Electronic Supplementary Material (ESI) for New Journal of Chemistry
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Supplementary information

Experimental and Theoretical Evidence of Unsupported Ag–Ag Interactions in Complexes with Triazine-based Ligands. Subtle Effects of the Symmetry of the Triazine Substituents

New Journal of Chemistry

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Figure S6. Electronic density and Laplacian of the charge density for the optimized compounds **2b** and **4b** in the plane defined by the atoms Ag(1)-Ag(2)-N(3).

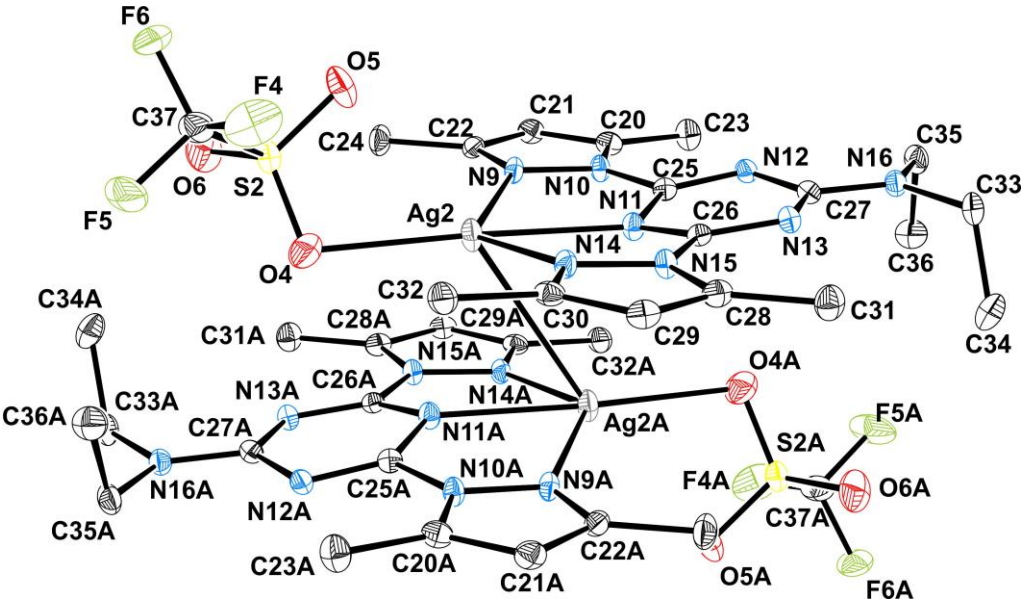

Figure S1. ORTEP representation of complex **2b** B.

