Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Self pairing of 1-methylthymine and thymidine mediated by two and three Ag(I) ions: a gas phase study using infrared dissociation spectroscopy and density functional theory

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Electronic supplementary information (ESI)

The isomers encoding is based on locating the protonation (hX) and silver coordination (agXY) sites of the ligands. The positions (X,Y) are indicated according to the standard ring numbering of thymine starting from the methylated nitrogen atom (glycosidic site) with another nitrogen atom acquiring number three. So, the two carbonyl groups are described thus as positions two and four (see Fig. 1). The orientation of the OH bond approximately perpendicular to the N3C6 axis is indicated by the prime (') sign. For example, the ag2343h4' abbreviation describes a complex characterized by the C2O-Ag^{I}-N3 and C4O-Ag^{I}-N3 coordinative bridges with the O4H bond being ca. perpendicular to the N3C6 axis of the corresponding ligand (Fig. S1g).

Table S1. Single point energies (E_{sp}(B3LYP), in hartree), relative Gibbs energies (ΔG_T) at T=0 and T=298 K (in kJ/mol) and Ag-Ag distances (in pm) for selected isomers of $[Ag_2(1MT\text{-}H)(1MT)]^+$ calculated at the B3LYP/B3LYP-D3/CPCM-B3LYP-D3 level (basis set: aug-cc-pVDZ/ECP), as well as corresponding Boltzmann populations (in %).

isomer	E_{sp}	d(Ag-Ag)	ΔG_0	ΔG_{298}	Population
ag2433h4	-1280.3118450	282.3/282.5/283.2	0.0/0.0/0.0	0.0/0.0/1.5	49.0/65.6/20.4
ag2424h3	-1280.3112654	475.6/473.9/467.8	3.1/6.1/13.1	3.1/6.1/14.0	14.4/5.9/0.1
ag2244h3	-1280.3111489	475.5/473.8/467.8	3.4/6.5/13.2	3.4/6.4/14.1	12.8/5.3/0.1
ag2433h4'	-1280.3097174	284.9/285.0/284.4	5.2/5.2/1.4	4.5/4.7/4.2	8.3/10.3/7.0
ag2343h4'	-1280.3091174	286.2/285.8/283.6	6.6/6.5/0.1	5.2/5.9/0.2	6.3/6.4/34.0
ag2343h4	-1280.308995	284.7/284.4/282.8	7.1/8.3/0.0	5.6/7.1/0.0	5.4/4.0/36.8
ag2233h4	-1280.3087312	286.1/284.4/286.0	7.8/9.0/5.8	6.6/8.4/8.2	3.6/2.4/1.5
ag4433h2	-1280.3059693	281.6/281.6/283.4	15.1/15.2/14.4	14.8/14.9/16.8	0.1/0.2/0.0
ag2323h4'	-1280.3052445	292.6/289.5/285.2	16.0/17.4/5.9	12.5/15.6/5.7	0.4/0.1/3.9
ag4233h2	-1280.3030926	284.2/283.4/284.8	22.5/23.4/19.7	21.6/22.6/21.7	
ag4343h2'	-1280.2966037	284.8/284.4/282.0	38.1/38.1/23.6	36.3/36.9/25.1	
ag4323h2'	-1280.2925086	289.7/287.3/283.4	48.2/49.5/29.1	44.4/47.3/29.4	

Table S2. Experimentally observed vibrational frequencies (in cm^{-1}) and assignments for the investigated silver complexes of 1-methylthymine and thymidine.

$[Ag_2(1MT\text{-}H)(1MT)]^+$	$[Ag_3(1MT\text{-}H)_2]^+$	$[Ag_3(dT\text{-}H)_2]^+$	Assignment[a]
		3655	$\nu(OH)^f$(sugar)
3598			$\nu(OH)^f$
3488			$\nu(OH)^{Ag}$
2988/2867/2940		2943	$\nu(CH/CH_2/CH_3)$
1667	~1660	1648	ν(C5C6)
1632			$\nu(C2O)^{Ag}$ (xT) + $\nu(C2O)^f$ (xT-H)
	1580	1579	$\nu(C2O)^{Ag}$ (xT-H)
1560/1555			$\beta(OH)^{Ag}/\beta(OH)^f$
1518	1536	1535	$\nu(C4O)^{Ag}$ (xT-H)
1484/1463/1437			$\beta(CH_3)$ +ring def.
1374/1336			β(C6H)

