Supplementary Information

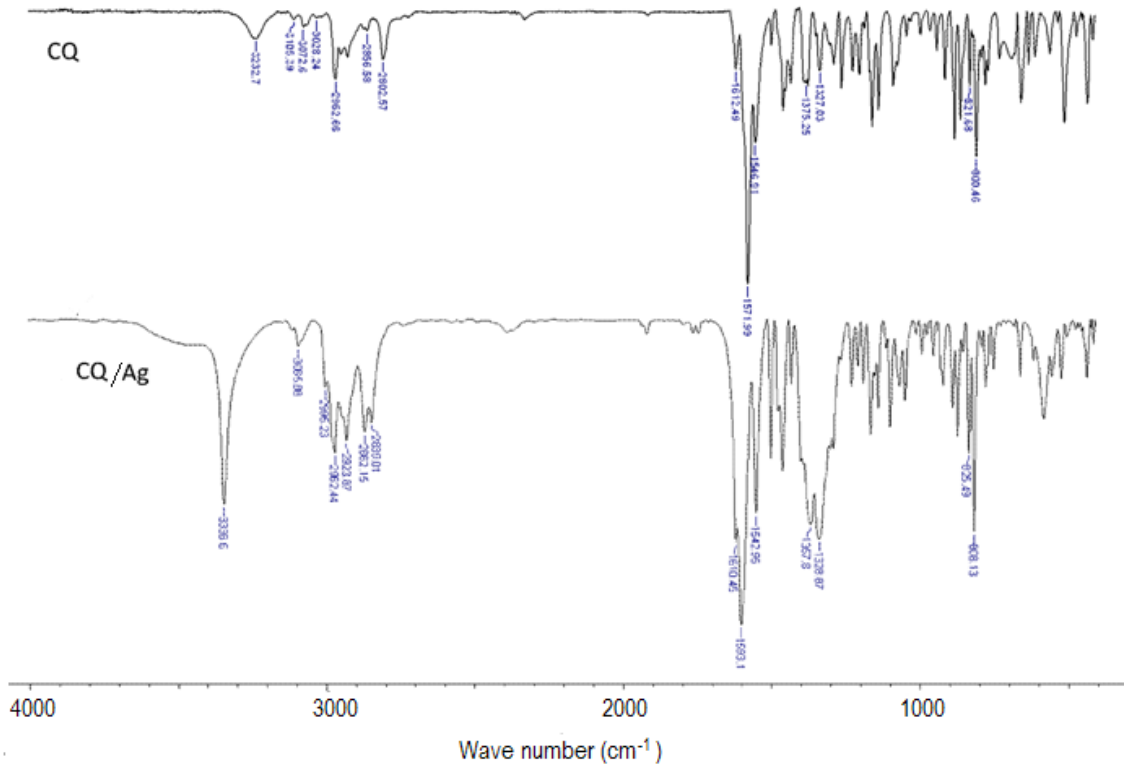
Silver complex of chloroquine: synthesis, characterization and structural properties.