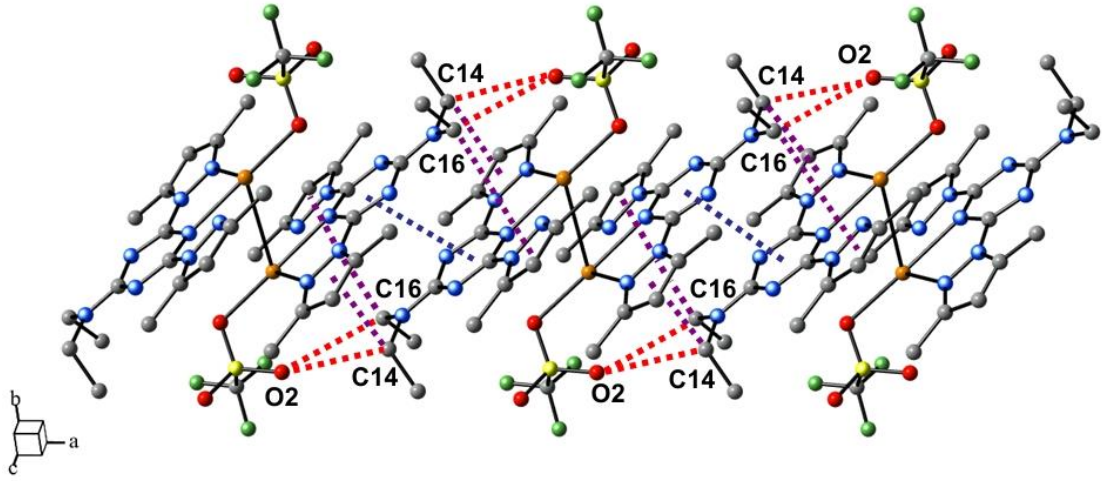

Figure S2. Complex **2b A**. Columns of dimers that extend along the *a* axis. The non-covalent interactions between dimers are indicated with dashed lines: red = hydrogen bonds; blue = π–π stacking, purple = CH–π.

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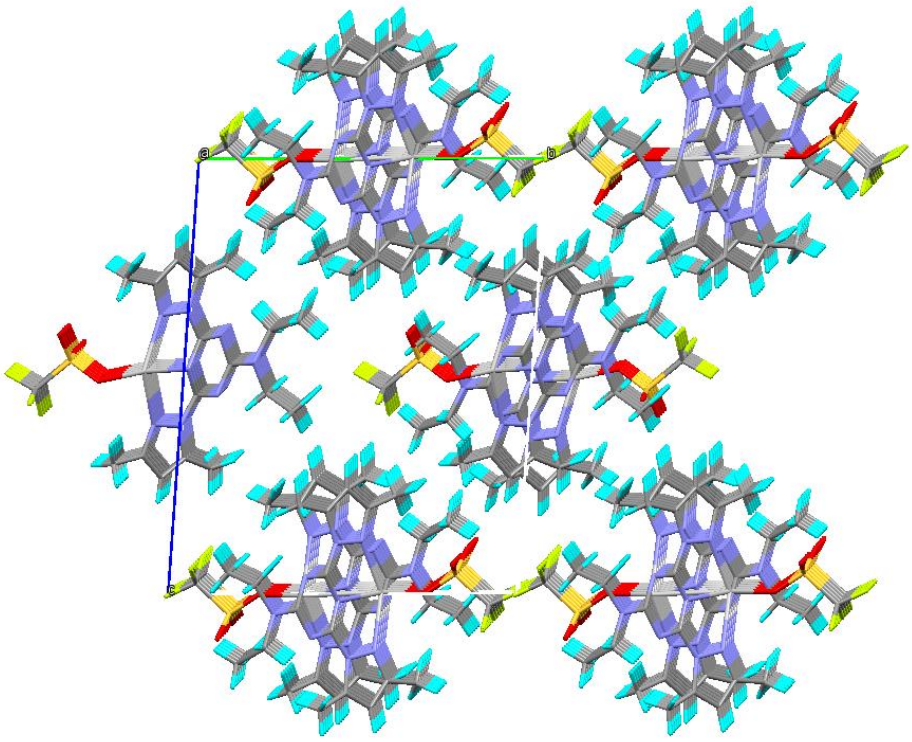

Figure S3. 3D structure of complex **2b**.

Way of calculation of I and II as the parameters to measure the lateral and frontal displacement of the monomers

Differences in the relative position of the two monomer units are defined in Table S1 using three parameters (**F**, **I** and **II**). This criterion has been applied for both the experimental (**2b**A, **2b** B and **4b**) and calculated structures (**2bopt** and **4opt**). The first parameter, **F**, defines the separation (Å) of the respective planar bpzT ligands of both monomer units. All the non-hydrogen atoms (N and C) have been considered in the calculation of these averaged planes (P1 and P2). Planes P1 and P2 are parallel (dihedral angle 0 °) in the experimental structures, due to the existence of a crystallographic inversion center in the Ag···Ag axis and this angle is practically also 0º in the calculated structures.

