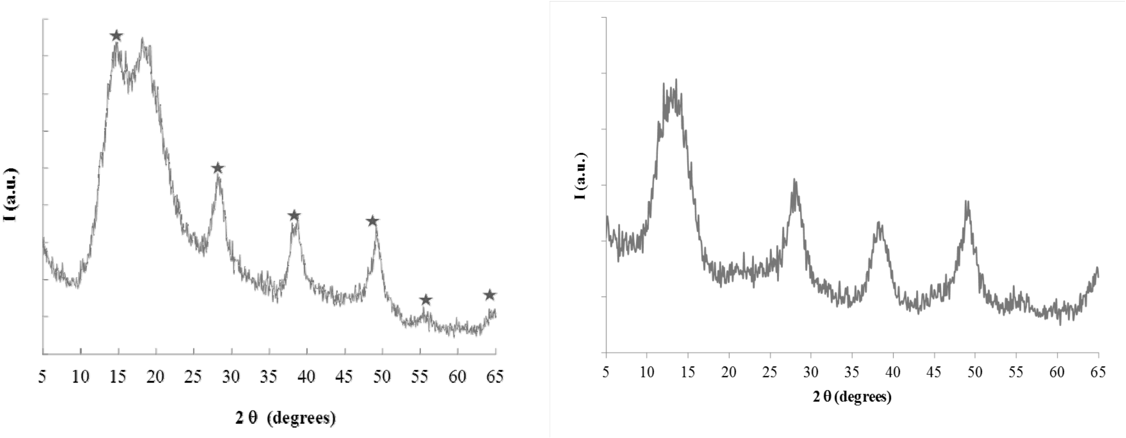


**Figure 1S.-**X-ray powder diffraction pattern of MSq (left) and BSq (right).

BSq presents peaks at 13.71, 28.31, 38.41, 49.21 and 64.81 2θ which are characteristic of the boehmite structure and confirms that the matrix has not been disrupted throughout the synthetic procedure. In MSq system the second component silica is amorphous silica as evidenced by the absence of peaks in the RX spectrum.

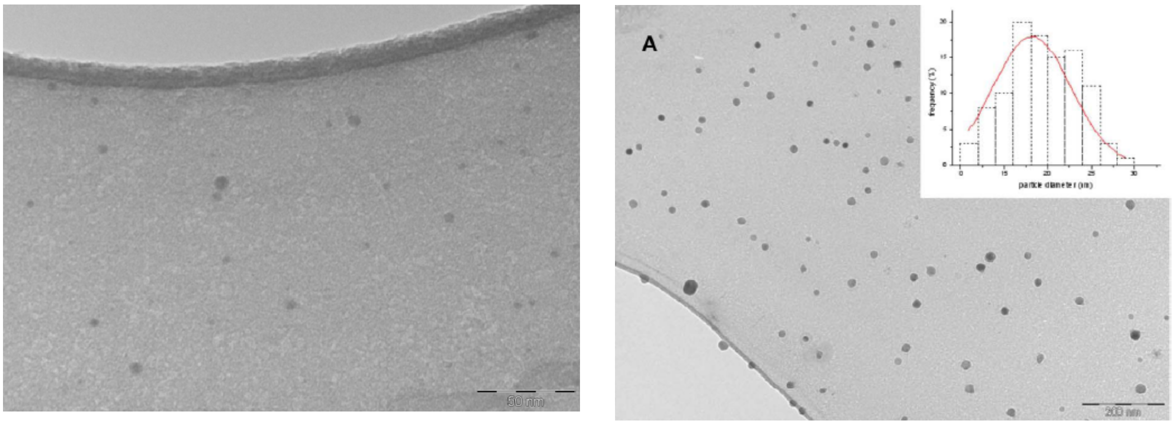


**Figure 2S.-**TEM image of MSq hybrid system. Inset shows size distribution of the nanoparticles (left) and BSq (right).

### UV-Vis titrations

All titrations were performed at 25 ºC in pure water and recorded on Agilent 8453 spectroscopy system. Bromocresol green ($1.48x10^{-5}$ M) was prepared in an acetic buffer (0.016 M). These conditions were used for the titrations of both systems **BSq** and **MSq**, and also for the indicator displacement assays (IDA) with the anions. The solution was buffered at pH 3.4 with an HAc-NaAc buffer. This pH value was chosen to keep the solution close to the beginning of the colour change transition from the acidic (phenolic) to the basic (phenolate) form of BG. The constancy of the pH throughout the titrations was checked for all the experiments.