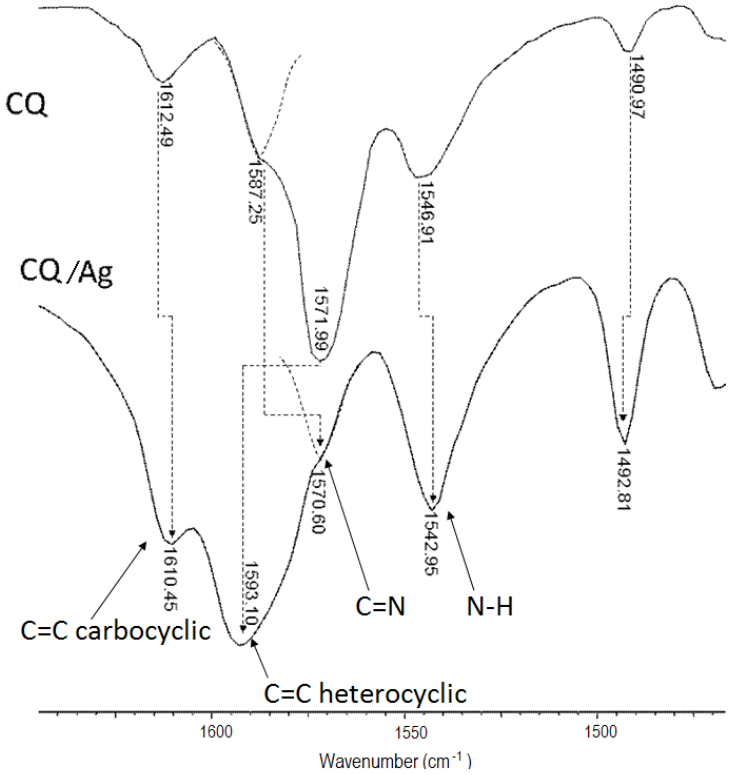
Juan Z. Dávalos, Javier González, Andrés Guerrero, Ana C. Valderrama-Negrón, Larry D. Aguirre Méndez, Rosa M. Claramunt, Dolores Santa María, Ibon Alkorta, and José Elguero

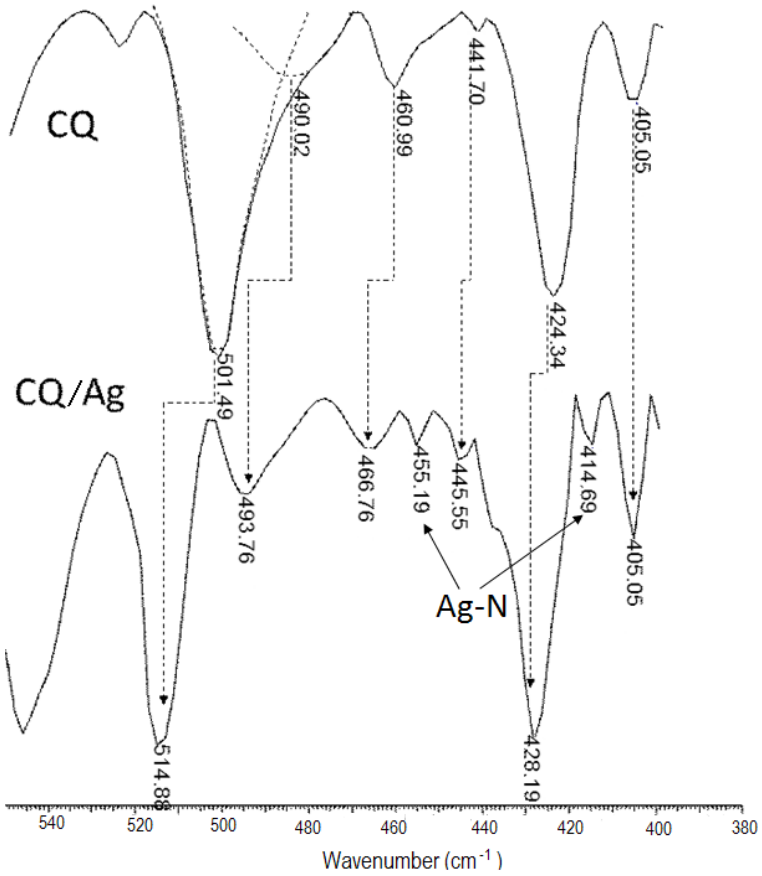
Contribution from: Instituto de Química Física Rocasolano, CSIC. C/Serrano, 119. E-28006 Madrid, Spain. Facultad de Ciencias, Universidad Nacional de Ingeniería, Av Túpac Amaru 210, PE-LIMA025, Lima, Perú. Departamento de Química Orgánica y Bio-Orgánica, Facultad de Ciencias, UNED, Senda del Rey 9, E-28040 Madrid, Spain. Instituto de Química Médica, CSIC, C/Juan de la Cierva, 3. E-28006 Madrid, Spain.

