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

Supplementary Information for

Molecular structure and vibrations of NTCDA monolayers on Ag(111) from density-functional theory and infrared absorption spectroscopy

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Table S1. Lattice contants a_0 (in Å), bulk modulus B_0 (in GPa), and volume per atom V_0 (in Å^3) for the Ag bulk (fcc) with different dispersion correction methods in comparison to experimental reference data.

	PBE	PBE-D2$_{PBC}$	PBE-D3$_{PBC}$	Experiment [a]
a_0	4.147	4.131	4.073	4.069
B_0	91.8	67.7	111.5	109
V_0	71.3	70.5	67.6	67.4

[a] Values taken from V. N. Staroverov, G. E. Scuseria, J. Tao, J. P. Perdew *Phys. Rev. B* 69, 075102 (2004).

Table S2 Calculated vertical distances and corrugation of Ag-surface and Ag sub-surface layer for all adsorption configurations [a]. The topmost Ag surface layer before relaxation (extrapolated bulk position of Ag surface atoms) is taken as reference layer ($z_{Ref} = 0$) for the derived distances. Our choice of $z_{Ref} = 0$ ensures direct comparison to NIXSW data. Note that the averaged vertical position of the Ag surface layer is then found at -0.02815Å. All values are given in [Å].

d(A – B)	$Bridge_1$	$Bridge_1$ (PBE)[b]	$Bridge_2$	Top_1	Top_2
$O_{acyl.}$ – Ag	2.577 (+0.004/-0.003)	3.276 (+0.011/-0.010)	2.526 (+/-0.004)	2.622 (+/-0.003)	2.644 (+0.010/-0.012)
$O_{anh.}$ – Ag	2.806 (+/-0.001)	3.418	2.822 (+/-0.003)	2.798 (+/-0.001)	2.862 (+/-0.016)
C_{all} – Ag[c]	2.905 (+0.109-0.104)		3.005 (+0.152/-0.178)	2.890 (+0.086/-0.090)	2.911 (+0.085/-0.091)
C_{ring} – Ag[d]	2.946 (+0.068/-0.050)	3.534 (+0.042/-0.032)	3.074 (+0.082/-0.046)	2.925 (+0.051/-0.036)	2.943 (0.053/-0.036)
O_{acyl} – C_{ring}	-0.369 (+0.054/-0.070)	-0.259 (+0.043/-0.052)	-0.548 (+0.050/-0.086)	-0.307 (+0.036/-0.052)	-0.300 (+0.046/-0.066)
$O_{anh.}$ – C_{ring}	-0.140 (+0.050/-0.068)	-0.116 (+0.032/-0.042)	-0.252 (+0.049/-0.085)	-0.134 (+0.036/-0.051)	-0.082 (+0.052/-0.069)
$O_{anh.}$ – O_{acyl}	0.230 (+0.003/-0.004)	0.143 (+0.011/-0.012)	0.296 (+/-0.007)	0.173 (+/-0.005)	0.218 (+0.028/-0.026)
$\delta z_{Ag\text{-}Ag}$[e]	0.134	0.077	0.160	0.208	0.198
$\delta z_{Ag/sub\text{-}Ag/sub}$[f]	0.025	0.021	0.055	0.076	0.062

[a] Averaged values for equivalent atoms. In parentheses, maximum positive and negative deviations of individual atomic positions within the entity from this averaged value are given. These numbers should not be confused with errors and inaccuracies associated with the calculations and used functionals.
[b] Structure optimized without dispersion correction (PBE).
[c] Averaged position of all carbon atoms above $z_{Ref} = 0$.
[d] Averaged position of ring carbon atoms (C_{ring} – see scheme 1) above $z_{Ref} = 0$.
[e] Difference in z-coordinates of Ag atoms (corrugation) of the topmost layer.
[f] Difference in z-coordinates of Ag atoms (corrugation) of the sub-surface layer.

Table S3

All computed vibrational modes for molecular (free) NTCDA with MP2/TZ, PBE-D3/TZ and PBE-D3$_{PBC}$ together with modes for NTCDA adsorbed on Ag(111) (Bridge$_1$, PBE-D3$_{PBC}$). Given are vibrational frequencies (**ν**, in cm^{-1}) and IR-intensities (**I**, normalized to the most intense mode). The mode character is specified for selected modes only.

