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Electronic Supplementary Information

Dual role of silver in a fluorogenic N-squaraine probe based on Ag(I)-π interactions

Manel Vega,[†] Salvador Blasco,[‡] Enrique García-España,[‡] Bartolomé Soberats,[†] Antonio Frontera,[†]
Carmen Rotger[†] and Antonio Costa[†,*]

[†] *Department of Chemistry, Universitat de les Illes Balears, Ctra. Valldemossa km 7.5, 07122, Palma (Spain)*

[‡] *Instituto de Ciencia Molecular (ICMOL). Universidad de Valencia, C/ Catedrático José Beltrán 2, 46980 Valencia (Spain)*

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1. Reagents and apparatus

All chemicals were obtained from commercial sources and used without further purification unless otherwise indicated. All reactions were performed in a single-mode Biotage Initiator microwave reactor according to the parameters described below.

NMR spectroscopy: Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear resonance (^{13}C NMR) were recorded at room temperature on a Bruker Avance and Bruker Avance III spectrometers operating at 300 and 600 MHz for ^{1}H and at 75.4 and 150.9 MHz for 13-carbon, respectively. The residual proton signal in the NMR solvent was used as reference (DMSO: δ 2.50 ppm, for proton, and δ 39.51 ppm, respectively for 13-carbon) unless specifically stated otherwise. Chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. Multiplicities for proton signals are abbreviated as s, t, m, and br for singlet, triplet, multiplet, and broad signal, respectively. ^{13}C-*CP-MAS NMR* were obtained with 4 mm ZrO_2 MAS rotors on a Bruker SB-MAS probe head.

Mass Spectrometry: High-resolution mass spectra (HRMS) were recorded on a Thermo Scientific Orbitrap Q-Exactive mass spectrometer equipped with a heated electrospray module (HESI-HRMS).

Absorbance (UV-Vis) spectroscopy: UV/Vis absorption spectra were recorded on Cary 60, Cary 300 UV-Vis-NIR or, JASCO V-750 spectrophotometers. JASCO V-750 was equipped with a Peltier thermostated cell holder device temperature-control unit ($\Delta T = \pm 0.05$ °C).

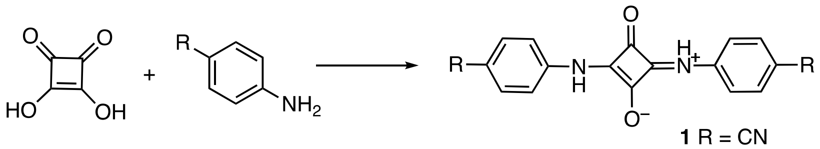
Fluorescence spectroscopy and Quantum Yield: fluorescence excitation-emission spectra were recorded on a Cary Eclypse spectrophotometer. The measurements were carried out in 1 cm quartz glass cuvettes using spectroscopic grade solvents. Slit widths were set to 5 mm bandpass for both excitation and emission. All spectra were recorded at 25 ± 1 °C. Solutions of N-squaraines were prepared in DMF or DMF-H_2O mixtures of variable composition, as indicated in the text. The solutions were allowed to stand for 5 min before obtaining absorption and emission spectra. The quantum yield for Ag_2(SQ**1**) was obtained by comparison of the integrated area of the emission spectrum of the sample with that of fluorescein in 0.1 N NaOH, which has a quantum efficiency of 0.925.[1] The quantum efficiency of Ag_2(SQ**1**) was evaluated by registering the UV-vis and emission spectra of diluted samples prepared from squaraine **1** (~ 1.273×10^{-6} M, Abs < 0.1) in DMF containing 0.4 mM $AgNO_3$ and 2% v/v of an aqueous solution 0.1 M of NaOAc. Emission for Ag_2(SQ**1**) was integrated from 500 to 650 nm with excitation at 490 nm. Refractive indexes: 1.33 for water and 1.428 for DMF. All measurements were made in triplicate and averaged. The quantum yield was evaluated with the expression in eq. 1.

$$\Phi_F = \Phi_{ref}\left(\frac{I_F}{I_{ref}}\right)\left(\frac{A_{ref}}{A_F}\right)\left(\frac{\eta_F^2}{\eta_{ref}^2}\right) \qquad \text{Eq. 1}$$

Φ_F; $\Phi_{ref.}$, fluorescence quantum yield of sample and reference. I_F; I_{ref}: Integrated fluorescence intensity. (area under spectrum). η_F; η_{ref}: Refractive index.

Infrared spectroscopy: FT-IR spectra were obtained on Bruker FT-IR Tensor 27 on KBr pellets. Spectral features are tabulated as follows: wavenumb[1]r (cm^{-1}); intensity: strong (s), medium (m), weak (w).

2. Synthesis and characterization



1 R = CN
2 R = OMe

2-((4-cyanophenyl)amino)-4-((4-cyanophenyl)iminio)-3-oxocyclobut-1-en-1-olate. (**N-squaraine 1**; R = CN).

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[1] A. M. Brouwer, *Pure Appl. Chem.* 2011, **83**, 2213–2228.

A mixture of 4-aminobenzonitrile (142 mg, 1.2 mmol) and squaric acid (57 mg, 0.5 mmol) in water (1.5 mL) were microwave heated at 120 °C for 1 h in a closed 0.5-2 mL vials. After cooling, the slurry was filtered and the solid washed sequentially with HCl (1N) solution (3 × 10 mL), ethyl acetate-DMSO (10% v/v) (3 × 10 mL), and ethyl acetate (3 × 10 mL). The remaining solid N-squaraine was dried at 100 °C for 1h to give N-squaraine **1** (150 mg, 95 % yield). M.p. > 300 °C. ^{1}H NMR (*d$_6$*-DMSO) δ_{H} 12.04 (s, 2H), 7.99 (d, *J* = 8.4 Hz, 4H), 7.89 (d, *J* = 8.4 Hz, 4H) ppm. ^{13}C CP-MAS NMR δ_{C} 173.8, 169.3, 138.7, 135.78, 119.3, 117.8, 112.0 ppm. IR(KBr) ν 3235(m), 3062(m), 2980(m), 2236(m), 1596(s), 1537(s), 1417(s), 1385(s) cm^{-1}. ESI(−)-HRMS *m/z* (%) calcd for $C_{18}H_{9}N_{4}O_{2}$: [M–H]$^{-}$ 313.0731; found 313.0732. Anal Calcd for $C_{18}H_{10}N_{4}O_{2}$: C, 68.79; H, 3.21; N, 17.83; found: C, 68.54; H, 3.31; N, 17.68.

[TBA(HSQ**1**)] Crystals suitable for X-ray diffraction analysis of N-squaraine **1** (as TBA salt) were grown by slow evaporation from a MeOH solution containing N-squaraine **1** and excess TBAF until complete dissolution of the N-squaraine.

[TMA(HSQ**1**)] Used for comparison in the ^{13}C CP MAS spectrum, was prepared from a mixture of N-squaraine **1** (100 mg) and two equiv of (TMA)OAc suspended in MeCN (10 mL). After sonication in an ultrasonic bath for several minutes, the solvent was evaporated to dryness.

[Ag(HSQ**1**)]·2H$_2$O A mixture of N-squaraine **1** (100 mg) and two equiv of (TMA)OAc in MeCN was dissolved by sonication as above. Then, a solution of $AgNO_3$ (1 equiv) in MeCN (2 mL) was added and left with continuous agitation until complete precipitation. After an additional one-hour period for aging, the resulting dark green precipitate was filtered, washed with MeCN (2 x 5 mL), and dried to afford amorphous [Ag(HSQ**1**)] (112 mg) as a dihydrate. ^{1}H NMR (*d$_6$*-DMSO) δ_{H} 9.92 (br, 1H), 7.78 (d, *J* = 8.1 Hz, 2H), 7.63 (br, 4H)), 7.48 (br, 2H) ppm. ^{13}C CP-MAS NMR δ_{C} 184.2, 176.4, 169.5, 166.0, 152.1, 145.5, 130.6, 1234.5, 119.4, 102.0, 99.6 ppm. Anal Calcd for $C_{18}H_{13}AgN_{4}O_{4}$: C, 47.29; H, 2.87; N, 12.25; found: C, 47.24; H, 2.82; N, 12.26.

The ^{13}C CP-MAS spectra of the TMA and Ag salts of N-squaraine **1**, show the loss of symmetry characteristic of the N-squaraine **1** monoanion (see ^{13}C NMR spectra of these salts in Figure S3).

2-((4-methoxyphenyl)amino)-4-((4-methoxyphenyl)iminio)-3-oxocyclobut-1-en-1-olate. (N-squaraine 2; R = OMe). This compound was prepared.[1]starting from a mixture of squaric acid (0.5 g, 4.3 mmol) and *p*-Anisidine (1.7 g, 13.7 mmol) were introduced in a Schlenk flask tube. The mixture was disaggregated and homogenized well before closing the flask. Then, the mixture was heated at 120 ºC for 12 h in an oil bath. The resulting dark green solid was taken in HCl 1N (20 mL) and sonicated in a bath for 15 min. The mixture was filtered and the solid washed with HCl 1N (5 × 20 mL), ethyl acetate-DMSO (30% v/v) (5 × 20 mL) to remove a residue of the competitive squaramide, and ethyl acetate (5 × 10 mL) and dried at 100°C to afford a green amorphous solid (1.09 g, 90 % yield). mp > 300 °C. ^{1}H NMR (*d$_6$*-DMSO) δ_{H} 11.18 (s, 2H), 7.71 (br, 4H), 6.95 (d, *J* = 8.7 Hz, 4H), 3.75 (s, 6H ppm. ESI(−)-HRMS *m/z* (%) calcd for $C_{18}H_{15}O_{4}N_{2}$: [M–H]$^{-}$ 323.10367; found 323.10373. Anal Calcd for

$C_{18}H_{16}N_2O_4$: C, 66.66; H, 4.97; N, 8.64; found: C, 66.12; H, 4.96; N, 8.64. IR(KBr) *v* 3243(m), 3127(m), 3070(m), 2961(s), 2835(m), 1619-1512(s), 1429(s), 1183(s) cm^{-1}.