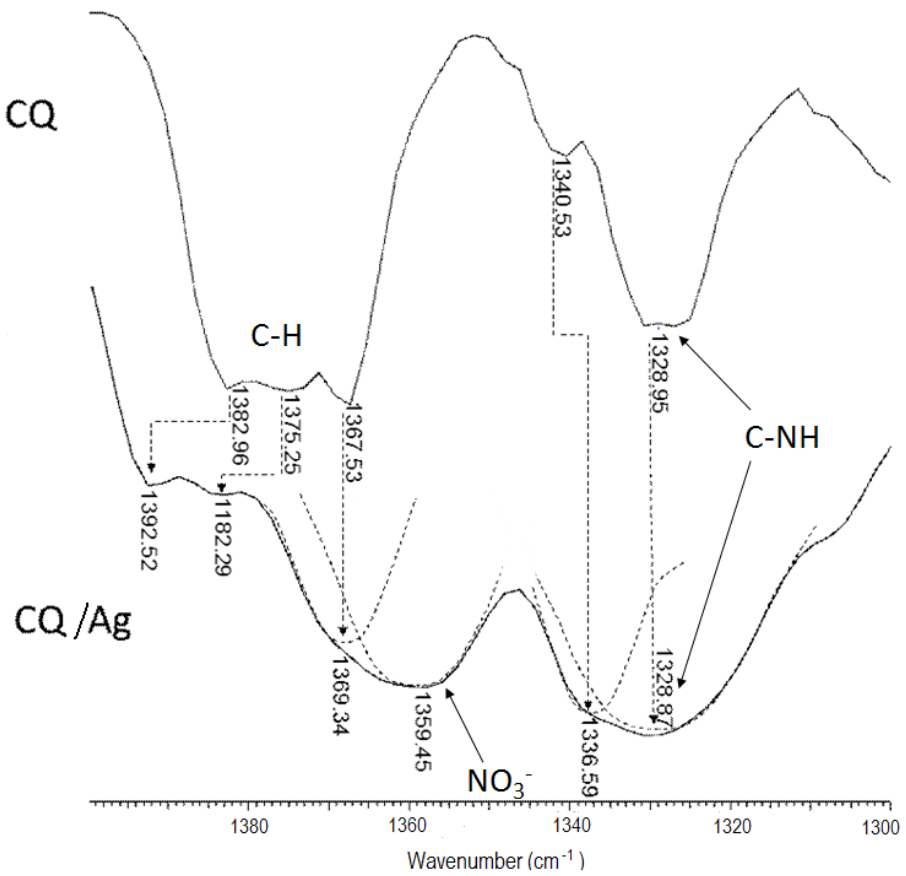
Topics

S1. Comparative FTIR spectra of CQ and CQ/Ag complex

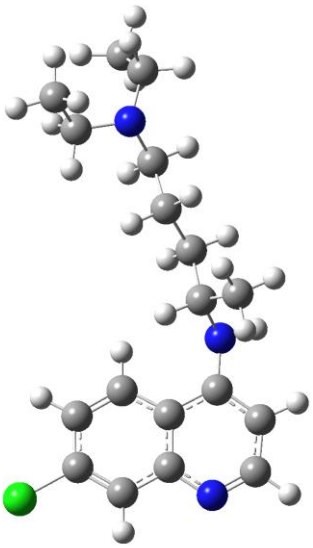






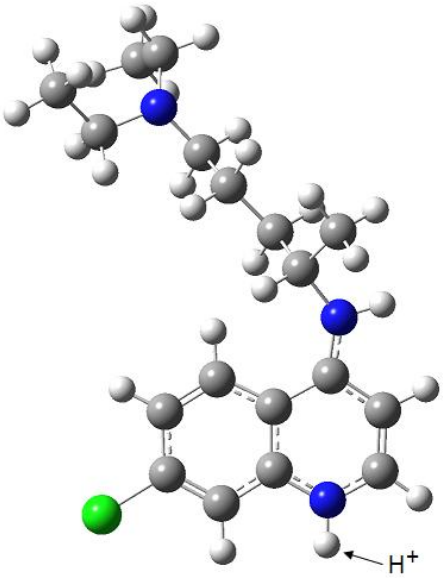


S2. Computational results: Structures optimized at B3LYP/6-31G(d)/LANL2DZ ECP level. Interatomic distances in Å.



CQ

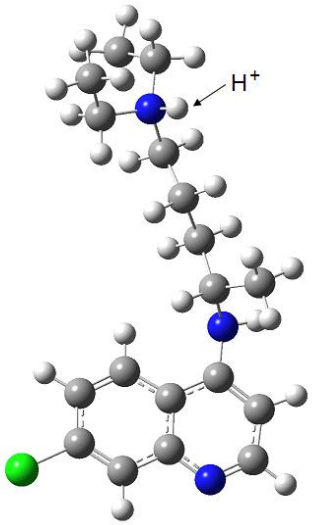
Protonated chloroquines