Parameters **I** and **II** measure the respective lateral and frontal displacement of the monomer units relative to each other (see Figure S4). Parameter **I** is defined as the distance (Å) between the straight line running from C^6 to N^3 of the triazine ring in plane P1and the projection, on this plane, of the corresponding straight line of the second triazine. In order to calculate **I**, an auxiliary plane (σ_{aux}) is defined in each of the structures with the four atoms, C^6 and N^3 of both triazine rings. The dihedral angle between planes **P1** and σ_{aux}(θ) defines one of the angles of a right-angle triangle defined by **F** and **I** as the triangle cathetus (see Figure S4). Knowing the values of θ and **F**, it is possible calculate the value of **I** as:

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$$\mathbf{I} = \frac{\mathbf{F}}{\boldsymbol{tan}\,\theta}$$

Analogously, the lateral displacement, measured with the parameter **II**, is defined as the distance (Å) between the two straight lines running between the N-donor atoms of the pyrazole rings of each monomer (direct and projection on plane P1). **II** is calculated in a similar way from the interplanar distance **F** and the dihedral angle (**θ'**) formed between plane P1 and an auxiliar plane ($\boldsymbol{\sigma'_{aux}}$) that has been created, in this occation,with the considered four N-donor atoms of the pyrazole rings. In this case:

$$\mathbf{II} = \frac{\mathbf{F}}{\boldsymbol{tan}\,\theta'}$$

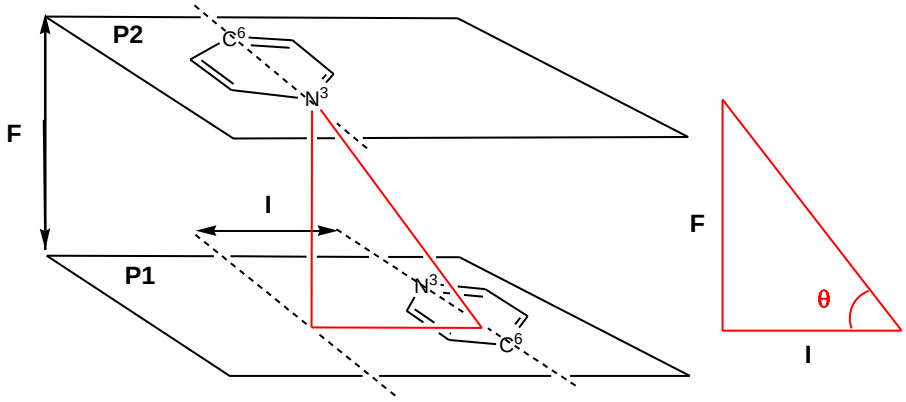

Figure S4.θ is the dihedral angle formed between planes$\boldsymbol{\sigma_{aux}}$ and **P1**. Plane $\boldsymbol{\sigma_{aux}}$is constructed from the coordinates of atoms N^1 and C^4 of the two triazine rings.

Table S1. Strucutral parameters for **2b (A** and **B)**, **4b** and the corresponding optimized structures.

Compound	**F (Å)**[a]	**θ (º)**	**θ' (º)**	**Lateral disp. I (Å)**[b]	**Frontal disp. II (Å)**[b]
2b A	3.29	85.64	83.72	0.25	0.36
2b B	3.20	88.85	84.82	0.06	0.29
2b opt	3.62	71.70	53.97	1.20	2.63
4b	3.11	57.86	67.02	1.95	1.32
4b opt	3.46	63.46	68.21	1.73	1.38

[a]**F** is the distance between the planes of the two ligands of each dimer. [b]See above and Figure S3 for the method used for obtaining its value.