3. NMR spectra

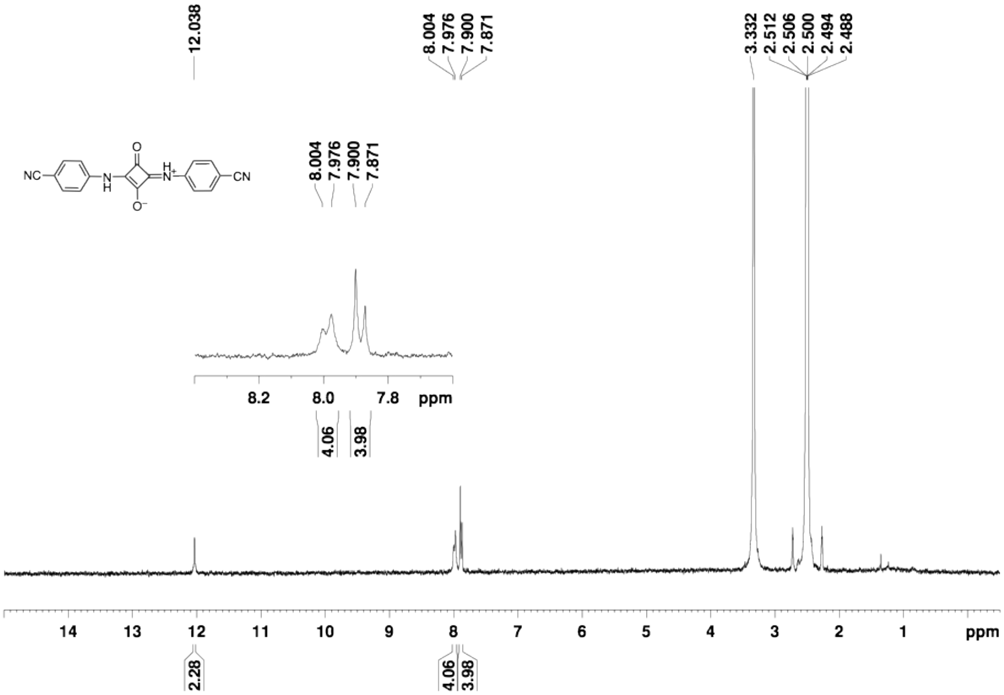
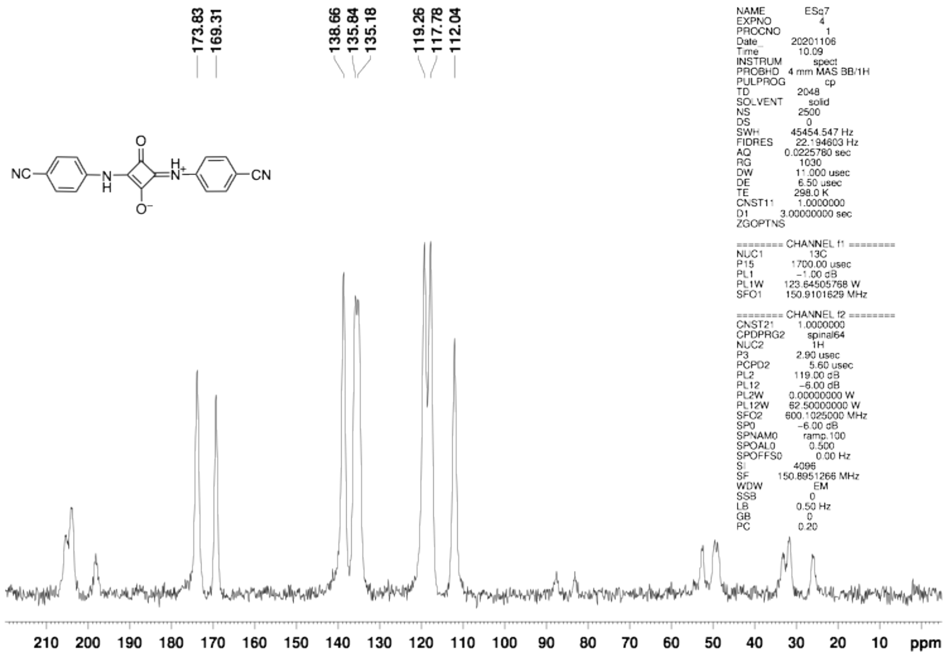


Figure S1. ^{1}H NMR spectrum of N-squaraine **1** (H2SQ**1**) in *d6*-DMSO



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PROCNO            1
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Time          10.09
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PULPROG          cp
TD             2048
SOLVENT       solid
NS             2500
DS                0
SWH      45454.547 Hz
FIDRES   22.194603 Hz
AQ      0.0225780 sec
RG             1030
DW        11.000 usec
DE          6.50 usec
TE          298.0 K
CNST11    1.0000000
D1     3.00000000 sec
ZGOPTNS

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NUC1            13C
P15       1700.00 usec
PL1         -1.00 dB
PL1W   123.64505768 W
SFO1   150.9101629 MHz

======== CHANNEL f2 ========
CNST21    1.0000000
CPDPRG2    spinal64
NUC2             1H
P3          2.90 usec
PCPD2         5.60 usec
PL2        119.00 dB
PL12        -6.00 dB
PL2W     0.00000000 W
PL12W   62.50000000 W
SFO2   600.1025000 MHz
SP0         -6.00 dB
SPNAM0     ramp.100
SPOAL0        0.500
SPOFFS0        0.00 Hz
SI            4096
SF     150.8951266 MHz
WDW              EM
SSB               0
LB          0.50 Hz
GB                0
PC             0.20
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Figure S2. ${}^{13}C$ CP-MAS NMR spectrum of N-squaraine **1** (H2SQ**1**).

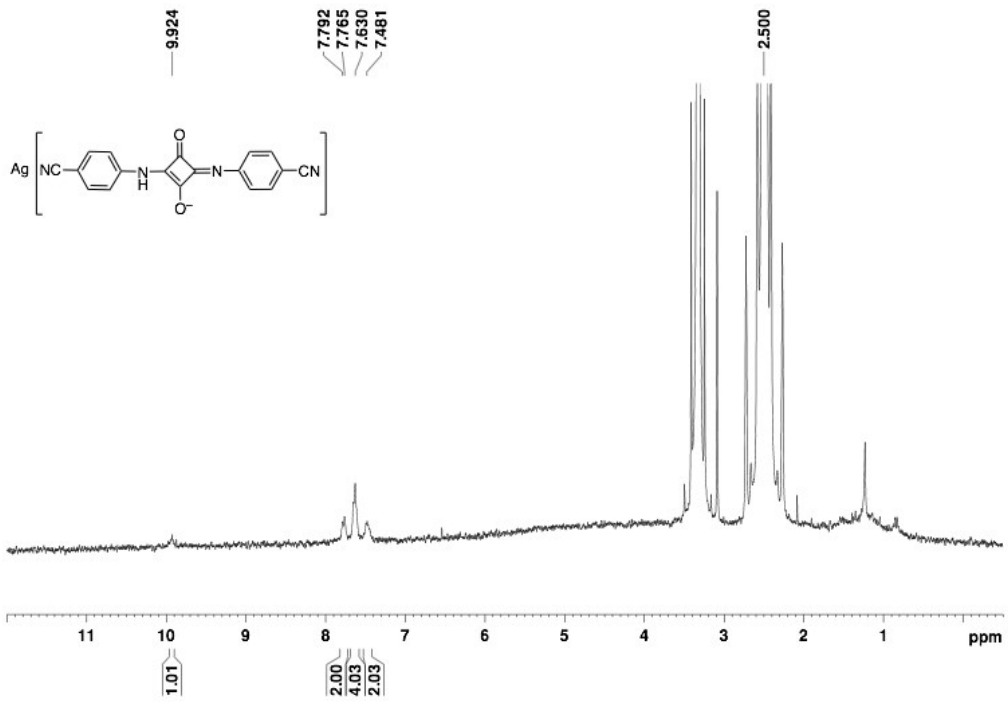

Figure S3. ${}^{1}H$ NMR spectrum of silver salt of N-squaraine **1** [Ag(H2SQ**1**)].