CQH^+[1]: protonated on N sp^2

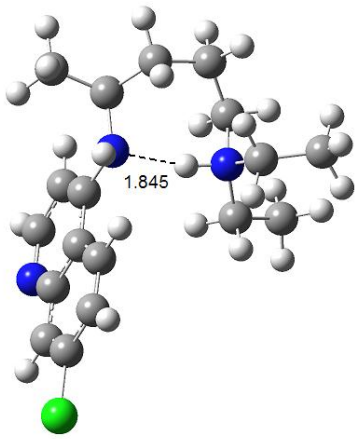
PA= 1017.8 $kJ \cdot mol^{-1}$

Protonated on N sp^3:



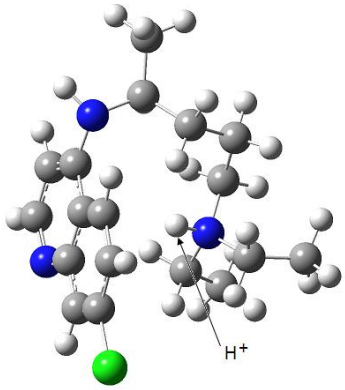
CQH^+[2a]

PA= 975.0 kJ·mol^{-1}



CQH^+[2b]

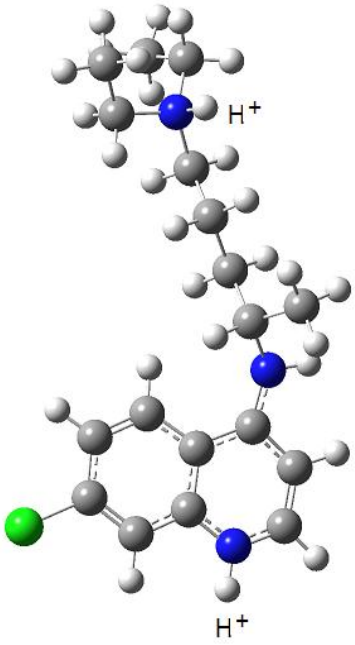
PA= 1009.8 kJ·mol^{-1}



CQH^+[2c]

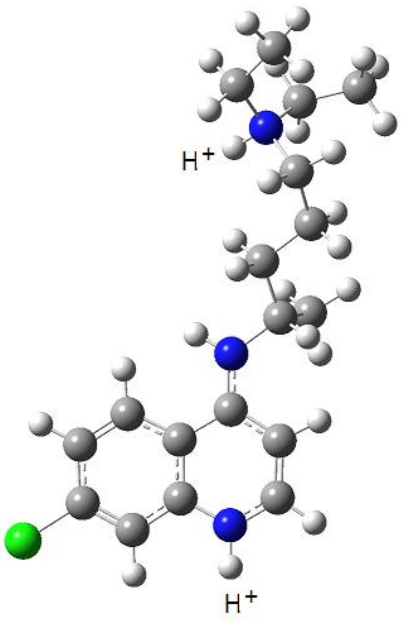
PA= 968.0 kJ·mol^{-1}

Diprotonated chloroquines



CQH_2^{2+}[a]