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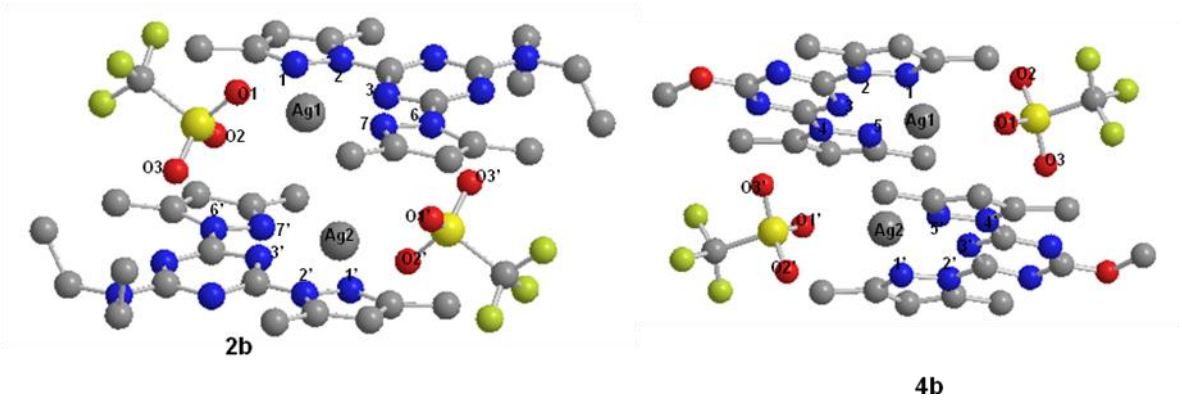

Figure S5. Drawings of the optimized structures for compounds **2b** and **4b**

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Table S2 . Cartesian coordinates and absoluted enenrgies and Gibbs energies (in hartrees/molec) of the calculated species (PBE1PBE calulations):

2b

E(gas): - 4413.60984860 a.u.

G(gas): -4412.839033 a.u.

C	1.380553	-5.105986	0.814729
C	0.294516	-4.396570	0.241850
N	0.723355	-3.289854	-0.334771
N	2.071587	-3.268760	-0.152720
C	2.509161	-4.371912	0.549041
C	2.811195	-2.212226	-0.698494
N	2.092835	-1.195198	-1.163888
C	2.818734	-0.253213	-1.764443
N	4.126970	-0.232011	-1.879822
C	4.756829	-1.269242	-1.285061
N	4.120648	-2.320010	-0.716662
N	2.087092	0.781035	-2.351044
C	2.528935	1.985112	-2.847518
C	1.411790	2.610428	-3.341089
C	0.320883	1.739536	-3.101906
N	0.740364	0.640896	-2.498355
C	-1.112817	1.944991	-3.443340
C	3.923215	2.495761	-2.777622
N	6.098618	-1.297224	-1.312451
C	6.820505	-2.360689	-0.621668
C	6.968598	-2.135336	0.879003
C	-1.147210	-4.768341	0.219850
C	3.914919	-4.659239	0.942157
C	6.854884	-0.217259	-1.934081
C	7.287492	0.877474	-0.966754
H	1.343372	-6.041209	1.356506
H	1.382030	3.583832	-3.811098
H	-1.699609	1.044524	-3.242857
H	-1.526643	2.779502	-2.864550
H	-1.220341	2.198751	-4.504000
H	4.284770	2.496429	-1.745164
H	4.613254	1.888890	-3.369297
H	3.936734	3.520886	-3.158652
H	6.291925	-3.299225	-0.807796
H	7.803116	-2.436426	-1.099826
H	7.414476	-3.021855	1.344445
H	7.610951	-1.277884	1.097998
H	5.995743	-1.941817	1.338201
H	-1.517643	-4.940813	1.236209
H	-1.741509	-3.973341	-0.235044

