Electronic Supplementary Material (ESI) for Nanoscale Advances.

Supplementary Materials

How gap distance between gold nanoparticles in dimers and trimers on metallic and non-metallic SERS substrates can impact signal enhancement

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Table S1. Results for AuNPs on the surface of Au substrate

Au	Id/Is	St. E	EFd/EF s	St. E	Dimers #	Int Dimers	Monomers #	Int Monomers
C6	9,0	1,5	4,0	0,6	21	456,8	17	50,7
C4	6,8	1,1	2,7	0,5	14	415,1	14	61,2
C8	5,4	0,6	2,4	0,3	24	476,1	29	88,8
C12	2,4	0,3	1,2	0,2	26	70,1	24	28,7
C16	1,7	0,1	0,8	0,1	18	53,5	20	30,3

Id/Is - dimer intensity/monomer intensity, Int - Raman Intensity, EF - enhancement factor, St. E - standard error.

Table S2. Results for AuNPs on the surface of Al substrate

Al	Id/Is	StE	EF	StE in EF	Dimers #	Int Dimers	Monomers #	Int Monomers
C4	3,8	0,9	1,6	0,4	56	51,6	71	13,4
C8	1,9	0,5	0,8	0,2	40	43,8	58	23,0
C12	1,7	0,3	0,7	0,1	61	28,2	59	16,2
C16	1,1	0,1	0,5	0,1	43	23,4	59	21,1

Id/Is - dimer intensity/monomer intensity, Int - Raman Intensity, EF - enhancement factor, St. E - standard error.

Table S3. Results for AuNPs on the surface of Si substrate

Si	Id/Is	StE	EF	StE in EF	Dimers #	Int Dimers	Monomers #	Int Monomers
C6	8,6	0,9	4,3	1,8	27	104,24	9	12,15
C8	4,2	0,5	2,1	0,9	5	59,38	5	14,22
C12	3,3	0,1	1,7	0,3	16	36,83	3	11,19
C16	1,9	0,2	0,9	0,4	7	29,03	25	15,38

Id/Is - dimer intensity/monomer intensity, Int - Raman Intensity, EF - enhancement factor, St. E - standard error.

Table S4. Results for AuNPs on the surface of Ag substrate

Ag	Id/Is	St. E	Dimers #	Int Dimers	Monomers #	Int Monomers
C3	4,3	0,8	31	103,6	82	24,0
C8	2,8	0,5	69	172,8	74	62,6
C12	1,4	0,3	28	68,9	30	47,9
C16	1,4	0,3	42	82,5	63	54,5

Id/Is - dimer intensity/monomer intensity, Int - Raman Intensity, EF - enhancement factor, St. E - standard error.

Table S5. Results for linear trimers on the surface of Al substrate

Al	It/Im	St. E	Trimers #	Int Trimers	Monomers #	Int Monomers
4,0	7,7	3,1	15	66,4	71	8,6
8,0	2,7	1,6	6	37,6	58	14,0
12,0	1,2	0,3	5	12,0	59	9,8
16,0	0,9	0,1	6	11,3	59	12,7

It/Is - trimer intensity/monomer intensity, Int - Raman Intensity, EF - enhancement factor, St. E - standard error. Grubbs outlier test is applied for both trimer and monomer intensities and up to 1 outlier excluded from average calculation (e.g. in C4 monomer intensity calculation)

Table S6. Results for linear trimers on the surface of Au substrate

Au	It/Im	StE	Trimers #	Int Trimers	Monomers #	Int Monomers
C6	6,2	1,2	6	312,6	17	50,7
C8	4,7	1,1	3	414,1	29	88,8
C12	2,6	0,7	2	73,8	24	28,7

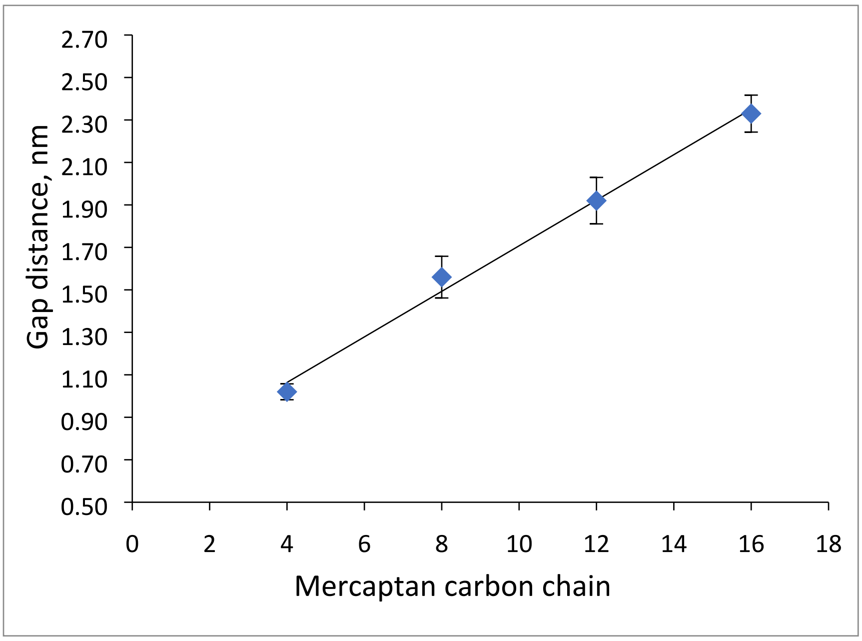
It/Is - trimer intensity/monomer intensity, Int - Raman Intensity, EF - enhancement factor, St. E - standard error.

Comments:

Ratio of EFd/EFm is calculated as ratio of average Raman intensity per nm^2 for dimers divided by average Raman intensity per nm^2 for singles (monomers). Raman intensity per nm^2 is calculated for each dimer or single AuNP using the spherical approximation. This approach is described in details about this approach can be found in publication of Sergiienko et. al. Briefly Raman Intensity of each monomer, dimer or trimer is divided by the sum of surface areas of nanoparticles in nanostructure. For instance, for a given dimer x. $EF_{dx} = I_{dx}/(4 * \pi * R_{x1} + 4 * \pi * R_{x2})$, where R_{x1} and R_{x2} are ½ of the height of each nanoparticle in a given dimer, measured by AFM. The average EFd and average EFm are calculated for each sample and their ratio is reported as EFd/EFm.

Table S7. TEM results for interparticle distance measurement in nm. MIN – minimum gap, MAX – maximum gap, STD DEV – standard deviation, RSDEV – relative standard deviation, St Error – standard error.

№	C4	C6	C8	C12	C16
1	1,06	0,68	1,79	1,9	2,94
2	0,93	0,94	1,46	1,84	2,46
3	0,93	0,91	1,84	1,64	2,26
4	1,28	0,46	1,96	1,57	2,55
5	0,91	1,02	2,29	1,38	2,2
6	1,14	0,91	1,22	1,39	2,38
7	0,81	1,02	1,74	1,82	2,1
8	1,15	0,91	1,33	2,16	2,48
9	1,17	0,91	2,2	2,15	1,79
10	0,98	0,68	1,29	2,22	2,54
11	1,02	0,94	1,33	2,1	1,64
12	1,17	1,14	1,28	2,93	2,66
13	0,91	0,91	1,33	1,36	2,55
14	0,77	0,77	1,06	2,24	2,04
15	1,02	0,73	1,29	2,15	2,3
Average	1,02	0,86	1,6	1,9	2,3
MIN	0,8	0,5	1,1	1,4	1,6
MAX	1,3	1,1	2,3	2,9	2,9
STD DEV	0,1	0,2	0,4	0,4	0,3
RSDEV	0,14	0,20	0,24	0,22	0,14
St Error	0,04	0,04	0,10	0,11	0,09



Insert Figure for Table S7. Graph of mercaptan chain length versus gap distance in nm.

Table S8. R^2 values and fit equations for all graphs.

R^2 Table	R^2 Exponential	Equation	R^2 Linear	Equation	R^2 Power	Equation
Au film Int	0,951	$y = 23{,}478e^{-1{,}111x}$	0,943	$y = -4{,}794x + 12{,}44$	0,914	$y = 7{,}561x^{-1{,}589}$
Au film EF	0,937	$y = 9{,}368e^{-1{,}041x}$	0,912	$y = -1{,}984x + 5{,}263$	0,897	$y = 3{,}237x^{-1{,}487}$
Al film Int (2 pt)	0,958	$y = 9{,}087e^{-0{,}906x}$	0,896	$y = -2{,}009x + 5{,}578$	0,969	$y = 3{,}905x^{-1{,}43}$
Al film EF (2 pt)	0,955	$y = 3{,}214e^{-0{,}78x}$	0,892	$y = -0{,}755x + 2{,}207$	0,981	$y = 1{,}560x^{-1{,}241}$
Si wafer Int	0,989	$y = 10{,}284e^{-1{,}003x}$	0,961	$y = -2{,}272x + 6{,}031$	0,958	$y = 3{,}659x^{-1{,}426}$
Si wafer EF	0,990	$y = 20{,}498e^{-1{,}001x}$	0,961	$y = -4{,}54x + 12{,}055$	0,960	$y = 7{,}313x^{-1{,}424}$
Ag film	0,924	$y = 5{,}592e^{-0{,}096x}$	0,928	$y = -0{,}239x + 4{,}799$	0,923	$y=4.243x^{-1.386}$
Al film Trimer	0,951	$y = 13{,}358e^{-0{,}182x}$	0,806	$y = -0{,}546x + 8{,}580$	0,996	$y = 70{,}515x^{-1{,}595}$
Au fim Trimer	1,000	$y = 14{,}915e^{-0{,}146x}$	0,991	$y = -0{,}589x + 9{,}568$	0,988	$y = 62{,}685x^{-1{,}276}$
Average All R^2	0,963		0,921		0,954	
Average R^2 for dimer ratios	0.960		0.927		0.944	

Int – intensity, EF – enhancement factor Maximum intensity in one point is taken for calulation of average intensities, unless specified otherwise (for 2 rows of data on Al film, sum intensity of 2 max intensity points is taken for calculation of average, where single point average have very high error bars)

Table S9 Enhancement Factor Calculation of dimers (dim) and monomers (mon) for all samples on 4 substrates