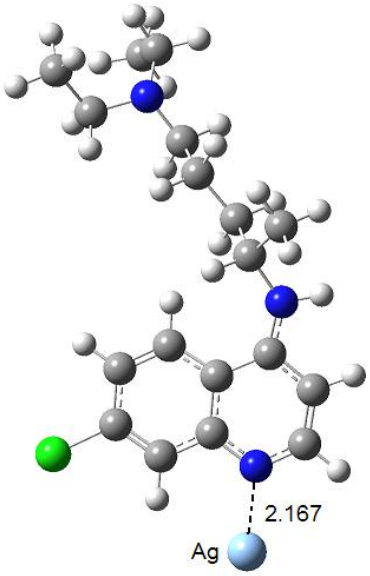
$\Delta_r H^0$ = 795.4 kJ·mol^{-1}



CQH_2^{2+}[b]

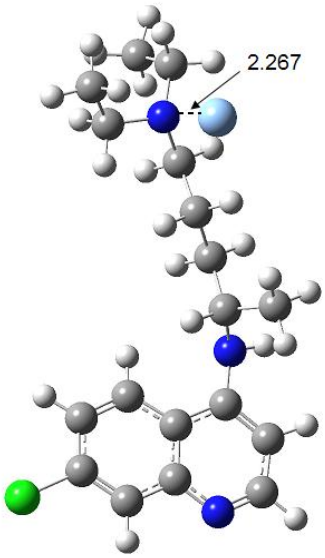
$\Delta_r H^0$ = 797.4 kJ·mol^{-1}

CQAg$^+$ cations



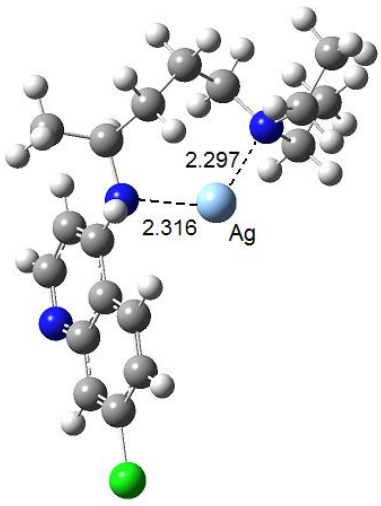
CQAg$^+$[1]

$\Delta_r H^0 = 207.6$ kJ·mol^{-1}



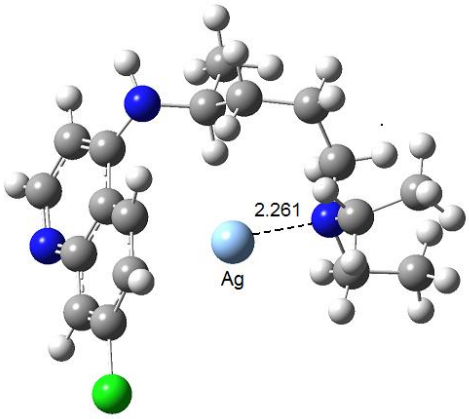
CQAg$^+$[2a]

$\Delta_r H^0 = 168.5$ kJ·mol^{-1}



CQAg$^+$[2b]