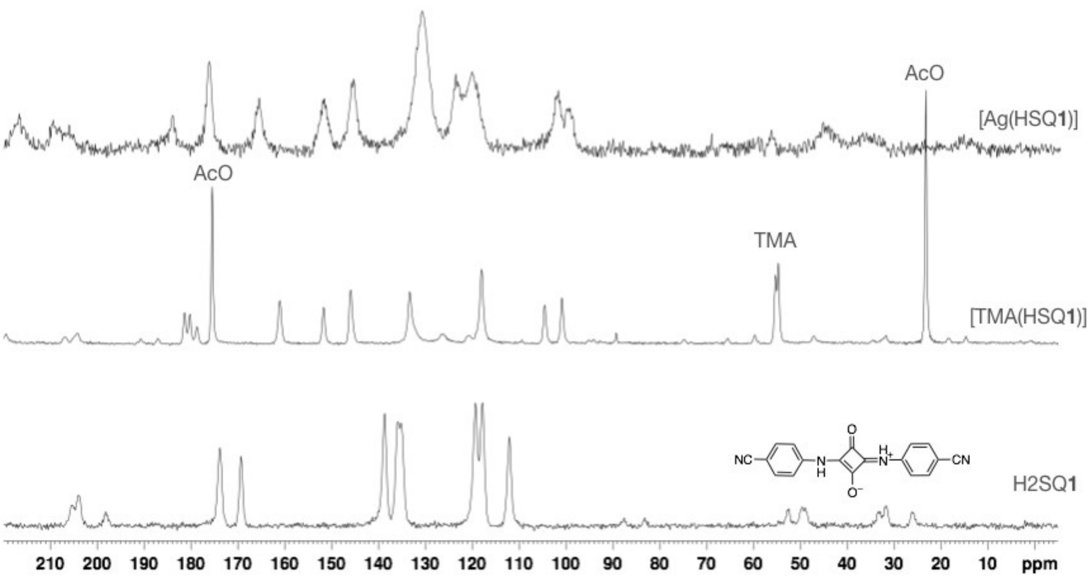

Figure S4. ^{13}C CP-MAS NMR spectra of N-squaraine **1** (H2SQ**1**) and its monoanion as tetramethylammonium [TMA(HSQ**1**)] and silver [Ag(HSQ**1**) salts respectivly.

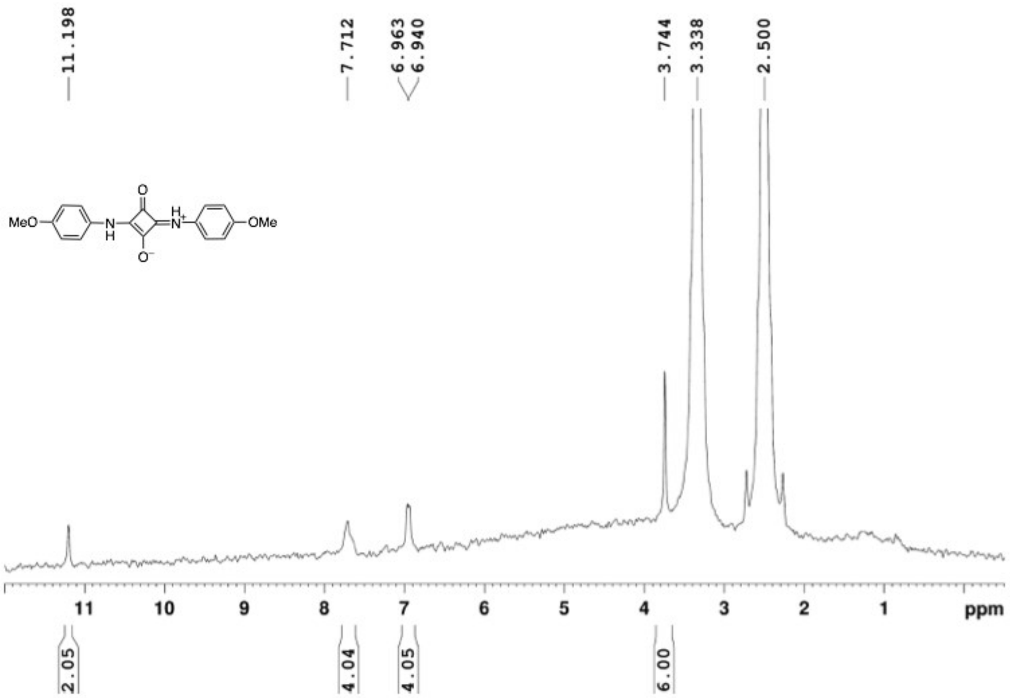

Figure S5. ^{1}H NMR spectrum of N-squaraine **2** (H2SQ**2**) in *d6*-DMSO

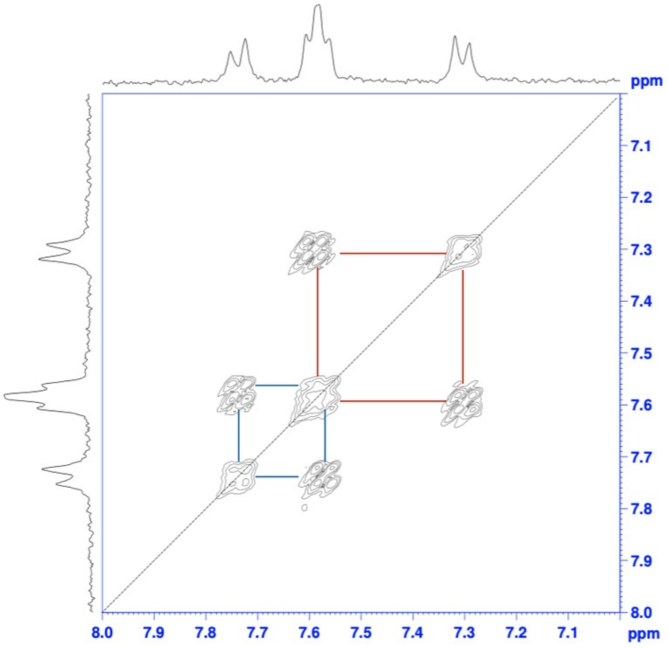

Figure S6. Partial 2D COSY NMR spectrum of N-squaraine **1** monoanion (HSQ**1**) in *d6*-DMSO containing 10 equiv. of NaOAc.

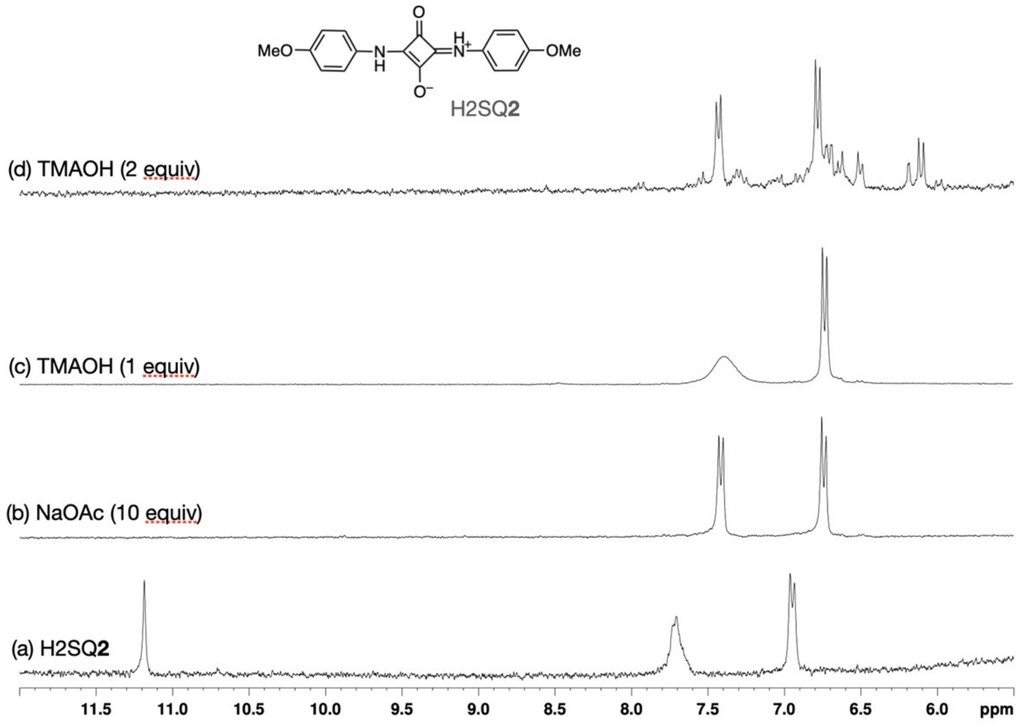

Figure S7. Stack plot of partial ^{1}H-NMR spectra of N-squaraine **2 (**H2SQ**2)** in DMSO-d_6 before (a) and after addition of bases. (b) NaOAc (10 equiv); (c) TMAOH (1 equiv) and (d) TMAOH (2 equiv), respectively. Spectrum (d) shows partial degradation of H2SQ**2** in the presence of a slight excess of TMAOH, thus precluding further additions of base.

4. Spectrophotometric pK_a determination of N-squaraine 1

The apparent pK_a values of N-squaraine **1** (1.75×10^{-5} M) in water (0.1M NaCl, ionic strength) was measured by registering the UV/vis absorption spectra in the range 250-550 nm against pH starting from pH = 9 and adding standardized 0.19 M NaOH up to pH = 13. Data sets were evaluated with HypSpec6 (Protonic Software). Output files include the calculated spectra for all species considered (H2SQ**1**), (HSQ**1**) and (SQ**1**). The titration was repeated two times.