Substrate	Chain	I dim	I mon	EF dim	EF mon	Id /I m	EFd/EFm
Au/gold	C6	456.8	50.7	4.32E+06	9.59E+05	9.01	4.51
	C4	415.1	61.2	3.93E+06	1.16E+06	6.78	3.39
	C8	476.1	88.8	4.51E+06	1.68E+06	5.36	2.68
	C12	70.1	28.7	6.64E+05	5.43E+05	2.44	1.22
	C16	53.5	30.3	5.06E+05	5.74E+05	1.76	0.88
Al	**Chain**	**I dim**	**I mon**	**EF dim**	**EF mon**	**Id /I m**	**EFd/EFm**
	C4	60.9	9.2	5.76E+05	1.74E+05	6.62	3.31
	C8	39.51	14.02	3.74E+05	2.65E+05	2.82	1.41
	C12	22.47	9.78	2.13E+05	1.85E+05	2.30	1.15
	C16	13.73	13.14	1.30E+05	2.49E+05	1.04	0.52
Ag film	**Chain**	**I dim**	**I mon**	**EF dim**	**EF mon**	**Id /I m**	**EFd/EFm**
	C3	103.6	24.00	9.80E+05	4.54E+05	4.32	2.16
	C8	172.80	62.60	1.64E+06	1.18E+06	2.76	1.38
	C12	68.90	47.90	6.52E+05	9.07E+05	1.44	0.72
	C16	82.50	54.50	7.81E+05	1.03E+06	1.51	0.76
Si wafer	**Chain**	**I dim**	**I mon**	**EF dim**	**EF mon**	**Id /I m**	**EFd/EFm**
	C6	104.24	12.15	9.87E+05	2.30E+05	8.58	4.29
	C8	59.38	14.22	5.62E+05	2.69E+05	4.18	2.09
	C12	36.83	11.19	3.49E+05	2.12E+05	3.29	1.65
	C16	29.03	15.38	2.75E+05	2.91E+05	1.89	0.94

The following data were used to calculate EFs each NP is assumed to be sphere 100 nm diameter

MOTP molar mass	140.2	g/mole
MOTP surface CS	0.2	nm^2
MOTP density	1.152	g/cm^3
laser focal volume	24.98	μm^3
I raman	41.56	a. u
N sers	157080	molecules/NP
N raman	1.24E+11	molecules
S Area sphere	31416	nm^2

Average I_{SERS} is taken from the table for each sample I dim or I mon monomer or dimer

$$N_{Raman} = \left(\frac{MOTP\ density * Nav}{MOTP\ molar\ mass}\right) * \left(\frac{Laser\ focal\ volume\ \mu m^3}{\frac{10^{12}\mu m^3}{cm^3}}\right)$$

$EFd = (Idim/Nsers)/(Iraman/Nraman)$ = ((456.8/(2*157080))/(41.56/1.24x 10^{11}) = 4.32 x 10^{6}. (example of calculation for C6 dimer on gold film)

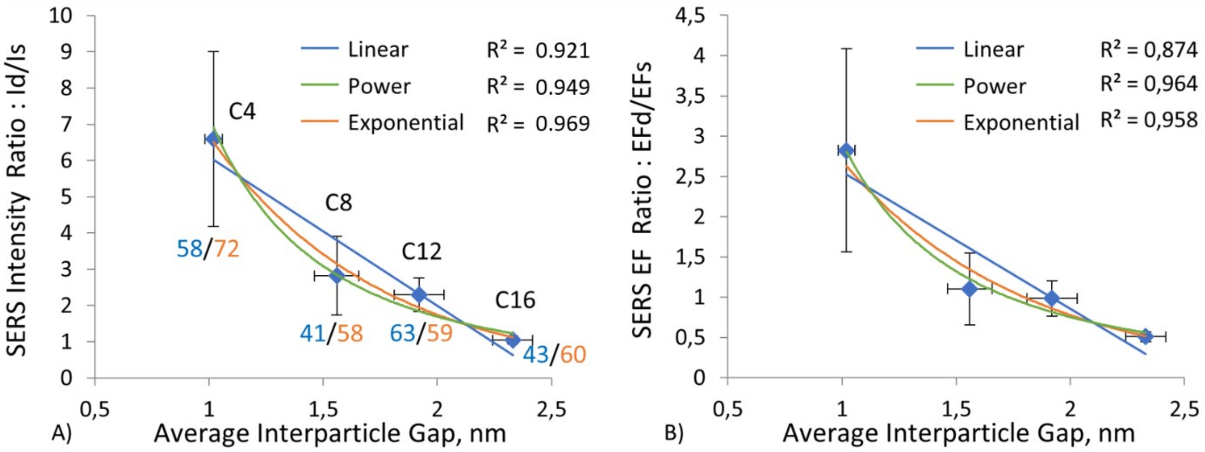


Figure S1 Ratio Id/Is and EFd/EFs (where I d and I s are intensities of dimers and singles/monomers, EFd and EFs average enhancement factors of dimers and singles respectively) for samples on Al film. The Maximum intensity in a single point is taken as SERS intensity in the same way as intensity or EF graphs on Figures 4,6,7,8 of the paper

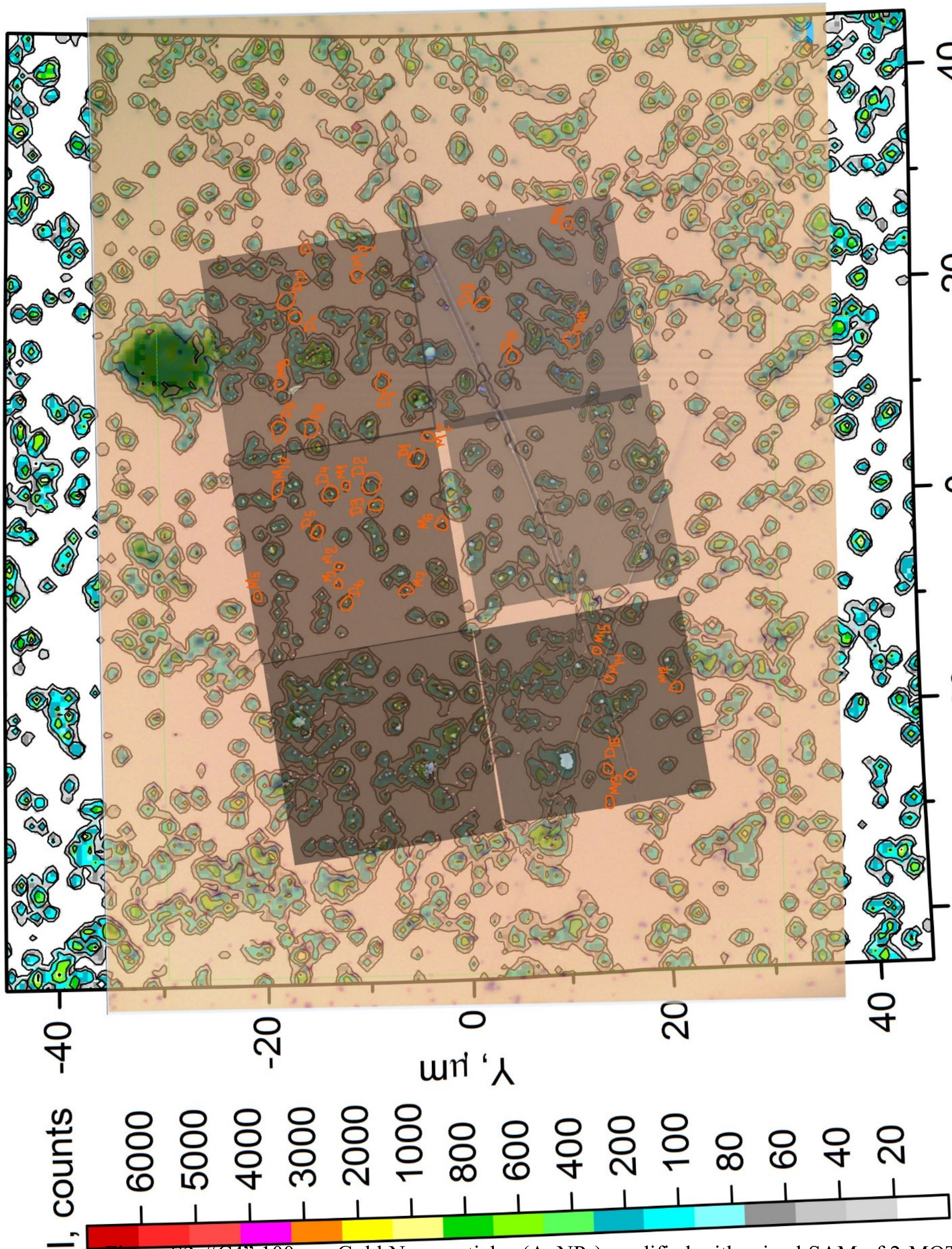
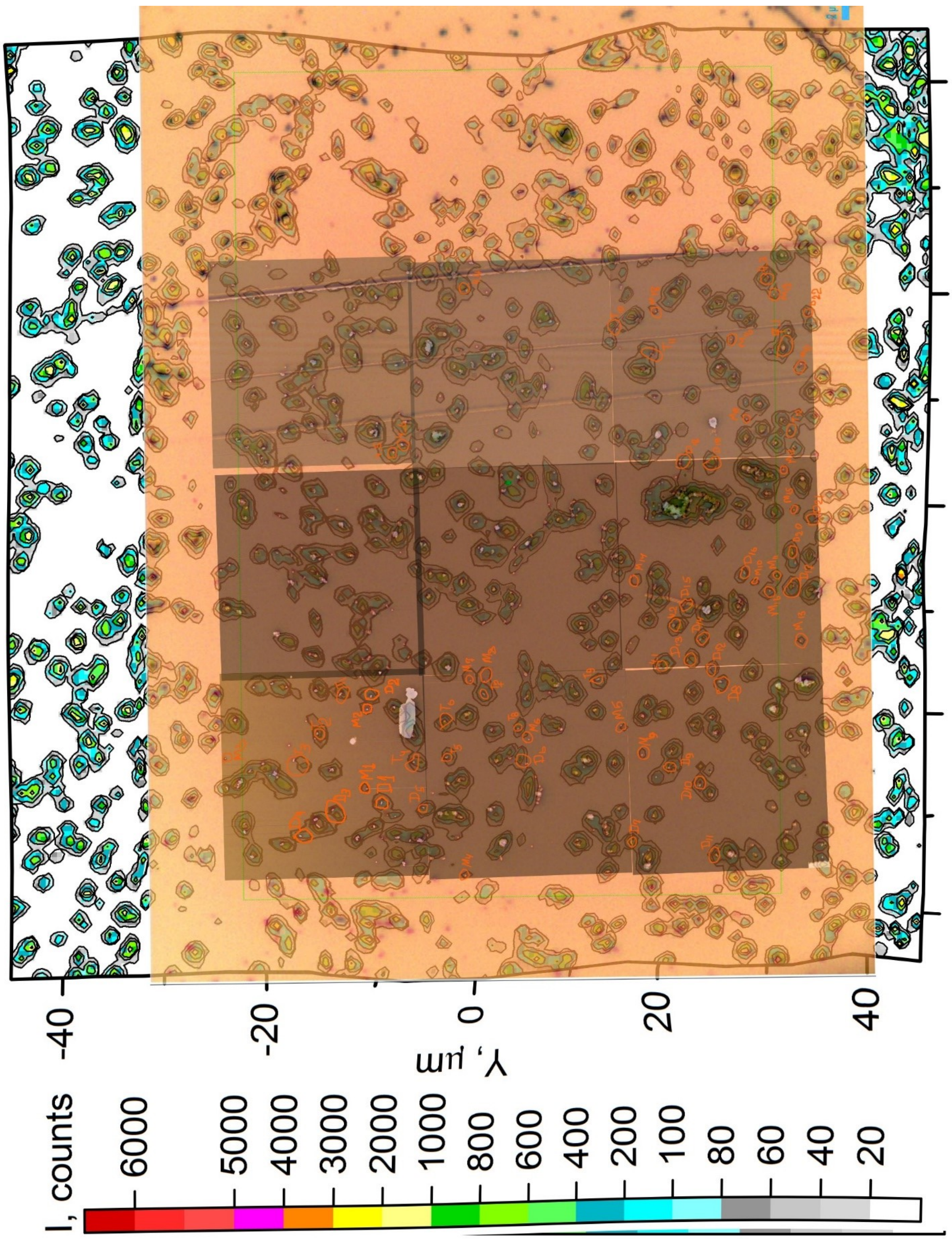