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H	-1.299510	-5.692613	-0.349701
H	3.922724	-5.547608	1.579878
H	4.547725	-4.844676	0.069613
H	4.361523	-3.824460	1.489289
H	7.728540	-0.673637	-2.414636
H	6.230485	0.206136	-2.722451
H	7.757853	1.696362	-1.522931
H	6.428543	1.271591	-0.418209
H	8.015714	0.509269	-0.237601
Ag	-0.274451	-1.136506	-1.252083
O	-2.510533	-1.548858	-0.572775
S	-3.452068	-1.193585	-1.682662
C	-4.385049	-2.767416	-1.885417
F	-3.554610	-3.767143	-2.187385
O	-4.472160	-0.208803	-1.306531
O	-2.779941	-0.996907	-2.973447
F	-5.016258	-3.084424	-0.745819
F	-5.292079	-2.660022	-2.849850
Ag	0.274352	1.136784	1.253123
O	2.510464	1.548114	0.573296
S	3.452053	1.193045	1.683211
O	4.471813	0.207909	1.307191
C	4.385328	2.766756	1.885646
F	5.016808	3.083473	0.746109
F	3.555027	3.766692	2.187280
F	5.292180	2.659363	2.850246
O	2.780056	0.996961	2.974161
N	-0.723033	3.289183	0.334438
C	-0.293773	4.395907	-0.241857
C	-1.379535	5.105826	-0.814636
C	-2.508417	4.372087	-0.549144
N	-2.071272	3.268606	0.152325
C	-3.914088	4.660023	-0.942130
C	1.148044	4.767313	-0.219348
C	-2.811233	2.212245	0.697963
N	-4.120671	2.320271	0.715940
C	-4.757089	1.269549	1.284196
N	-4.127464	0.232511	1.879586
C	-2.819226	0.253507	1.764360
N	-2.093141	1.195115	1.163481
N	-6.098881	1.297367	1.310653
C	-6.855527	0.217607	1.932173
C	-7.288333	-0.876955	0.964737
N	-2.087690	-0.780580	2.351424
N	-0.740947	-0.640529	2.498584
C	-0.321494	-1.739038	3.102417
C	-1.412474	-2.609697	3.342039
C	-2.529618	-1.984395	2.848409
C	-3.924020	-2.494795	2.779192
C	1.112363	-1.944815	3.443028

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C	-6.820388	2.360582	0.619068
C	-6.966754	2.135111	-0.881758
H	-1.342014	6.041270	-1.356008
H	-4.360966	3.825606	-1.489591
H	-4.546824	4.845296	-0.069499
H	-3.921626	5.548647	-1.579497
H	1.742374	3.970742	0.232761
H	1.518071	4.943156	-1.235265
H	1.300768	5.689654	0.353233
H	-6.231338	-0.205996	2.720587
H	-7.729119	0.674214	2.412639
H	-7.759399	-1.695524	1.520787
H	-8.016049	-0.508379	0.235266
H	-6.429377	-1.271599	0.416570
H	-1.382803	-3.582894	3.812483
H	-3.937636	-3.519709	3.160789
H	-4.613702	-1.887468	3.370824
H	-4.286029	-2.495950	1.746894
H	1.220191	-2.202930	4.502586
H	1.526609	-2.776597	2.860620
H	1.698567	-1.043209	3.245931
H	-7.803548	2.435952	1.096152
H	-6.292374	3.299331	0.805764
H	-7.412262	3.021518	-1.347765
H	-5.993348	1.941675	-1.339823
H	-7.608689	1.277511	-1.101401

4b

E(gas): - 4217.69553637 a.u.

G(gas): -4217.111367 a.u.

Ag	0.868308	1.253620	0.332909
S	-0.869483	3.983597	-0.490045
O	-0.563236	3.020031	0.621815
O	0.290789	4.492936	-1.218429
O	-2.030224	3.581272	-1.296441
N	2.034040	1.264006	2.554652
N	4.236643	-1.439084	1.875061
N	1.545022	0.247957	-1.766478
N	4.009098	-1.964594	-0.437862
N	2.461564	-0.759257	-1.701821
N	2.878003	0.219443	2.775427
N	2.593932	-0.366271	0.562553
O	5.431778	-3.080320	0.963237
C	2.709216	-1.299115	-2.945896
C	3.044122	-1.059457	-0.474589
C	0.261337	1.402836	-3.511827
H	-0.208293	1.926430	-2.676436