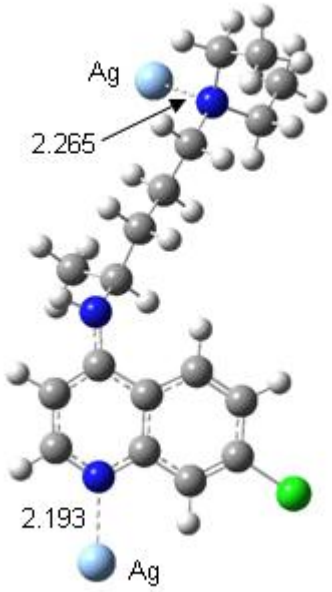
$\Delta_r H^0 = 228.9$ kJ·mol^{-1}



CQAg$^+$[2c]

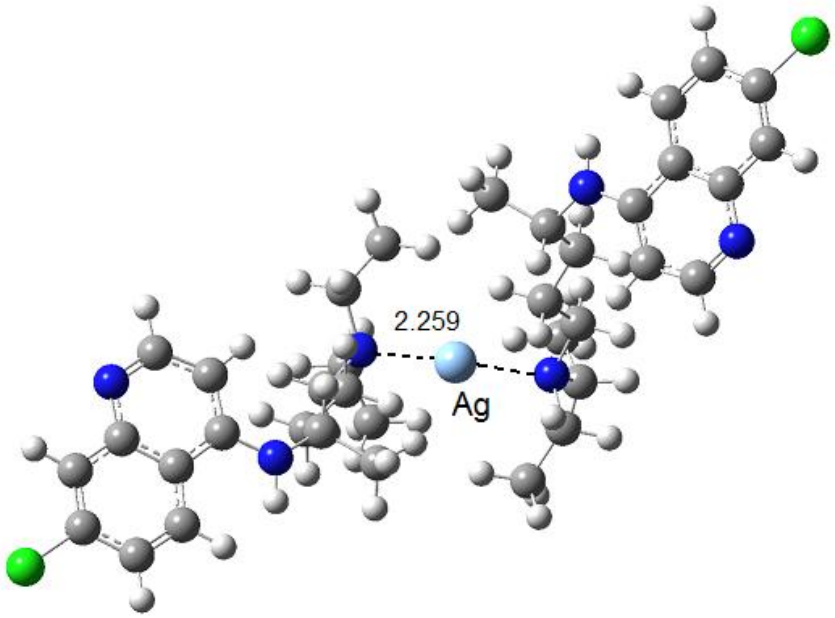
$\Delta_r H^0 = 229.5$ kJ·mol^{-1}

$CQAg_2^{2+}$ dication



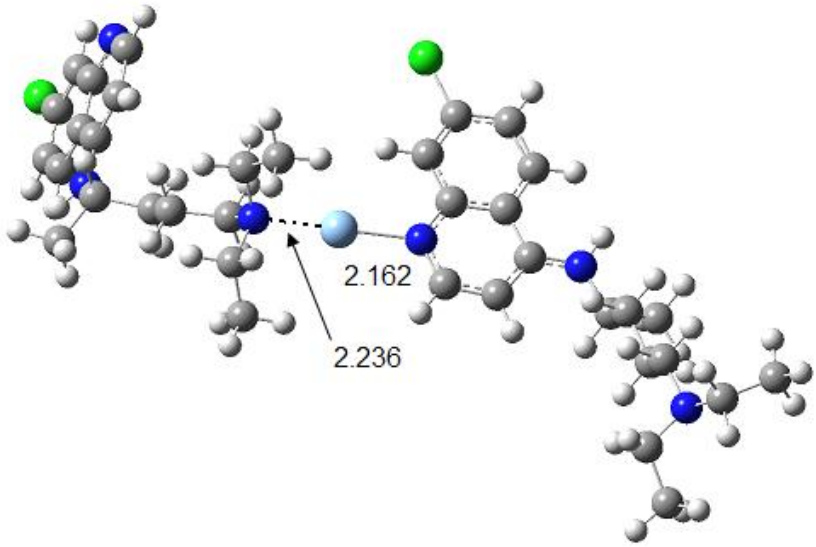
$\Delta_r H^0 = 49.2\ \text{kJ}\cdot\text{mol}^{-1}$