		Free NTCDA molecule						NTCDA/Ag(111)				Mode character
	Mode[a]	MP2/TZ		PBE-D3/TZ		PBE-D3$_{PBC}$		PBE-D3$_{PBC}$				
#	Sym-metry	**ν**	**I**	**ν**	**I**	**ν**	**I**	**ν**	**I$_z$[b]**	**$\lvert\nu_{min} - \nu_{max}\rvert$ [c]**	**Δν[d]**	
T_x	b_{1u}							22.2				
T_y	b_{2u}							34.8				
R_z	b_{3g}							37.2				
T_z	b_{3u}							74.8				
R_x	b_{1g}							84.1				
R_y	b_{2g}							79.6				
1	a_u	41.32	0.000	39.66	0.000	29.49	0.000	89.6	0.000	40.5	60.1	
2	b_{1g}	73.34	0.000	71.86	0.000	73.63	0.000	130.6	0.000	19.7	57	
3	b_{3u}	83.20	0.015	77.03	0.015	74.85	0.015	102.8	0.006	9.5	17.9	
4	b_{3u}	119.98	0.001	123.90	0.002	119.35	0.002	169.3	0.006	13.5	49.9	
5	b_{2g}	122.26	0.000	127.14	0.000	121.57	0.000	176.4	0.000	22.3	54.8	
6	b_{3u}	182.48	0.004	182.94	0.004	183.15	0.004	247.9	0.000	16.6	64.7	
7	b_{2u}	216.51	0.019	212.23	0.018	215.71	0.018	222.4	0.000	5.4	6.7	
8	b_{2g}	237.58	0.000	234.49	0.000	233.78	0.000	231.0	0.000	4.7	-2.8	
9	a_u	272.84	0.000	272.57	0.000	272.40	0.000	262.2	0.000	12.6	-10.2	
10	a_g	313.87	0.000	306.17	0.000	310.80	0.000	318.1	0.000	9.1	7.3	

11	b_{3g}	335.35	0.000	328.58	0.000	334.44	0.000	336.6	0.000	5.4	2.2	
12	b_{1u}	372.41	0.057	364.37	0.053	367.77	0.102	370.4	0.000	5.0	2.6	
13	b_{3g}	406.62	0.000	394.24	0.000	400.03	0.000	407.4	0.000	4.6	7.4	
14	a_g	408.96	0.000	397.09	0.000	399.33	0.000	396.1	0.009	3.3	-3.2	
15	b_{1g}	425.53	0.000	427.44	0.000	424.56	0.000	361.1	0.000	14.9	-63.5	
16	b_{2u}	440.31	0.008	427.45	0.010	430.37	0.013	449.9	0.000	3.3	19.5	
17	b_{2g}	442.61	0.000	454.43	0.000	452.58	0.000	502.8	0.000	6.8	50.2	
18	b_{1u}	471.14	0.000	455.17	0.002	469.75	0.035	461.0	0.000	7.3	-8.8	
19	b_{2g}	478.41	0.000	827.98[e]	0.000	826.07[e]	0.000	795.9[e]	0.000	8.6	-30.2	
20	b_{3u}	530.52	0.020	540.26	0.021	535.86	0.024	510.5	0.024	7.1	-25.4	
21	a_u	544.48	0.000	600.29	0.000	596.91	0.000	571.8	0.000	5.0	-25.1	
22	a_g	546.07	0.000	529.44	0.000	533.79	0.000	535.9	0.054	9.1	2.1	
23	b_{1u}	599.05	0.003	584.82	0.002	592.03	0.138	605.3	0.000	4.5	13.3	
24	b_{3g}	600.48	0.000	591.76	0.000	593.49	0.000	603.1	0.000	3.9	9.6	
25	a_g	664.40	0.000	650.05	0.000	652.21	0.000	648.1	0.004	2.9	-4.1	
26	b_{2u}	696.86	0.039	681.12	0.033	681.69	0.036	673.8	0.000	2.3	-7.9	
27	b_{2g}	727.63	0.000	691.79	0.000	686.92	0.000	665.4	0.000	7.1	-21.5	
28	b_{1g}	732.14	0.000	718.50	0.000	713.89	0.000	689.5	0.000	6.7	-24.4	
29	b_{3u}	747.73	0.091	753.19	0.084	747.11	0.093	717.9	0.058	6.7	-29.2	
30	a_u	751.45	0.000	759.86	0.000	753.87	0.000	720.8	0.000	6.5	-33.1	
31	b_{1u}	752.23	0.003	737.26	0.000	745.28	0.072	748.8	0.000	4.8	3.5	
32	b_{3g}	806.67	0.000	786.40	0.000	787.72	0.000	789.2	0.000	3.9	1.5	
33	b_{1u}	828.55	0.000	806.60	0.003	812.35	0.052	813.6	0.001	4.6	1.2	
34	b_{1g}	880.72	0.000	876.24	0.000	874.43	0.000	808.0	0.000	6.6	-66.4	
35	b_{3u}	881.92	0.051	877.25	0.034	874.57	0.036	813.0	0.002	5.4	-61.6	
36	a_u	947.00	0.000	982.86	0.000	982.07	0.000	937.8	0.000	6.4	-44.3	
37	b_{2u}	954.02	0.016	923.94	0.088	934.00	0.050	916.3	0.000	8.7	-17.7	
38	b_{2g}	961.35	0.000	983.16	0.000	982.31	0.000	943.3	0.000	7.0	-39.0	
39	a_g	1014.61	0.000	984.52	0.000	990.32	0.000	987.0	0.002	6.0	-3.3	
40	b_{3g}	1049.07	0.000	962.85	0.000	986.68	0.000	958.6	0.000	15.2	-28.1	C-O_{Anh} stretch
41	b_{2u}	1068.54	0.883	994.06	0.756	1011.60	0.789	959.5	0.000	11.6	-52.1	C-O_{Anh} stretch
42	a_g	1125.03	0.000	1091.81	0.000	1101.02	0.000	1104.2	0.021	8.1	3.2	