Table S1. Logarithms of the stepwise and cumulative protonation constants for H2SQ**1**, determined at 298.1 ± 0.1 K.

Reaction[a]	**Log K**
$L + H \rightleftarrows HL$	12.18(8)
$HL + L \rightleftarrows H_2L$	11.39(3)
log β[b]	23.48(1)[c]

[a] Charges are omitted.
[b] Cumulative acid dissociation constant was calculated as $\log \beta = \sum \log K_{HjL.}$
[c] Values in parenthesis are standard deviations in the last significant figures

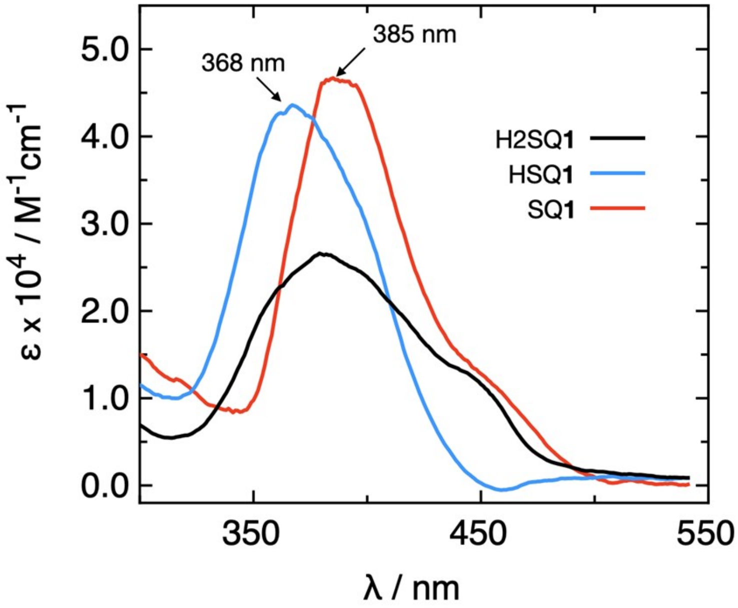

Figure S8. Calculated UV-vis spectra of N-squaraine **1** in water corresponding to the fully protonated (H2SQ**1**), monoanion (HSQ**1**), and dianion (SQ**1**) forms, as provided by HypSpec data.

5. X-ray structure of N-squaraine 1 [TBA(HSQ**1**]

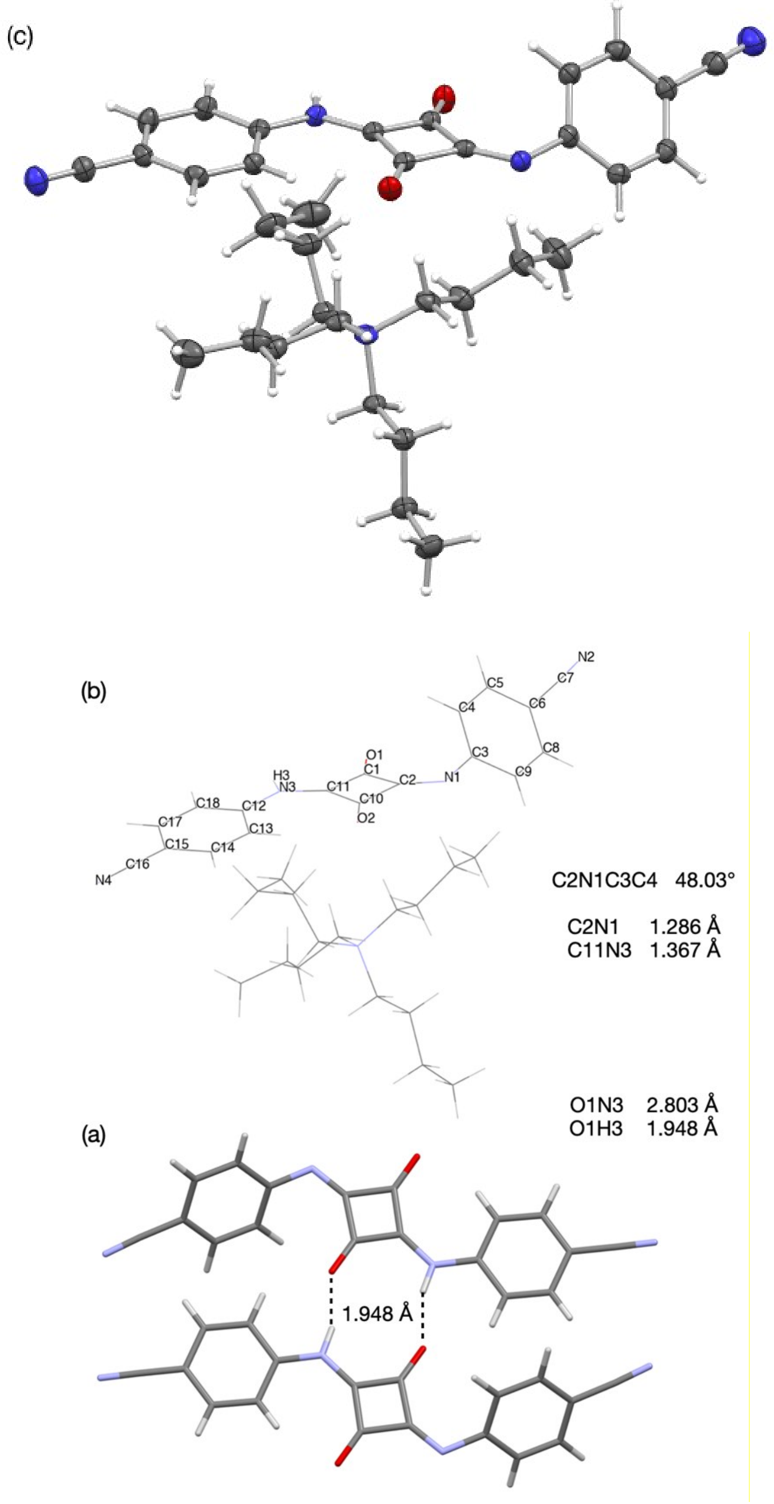

Figure S9. (a) ORTEP model of [TBA(HSQ**1**)] at 50% probability level. (b) Labelled structure and selected distances and angles of HSQ**1**. (a) X-ray dimeric structure of [TBA(HSQ**1**)]. TBA counter ions have been removed for clarity.

6. UV-vis spectra

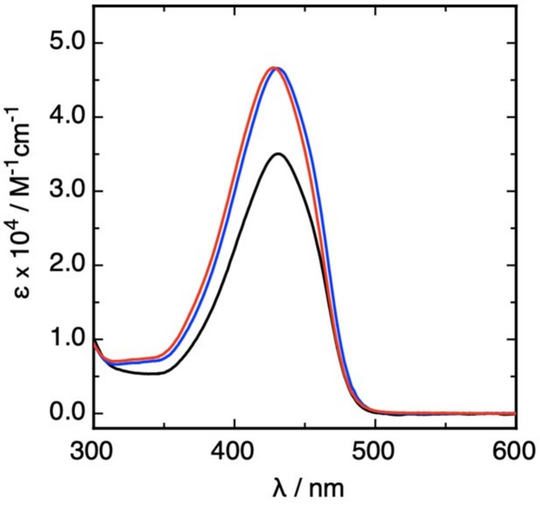

Figure S10. UV-vis spectra of [H2SQ**1**] (1.0×10^{-5} M) dissolved in DMF (black line), DMF containing 10 equiv. of NaOAc added as a solid (blue line), and DMF containing 10 equiv. of NaOAc and, additionally, adding a 2% v/v of an aqueous solution 0.1 M of NaOAc (red line), respectively, to give the monoanion HSQ**1**.

The formation of HSQ**1** (λ_{max} 428 nm) in DMF containing 10 equiv. of NaOAc shows a notable hyperchromic effect compared to the fully protonagted form H2SQ**1** **(**Fig. S10). The same trend, but at shorter wavelength, was observed for the calculated spectra of HSQ**1** (λ_{max} 368 nm), in the acid-base titration of H2SQ**1** in water (cf. Figure S8)

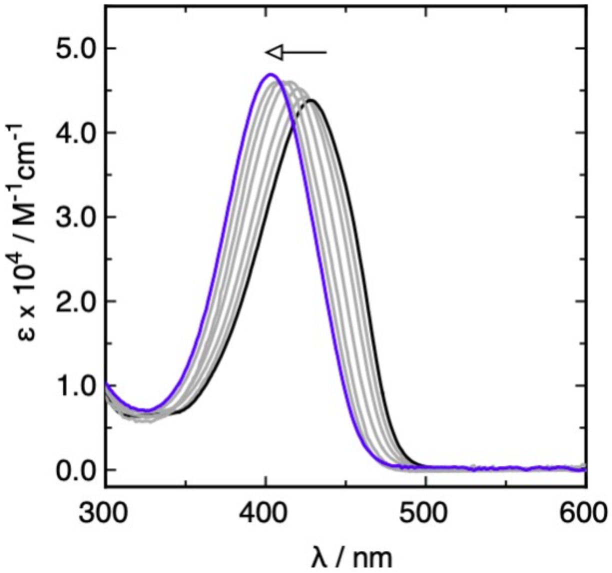

Figure S11. UV-vis spectra of [H2SQ**1**] (1.0 × 10^{-5} M) dissolved in DMF containing 10 equiv of NaOAc (black line) and, additionally, 2; 5; 10; 20; 30; 40; 50 % v/v of an aqueous solution H_2O (NaOAc, 0.1 M), respectively.