[a] xT = 1-metylthymine/thymidine

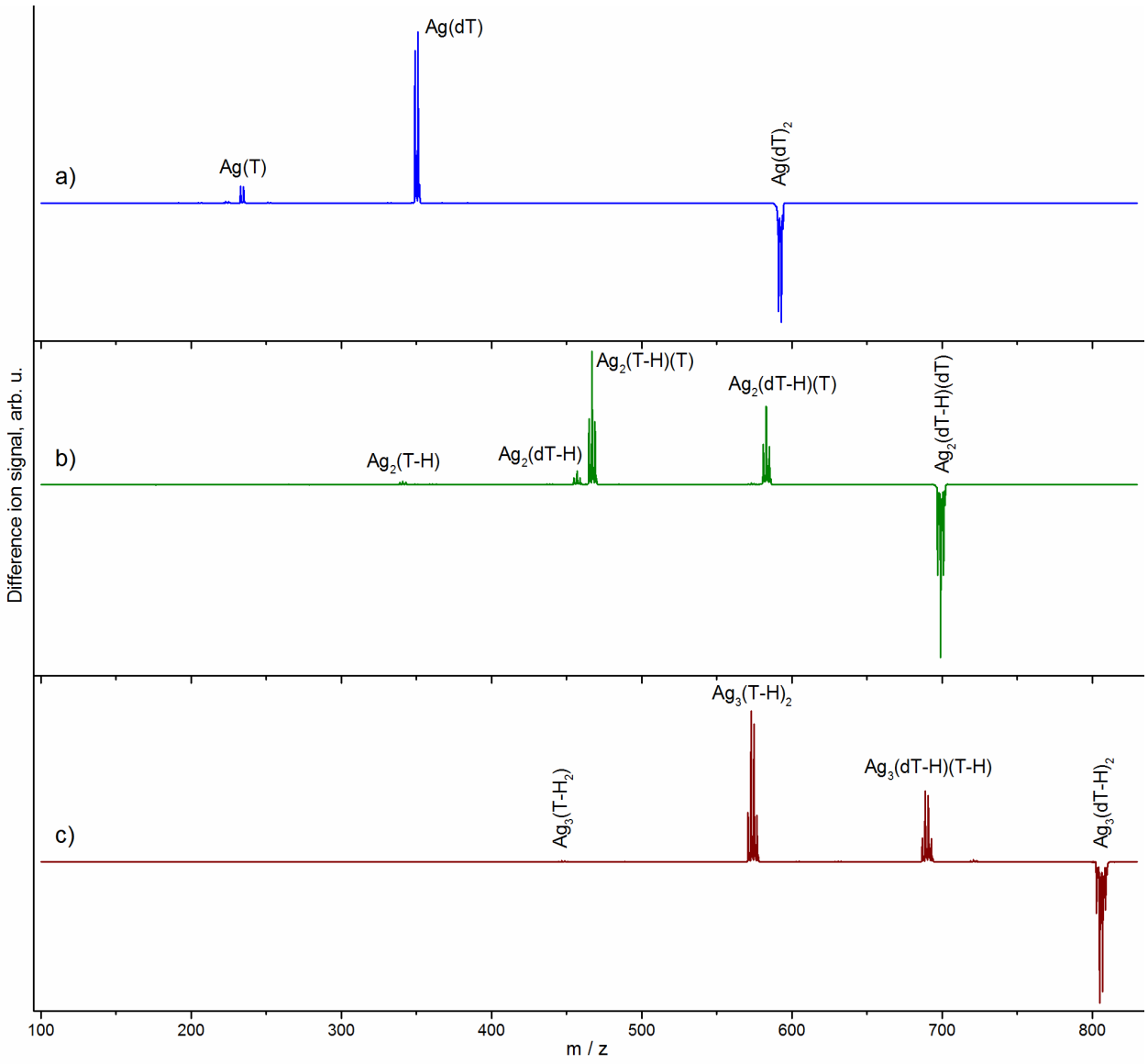

Figure S1. Difference mass spectra emphasizing IR induced fragmentations measured at the corresponding C=O stretch modes for the a) $[Ag(dT)_2]^+$, b) $[Ag_2(dT\text{-}H)(dT)]^+$ and c) $[Ag_3(dT\text{-}H)_2]^+$ complexes. The negative signals indicate depletion of the parent ions; the positive peaks show appearance of the related ion fragments. Assignments for the major ionic fragments are given.