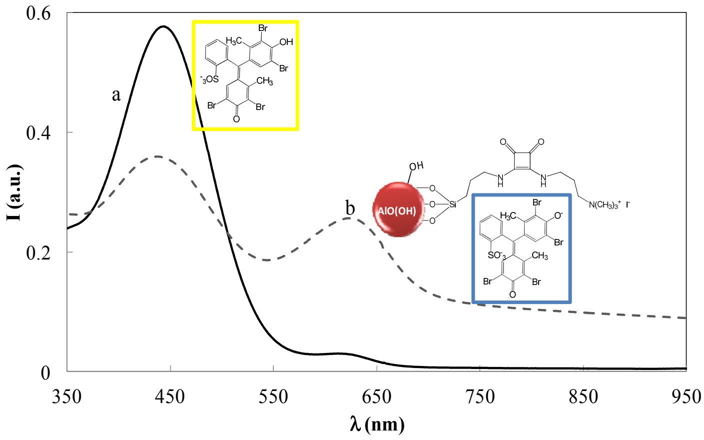


**Figure 3S.-**UV-vis spectra of a solution of Bromocresol green ($1.48x10^{-5}$ M) (a) before and (b) after the addition of hybrid B-Sq at 25ºC.

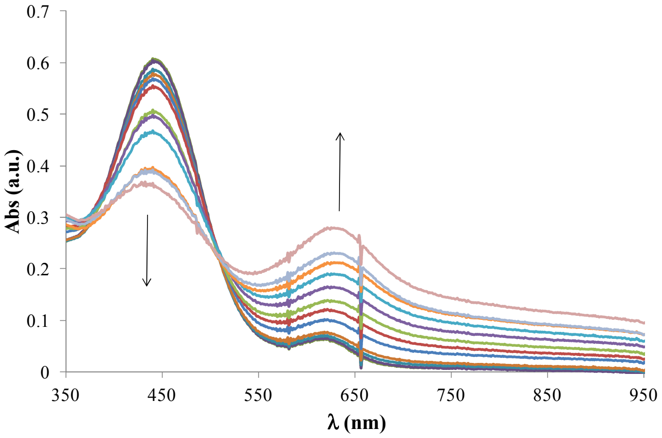


**Figure 4S.-**UV/VIS spectra resulting from the addition of MSq to a BG aqueous solution at pH =3.4.

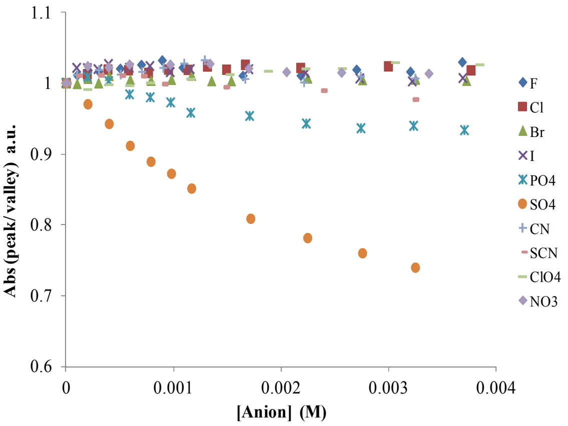


**Figure 5S.-**Changes in the absorption spectrum BG-MSq system upon addition of different anions. BG(1.48x10$^{-5}$ M).

**Table 1S.-**Protonation constants of the different acids used in this work.

| | Malo | Mal | Cit | 1,2,3-BTC | 1,2,4-BTC | $PO_4^{3-}$ | $SO_4^{2-}$ |
|---|---|---|---|---|---|---|---|
| H+ A = HA | 5.36[a] | 5.86[a] | 5.44[b] | 5.40[b] | 5.51[c] | 11.74[a] | 1.55[a] |
| H + HA = $H_2A$ | 2.52 | 1.71 | 4.17 | 3.90 | 4.06 | 6.71 | |
| H + $H_2A$ = $H_3A$ | | | 2.74 | 2.65 | 2.76 | 1.92 | |

a) Taken from A. E. Martell, R. M. Motekaitis, NIST Critically Selected Stability Constants of Metal Complexes Database, NIST Standard Reference Database Version 4, 1997.

b) A. Bencini, A. Bianchi, M. I. Burguete, E. García-España, S. V. Luis and J. A. Ramirez, J. Am. Chem. Soc., 1992, 114, 1919-1920.