CQ_2Ag^+ cations



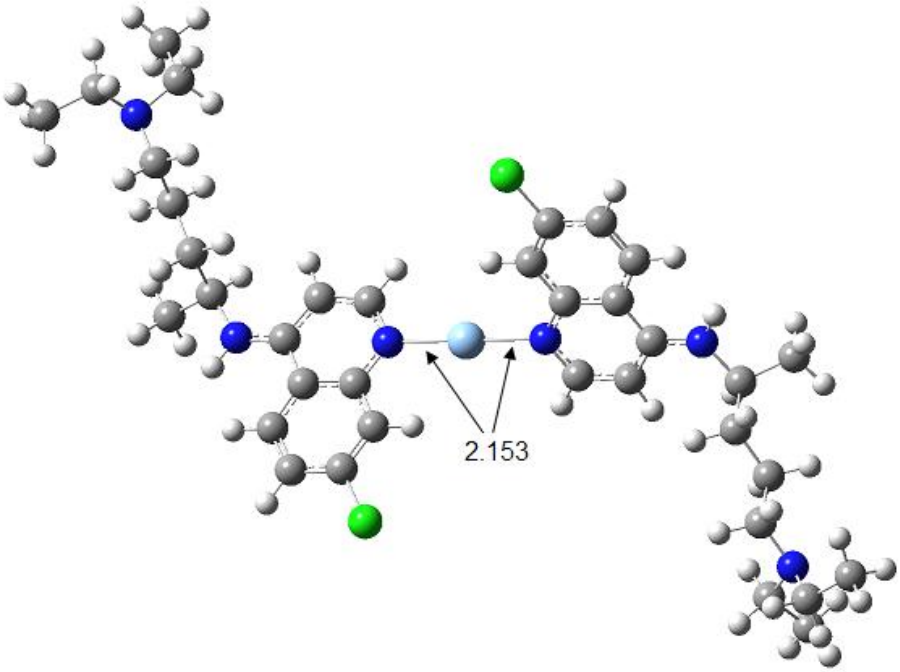
CQ_2Ag^+ "tail-tail" (N sp^3–Ag–N sp^3 bonds),