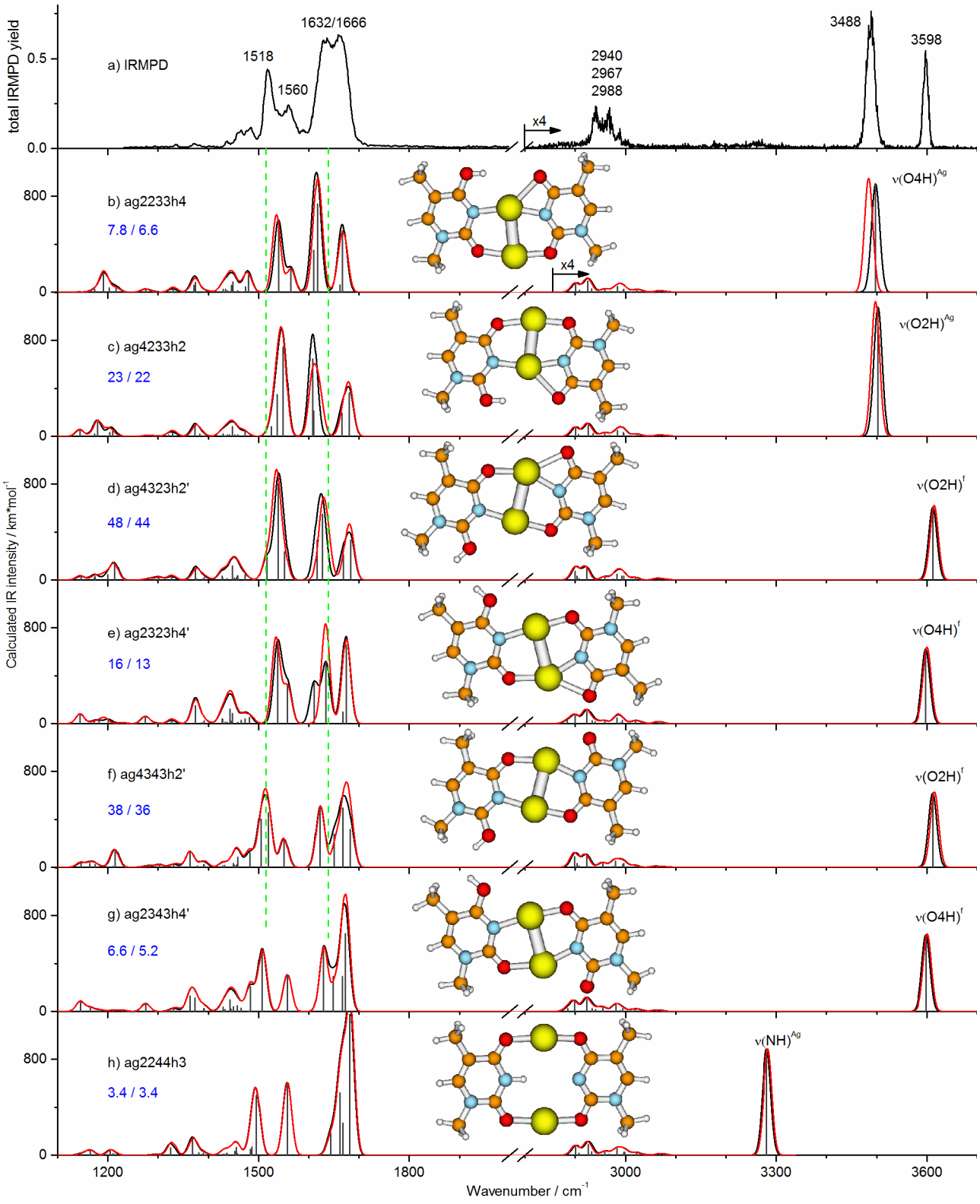

Figure S2. a) IRMPD of $[Ag_2(1MT\text{-}H)(1MT)]^+$ and b)-h) linear IR absorption spectra of its selected isomers calculated at the B3LYP/aug-cc-pVDZ/ECP level and simulated with Gaussian beam profile of fwhm=20 cm^{-1} (black lines). The red traces show the spectra based on B3LYP-D3 calculations. Calculated vibrational frequencies above and below 2000 cm^{-1} were scaled by 0.954 and 0.986, respectively. The optimized structures as well as relative Gibbs free energies at 0/298 K are shown.

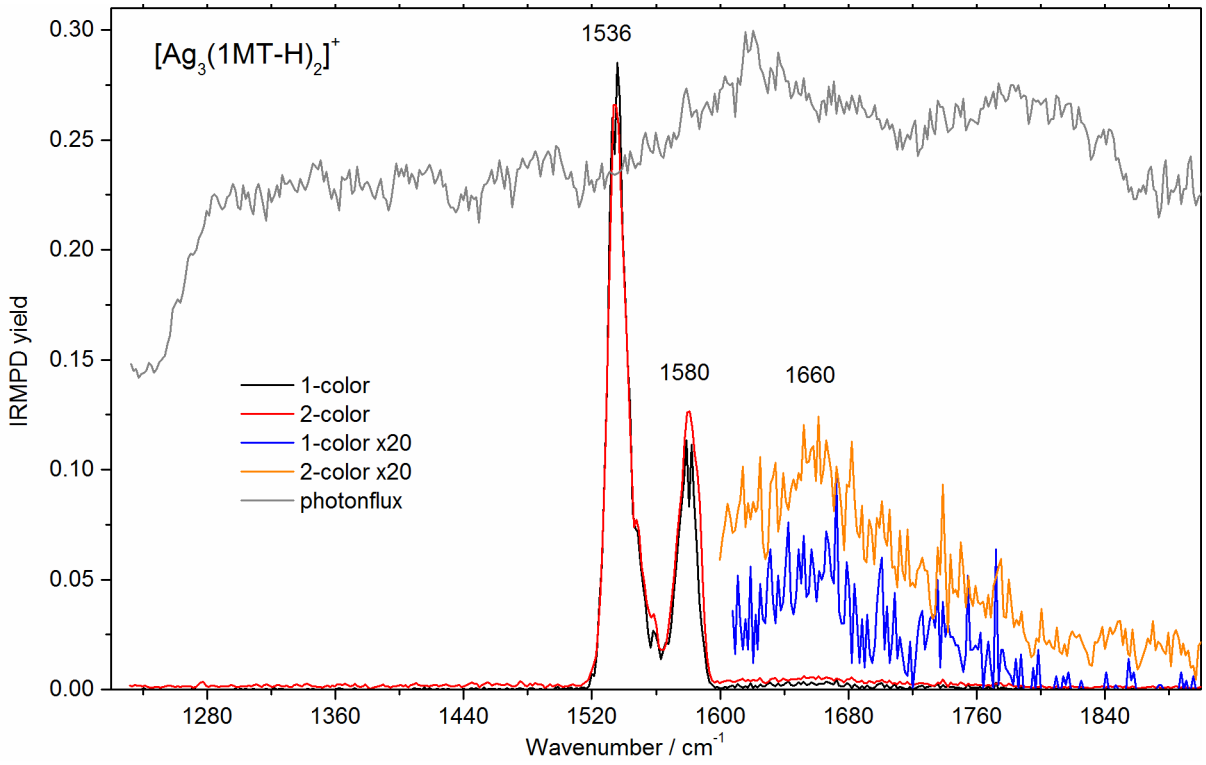

Figure S3. 1C- and 2C-IRMPD spectra of $[Ag_3(1MT\text{-}H)_2]^+$ (above 1600 cm^{-1} also x20 zoomed) along with the laser photon flux curve.