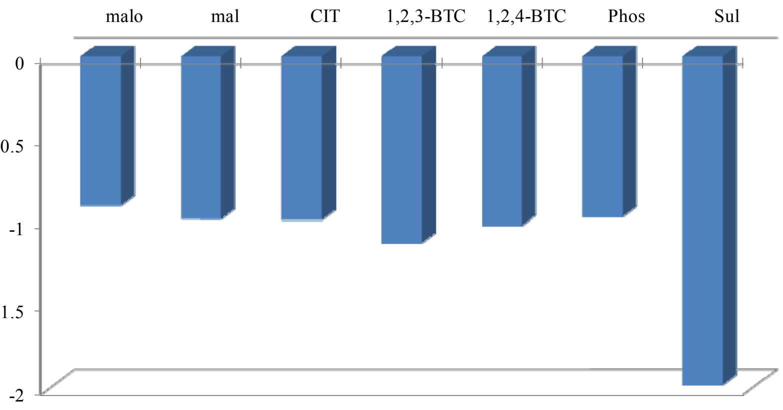
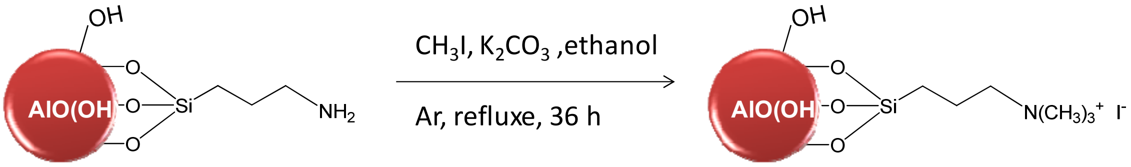


**Fig 6S.-** Actual net charge at pH 3.4 of the different anions used.

## Preparation of nanoparticles containing just quaternised amino groups.

Boehmite nanoparticles were synthetised with a quaternary nitrogen at its surface [3] The synthesis was carried out as is shown in the next scheme. A mixture of aminopropylsilyl boehmite nanoparticles, MeI and $K_2CO_3$ in acetonitrile was refluxed with stirring at 90ºC for 36 hours. Then, several cleanings in dicloromethane were performed by centrifugation. Finally, a ninhidrin solution was used to check the completeness of the reaction.



To test the viability of this new system, we repeated the titration depicted in figure 4S with the quaternised ammonium salt on the nanoparticles ($BN^+$). As is shown below, only the squaramide nanoparticles (BSq) are able to shift the indicator from the acidic (yellow colour) to the basic form (blue colour) while either boehmite nanoparticles (BSq) or quaternised ammonium boehmite do not produce such a change.

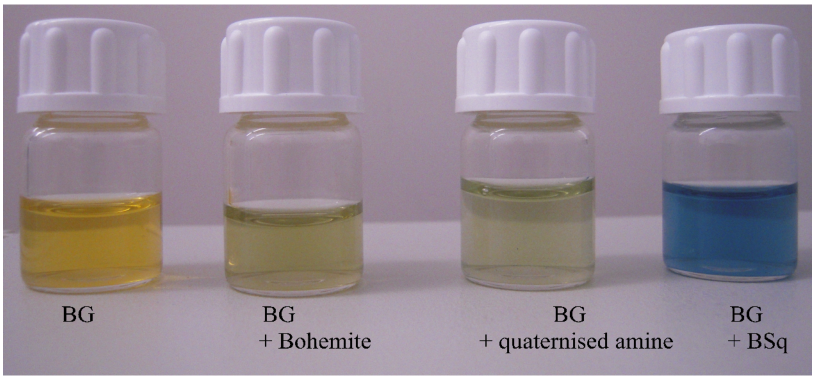


**Fig 7S.-** From left to right: BG solution, addition of boehmite, quaternised boehmite ($BN^+$) and BSq to a BG aqueous solution at pH =3.4.

---

[1] R. Aucejo, P. Díaz, E. García-España, J. Alarcón, E. Delgado-Pinar, F. Torres, C. Soriano and M. C. Guillem, *New J. Chem.*, 2007, **31**, 44–51.

[2] E. Delgado-Pinar, N. Montoya, M. Galiana, M. T. Albelda, J. C. Frías, H. R. Jiménez, E. García-España and J. Alarcón, *New J. Chem.*, 2010, **34**, 567–570.

[3] J. F. W. Keana, Y. Wu andG. Wu, *J. Org. Chem.*, 1987, **52**, 2571-2576.