43	b_{1u}	1135.20	0.347	1097.45	0.298	1108.14	0.108	1084.5	0.000	8.3	-23.6	
44	b_{3g}	1164.73	0.000	1131.82	0.000	1139.85	0.000	1123.9	0.000	7.2	-16.0	
45	b_{2u}	1187.44	0.208	1143.76	0.108	1156.50	0.128	1155.8	0.000	7.2	-0.7	
46	b_{3g}	1235.79	0.000	1189.76	0.000	1198.45	0.000	1208.2	0.000	6.2	9.7	
47	b_{2u}	1280.92	0.265	1229.69	0.146	1239.40	0.186	1211.1	0.000	7.5	-28.3	
48	a_g	1285.24	0.000	1238.11	0.000	1248.20	0.000	1256.9	0.038	6.7	8.7	
49	b_{1u}	1316.91	0.480	1269.47	0.517	1283.85	0.499	1282.5	0.000	7.1	-1.4	
50	a_g	1392.19	0.000	1352.90	0.000	1357.93	0.000	1345.5	0.581	9.0	-12.4	
51	b_{1u}	1475.33	0.039	1423.98	0.049	1432.64	0.088	1435.8	0.000	8.2	3.2	
52	a_g	1492.64	0.000	1420.16	0.000	1428.95	0.000	1404.8	0.133	13.7	-24.2	
53	b_{3g}	1498.59	0.000	1456.46	0.000	1462.51	0.000	1419.8	0.000	7.5	-42.7	
54	b_{2u}	1527.48	0.000	1383.67	0.004	1392.74	0.005	1430.4	0.000	12.6	37.7	
55	b_{2u}	1559.87	0.009	1512.23	0.027	1519.52	0.023	1509.8	0.000	9.7	-9.7	
56	b_{1u}	1613.96	0.040	1571.79	0.098	1575.83	0.066	1493.6	0.000	12.5	-82.2	
57	a_g	1628.64	0.000	1586.12	0.000	1593.96	0.000	1565.6	1.000	7.8	-28.4	
58	b_{3g}	1669.26	0.000	1610.55	0.000	1617.84	0.000	1541.2	0.000	12.5	-76.6	
59	b_{2u}	1788.56	1.000	1744.69	0.955	1733.07	1.000	1580.9	0.000	21.6	-152.2	C=O/C=O-Ag
60	b_{3g}	1791.65	0.000	1745.98	0.000	1733.99	0.000	1593.0	0.000	29.2	-141.0	C=O/C=O-Ag
61	a_g	1819.90	0.000	1781.18	0.000	1770.63	0.000	1625.7	0.264	22.1	-144.9	C=O/C=O-Ag
62	b_{1u}	1824.06	0.729	1775.49	1.000	1802.49	0.248	1628.9	0.024	17.0	-173.6	C=O/C=O-Ag
63	b_{1u}	3230.52	0.004	3133.42	0.002	3114.27	0.003	3113.8	0.000	5.1	-2.1	C-H stretch
64	b_{3g}	3230.66	0.000	3133.67	0.000	3114.00	0.000	3112.2	0.000	6.0	-0.2	C-H stretch
65	b_{2u}	3242.39	0.008	3143.74	0.002	3125.17	0.005	3122.9	0.000	3.8	-2.3	C-H stretch
66	a_g	3242.52	0.000	3143.88	0.000	3125.07	0.000	3126.5	0.000	6.5	1.4	C-H stretch