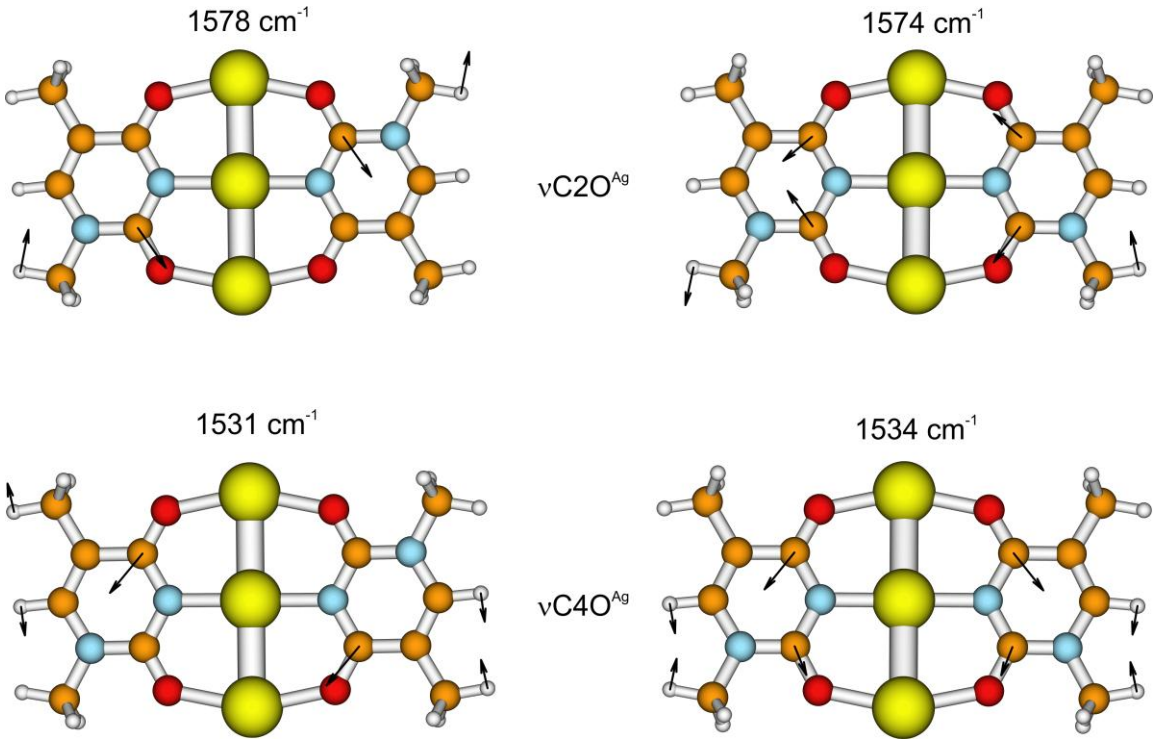

Figure S4. Normal coordinates of the ag243342 (left) and ag223344 (right) isomers corresponding to the allowed carbonyl stretch modes, calculated at the B3LYP/aug-cc-pVDZ level. The wavenumbers are scaled by the 0.986 factor. Insignificant vector displacements are omitted for clarity.