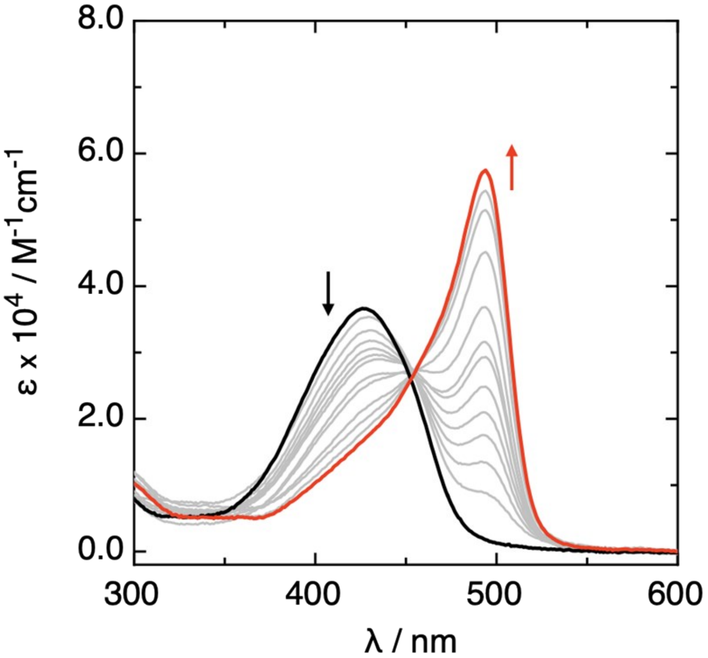

Figure S12. UV-vis titration of [Ag(HSQ**1**)] (2.0 × 10^{-6} M) with an increasing amount of Ag(I) in DMF (2% v/v 0.1 M of NaOAc in water) with Ag(I) .

6. Fluorescence spectra

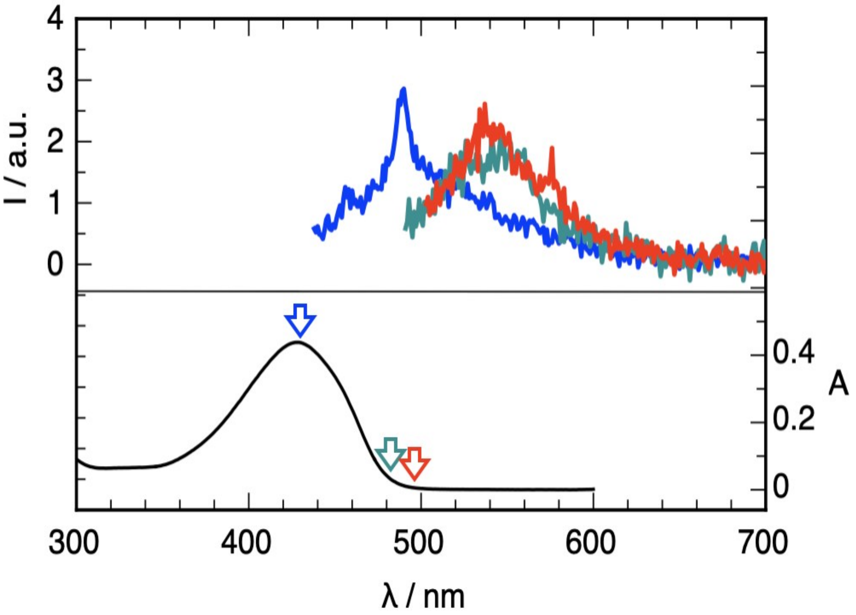

Figure S13. Emission spectra of [HSQ**1**] (1.0×10^{-6} M) in DMF(10 equiv NaOAc)-H_2O (2% v/v, 0.1M NaOAc) recorded by exciting at 428(blue), 480(green) and 494(red) nm, respectively. The UV-vis absorption spectrum of [HSQ**1**] (1.0×10^{-5} M) registered in the same solvent media is included.

7. TD-DFT calculations

7.1 Theoretical methods

The neutral squaraine (H_2SQ**1**), its anionic form (HSQ**1**$^{-}$) and complexes with silver (AgHSQ**1** and Ag_2SQ**1**) in their singlet ground state (S_0) were optimized by DFT and time-dependent DFT (TDDFT)[1-2] methods with the B3LYP[3]-D3[4] functional approach associated with the conductor-like polarizable continuum model (CPCM).[5-7]

We calculated 20 singlet–singlet transitions using the ground S_0 state geometries and the conductor-like polarizable continuum model. In some cases, explicit solvent molecules have been used coordinated to the silver atom (*vide infra*). The def2-TZVP as basis set[8] has been used. The def2-TZVP implementation used in this work employs for Ag the ECP-28 set and scalar relativistic effects.[8] In particular, the core AOs for Ag comprise from 1s to 3d.[9] The calculated electronic density plots for the frontier molecular orbitals were prepared by using the GaussView 6.0 software.[10] All the TDDFT calculations were performed with the Gaussian 16 software package.[11]

6.2 Additional results and discussion

In Figure S14, the optimized structure of squaraine (H_2SQ**1**) and the frontier orbitals are represented. The HOMO is localized in the four membered ring and its shape embracing the whole ring is typical of aromatic rings. The results from the TD-DFT calculation for this compound using the first 20 excited states are summarized in Table S1. The lowest lying UV-band correspond to the $S_0 \rightarrow S_1$ excitation that is composed by a single transition (HOMO → LUMO). The theoretical value $\lambda_{abs} = 422.2$ nm is in reasonable agreement with the experimental one (slightly underestimated by 9 nm). The TD-DFT analysis of the optimized first excited state predicts an emission band at 448.2 nm with a modest oscillator strength ($f = 0.4083$) in agreement with the almost negligible fluorescence observed for this squaraine derivative.

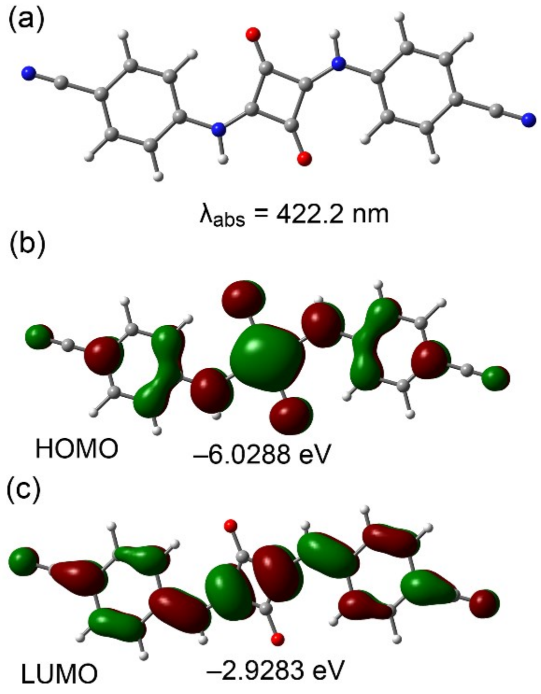

Figure S14. B3LYP-D3/def2-TZVP optimized geometry (a) and frontier orbitals (b,c) of H_2SQ**1**.

Table S1. Selected parameters for the vertical excitation (UV–Vis absorptions) and emission (from S_1) of complex H_2SQ**1** electronic excitation energies (eV) and oscillator strengths (*f*), configuration of the excited states, energy gap based on optimized ground–state geometry (DMF used as solvent).

Process	Composition	Excitation energy	Osc. strength (*f*)	%	λ_{exp}(nm)
$S_0 \rightarrow S_1$ (absorption)	HOMO → LUMO	2.9364 eV 422.2 nm	1.3977	100 %	430
$S_1 \rightarrow S_0$ (emission)	HOMO → LUMO	2.7660 eV 448.24 nm	0.4083	100 %	????

Figure S15a shows the optimized structures of the complex between squaraine monoanion (HSQ**1**$^{-}$) and silver(I). The silver atom is coordinated to the anionic N-atom and the adjacent O-atom of the four-membered ring. It is worthy to clarify that we have treat solvent effects (DMF) using a polarized continuum model (PCM) as implemented in Gaussian-16 program. Moreover, we have also evaluated the effect of using an explicit DMF molecule coordinated to Ag(I) in addition to the continuum model (Figure 2a). It can be observed that the presence/absence of the solvent molecule does not influence the shape of the frontier orbitals, since he DMF molecule is not involved in any of both orbitals. Moreover, the agreement between the experimental and theoretical values of λ_{abs} is better for the complex without the inclusion of the DMF molecule coordinated to silver. Therefore, we have simply used the PCM model to treat solvent effects without the utilization of explicit solvent molecules. Both HOMO and LUMO orbitals are π-type with participation of the four and six membered rings. The silver atom does not participate in any of both MOs and the transition is interligand π → π* type and almost equivalent to the one observed for the free ligand (see Figure S14).

Additionally, we have studied the effect of using water as solvent due to the fact that the elementary analysis suggests the presence of two water molecules. We have computed two situations, where the silver is coordinated to one or two water molecules. The results are shown in Figure S15, confirming the fact that the solvent is a mere spectator, since it does not participate in any of both frontier orbitals and its influence upon the theoretical λ_{abs} values is minimum.