Statistics[f]	vs MP2/TZ	vs. PBE-D3/TZ
Max	56	24
Min	-144	-20 (-12)
RMS	32 (28)	7 (6)

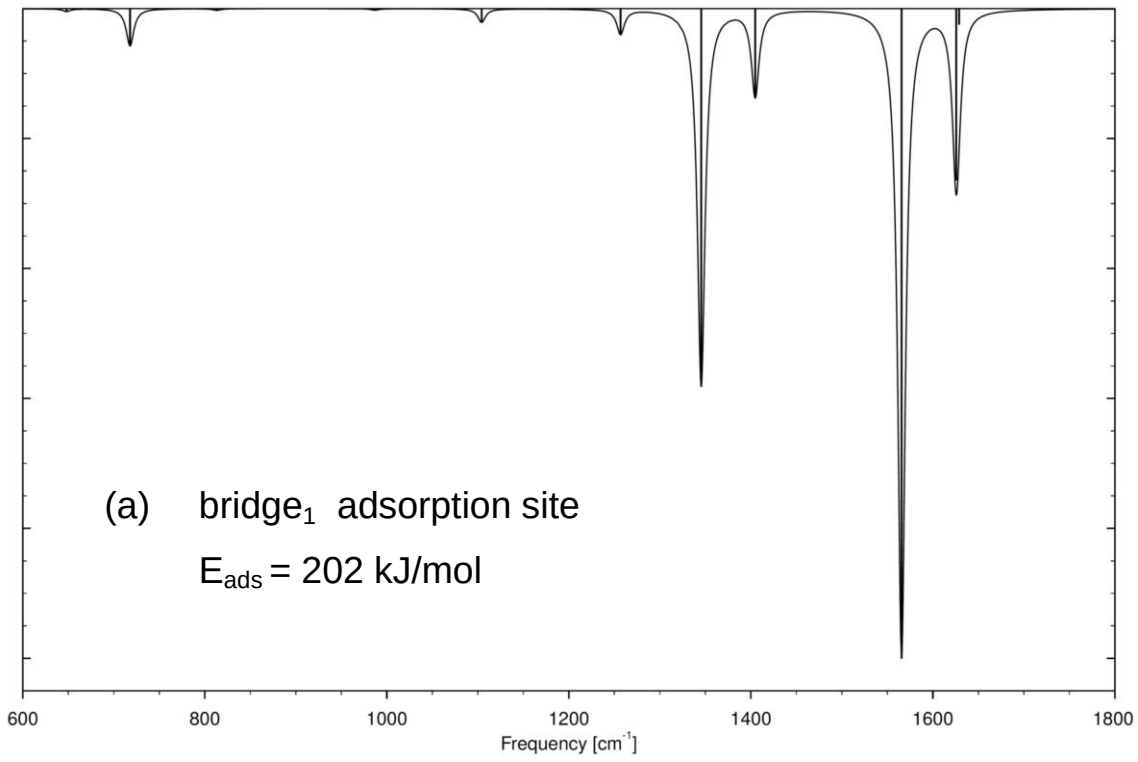
[a] The sorting of modes and the symmetry assignment refers to the MP2/TZ data (D_{2h} symmetry). Matching of the vibrational modes for the different levels of approximation has been carried out by visual inspection of the displacement pattern and comparison to MP2/TZ.
[b] Intensities computed considering dipole changes perpendicular to the surface only.
[c] Magnitude of spread of the vibrational modes when considering all adsorption geometries for NTCDA/Ag(111) depicted in Figure 1.
[d] Change in vibrational frequency upon adsorption via dynamical dipole approach.
[e] Very strongly shifted mode (MP2 compared to PBE) which has been excluded from the statistical measures.
[f] Maximal and minimal deviation together with root-mean-square error for the modes given in that column relative to the level of approximation indicated. Values in brackets are deviations excluding the C-H stretch modes (modes 63-66).