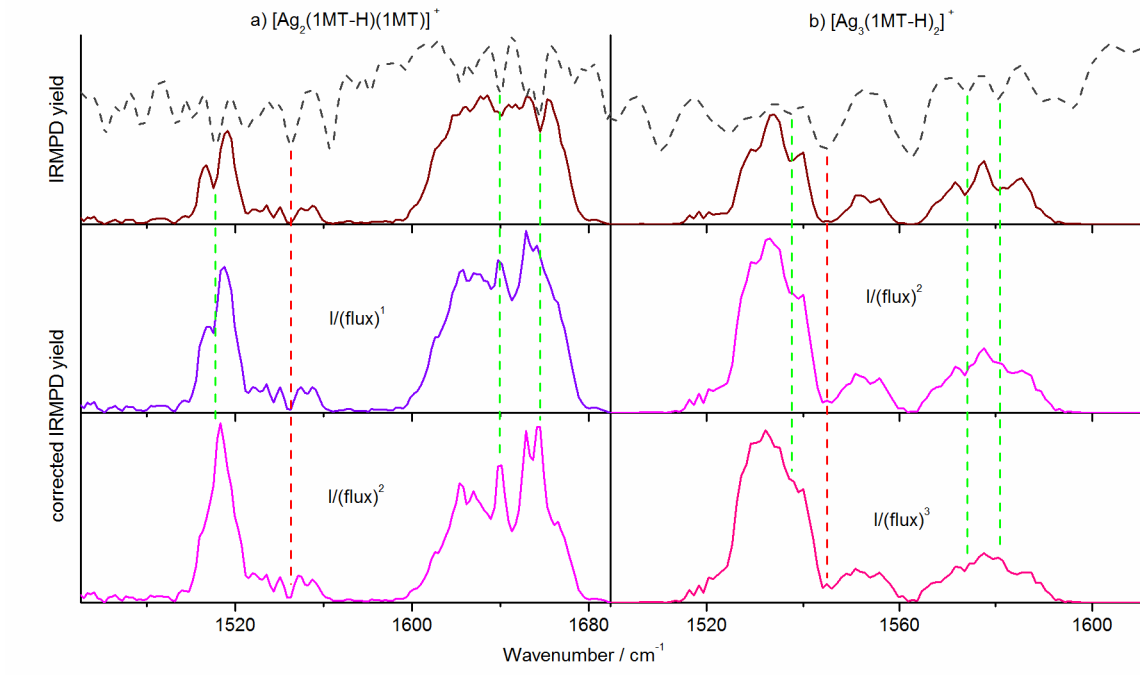

Figure S5. Top raw: the IRMPD spectra (continuous lines) of the 1MT self pair mediated by a) two and b) three Ag^{I} ions measured in the carbonyl stretch region under ca. 10% of the relative humidity so that the laser photon flux curves (dashed lines) were significantly modulated due to atmospheric water absorption. The lower raws represent the corresponding IRMPD spectra corrected for suitable power functions of the photon flux. While the bands above 1600 cm^{-1}, when not saturated, respond linearly to the flux, the <1600 cm^{-1} bands of the $[Ag_2(1MT\text{-}H)(1MT)]^+$ and $[Ag_3(1MT\text{-}H)_2]^+$ ions show up to quadratic and cubic dependencies, respectively. The signal dips at 1545 cm^{-1}, which could not be corrected within the applied models, clearly demonstrate the threshold character of the IRMPD process.

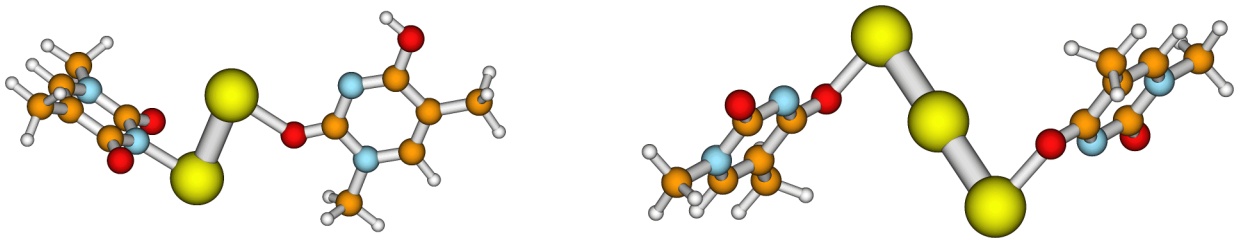

Figure S6. The model structures of the $[Ag_2(1MT\text{-}H)(1MT)]^+$ and $[Ag_3(1MT\text{-}H)_2]^+$ complexes used for estimation of the Ag-Ag interaction.

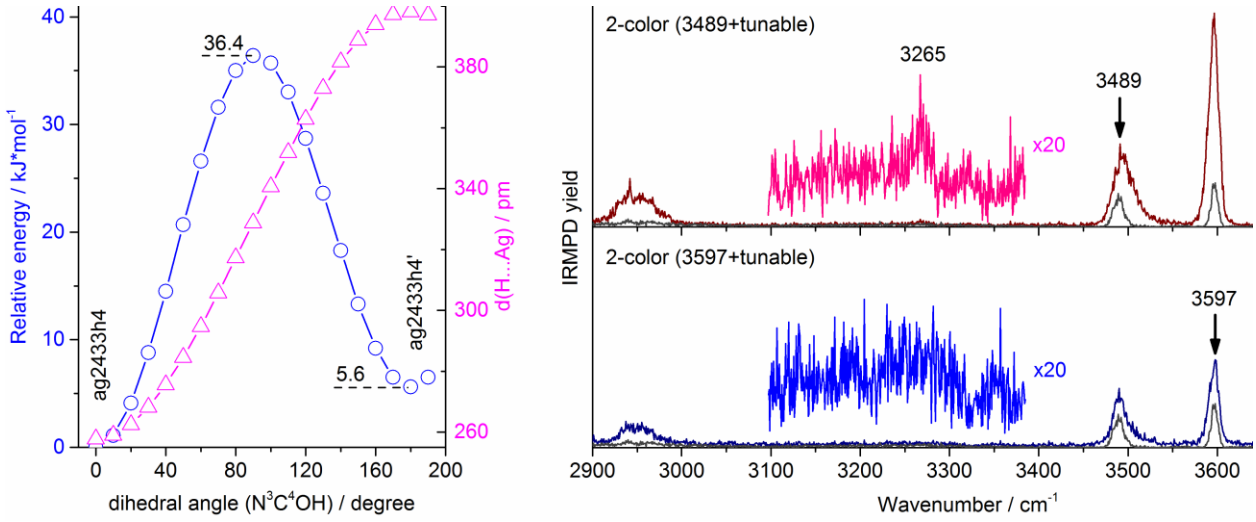

Figure S7. Right: fixed pump – tunable probe 2C-IRMPD spectra of $[Ag_2(1MT\text{-}H)(1MT)]^+$ with the pump frequencies fixed as indicated by the arrows. Black trace represent the 1C-IRMPD spectrum recorded at otherwise the same conditions. Left: relaxed potential energy surface scan (B3LYP/aug-cc-pVDZ/ECP) for the energy minimum structure of $[Ag_2(1MT\text{-}H)(1MT)]^+$ along the hydroxyl group torsion coordinate (blue circles) and the corresponding distances between the hydroxyl hydrogen atom and the silver centre (magenta triangles). The counterintuitive IR induced blue shift of the 3488 cm^{-1} band can be understood in terms of weakening of the OH…Ag interaction upon "warming up" the low frequency out-of-plane vibrational degrees of freedom.