Figure S2. “C4” 100 nm Gold Nanoparticles (AuNPs) modified with mixed SAM of 2-MOTP and 4-mercaptobenzoic acid (hereafter called just C4 samples) on Gold film



acid (hereafter called just C6 samples) on Gold film

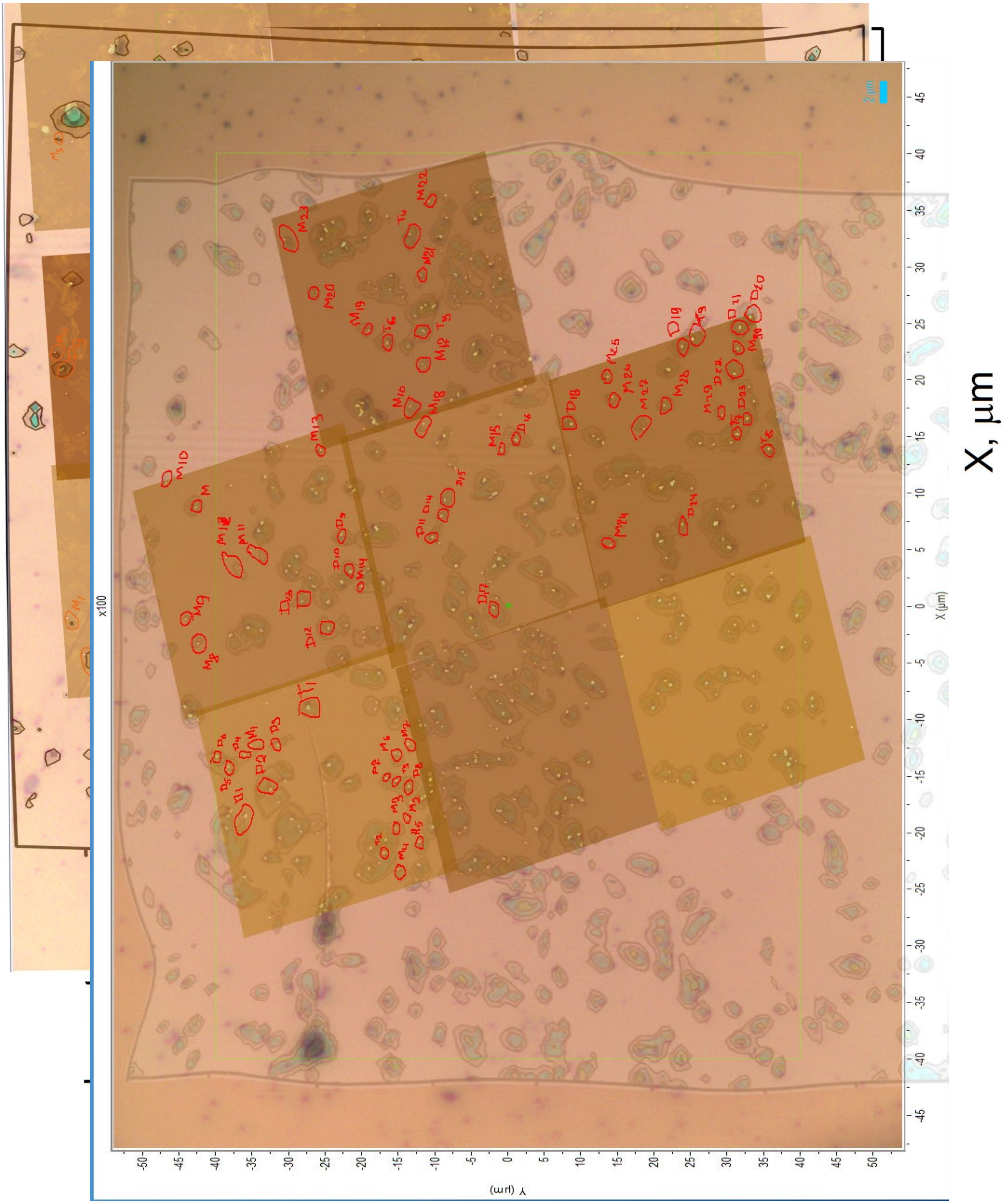


Figure S5. “C12” 100 nm AuNPs modified with mixed SAM of 2-MOTP and 12-Mercaptododecanoic acid - (hereafter called just C12 samples) on Gold film

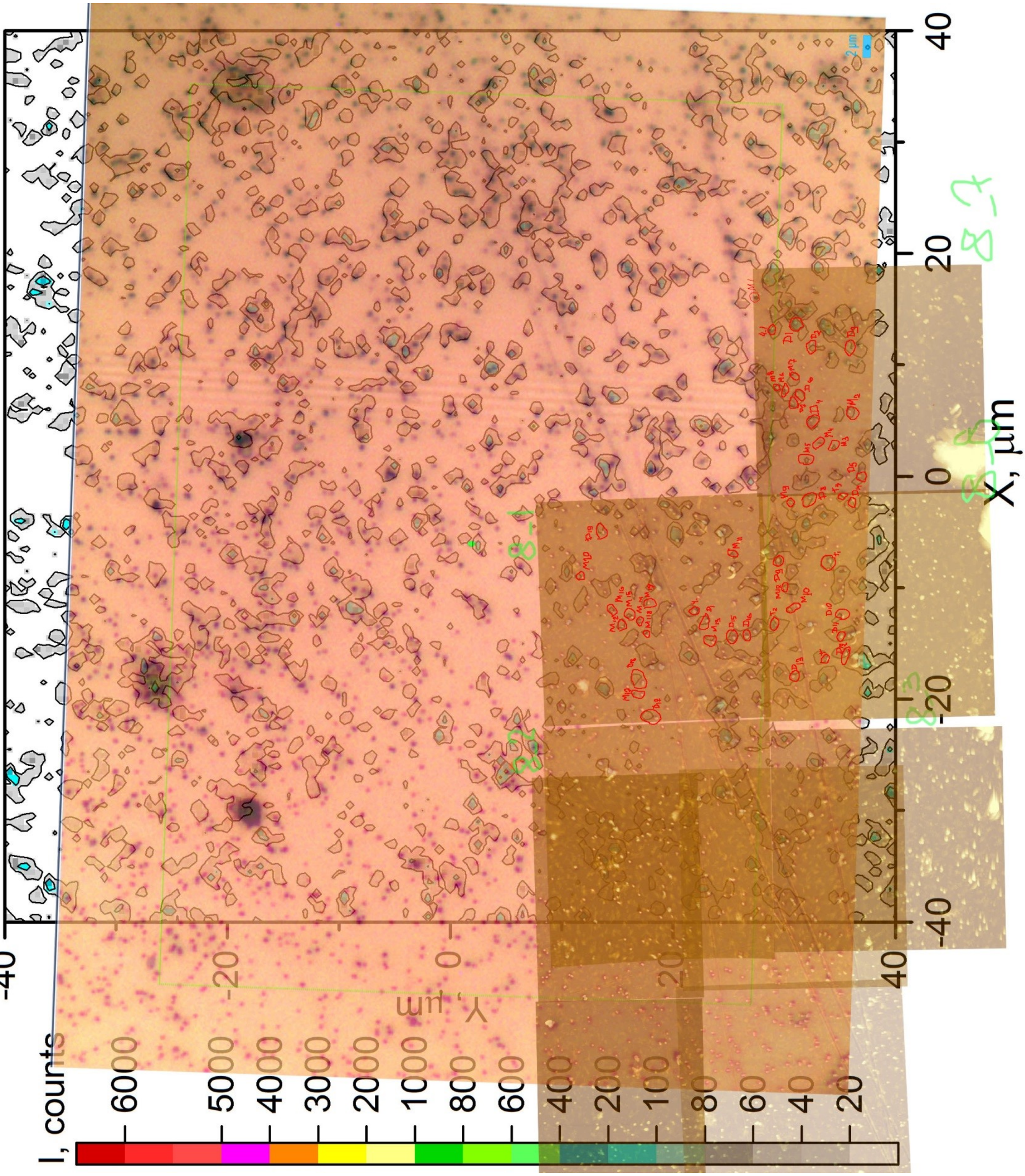


Figure S6. “C16” 100 nm AuNPs modified with mixed SAM of 2-MOTP and 16-Mercaptohexadecanoic acid - (hereafter called C16) on Gold film