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H	-0.518143	0.949060	-4.133659
H	0.777566	2.153115	-4.121615
C	3.257548	-0.577044	1.696492
C	3.271476	0.147156	4.096619
C	1.221135	0.368648	-3.041803
C	4.518762	-2.151934	0.780595
C	1.928527	-0.583937	-3.816881
H	1.871443	-0.729585	-4.886737
C	1.886437	1.865538	3.719078
C	2.640426	1.195246	4.718251
H	2.715915	1.450013	5.766491
C	3.612925	-2.443113	-3.235278
H	3.553587	-2.670092	-4.303231
H	3.317508	-3.326966	-2.664251
H	4.651489	-2.218697	-2.977420
C	1.036298	3.081678	3.850193
H	0.597107	3.352050	2.886082
H	1.629061	3.927370	4.217011
H	0.225281	2.913421	4.567728
C	4.168184	-0.886592	4.680428
H	4.213221	-0.736908	5.762580
H	5.178788	-0.826425	4.267817
H	3.805782	-1.897635	4.472934
C	-1.456147	5.429536	0.490352
F	-2.566752	5.120757	1.184210
F	-0.526093	5.814024	1.362056
F	-1.744550	6.449956	-0.309499
C	5.714971	-3.953093	-0.128620
H	4.807769	-4.475514	-0.437861
H	6.451613	-4.657509	0.257446
H	6.128270	-3.395558	-0.973594
Ag	-0.868308	-1.253620	-0.332909
S	0.869483	-3.983597	0.490045
O	0.563236	-3.020031	-0.621815
O	-0.290789	-4.492936	1.218429
O	2.030224	-3.581272	1.296441
N	-2.034040	-1.264006	-2.554652
N	-4.236643	1.439084	-1.875061
N	-1.545022	-0.247957	1.766478
N	-4.009098	1.964594	0.437862
N	-2.461564	0.759257	1.701821
N	-2.878003	-0.219443	-2.775427
N	-2.593932	0.366271	-0.562553
O	-5.431778	3.080320	-0.963237
C	-2.709216	1.299115	2.945896
C	-3.044122	1.059457	0.474589
C	-0.261337	-1.402836	3.511827
H	0.208293	-1.926430	2.676436
H	0.518143	-0.949060	4.133659
H	-0.777566	-2.153115	4.121615

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C	-3.257548	0.577044	-1.696492
C	-3.271476	-0.147156	-4.096619
C	-1.221135	-0.368648	3.041803
C	-4.518762	2.151934	-0.780595
C	-1.928527	0.583937	3.816881
H	-1.871443	0.729585	4.886737
C	-1.886437	-1.865538	-3.719078
C	-2.640426	-1.195246	-4.718251
H	-2.715915	-1.450013	-5.766491
C	-3.612925	2.443113	3.235278
H	-3.553587	2.670092	4.303231
H	-3.317508	3.326966	2.664251
H	-4.651489	2.218697	2.977420
C	-1.036298	-3.081678	-3.850193
H	-0.597107	-3.352050	-2.886082
H	-1.629061	-3.927370	-4.217011
H	-0.225281	-2.913421	-4.567728
C	-4.168184	0.886592	-4.680428
H	-4.213221	0.736908	-5.762580
H	-5.178788	0.826425	-4.267817
H	-3.805782	1.897635	-4.472934
C	1.456147	-5.429536	-0.490352
F	2.566752	-5.120757	-1.184210
F	0.526093	-5.814024	-1.362056
F	1.744550	-6.449956	0.309499
C	-5.714971	3.953093	0.128620
H	-4.807769	4.475514	0.437861
H	-6.451613	4.657509	-0.257446
H	-6.128270	3.395558	0.973594

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Table S3. Selected Geometrical distances (in Å) involving the Ag atoms for 2b y 4b structures. Rx refers to the crystal structure determined using X-ray diffraction. The theoretical values are obtained through DFT calculations at the PBE1PBE /6-31G* level of theory (see Figure S4 for the numeration).