Cartesian coordinates of selected isomers under study.

ag243342

N	-2.20653	0.64001	0.03912
C	-2.94234	1.7828	-0.00549
N	-4.30574	1.69139	0.16036
C	-4.8974	0.46575	0.36273
C	-4.19501	-0.69786	0.41149
C	-2.75882	-0.59972	0.2385
O	-2.04598	-1.64748	0.27373
O	-2.4452	2.93182	-0.19122
C	-4.83536	-2.03839	0.63265
Ag	-0.11738	0.81162	-0.20842
H	-5.97854	0.48822	0.48304
H	-4.62614	-2.71401	-0.20778
H	-5.92172	-1.9409	0.74185
H	-4.43353	-2.51824	1.5354
C	-5.10326	2.92642	0.11583
H	-4.98001	3.41715	-0.85553
H	-4.77424	3.61296	0.90322
H	-6.15326	2.66411	0.26805
C	2.70804	-0.15867	-0.40523
C	2.5244	2.2238	-0.65002
N	1.97205	0.98395	-0.45182
Ag	0.11303	-1.90784	0.07908
Ag	-0.34736	3.53188	-0.48813
O	1.81142	3.27142	-0.68593
O	2.21074	-1.30753	-0.21909
N	4.07157	-0.06713	-0.56954
C	4.86931	-1.30193	-0.5231
H	4.74525	-1.79184	0.44859
H	4.54118	-1.98927	-1.31017
H	5.91944	-1.03955	-0.67457
C	3.96082	2.32212	-0.82117
C	4.60124	3.66273	-1.04181
H	5.68791	3.56552	-1.14847
H	4.38996	4.33887	-0.20233
H	4.20122	4.14182	-1.94583
C	4.66329	1.15861	-0.77146
H	5.74459	1.13624	-0.89043

ag2433h4

N	-2.38131	0.81386	0.01913
C	-3.14393	1.93527	-0.03978
C	-4.57899	1.80646	0.13
C	-5.05929	0.54835	0.33552
N	-4.25822	-0.56618	0.38754
C	-2.88765	-0.44599	0.2282
O	-2.13279	-1.43019	0.2697
O	-2.6316	3.08638	-0.23915
C	-4.80834	-1.90848	0.61073
Ag	-0.27337	0.54793	-0.17038
H	-6.12324	0.36182	0.47092
H	-4.55868	-2.55993	-0.23413
H	-5.89419	-1.82804	0.71038
H	-4.38147	-2.34101	1.52252
C	-5.45747	3.02492	0.07458
H	-5.35712	3.53839	-0.89143
H	-5.17491	3.74872	0.85133
H	-6.51028	2.75395	0.21762
C	2.70731	-0.30296	-0.39237
C	2.36385	2.0135	-0.62375
N	1.87613	0.74329	-0.42448
Ag	-0.53128	3.34073	-0.49349
O	1.6513	3.03865	-0.66751
O	2.22626	-1.52265	-0.19971
H	1.25712	-1.52544	-0.09532
C	4.11622	-0.19375	-0.55642
C	5.01364	-1.3998	-0.51562
H	4.92683	-1.92162	0.44665
H	4.74159	-2.11807	-1.30047
H	6.05952	-1.10704	-0.65961
N	3.73194	2.16206	-0.78486
C	4.25267	3.52576	-0.99586
H	5.33842	3.4675	-1.10293
H	3.99186	4.15533	-0.13894
H	3.80749	3.95337	-1.90011
C	4.56653	1.08419	-0.75004
H	5.62378	1.30204	-0.88695

ag2424h3

N	-2.16358	0.00718	0.0015
C	-2.7694	-1.22615	0.00692
N	-4.13623	-1.21451	0.00942
C	-4.82931	-0.0193	0.00675
C	-4.23981	1.20902	0.00075
C	-2.79503	1.24257	-0.00215
O	-2.11961	2.2914	-0.00736
O	-2.12085	-2.29002	0.00937
C	-5.00653	2.50076	-0.00248
H	-1.1414	0.00304	0.00005
H	-5.91225	-0.12423	0.00972
H	-4.7481	3.10789	0.87554
H	-6.08607	2.31473	0.00502
H	-4.75866	3.09725	-0.89084
C	-4.8346	-2.51446	0.01457
H	-4.55493	-3.08154	0.90863
H	-4.55704	-3.08735	-0.87646
H	-5.91031	-2.32454	0.01516
C	2.71249	1.15771	0.00701
C	2.74391	-1.17965	-0.00397
N	2.05399	-0.01288	0.00025
Ag	0.03884	2.37974	-0.00778
Ag	0.05226	-2.37564	-0.00414
O	2.13613	-2.30669	-0.01038
O	2.12446	2.29393	0.00956
N	4.09193	1.19736	0.0124
C	4.76992	2.50035	0.02181
H	4.49122	3.07626	-0.86739
H	4.48063	3.06856	0.91254
H	5.84957	2.32778	0.02758
C	4.19503	-1.19223	-0.00149
C	4.94753	-2.49209	-0.0076
H	6.0304	-2.31915	-0.00879
H	4.68669	-3.09059	-0.89114
H	4.68986	-3.09717	0.87245
C	4.80384	0.02293	0.00712
H	5.88669	0.13038	0.01024