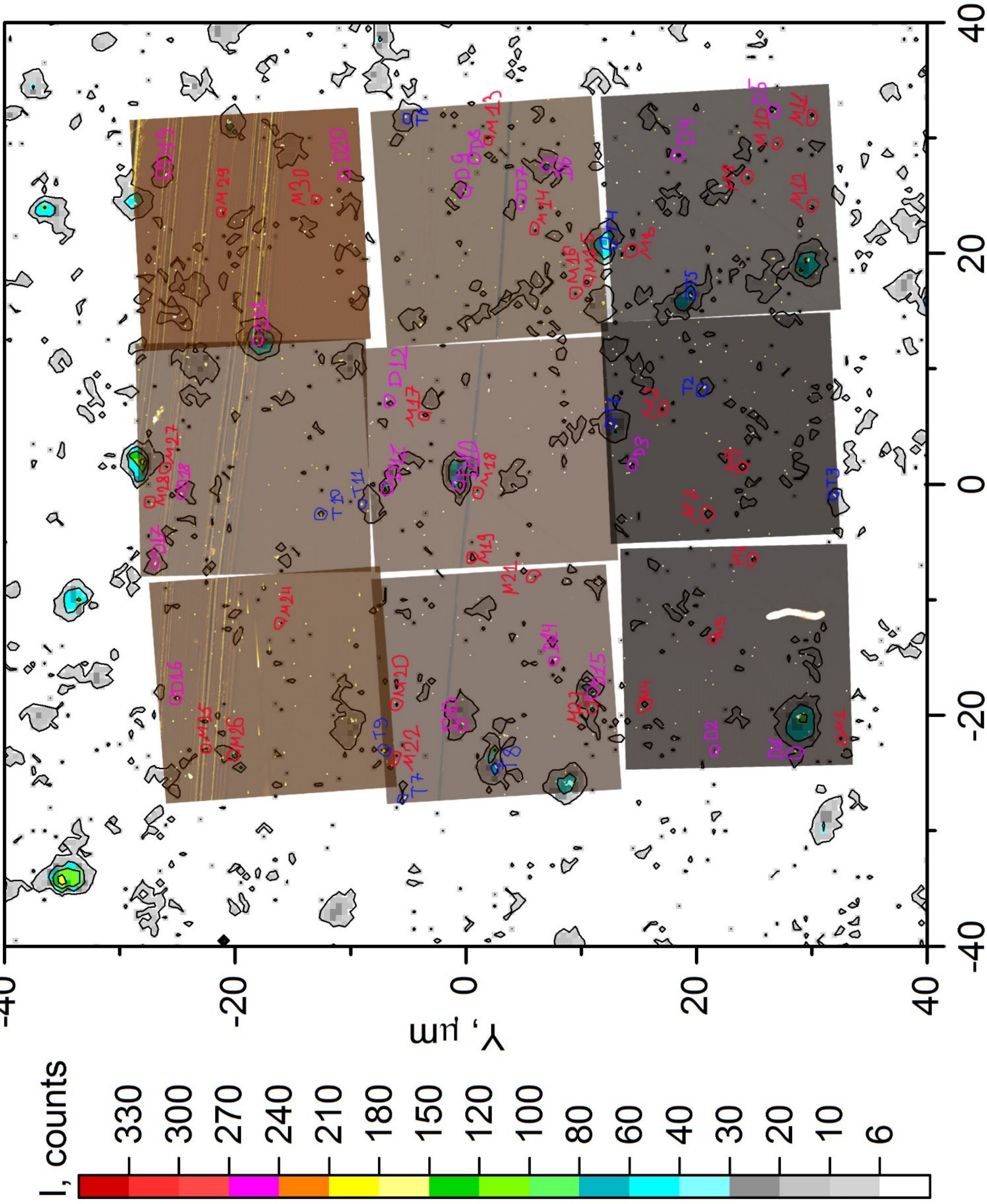
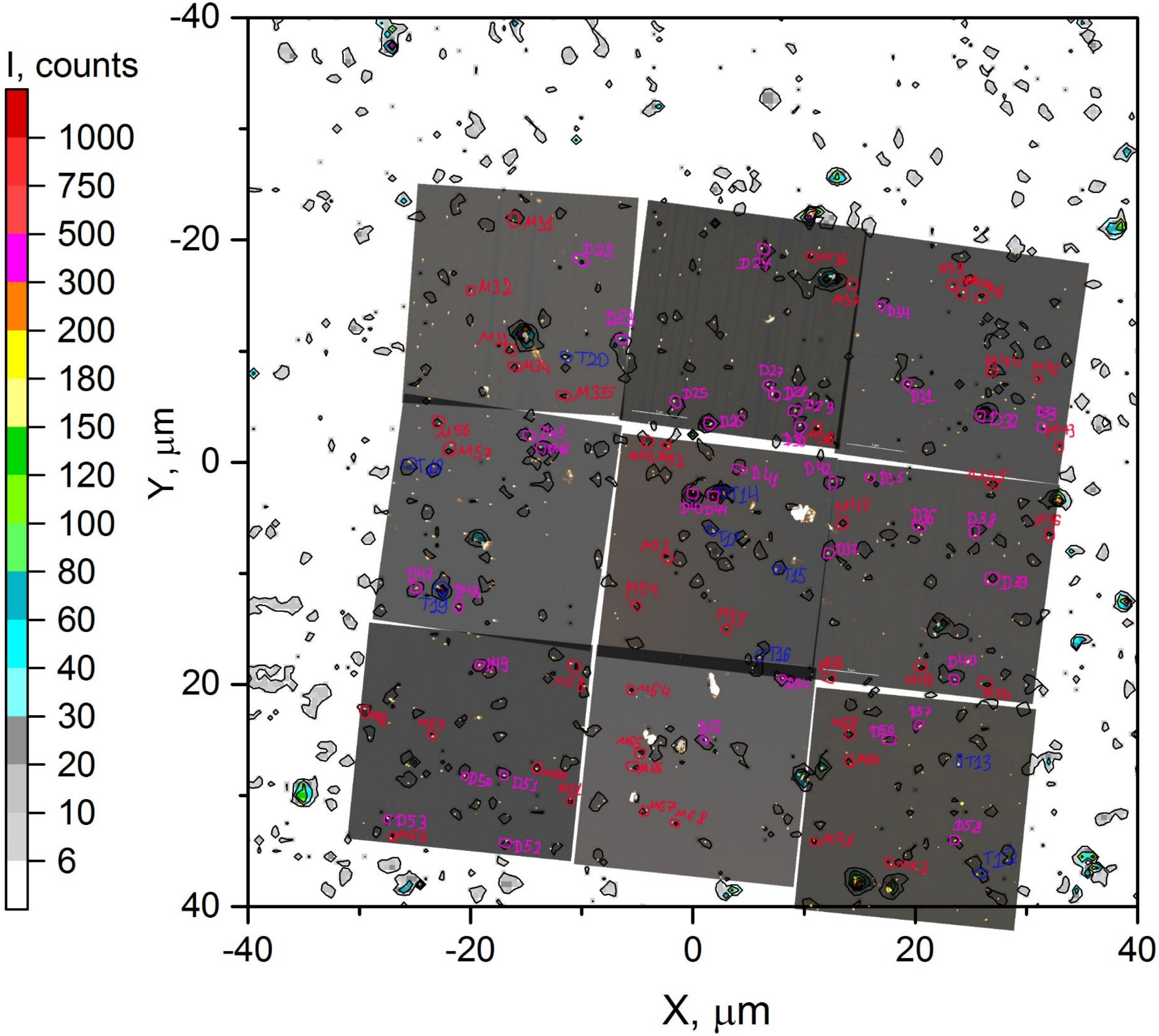


Figure S7. “C4” 100 nm Gold Nanoparticles (AuNPs) modified with mixed SAM of 2-MOTP and 4-mercaptobenzoic acid (hereafter called just C4 samples) on Al film



I, counts
1000
750
500
300
200
180
150
120
100
80
60
40
30
20
10
6
Y, μm
X, μm
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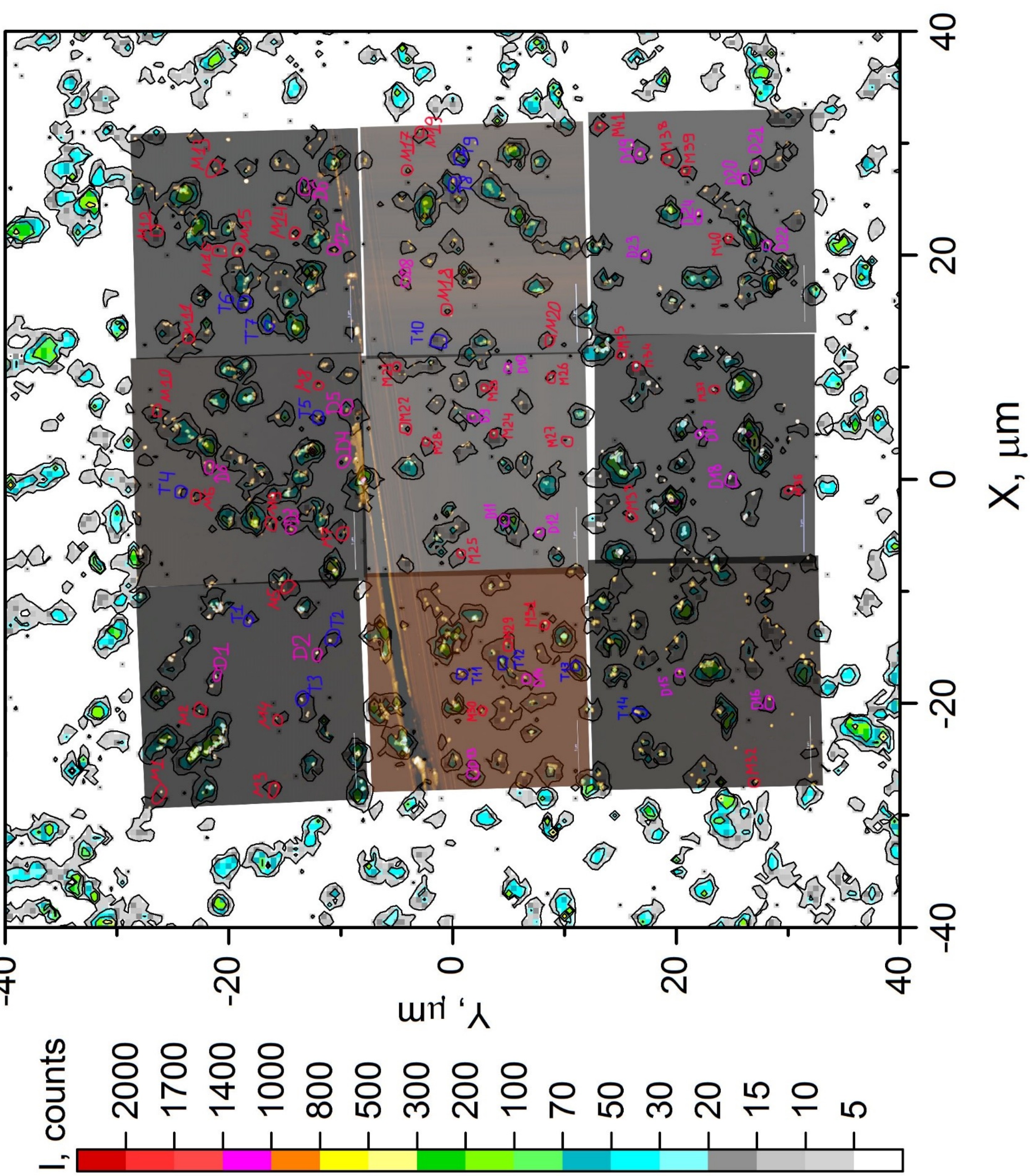
0
20
40