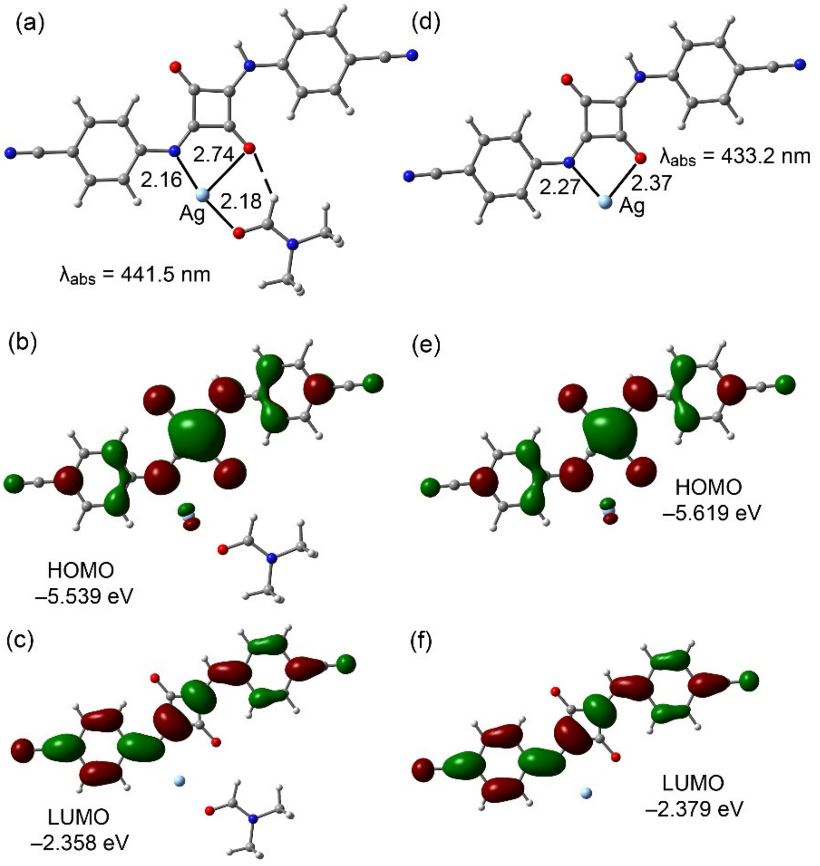

Figure S15. B3LYP-D3/def2-TZVP optimized geometries (a,b) and frontier orbitals (b,c,e,f) of Ag(DMF)(HSQ**1**) and Ag(HSQ**1**) complexes. Distances in Å.

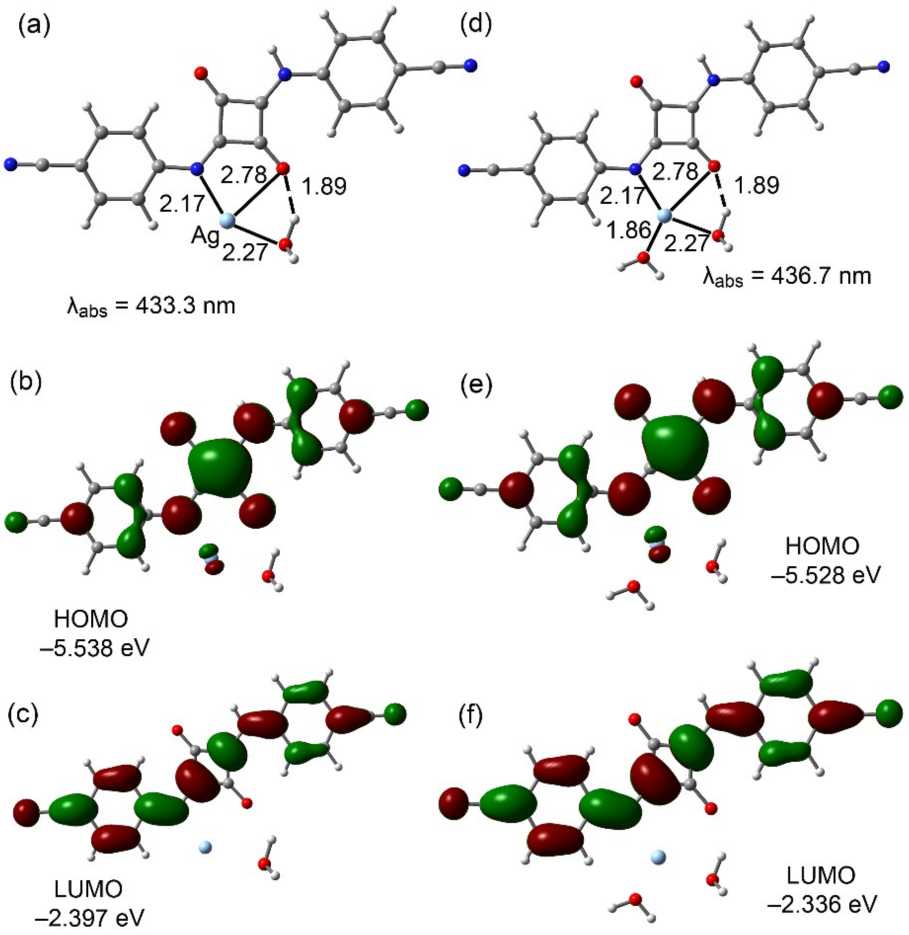

Figure S16. B3LYP-D3/def2-TZVP optimized geometries (a,b) and frontier orbitals (b,c,e,f) of Ag(H_2O)(HSQ**1**) and Ag(H_2O)$_2$(HSQ**1**) complexes. Distances in Å.

In Table S2 we summarize the results from the TD-DFT calculations. In all models the lowest lying energy excitation corresponds to the $S_0 \rightarrow S_1$ that is composed by a single HOMO → LUMO transition. As commented above, the theoretical λ_{abs} is 433.2 nm (f = 1.4763) for the Ag(HSQ**1**) complex that is in excellent agreement with the experimental value (λ_{exp} = 431 nm).

Table S2. Selected parameters for the vertical excitation (UV–Vis absorptions) of complexes Ag(HSQ**1**), and Ag(DMF)(HSQ**1**) electronic excitation energies (eV), oscillator strengths (f), configuration of the excited states, energy gap based on optimized ground–state geometry (DMF used as solvent).

Process	Composition	Excitation energy	Oscillator strength (f)	%	λ_{exp}(nm)
		Ag(HSQ**1**)			
$S_0 \rightarrow S_1$	HOMO →	2.8621 eV	1.0763	100 %	431

	LUMO	433.2 nm			
Ag(HSQ**1**)(DMF)					
$S_0 \rightarrow S_1$	HOMO → LUMO	2.8082 eV 441.5 nm	1.0733	100 %	431
Ag(H_2O)(HSQ**1**)					
$S_0 \rightarrow S_1$	HOMO → LUMO	2.8614 eV 433.3 nm	1.4261	100 %	431
Ag(H_2O)$_2$(HSQ**1**)					
$S_0 \rightarrow S_1$	HOMO → LUMO	2.8392 eV 436.7 nm	1.4148	100 %	431

Figure S17a shows the DFT-optimized structure of the complex with stoichiometry 2:1, Ag_2(SQ**1**). Each Ag atom is coordinated to one O-atom from the squaraine ring and establishes a π-interaction with one C-atom of the six-membered ring (2.34 Å). This provokes a loss of conjugation between the four and six-membered rings. This binding mode is different in comparison to the 1:1 complex where the Ag is coordinated to the N and O-atoms of the SQ ring and the conjugation between the six and four membered ring remains unaltered. This different binding mode is favored because it reduces the Ag(+)···Ag(+) repulsion by increasing the Ag···Ag distance with respect to the hypothetical complex where both Ag(+) would be located in the SQ plane and coordinated to the O and N-atoms. The frontier orbitals are represented in Figure S17b,c and it can be observed that the silver atomic orbitals have a negligible participation in the HOMO but a significant participation of the LUMO, thus changing the electronic characteristics of the system. The loss of conjugation increases the energy of the HOMO and consequently increases the theoretical value of λ_{abs} = 481.7 nm that is in reasonable agreement with the experimental value (λ_{exp} = 494 nm). More importantly, there is also a very good agreement between the experimental and theoretical λ_{em} values, thus giving reliability to the proposed geometry of the 2:1 complex and mechanism. In both the absorption and emission bands, each process is composed by two transitions where the HOMO → LUMO dominates (≥ 96%).