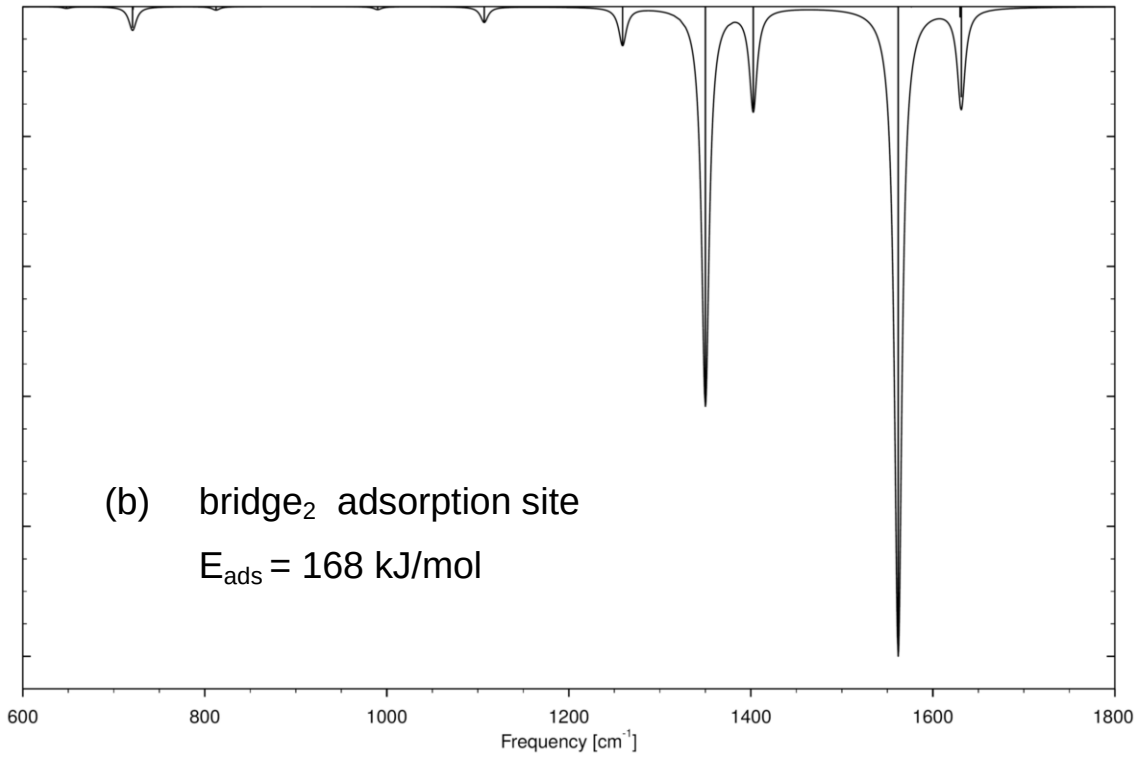
Table S4. Vibrational modes of NTCDA/Ag (PBE-D3$_{PBC}$) for all adsorption geometries considered in this study. Given are vibrational frequencies (**ν**, in cm^{-1}) and IR-intensities (**I**, normalized to the most intense mode). The ordering is taken from table S3.