acid (hereafter called just C8 samples) on Al film

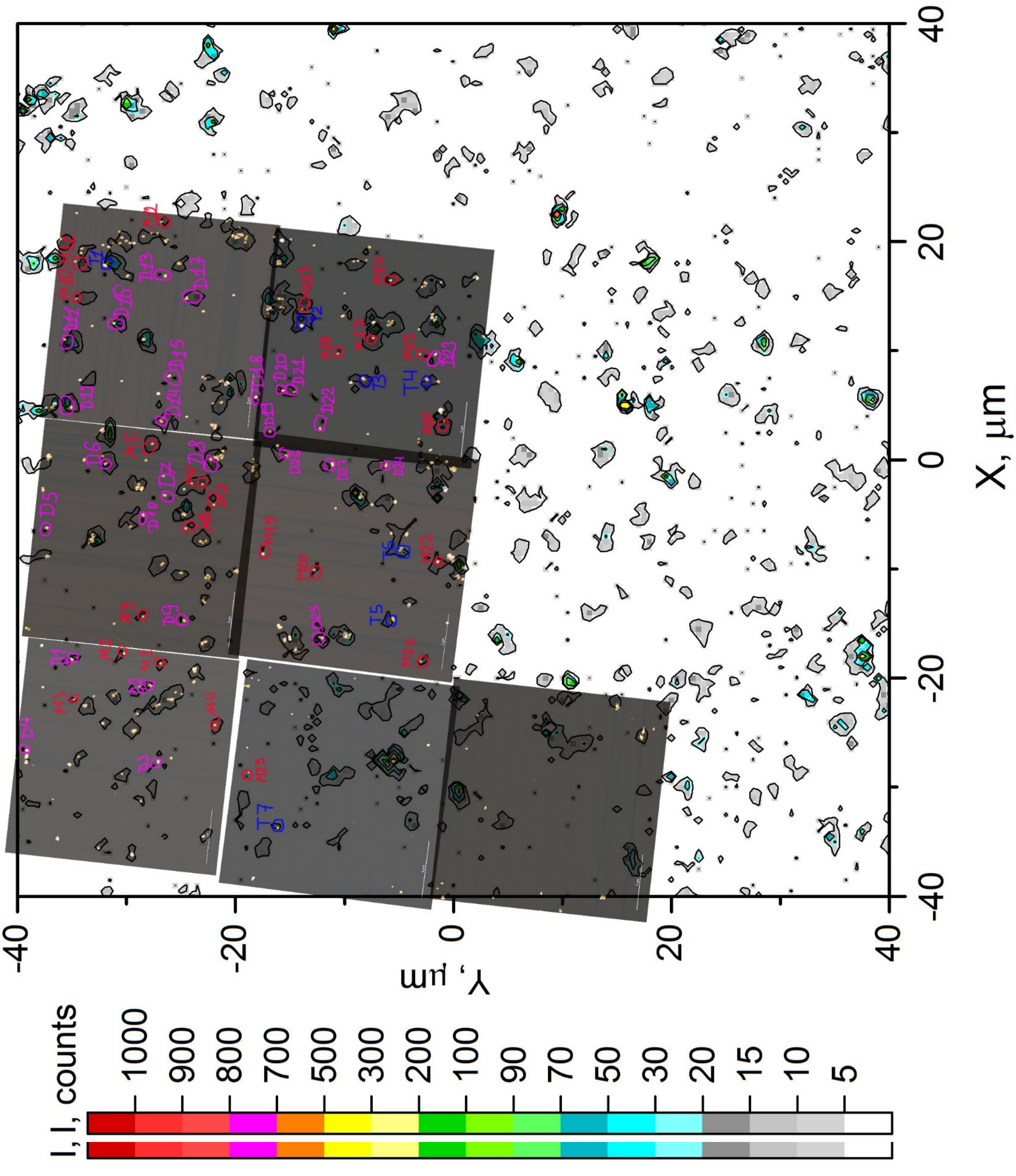


Figure S11. “C12” 100 nm AuNPs modified with mixed SAM of 2-MOTP and 12-Mercaptododecanoic acid - (hereafter called just C12 samples) on Al film

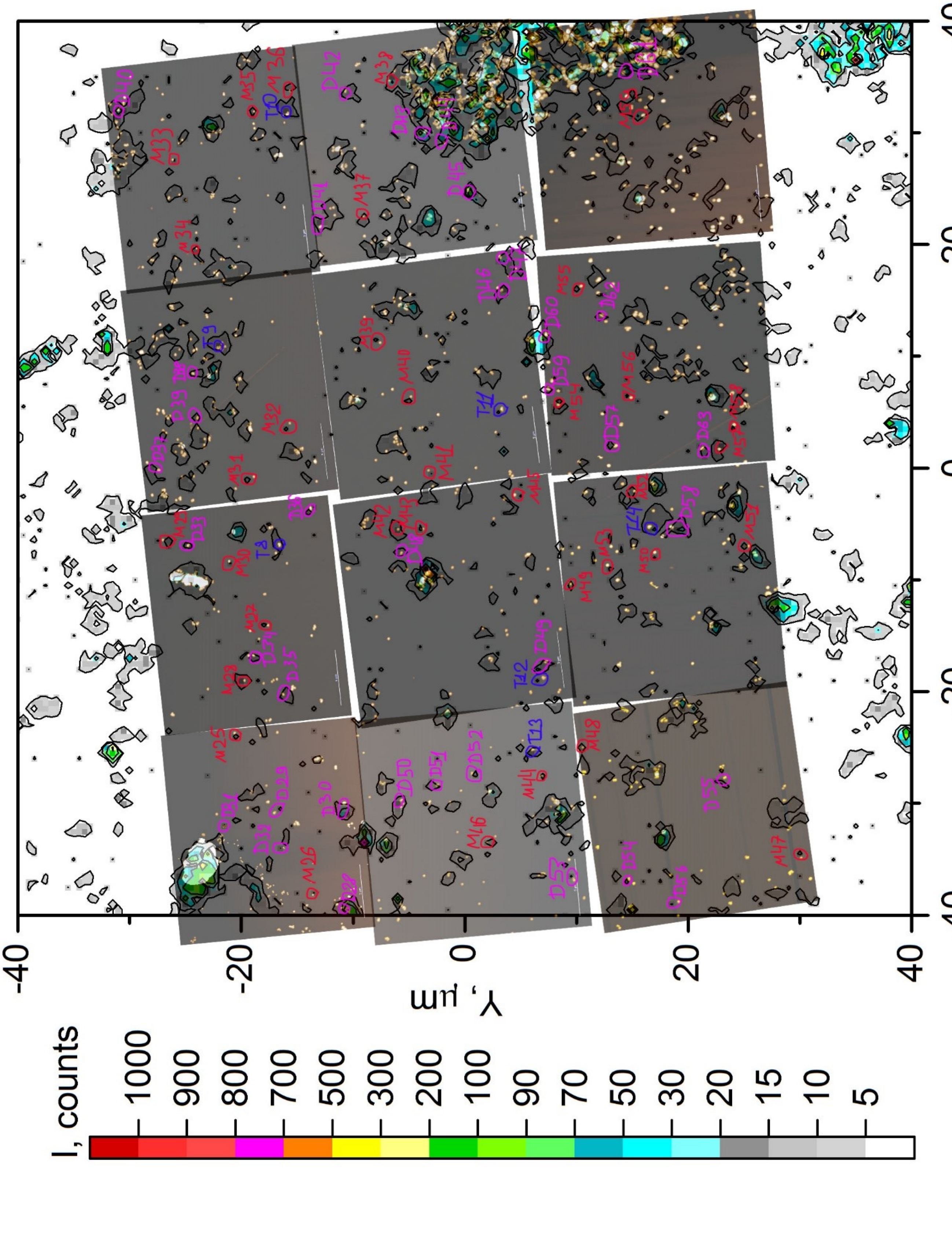


Figure S12. “C12” 100 nm AuNPs modified with mixed SAM of 2-MOTP and 12-Mercaptododecanoic acid - (hereafter called just C12 samples) on Al film