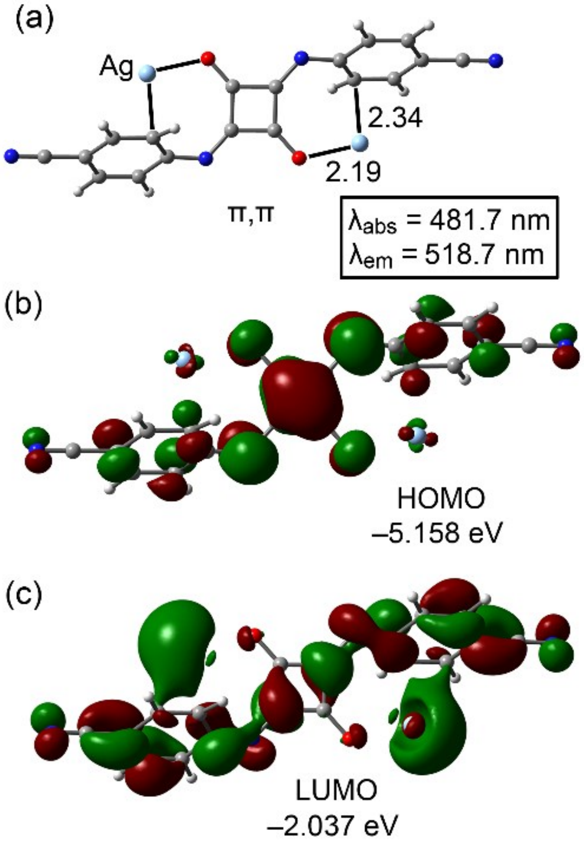

Figure S17. B3LYP-D3/def2-TZVP optimized geometries (a,b) and frontier orbitals (b,c,e,f) of Ag_2(SQA) complex. Distances in Å.

Table S3. Selected parameters for the vertical excitation (UV–Vis absorptions) and emission (from S_1) of complex Ag_2(SQ) , electronic excitation energies (eV) and oscillator strengths (*f*), configuration of the excited states, energy gap based on optimized ground–state geometry (DMF used as solvent).

Process	Composition	Excitation energy	Osc. strength (*f*)	%	λ_{exp}(nm)
Ag_2(SQ**1**)					
$S_0 \rightarrow S_1$ (absorption)	HOMO → LUMO HOMO → LUMO+2	2.5741 eV 481.7 nm	1.0787	96 % 4%	494
$S_1 \rightarrow S_0$ (emission)	HOMO-1 → LUMO+1 HOMO → LUMO	2.3901 eV 518.7 nm	2.0270	8.2 % 91.8 %	517

Figure S18 shows a comparison of the optimized geometries of the *bis*-Ag(I) σ-coordinated complex (a) and bis-Ag(I) π-coordinated complex. It can be observed that the Ag···Ag distance is longer for the latter complexation mode. The theoretical absorption values are also indicated, showing that the value for the *bis*-Ag(I) σ-coordinated complex is in disagreement with the experimental value.

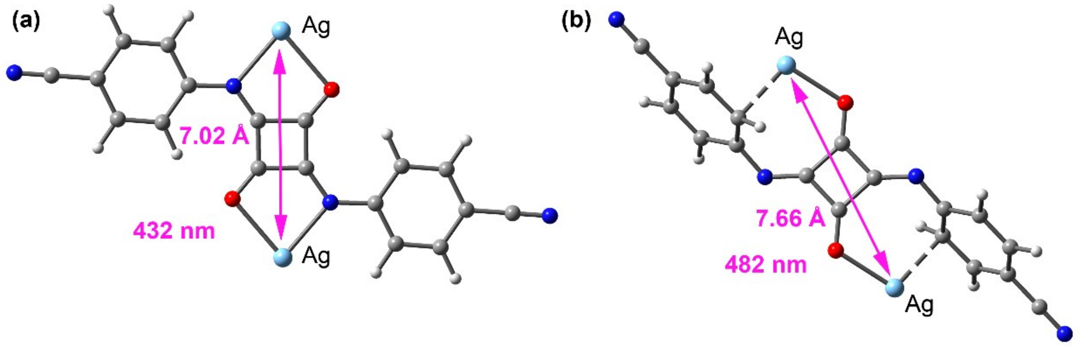

Figure S18. Optimized geometries of the *bis*-Ag(I) σ-coordinated complex (a) and bis-Ag(I) π-coordinated Ag(I) complex at the B3LYP/def2-TXVP level of theory.

7.3 References

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H. Nakai, T. Vreven, K. Throssell, J. a. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, 2016, Gaussian 16, Revision A.07, Gaussian, Inc., Wallingford CT, 2016.

6.4 X-ray coordinates

H2SQ**1**

```
---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
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      1          1           0        2.955076   -1.433091    0.000127
      2          6           0        3.725617   -0.672598    0.000090
      3          6           0        5.723107    1.284510   -0.000031
      4          6           0        3.389232    0.683469    0.000042
      5          6           0        5.059227   -1.039354    0.000064
      6          6           0        6.070102   -0.070818   -0.000010
      7          6           0        4.392528    1.657104   -0.000004
      8          1           0        5.324394   -2.087761    0.000108
      9          1           0        4.129443    2.708131   -0.000008
     10          1           0        6.498017    2.038540   -0.000071
     11          6           0        0.924689    0.420382    0.000043
     12          6           0       -0.432922    0.964361    0.000009
     13          8           0       -0.875623    2.101253    0.000049
     14          6           0        0.432854   -0.964278   -0.000033
     15          6           0       -0.924667   -0.420328    0.000018
     16          8           0        0.875525   -2.101214   -0.000028
     17          7           0       -2.055111   -1.119373    0.000021
     18          1           0       -1.910991   -2.123783    0.000015
     19          6           0       -3.389201   -0.683422    0.000007
     20          6           0       -6.070065    0.070778   -0.000021
     21          6           0       -3.725636    0.672657   -0.000019
     22          6           0       -4.392464   -1.657115    0.000022
     23          6           0       -5.723058   -1.284531    0.000008
     24          6           0       -5.059245    1.039367   -0.000033
     25          1           0       -2.955067    1.433115   -0.000020
     26          1           0       -4.129377   -2.708133    0.000044
     27          1           0       -6.497989   -2.038542    0.000019
     28          1           0       -5.324501    2.087753   -0.000054
     29          6           0       -7.443500    0.460459   -0.000038
     30          7           0       -8.552986    0.773214   -0.000052
     31          6           0        7.443501   -0.460577   -0.000068
     32          7           0        8.552977   -0.773370   -0.000110
     33          7           0        2.055152    1.119420    0.000044
     34          1           0        1.910970    2.123820    0.000082
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```

HSQ**1**

```
---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
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      3          6           0        5.740285    1.252671   -0.000665
      4          6           0        3.362691    0.720093    0.000069
      5          6           0        5.018524   -1.053704    0.000915
      6          6           0        6.060354   -0.112861    0.000144
      7          6           0        4.419556    1.652377   -0.000666
      8          1           0        5.258959   -2.109525    0.001567
```