ag2244h3

N	-2.16411	0.01525	0.00471
C	-2.75568	-1.22382	0.01267
N	-4.12205	-1.22831	0.01128
C	-4.82944	-0.04074	0.00182
C	-4.25439	1.19402	-0.0074
C	-2.80968	1.24457	-0.00558
O	-2.14516	2.29906	-0.01249
O	-2.09566	-2.28185	0.02073
C	-5.03536	2.47703	-0.01847
H	-1.14194	0.02759	0.00813
H	-5.91102	-0.15861	0.00188
H	-4.78594	3.09067	0.85763
H	-6.11283	2.2793	-0.01345
H	-4.79092	3.07241	-0.90852
C	-4.80601	-2.53579	0.01965
H	-4.5234	-3.09613	0.91705
H	-4.51963	-3.10938	-0.86813
H	-5.88372	-2.35771	0.01601
C	2.7217	1.19282	0.01054
C	2.73468	-1.14463	-0.01073
N	2.054	0.0129	-0.0008
Ag	0.01783	2.38872	-0.00573
Ag	0.07288	-2.36587	-0.00045
O	2.16585	-2.29137	-0.02042
O	2.09505	2.30864	0.01639
C	4.17277	1.23158	0.01614
C	4.90078	2.54519	0.03286
H	4.63352	3.15152	-0.84344
H	4.6267	3.13255	0.91994
H	5.98663	2.39255	0.0356
N	4.11418	-1.15948	-0.01142
C	4.81599	-2.44965	-0.02374
H	5.89222	-2.25707	-0.03105
H	4.53579	-3.02149	-0.91495
H	4.54963	-3.032	0.86521
C	4.80429	0.02822	0.00308
H	5.88895	-0.05953	0.00315

ag2433h4’

N	-2.43502	0.7764	0.0357
C	-3.17057	1.91471	-0.02232
C	-4.6098	1.82904	0.1441
C	-5.12818	0.58636	0.34696
N	-4.35865	-0.54862	0.39903
C	-2.98164	-0.46862	0.24268
O	-2.26316	-1.47626	0.28635
O	-2.63288	3.05569	-0.21891
C	-4.94488	-1.87498	0.61966
Ag	-0.31364	0.42738	-0.15223
H	-6.19751	0.43064	0.4797
H	-4.70779	-2.53362	-0.22333
H	-6.02893	-1.76622	0.7138
H	-4.53393	-2.31914	1.53331
C	-5.45098	3.07354	0.08742
H	-5.33521	3.58362	-0.87878
H	-5.1476	3.7895	0.86366
H	-6.51164	2.83432	0.23006
C	2.68861	-0.27045	-0.40524
C	2.34952	2.03691	-0.62625
N	1.86183	0.77224	-0.43199
Ag	-0.53729	3.24951	-0.46962
O	1.64454	3.06516	-0.66575
O	2.07472	-1.43567	-0.20804
H	2.69594	-2.17908	-0.19173
C	4.09783	-0.16777	-0.57027
C	5.0019	-1.37219	-0.53538
H	4.94763	-1.89329	0.4327
H	4.75094	-2.09148	-1.32997
H	6.04633	-1.077	-0.68528
N	3.72392	2.18693	-0.79033
C	4.24329	3.55175	-0.99707
H	5.32914	3.49604	-1.10588
H	3.98126	4.17734	-0.13766
H	3.79491	3.98168	-1.89861
C	4.55358	1.1113	-0.76075
H	5.61175	1.32564	-0.89825

ag2343h4’

N	-2.38062	-0.19087	0.0024
C	-3.42718	-1.08373	0.01146
N	-4.71452	-0.5608	0.01408
C	-4.91003	0.79638	0.00743
C	-3.88806	1.69733	-0.00197
C	-2.54341	1.15355	-0.00405
O	-1.54502	1.95224	-0.01189
O	-3.22129	-2.30324	0.01692
C	-4.10219	3.18521	-0.00988
Ag	0.45127	1.26885	-0.00875
H	-5.9504	1.11744	0.01003
H	-3.63623	3.65534	0.86713
H	-5.17214	3.42553	-0.00539
H	-3.64609	3.64439	-0.89783
C	-5.8344	-1.50849	0.02469
H	-5.78322	-2.13821	0.92004
H	-5.78392	-2.15639	-0.85751
H	-6.77057	-0.94329	0.01941
C	3.53337	1.09394	0.00928
C	2.55447	-1.03707	-0.00851
N	2.44366	0.33045	-0.00172
Ag	-0.59164	-1.39665	-0.00517
O	1.58717	-1.81913	-0.01944
O	3.27482	2.40235	0.0141
H	4.08656	2.93153	0.0219
C	4.85942	0.58051	0.01565
C	6.07001	1.47701	0.02869
H	6.1069	2.12478	-0.86064
H	6.09366	2.11673	0.92426
H	6.99086	0.88331	0.03282
N	3.83638	-1.58369	-0.00313
C	3.94859	-3.05458	-0.01059
H	5.00829	-3.3213	-0.00492
H	3.46267	-3.45384	-0.90674
H	3.4506	-3.46374	0.8744
C	4.93698	-0.78895	0.00877
H	5.89486	-1.30579	0.0126