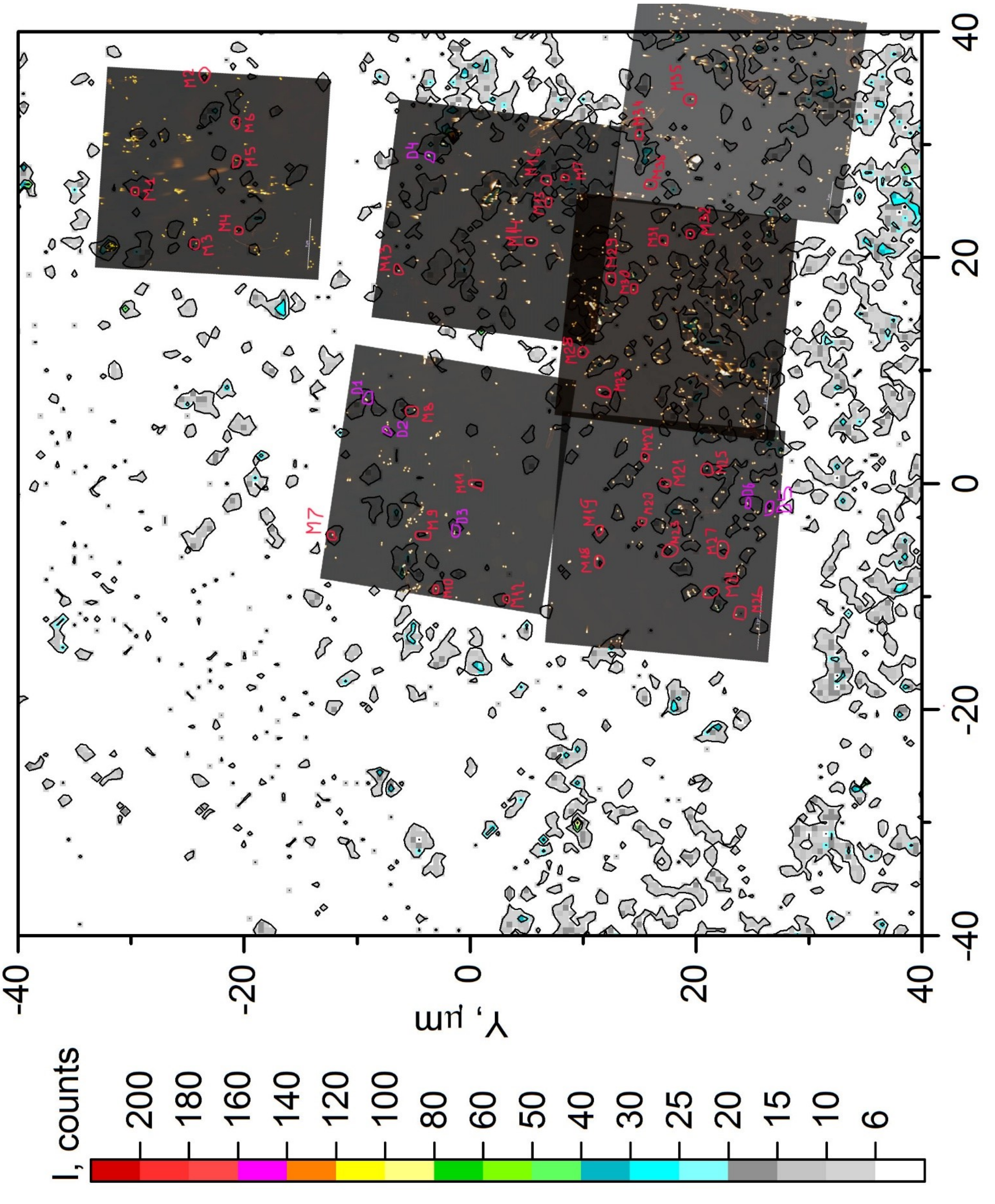


Figure S13. "C16" 100 nm AuNPs modified with mixed SAM of 2-MOTP and 16-Mercaptohexadecanoic acid - (hereafter called C16) on Al film

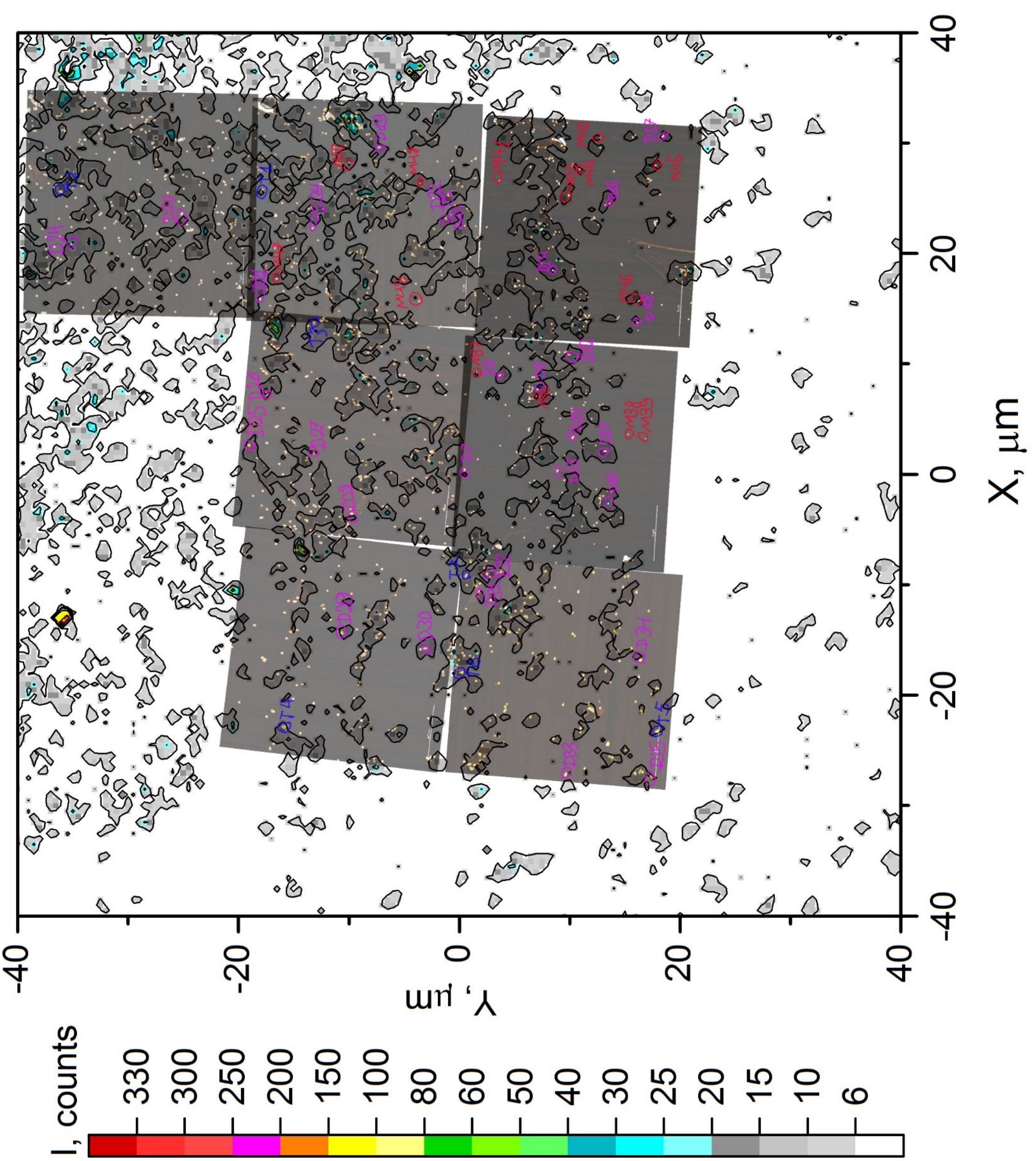
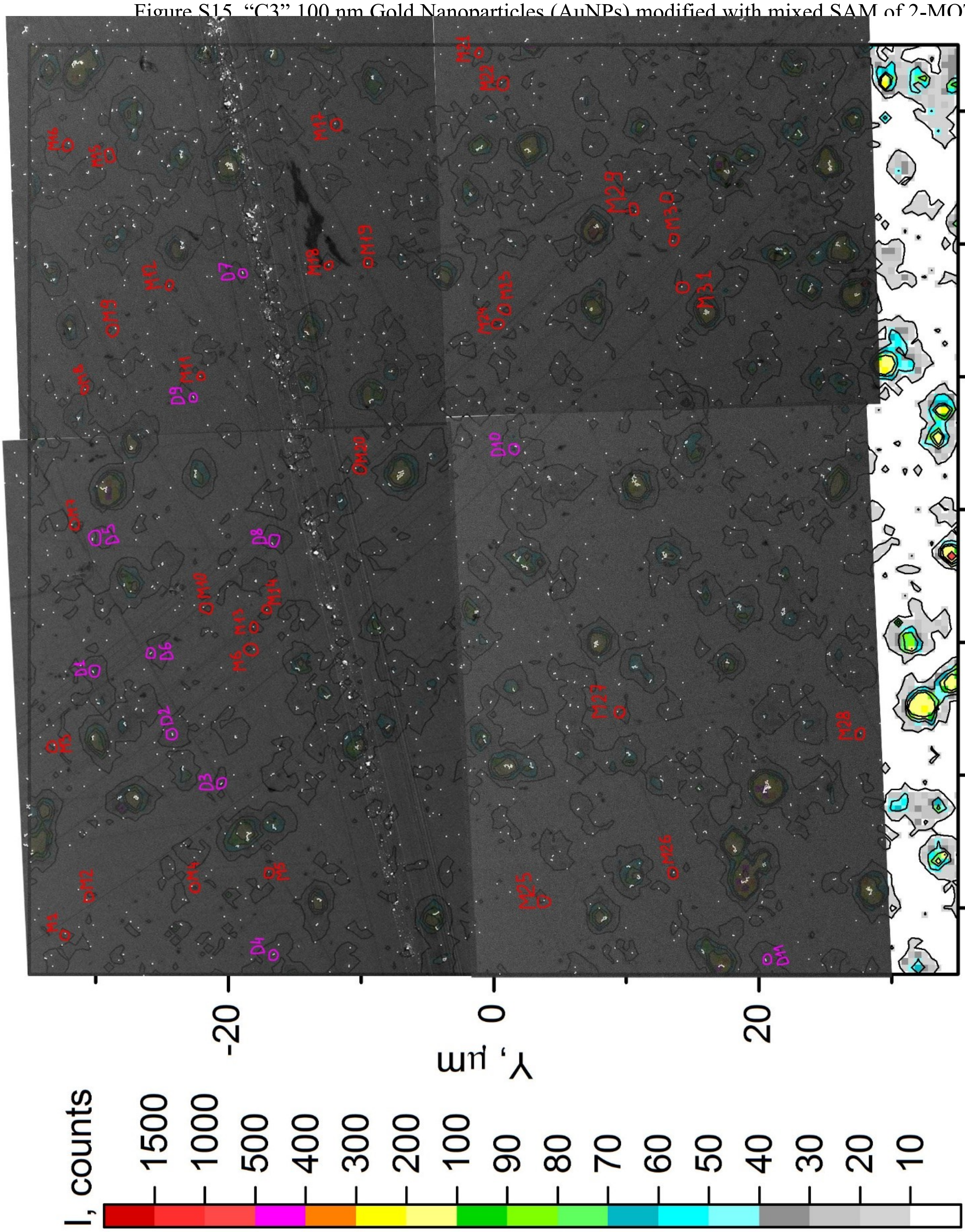