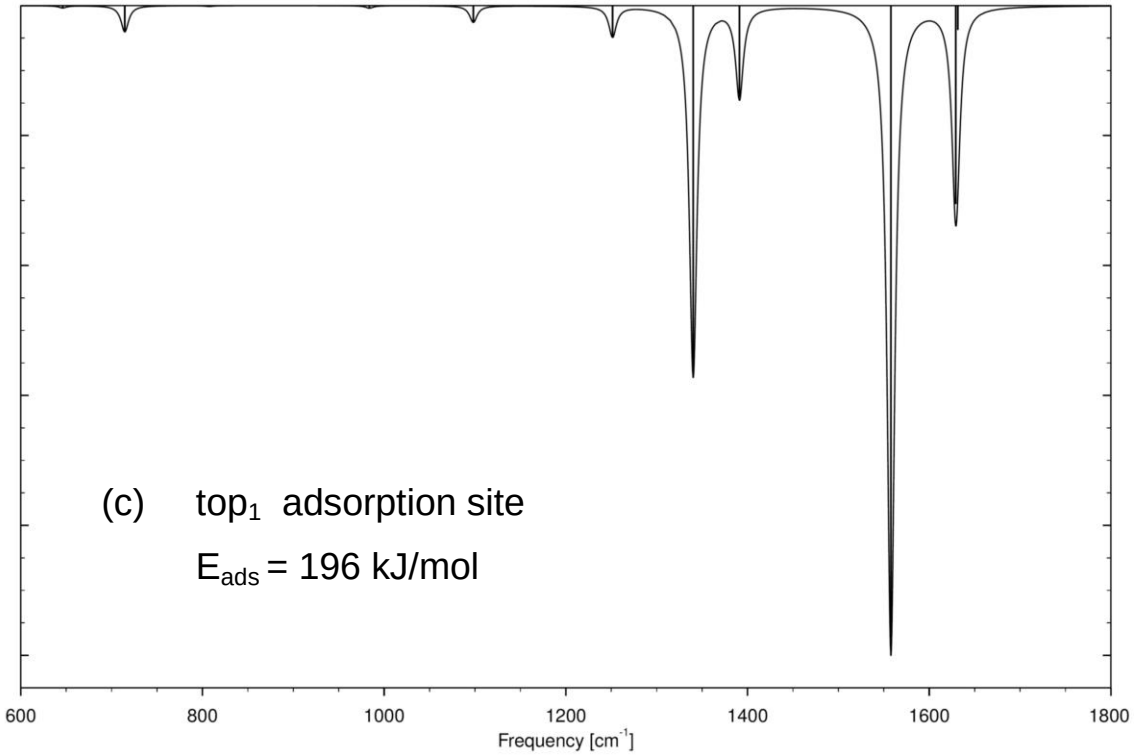
Mode		bridge$_1$		bridge$_2$		top$_1$		top$_2$	
		ν	I	ν	I	ν	I	ν	I
	T_x	22.2	0.00	-3.8	0.000	12.0	0.00	-10.8	0.000
	T_y	34.8	0.00	16.3	0.000	30.5	0.00	21.8	0.000
	R_z	37.2	0.00	-24.4	0.000	34.2	0.00	-12.9	0.000
	T_z	74.8	0.00	60.1	0.000	73.2	0.00	59.9	0.001
	R_x	84.1	0.00	61.7	0.000	91.0	0.00	61.6	0.000
	R_y	79.6	0.00	67.6	0.000	93.2	0.00	59.1	0.000
1	a_u	89.6	0.00	76.9	0.000	115.6	0.01	72.8	0.000
2	b_{1g}	130.6	0.00	115.9	0.000	132.9	0.00	119.2	0.000
3	b_{3u}	102.8	0.01	103.1	0.001	107.4	0.00	97.2	0.011
4	b_{3u}	169.3	0.01	160.9	0.004	173.3	0.01	160.1	0.005
5	b_{2g}	176.4	0.00	166.8	0.000	185.2	0.00	163.7	0.000
6	b_{3u}	247.9	0.00	233.6	0.000	232.7	0.00	238.2	0.000
7	b_{2u}	222.4	0.00	220.9	0.000	219.3	0.00	218.0	0.000
8	b_{2g}	231.0	0.00	230.0	0.000	232.3	0.00	229.0	0.000
9	a_u	262.2	0.00	263.6	0.000	273.2	0.00	263.8	0.000
10	a_g	318.1	0.00	324.7	0.001	315.0	0.00	316.4	0.000
11	b_{3g}	336.6	0.00	341.4	0.000	335.9	0.00	336.2	0.000
12	b_{1u}	370.4	0.00	372.1	0.000	368.5	0.00	367.6	0.000
13	b_{3g}	407.4	0.00	409.1	0.000	407.3	0.00	404.2	0.000
14	a_g	396.1	0.01	395.5	0.010	393.8	0.01	393.9	0.014
15	b_{1g}	361.1	0.00	358.8	0.000	358.1	0.00	355.6	0.000
16	b_{2u}	449.9	0.00	449.1	0.000	447.3	0.00	446.2	0.000
17	b_{2g}	502.8	0.00	496.8	0.000	499.3	0.00	497.1	0.000
18	b_{1u}	461.0	0.00	465.4	0.000	460.1	0.00	458.4	0.000
19	b_{2g}	795.9	0.00	802.1	0.000	795.1	0.00	810.9	0.003
20	b_{3u}	510.5	0.02	515.7	0.022	512.7	0.03	510.8	0.041
21	a_u	571.8	0.05	570.9	0.000	573.0	0.00	572.2	0.000
22	a_g	535.9	0.00	541.3	0.051	532.4	0.04	534.0	0.052
23	b_{1u}	605.3	0.00	605.0	0.000	603.1	0.00	600.7	0.000
24	b_{3g}	603.1	0.00	605.9	0.000	601.7	0.00	601.5	0.000
25	a_g	648.1	0.00	648.0	0.002	646.2	0.00	646.2	0.002
26	b_{2u}	673.8	0.00	674.9	0.000	672.8	0.00	672.9	0.000
27	b_{2g}	665.4	0.00	666.2	0.000	664.4	0.00	663.9	0.000
28	b_{1g}	689.5	0.00	687.4	0.000	688.2	0.00	688.1	0.000
29	b_{3u}	717.9	0.06	720.6	0.032	714.5	0.04	716.9	0.049
30	a_u	720.8	0.00	721.1	0.004	720.2	0.00	720.3	0.000
31	b_{1u}	748.8	0.00	750.7	0.000	746.0	0.00	746.8	0.000
32	b_{3g}	789.2	0.00	792.6	0.000	788.2	0.00	788.4	0.000