$\Delta_r H^0 = 307.2\ \text{kJ}\cdot\text{mol}^{-1}$



CQ_2Ag^+ "head-tail" (N sp^2–Ag–N sp^3 bonds),

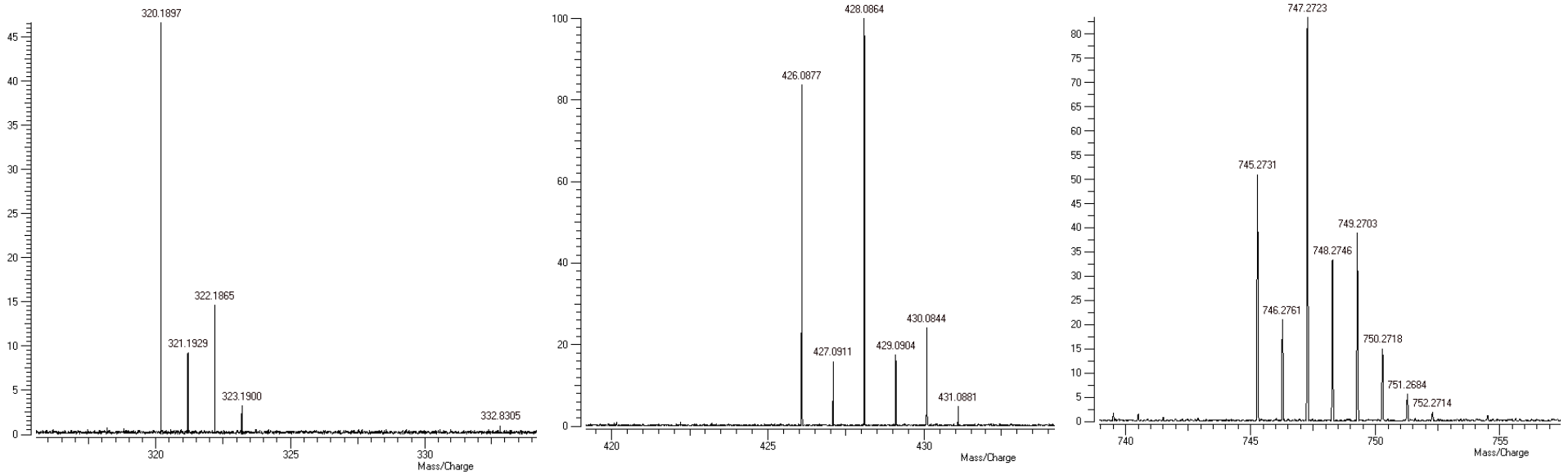
$\Delta_r H^0 = 356.5$ kJ·mol^{-1}



CQ_2Ag^+ "head-head" (N sp^2–Ag–N sp^2 bonds),

$\Delta_r H^0 = 407.1$ kJ·mol^{-1}

S3. ESI/FT-ICR Mass Spectrometry



(a) **CQH$^+$** (b) **CQAg$^+$** (c) **CQAgCQ$^+$**

Figure S4a. ESI/FT-ICR spectrum of isolated cations of **CQ**/Ag complex, solved in DMSO (100 μg/mL), showing their isotopic mass distribution

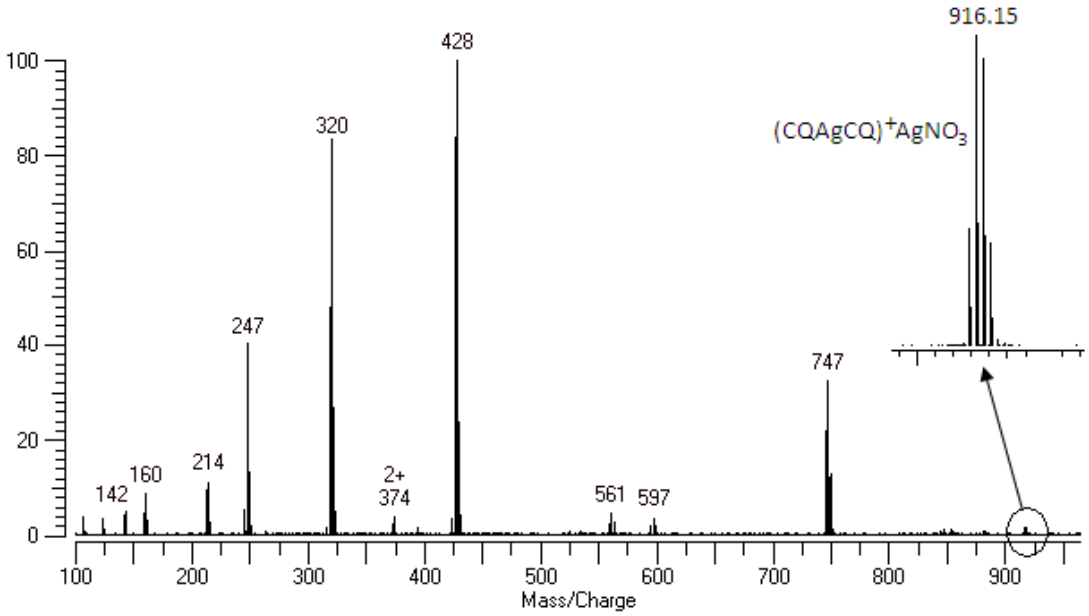


Figure S4b. ESI/FT-ICR spectrum of **CQ**/Ag complex, solved in DMSO:ACN (4:96, 100 μg/mL).