Figure S14. “C16” 100 nm AuNPs modified with mixed SAM of 2-MOTP and 16-Mercaptohexadecanoic acid - (hereafter called C16) on Al film

Figure S15. “C3” 100 nm Gold Nanoparticles (AuNPs) modified with mixed SAM of 2-MOTP and



3-mercaptopropionic acid (hereafter called just C3 samples) on Ag film

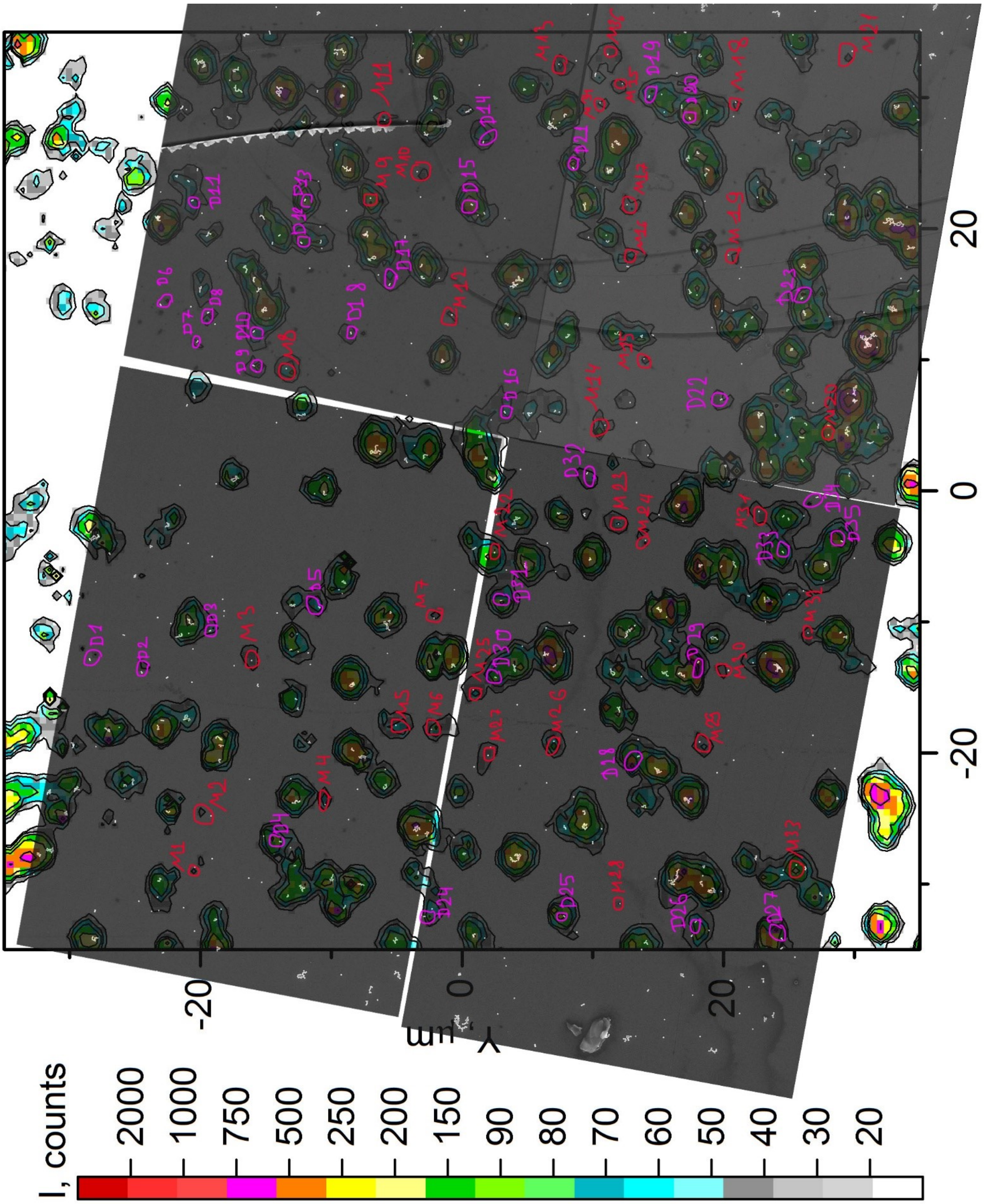


Figure S17. “C8” 100 nm AuNPs modified with mixed SAM of 2-MOTP and 8-Mercaptooctanoic acid (hereafter called just C8 samples) on Ag film

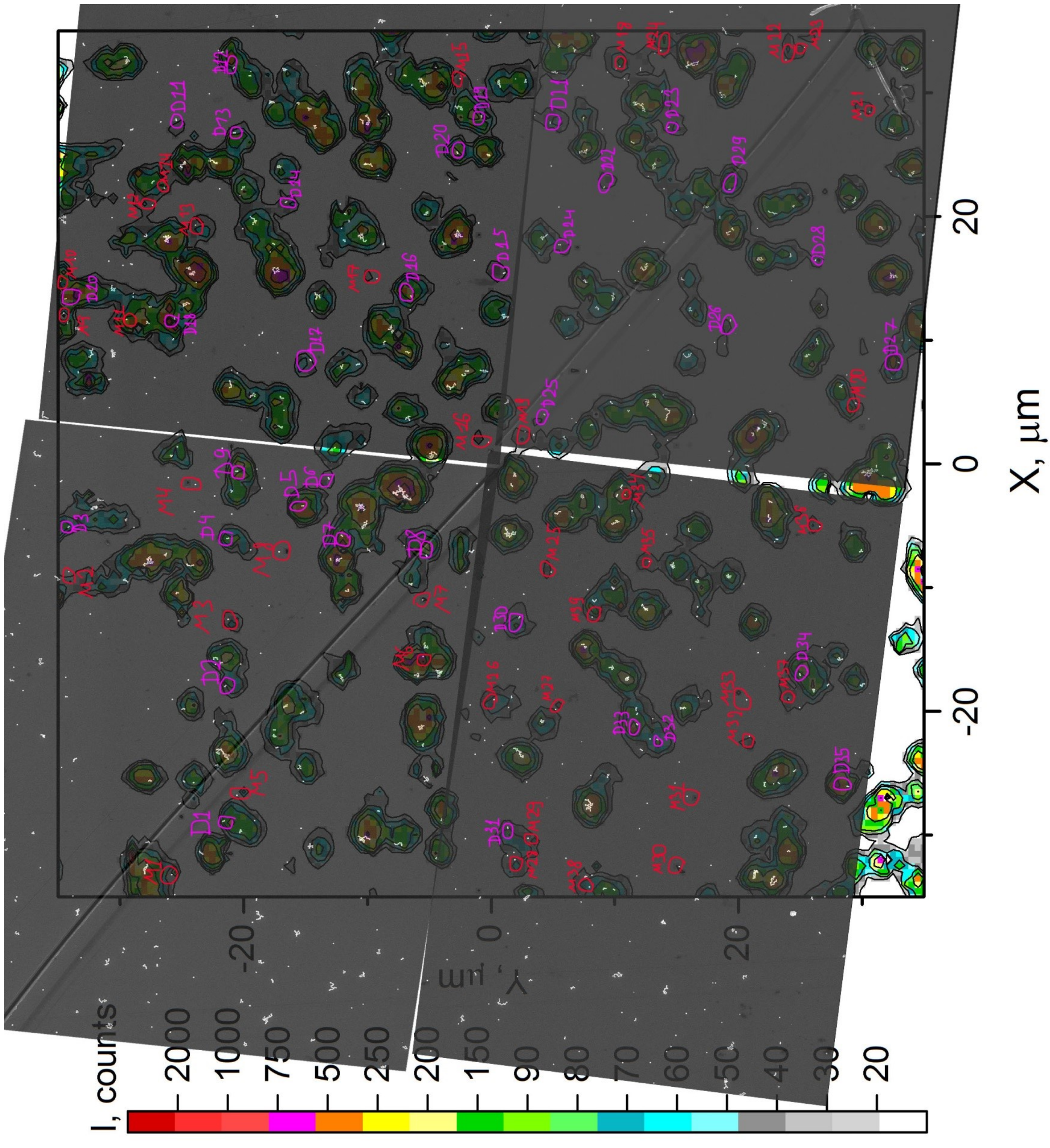


Figure S18. “C8” 100 nm AuNPs modified with mixed SAM of 2-MOTP and 8-Mercaptooctanoic acid (hereafter called just C8 samples) on Ag film