	2b		**4b**	
	Experimental	Calculated	Experimental	Calculated
d (Ag1- N1)	2.446	2.544	2.503	2.509
d (Ag1- N3)	2.394	2.370	2.393	2.378
d (Ag1-N7)	2.390	2.396	2.283	2.424
d (Ag1-Ag2)	3.194	3.427	3.132	3.122
d (Ag2- N1’)	2.446	2.544	2.503	2.509
d (Ag2- N3´)	2.394	2.370	2.393	2.378
d (Ag2-N7’)	2.391	2.396	2.383	2.424

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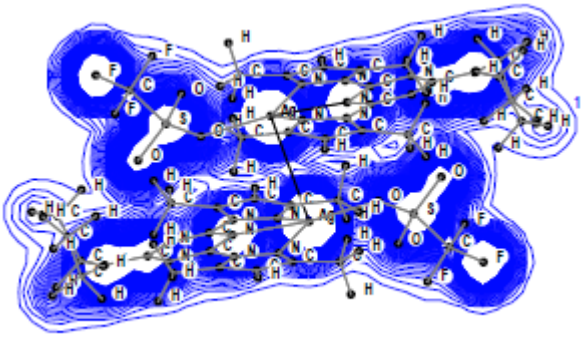
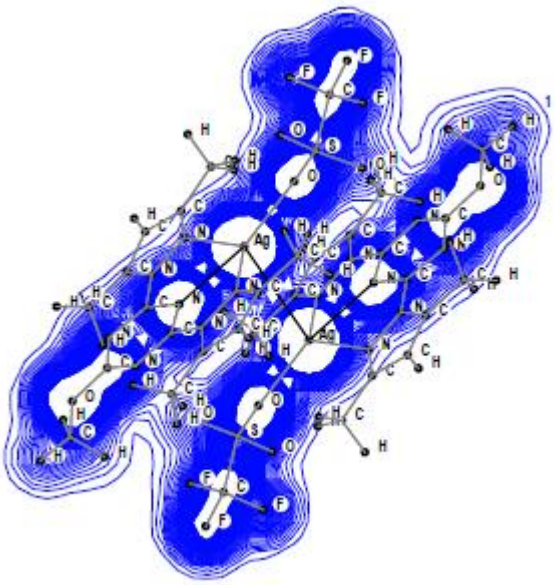
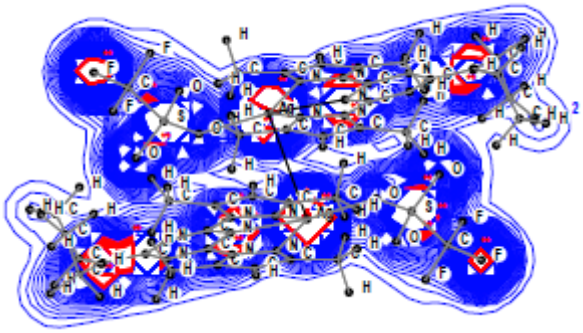
Figure S6. Electronic density and Laplacian of the charge density for the optimized compounds **2b** and **4b** in the plane defined by the atoms Ag(1)-Ag(2)-N(3) (see Figure S5 for the numeration). Blue contours indicate a positive value whereas the red contours correspond to negative values o the measured magnitude. To be noted that the Laplacian has a positive value at the critical points corresponding to the Ag-Ag bond.



a) Electronic density for compound **2b**



b) Electronic density for compound **4b**



c) Laplacian for compound **2b**

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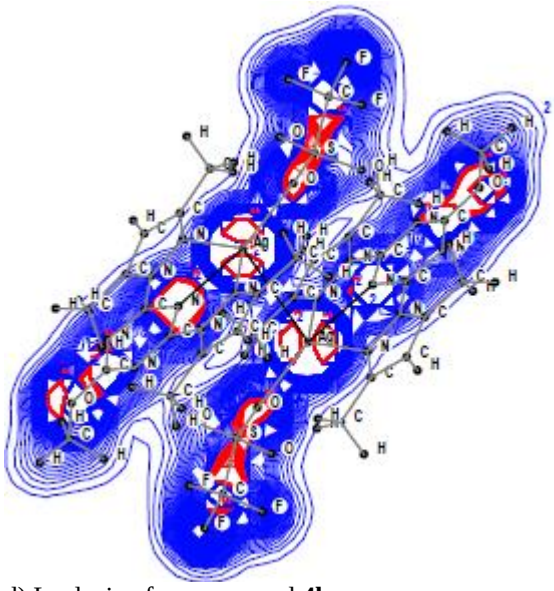

d) Laplacian for compound **4b**