ag2343h4

N	-2.60336	1.34097	-0.02643
C	-3.53531	2.35129	-0.0542
N	-4.86613	2.00111	0.12608
C	-5.21392	0.68939	0.32261
C	-4.30695	-0.32794	0.35386
C	-2.91835	0.03972	0.16526
O	-2.01679	-0.87095	0.1834
O	-3.18614	3.52536	-0.23414
C	-4.68918	-1.76576	0.56981
Ag	0.00411	-0.37128	-0.09369
H	-6.27866	0.50473	0.45499
H	-4.37629	-2.38879	-0.27939
H	-5.77403	-1.86679	0.69286
H	-4.19848	-2.17405	1.46408
C	-5.86509	3.07624	0.09676
H	-5.8359	3.58663	-0.87239
H	-5.64731	3.8089	0.88175
H	-6.85406	2.63871	0.25844
C	3.08659	-0.71007	-0.41077
C	2.35906	1.52204	-0.56589
N	2.09083	0.18164	-0.3925
Ag	-0.71769	2.3718	-0.34113
O	1.49012	2.41461	-0.56297
O	2.81769	-1.99843	-0.24316
H	1.8636	-2.14783	-0.1191
C	4.45275	-0.36679	-0.60266
C	5.53712	-1.40893	-0.61586
H	5.56579	-1.95921	0.33403
H	5.36632	-2.14444	-1.41321
H	6.51584	-0.94368	-0.77692
N	3.68128	1.89662	-0.75503
C	3.96185	3.33329	-0.93909
H	5.03868	3.45993	-1.07409
H	3.62406	3.88893	-0.05831
H	3.42521	3.70217	-1.81919
C	4.68181	0.97254	-0.77058
H	5.68486	1.36474	-0.92606

ag2233h4

N	-2.10401	0.38846	-0.00647
C	-2.85754	-0.72336	0.00391
N	-4.22776	-0.58612	0.00639
C	-4.79302	0.67581	0.00281
C	-4.06427	1.82302	-0.00429
C	-2.61706	1.67296	-0.00817
O	-1.80004	2.61644	-0.01242
O	-2.37229	-1.90113	0.01336
C	-4.67318	3.19534	-0.00701
Ag	0.0231	0.76368	-0.01005
H	-5.88132	0.68855	0.00654
H	-4.34347	3.76818	0.87069
H	-5.76841	3.14277	-0.00173
H	-4.35174	3.76118	-0.89233
C	-5.06054	-1.79578	0.01615
H	-4.85165	-2.39155	0.91163
H	-4.85059	-2.40582	-0.86936
H	-6.11063	-1.49207	0.013
C	3.03834	1.54755	0.00785
C	2.67463	-0.77576	-0.01238
N	2.19451	0.51222	-0.00562
H	1.59251	2.80849	0.01227
Ag	-0.23343	-2.0853	0.00805
O	1.94782	-1.79242	-0.02123
O	2.56644	2.78533	0.01799
C	4.45467	1.40823	0.01341
C	5.36579	2.60443	0.03034
H	5.19328	3.24139	-0.8473
H	5.18562	3.22188	0.92039
H	6.41556	2.29061	0.03142
N	4.04699	-0.95466	-0.01061
C	4.55956	-2.33743	-0.0214
H	5.6516	-2.30064	-0.02152
H	4.20045	-2.85537	-0.91672
H	4.20105	-2.86952	0.86571
C	4.89637	0.11354	0.00222
H	5.95715	-0.12842	0.00336

ag4433h2

N	2.17023	0.49058	0.00008
C	2.96638	1.54913	-0.00547
N	4.31235	1.47466	-0.0038
C	4.89655	0.22017	0.00612
C	4.16327	-0.92244	0.01201
C	2.71318	-0.79303	0.0073
O	1.98898	-1.81134	0.01033
O	2.48895	2.7877	-0.01328
C	4.77712	-2.29141	0.02261
Ag	0.0072	0.67969	0.00195
H	5.9838	0.21782	0.0086
H	4.44818	-2.8535	0.90705
H	5.87121	-2.23377	0.02584
H	4.45411	-2.86448	-0.85695
C	5.13141	2.70555	-0.01201
H	4.91231	3.30449	0.87779
H	4.9128	3.29213	-0.91017
H	6.18263	2.40941	-0.00982
C	-2.84682	-0.731	-0.00111
C	-2.64454	1.67106	0.00419
N	-2.10686	0.40765	0.00161
Ag	-0.18601	-2.12978	-0.00942
H	1.51488	2.79131	-0.01572
O	-1.90907	2.67129	0.00541
O	-2.30381	-1.88447	-0.00657
C	-4.29324	-0.61553	0.00236
C	-5.14795	-1.85195	0.00309
H	-4.94061	-2.47339	-0.87891
H	-4.94071	-2.47236	0.88579
H	-6.21286	-1.59067	0.00325
N	-4.02568	1.77785	0.00496
C	-4.61072	3.12371	0.00663
H	-4.28192	3.67526	-0.88107
H	-4.28603	3.67217	0.89798
H	-5.70013	3.0304	0.00426
C	-4.80542	0.64661	0.00439
H	-5.87956	0.82364	0.00556