33	b_{1u}	813.6	0.00	814.7	0.000	810.3	0.00	796.0	0.000
34	b_{1g}	808.0	0.00	807.8	0.000	801.4	0.00	805.5	0.000
35	b_{3u}	813.0	0.00	812.4	0.005	807.6	0.00	813.0	0.000
36	a_u	937.8	0.00	940.6	0.000	931.7	0.00	931.8	0.000
37	b_{2u}	916.3	0.00	925.1	0.000	916.2	0.00	917.3	0.000
38	b_{2g}	943.3	0.00	944.2	0.000	936.3	0.00	937.4	0.000
39	a_g	987.0	0.00	989.9	0.004	983.8	0.00	985.4	0.001
40	b_{3g}	958.6	0.00	971.3	0.000	956.6	0.00	958.5	0.000
41	b_{2u}	959.5	0.00	965.1	0.000	952.4	0.00	955.2	0.000
42	a_g	1104.2	0.02	1107.0	0.024	1098.2	0.03	1098.5	0.034
43	b_{1u}	1084.5	0.00	1091.0	0.000	1081.6	0.00	1085.1	0.000
44	b_{3g}	1123.9	0.00	1130.9	0.000	1123.3	0.00	1126.4	0.000
45	b_{2u}	1155.8	0.00	1157.4	0.000	1151.6	0.00	1150.2	0.000
46	b_{3g}	1208.2	0.00	1208.6	0.000	1202.2	0.00	1202.3	0.000
47	b_{2u}	1211.1	0.00	1213.9	0.000	1205.1	0.00	1207.9	0.000
48	a_g	1256.9	0.04	1259.1	0.058	1251.5	0.05	1254.6	0.096
49	b_{1u}	1282.5	0.00	1284.9	0.000	1277.8	0.00	1277.3	0.000
50	a_g	1345.5	0.58	1350.1	0.615	1340.2	0.57	1345.1	0.666
51	b_{1u}	1435.8	0.00	1436.1	0.000	1427.7	0.00	1435.5	0.000
52	a_g	1404.8	0.13	1402.7	0.157	1391.1	0.14	1398.9	0.186
53	b_{3g}	1419.8	0.00	1427.8	0.000	1420.0	0.00	1421.9	0.000
54	b_{2u}	1430.4	0.00	1421.8	0.000	1417.8	0.00	1423.2	0.000
55	b_{2u}	1509.8	0.00	1509.3	0.000	1500.1	0.00	1504.2	0.000
56	b_{1u}	1493.6	0.00	1507.0	0.000	1496.4	0.00	1498.2	0.000
57	a_g	1565.6	1.00	1561.9	1.000	1557.8	1.00	1562.6	1.000
58	b_{3g}	1541.2	0.00	1550.0	0.000	1536.2	0.00	1543.4	0.000
59	b_{2u}	1580.9	0.00	1576.3	0.001	1588.2	0.00	1598.6	0.000
60	b_{3g}	1593.0	0.00	1605.0	0.000	1599.1	0.00	1625.2	0.000
61	a_g	1625.7	0.26	1631.3	0.139	1629.2	0.30	1650.3	0.321
62	b_{1u}	1628.9	0.02	1629.9	0.016	1631.5	0.04	1647.5	0.091
63	b_{1u}	3112.2	0.00	3110.2	0.000	3107.1	0.00	3109.1	0.000
64	b_{3g}	3113.8	0.00	3110.4	0.000	3107.8	0.00	3110.7	0.000
65	b_{2u}	3122.9	0.00	3123.3	0.000	3119.1	0.00	3122.7	0.000
66	a_g	3126.5	0.00	3124.7	0.000	3120.0	0.00	3123.4	0.000