```
    9       1       0      4.158851    2.702577   -0.001262
   10       1       0      6.535012    1.987755   -0.001258
   11       6       0      1.001904    0.571237   -0.000075
   12       6       0     -0.424848    1.071831   -0.000083
   13       8       0     -0.940047    2.181559    0.000247
   14       6       0      0.456665   -0.845708   -0.000535
   15       6       0     -0.870065   -0.308613   -0.000291
   16       8       0      0.881041   -2.003725   -0.000735
   17       7       0     -2.011791   -1.061702   -0.000325
   18       1       0     -1.822271   -2.056649   -0.000537
   19       6       0     -3.329241   -0.677458   -0.000165
   20       6       0     -6.052166    0.019365    0.000140
   21       6       0     -3.714999    0.676775    0.000095
   22       6       0     -4.328774   -1.670665   -0.000265
   23       6       0     -5.663577   -1.329065   -0.000117
   24       6       0     -5.053933    1.007720    0.000245
   25       1       0     -2.955786    1.451555    0.000197
   26       1       0     -4.041822   -2.715930   -0.000461
   27       1       0     -6.419852   -2.103152   -0.000198
   28       1       0     -5.341775    2.051062    0.000449
   29       6       0     -7.430162    0.372014    0.000293
   30       7       0     -8.551275    0.652740    0.000418
   31       6       0      7.420143   -0.535812    0.000216
   32       7       0      8.524531   -0.876114    0.000290
   33       7       0      2.086425    1.259110    0.000070
 ---------------------------------------------------------------------
```

Ag(HSQ**1**)

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 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
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    4       7       0      1.786047    0.338236    0.000435
    5       6       0      0.095215   -1.742684    0.000468
    6       6       0     -1.226714   -1.113357    0.000287
    7       6       0      0.693469   -0.359284    0.000314
    8       6       0     -0.666807    0.201189    0.000162
    9       6       0      3.382550   -1.544888   -0.002618
   10       6       0      4.148589    0.743270    0.003202
   11       6       0     -3.709542   -1.248358    0.000185
   12       6       0     -6.353525   -0.345421    0.000164
   13       6       0     -5.289525    0.564051    0.000090
   14       6       0     -3.978378    0.124546    0.000094
   15       6       0     -6.077851   -1.717939    0.000250
   16       6       0     -7.702273    0.119832    0.000159
   17       6       0      3.088350   -0.171604    0.000349
   18       7       0     -8.792330    0.495893    0.000159
   19       6       0      5.462714    0.317060    0.003163
   20       6       0     -4.770787   -2.162705    0.000268
   21       6       0      4.696772   -1.973301   -0.002664
   22       6       0      5.751564   -1.051773    0.000190
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   24       6       0      7.106062   -1.501154    0.000046
   25       1       0      6.270099    1.036587    0.005410
   26       1       0     -3.170465    0.843298    0.000026
   27       1       0      3.928248    1.804473    0.005567
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   30       1       0      2.585775   -2.276567   -0.004614
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   33       1       0     -2.318701   -2.762323    0.000267
   34      47       0      1.062980    2.491195   -0.000718
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Ag(DMF)(HSQ**1**)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
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2	7	0	2.041325	-2.818386	0.017021
3	8	0	1.049496	0.450336	0.032883
4	7	0	-1.943105	-0.335347	0.014318
5	6	0	-0.432502	-2.537742	0.018008
6	6	0	0.937404	-2.056229	0.020595
7	6	0	-0.893843	-1.103546	0.020871
8	6	0	0.528569	-0.670532	0.027116
9	6	0	-3.637205	-2.143194	0.017634
10	6	0	-4.291324	0.175796	-0.023585
11	6	0	3.384411	-2.478539	0.005663
12	6	0	6.112427	-1.862502	-0.020467
13	6	0	5.157808	-0.844022	-0.016542
14	6	0	3.803902	-1.135761	-0.003406
15	6	0	5.690023	-3.196753	-0.011336
16	6	0	7.516945	-1.539793	-0.034207
17	6	0	-3.273260	-0.787470	0.003152
18	7	0	8.616040	-1.279217	-0.045361
19	6	0	-5.623797	-0.185919	-0.037025
20	6	0	4.342470	-3.497007	0.001287
21	6	0	-4.970452	-2.507868	0.004459
22	6	0	-5.981330	-1.538029	-0.023191
23	7	0	-8.469389	-2.228724	-0.048644
24	6	0	-7.351647	-1.920661	-0.037161
25	1	0	-6.394189	0.573744	-0.058693
26	1	0	3.073233	-0.339400	-0.000708
27	1	0	-4.023068	1.226155	-0.034916
28	1	0	4.024664	-4.531655	0.008404
29	1	0	-5.238063	-3.555512	0.015236
30	1	0	-2.880164	-2.915904	0.037385
31	1	0	5.477829	0.188616	-0.022822
32	1	0	6.422902	-3.994054	-0.013670
33	1	0	1.831153	-3.823126	0.014000
34	47	0	-1.360535	1.749342	0.017139
35	6	0	0.875569	3.681346	0.024367
36	8	0	-0.368125	3.690938	0.012712
37	7	0	1.623668	4.787921	-0.004208
38	1	0	1.437017	2.744652	0.058697
39	6	0	1.025263	6.112656	-0.056216
40	1	0	1.334770	6.693339	0.815872
41	1	0	1.356221	6.633409	-0.957914
42	1	0	-0.056099	6.020821	-0.066120
43	6	0	3.074974	4.710074	0.010187
44	1	0	3.486130	5.168609	-0.892012
45	1	0	3.471322	5.237222	0.880856
46	1	0	3.391271	3.670673	0.052806

Ag(H$_2$O)(HSQ**1**)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	1	0	-3.278280	0.706840	-0.039094
2	6	0	-4.071905	-0.027537	-0.023683
3	6	0	-6.123360	-1.922597	0.014751
4	6	0	-3.767512	-1.392914	0.001848
5	6	0	-5.393491	0.378324	-0.029052
6	6	0	-6.434297	-0.557818	-0.009605
7	6	0	-4.805358	-2.333892	0.020412
8	1	0	-5.628637	1.433938	-0.049680
9	1	0	-4.574137	-3.392241	0.039844
10	1	0	-6.919302	-2.654508	0.029434
11	6	0	-1.285945	-1.198770	0.007312
12	6	0	0.030771	-1.815957	0.005422
13	8	0	0.392956	-2.978546	0.005644

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    14        6          0       -0.742757    0.129548    0.010410
    15        6          0        0.629698   -0.434947    0.005263
    16        8          0       -1.173154    1.297074    0.016734
    17        7          0        1.763025    0.210702    0.001202
    18        6          0        3.037696   -0.377828   -0.001406
    19        6          0        5.654611   -1.400338   -0.005789
    20        6          0        3.260843   -1.763722    0.014139
    21        6          0        4.149050    0.475870   -0.019468
    22        6          0        5.438618   -0.018570   -0.021871
    23        6          0        4.550827   -2.261468    0.011867
    24        1          0        2.429349   -2.454667    0.026738
    25        1          0        3.991095    1.548854   -0.032937
    26        1          0        6.282041    0.658165   -0.036342
    27        1          0        4.709762   -3.331438    0.023912
    28        6          0        6.982877   -1.921921   -0.007051
    29        6          0       -7.794067   -0.126412   -0.014280
    30        7          0       -8.892735    0.223963   -0.017266
    31        7          0       -2.455527   -1.863201    0.008370
    32        1          0       -2.338426   -2.869544    0.012101
    33        7          0        8.057529   -2.340051   -0.007693
    34       47          0        1.400397    2.355145   -0.002490
    35        8          0       -0.262126    3.906755   -0.046062
    36        1          0       -0.450105    4.496740    0.692625
    37        1          0       -0.907283    3.169562   -0.007721
 ---------------------------------------------------------------------
```

Ag(H_2O)$_2$(HSQ**1**)

```
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
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     1        1          0       -3.236445    0.462618   -0.266824
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     3        6          0       -6.094654   -2.124080    0.105506
     4        6          0       -3.735395   -1.615637    0.021351
     5        6          0       -5.351696    0.152119   -0.202952
     6        6          0       -6.397909   -0.768658   -0.070677
     7        6          0       -4.779222   -2.541196    0.151221
     8        1          0       -5.579660    1.199906   -0.345385
     9        1          0       -4.554464   -3.591819    0.291081
    10        1          0       -6.894894   -2.844282    0.207395
    11        6          0       -1.256057   -1.424137    0.039961
    12        6          0        0.066016   -2.034043    0.053579
    13        8          0        0.436972   -3.192377    0.092162
    14        6          0       -0.717416   -0.096985    0.002447
    15        6          0        0.653779   -0.645932    0.005307
    16        8          0       -1.131993    1.075653   -0.030004
    17        7          0        1.769775    0.025435   -0.023765
    18        6          0        3.053914   -0.547943   -0.016681
    19        6          0        5.679911   -1.547197   -0.008061
    20        6          0        3.289894   -1.931636   -0.001416
    21        6          0        4.157209    0.316098   -0.027367
    22        6          0        5.451128   -0.167688   -0.022747
    23        6          0        4.584016   -2.418345    0.002813
    24        1          0        2.465897   -2.631413    0.009323
    25        1          0        3.990557    1.387140   -0.037081
    26        1          0        6.288315    0.516870   -0.030344
    27        1          0        4.752261   -3.486884    0.014634
    28        6          0        7.012829   -2.056938   -0.004293
    29        6          0       -7.755080   -0.331540   -0.115642
    30        7          0       -8.851653    0.023631   -0.150540
    31        7          0       -2.425949   -2.089213    0.071201
    32        1          0       -2.311299   -3.093857    0.130660
    33        7          0        8.091065   -2.465739   -0.001461
    34       47          0        1.431700    2.163231   -0.070016
    35        8          0       -1.677047    3.671649    0.479733
    36        1          0       -2.127170    3.829723    1.315178
    37        1          0       -1.627426    2.699196    0.357672
    38        8          0        0.833898    4.276773    0.012008
```

```
    39        1          0        0.941802    4.818375   -0.777172
    40        1          0       -0.145023    4.213911    0.204586
 ---------------------------------------------------------------------
```

Ag$_2$(SQ**1**)

```
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1          8           0        1.058773    1.379472   -1.475391
      2          7           0       -1.974821    1.116939   -0.613035
      3          8           0       -1.058773   -1.379472    1.475391
      4          7           0        1.974821   -1.116939    0.613035
      5          6           0        0.495209    0.628425   -0.642480
      6          6           0       -0.908718    0.444039   -0.286179
      7          6           0        0.908718   -0.444039    0.286179
      8          6           0       -0.495209   -0.628425    0.642480
      9          6           0        3.675118    0.643979    0.808652
     10          6           0        4.262688   -1.606122    0.109873
     11          6           0       -3.246202    0.690040   -0.483374
     12          6           0       -5.990621   -0.090643   -0.297058
     13          6           0       -5.026735   -1.013904   -0.717285
     14          6           0       -3.675118   -0.643979   -0.808652
     15          6           0       -5.581065    1.226545   -0.009848
     16          6           0       -7.355201   -0.476312   -0.181391
     17          6           0        3.246202   -0.690040    0.483374
     18          7           0       -8.459281   -0.796432   -0.078467
     19          6           0        5.581065   -1.226545    0.009848
     20          6           0       -4.262688    1.606122   -0.109873
     21          6           0        5.026735    1.013904    0.717285
     22          6           0        5.990621    0.090643    0.297058
     23          7           0        8.459281    0.796432    0.078467
     24          6           0        7.355201    0.476312    0.181391
     25          1           0        6.325753   -1.950573   -0.294379
     26          1           0       -2.975589   -1.294127   -1.323148
     27          1           0        3.967024   -2.625162   -0.099492
     28          1           0       -3.967024    2.625162    0.099492
     29          1           0        5.333866    2.001081    1.038940
     30          1           0        2.975589    1.294127    1.323148
     31          1           0       -5.333866   -2.001081   -1.038940
     32          1           0       -6.325753    1.950573    0.294379
     33         47           0        3.225855    1.628297   -1.269584
     34         47           0       -3.225855   -1.628297    1.269584
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