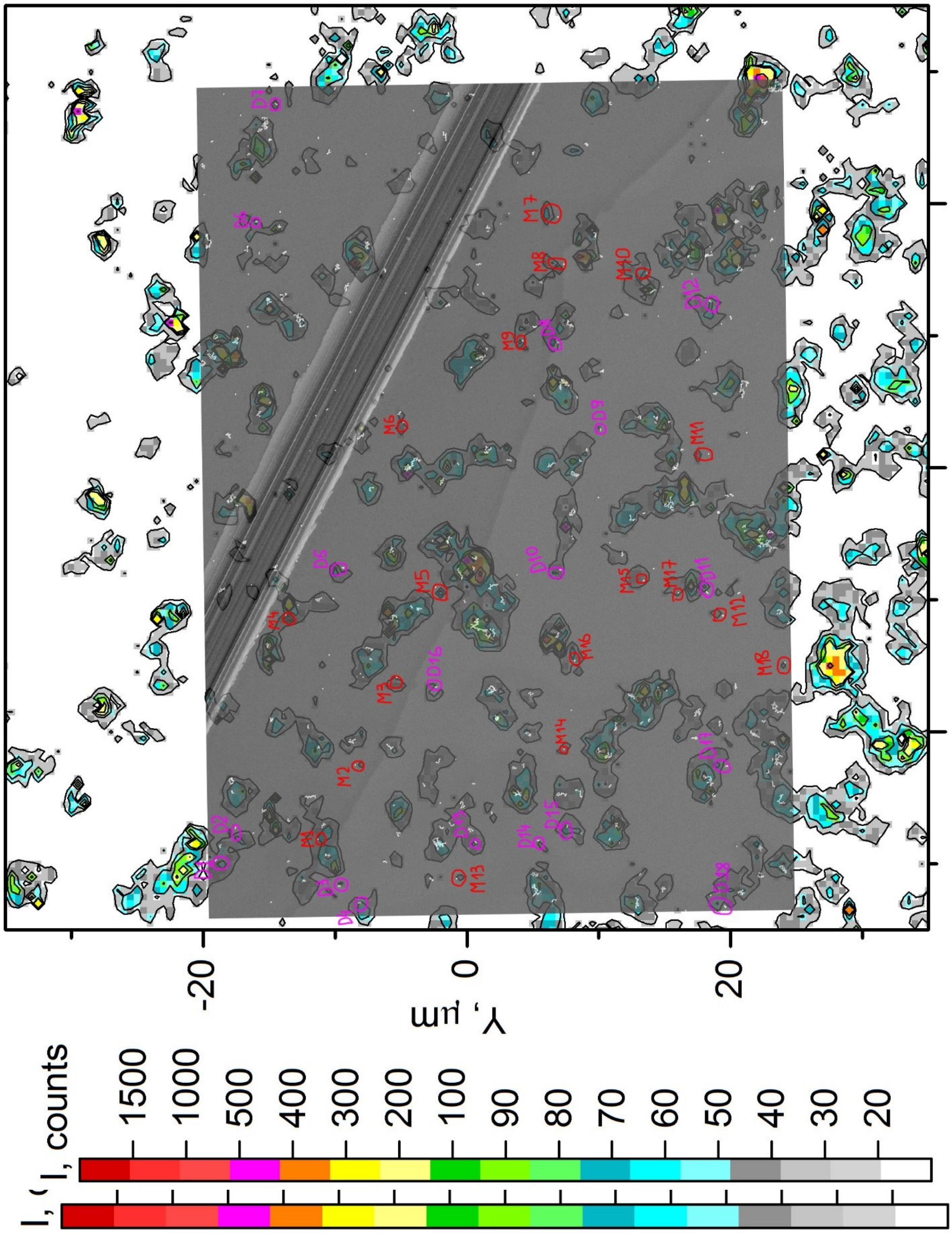


Figure S19. “C12” 100 nm AuNPs modified with mixed SAM of 2-MOTP and 12-Mercaptododecanoic acid - (hereafter called just C12 samples) on Ag film

Figure S20. “C12” 100 nm AuNPs modified with mixed SAM of 2-MOTP and 12-Mercaptododecanoic acid - (hereafter called just C12 samples) on Ag film

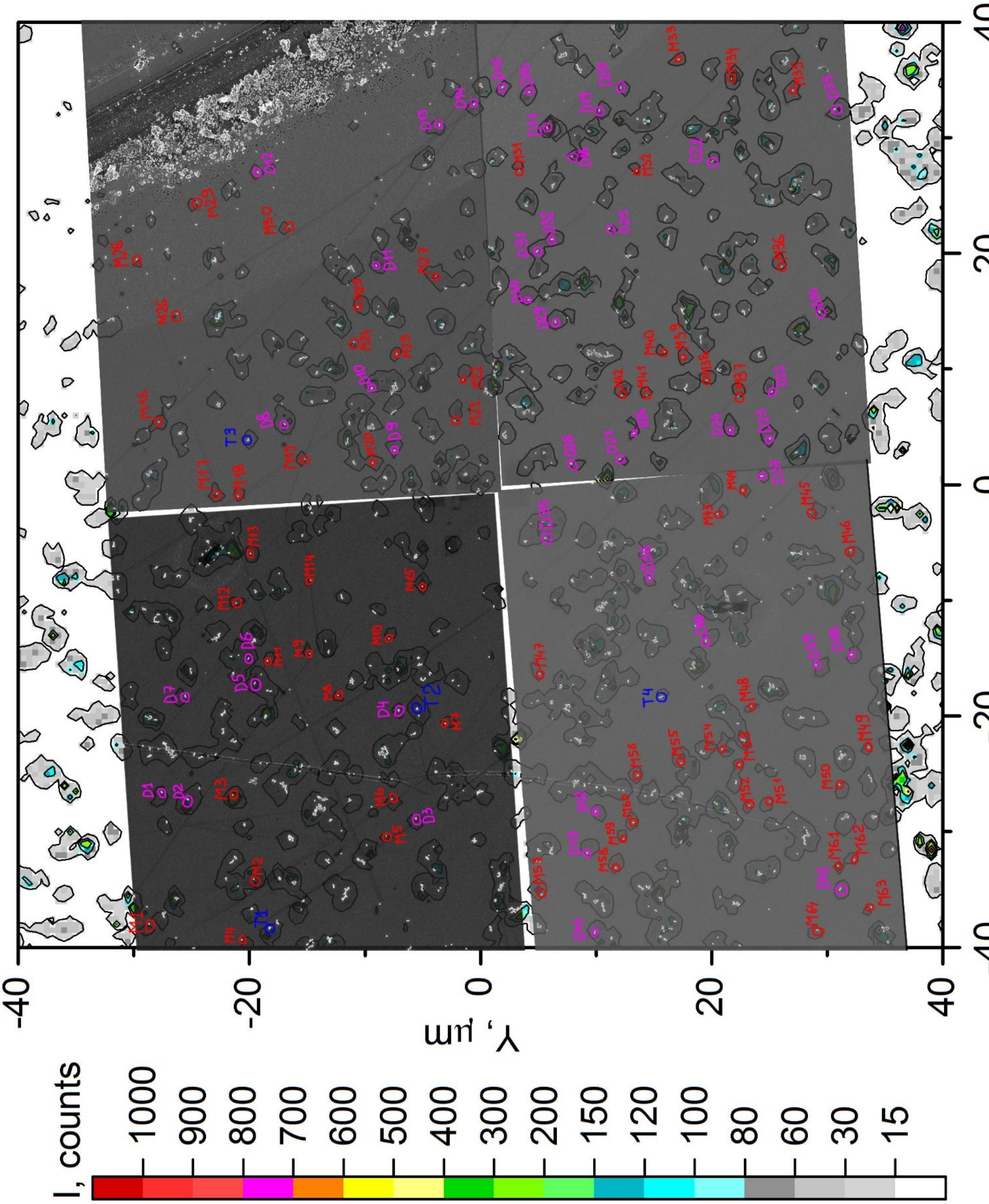


Figure S21. “C16” 100 nm AuNPs modified with mixed SAM of 2-MOTP and 16-Mercaptohexadecanoic acid - (hereafter called C16) on Ag film

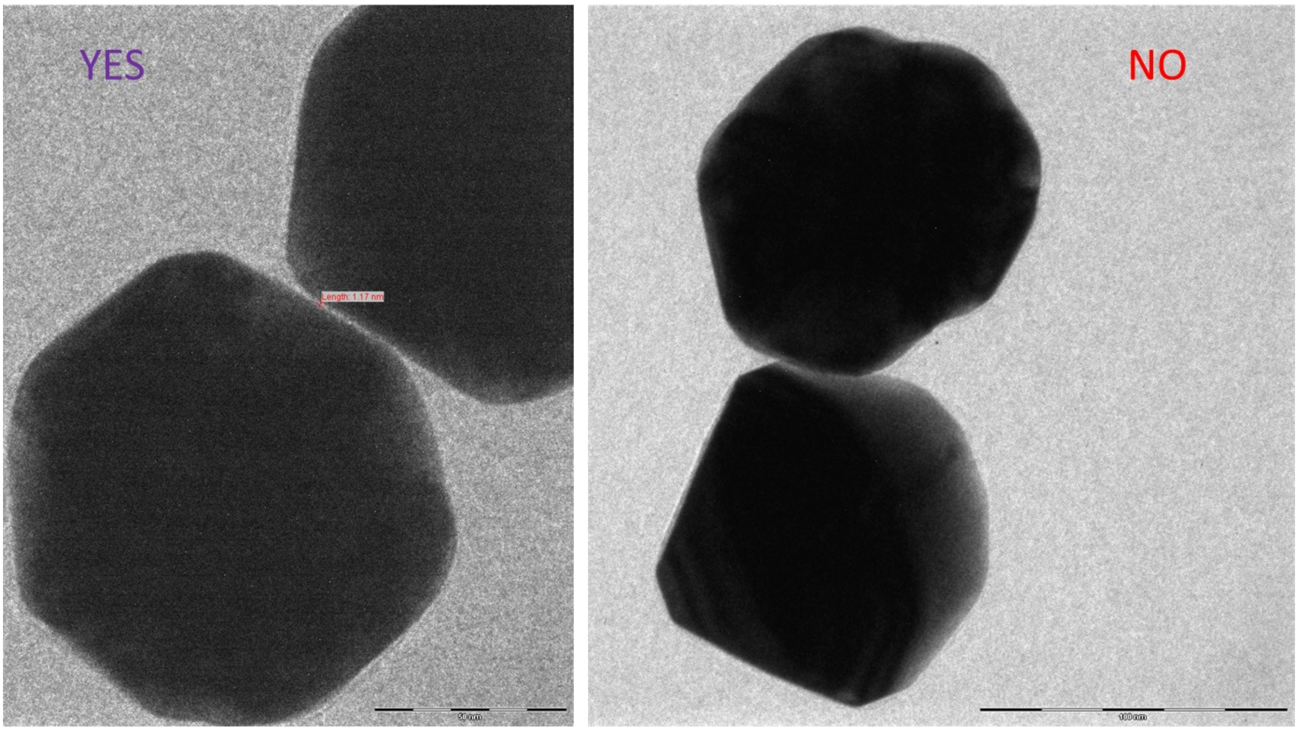


Figure S22 Representative High Resolution SEM Images (C6 mercapto carboxylic acid modified) of two dimers that shows clear gap view image , where gap is measured (left) and tilted/ obscure gap view (right) where gap cannot be reliably measured. Only clear gap view images were used for calculation of average gap distances.