Figure S1. Computed (PBE-D3$_{PBC}$) IR spectrum for all adsorption geometries of NTCDA on Ag(111), derived under consideration of dipole selection rules (screening of parallel dipoles by means of metal substrate).

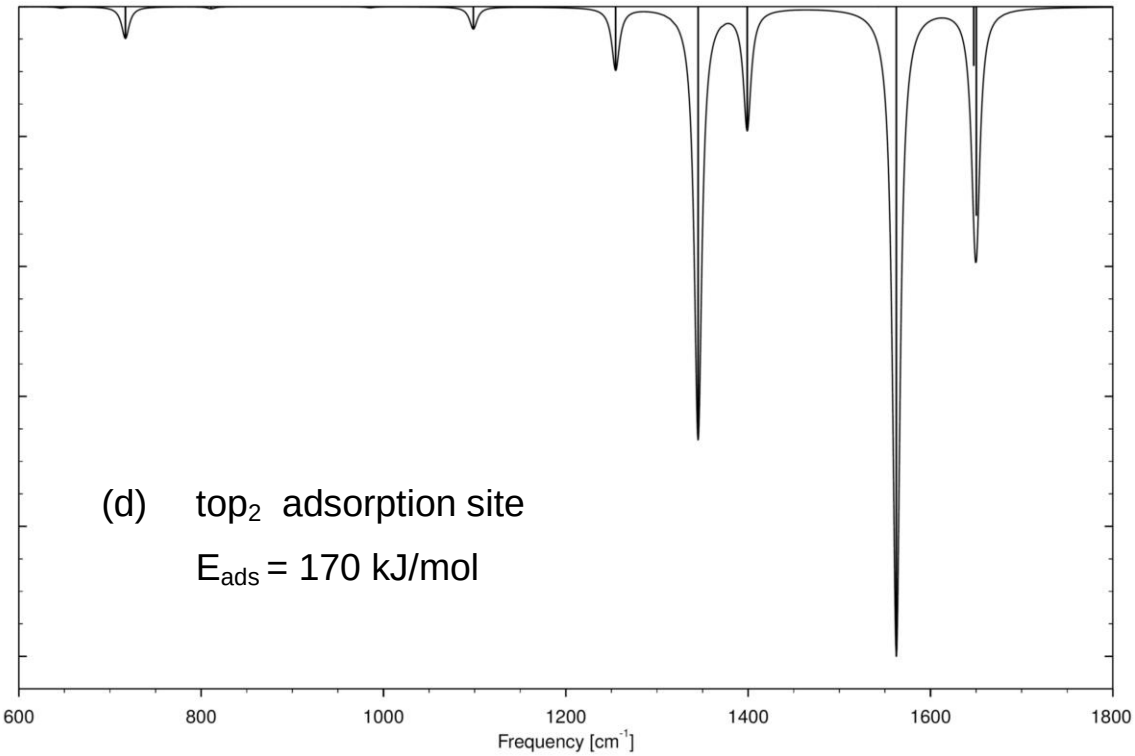






(c) top_1 adsorption site

E_{ads} = 196 kJ/mol



(d) top_2 adsorption site

E_{ads} = 170 kJ/mol

Figure S2. IRAS spectra (spectral range 630 - 1840 cm^{-1}) of 0.15 ML NTCDA on Ag(111), deposited at 28 K after annealing to successively higher temperatures. The series reveals the transformation of initially isolated NTCDA towards disordered aggregates and well-ordered 2D-islands (relaxed monolayer phase). The spectrum of the NTCDA/Ag(111) relaxed monolayer phase (coverage 0.9 ML) is displayed for comparison (top curve). All spectra were obtained at 28 K using a spectral resolution of 2 cm^{-1}. Spectra are offset vertically for clarity of presentation.