# **Electronic Supplementary Information**

# **PPH dendrimers grafted on silica nanoparticles: surface chemistry, characterization, silver colloids hosting and antibacterial activity.**

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# **Compounds**







/n

2d

О



Si-2

Si-3



⊙\_<sub>Ms</sub>









#### 2a, Mass Spectrometry

#### <u>2b, <sup>1</sup>H NMR</u>





#### **2b, Mass Spectrometry**



### <u>2c, <sup>1</sup>H NMR</u>



#### **2c, 13C NMR**



### **<u>2c. Mass Spectrometry</u>**



2d, <sup>1</sup>H NMR



### <u>2d, <sup>13</sup>C NMR</u>



#### 2d, Mass Spectrometry





### Dendrimer 1-G1: <sup>13</sup>C- {<sup>1</sup>H} CP-MAS NMR

#### Dendrimer 1-G1: <sup>31</sup>P- {<sup>1</sup>H} CP-MAS NMR











#### Si-2, <sup>29</sup>Si CP-MAS NMR





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Normalized (reference at 1046 cm<sup>-1</sup>)
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Normalized (reference at 1046 cm<sup>-1</sup>)







# Adsorption of 1-G<sub>1</sub> on Si-1



AH323: Dendrimer Gc'1 (**1-G**<sub>1</sub>) is solubilized in a suspension of Si-1 in a mixture MeOH/THF (7:3, V/V). The suspension is heated at 55°C overnight. After cooling, the silica is separated by filtration on a sintered glass filter, washed with THF (4x50 mL) and dichloromethane (4x25 mL) and dried under vacuum at 100°C. The resulting powder is AH323 (no trace of adsorbed dendrimer on the FTIR spectrum).

The washings are gathered, concentrated under reduced pressure and analyzed by proton and phosphorus NMR (see hereunder). The dendrimer  $1-G_1$  is recovered without any trace of degradation.





#### Si-4, <sup>31</sup>P CP-MAS NMR









#### Si-5, <sup>31</sup>P CP-MAS NMR







# HRTEM imaging and EDX spectroscopy of modified silicas.



Scal bar is 50 nm



# TEM imaging of silver NPs grown on Si-2 modified silica in the absence of reducing agent (14days).



# HRTEM imaging of silver NPs grown on Si-3 modified silica in the absence of reducing agent (14days).



HRTEM imaging of silver NPs grown on Si-3 modified silica in the absence of reducing agent (14days).



# HRTEM imaging of silver NPs grown on Si-5 modified silica in the absence of reducing agent (14days).



HRTEM imaging of silver NPs grown on Si-5 modified silica in the absence of reducing **agent** (14 days, 2/2).



# EDX spectroscopy of silver NPs grown on Si-3 modified silica in the absence of reducing agent.

At t= 18 hours







# EDX spectroscopy of silver NPs grown on Si-5 modified silica in the absence of reducing agent.

At t= 18 hours











# HRTEM imaging of silver NPs grown on Si-2 modified silica in the presence of NaBH<sub>4</sub> (18 hours)

(picture shot at T = 18 hours)



#### HRTEM imaging of silver NPs grown on Si-2 modified silica in the presence of NaBH4.

(picture shot at T = 18 hours)



# HRTEM imaging of silver NPs grown on Si-5 modified silica in the presence of NaBH<sub>4</sub> (1 hour)



#### HRTEM imaging of silver NPs grown on Si-5 modified silica in the presence of NaBH4.

(picture shot at T = 1 hour)



# HRTEM imaging of silver NPs grown on Si-5 modified silica in the presence of NaBH<sub>4</sub> (18 hours)

(picture shot à T = 18 hours)



#### HRTEM imaging of silver NPs grown on Si-5 modified silica in the presence of NaBH4.

(picture shot à T = 18 hours)



## EDX spectroscopy of silver NPs grown on Si-2 modified silica in the presence of NaBH<sub>4</sub>

#### At t= 18 hours











# EDX spectroscopy of silver NPs grown on Si-5 modified silica in the presence of NaBH<sub>4</sub>

#### At t= 18 hours











# **Cristallographic analysis**

#### Cristallographic data

# Ag Cubic

h	k	I	d [A]	2Theta	[deg] I [%]	
1	1	1	1	2,35040	38,262	100,0
2	2	0	0	2,03550	44,473	45,1
3	2	2	0	1,43930	64,714	22,3
4	3	1	1	1,22740	77,745	22,1
5	2	2	2	1,17520	81,910	6,1
6	4	0	0	1,01780	98,371	2,6
7	3	3	1	0,93400	111,123	7,9

# Ag Hexagonal

<u>.</u> h	n k	C I	(	:[A] 2The	ta[deg] I [	%]
1	1	0	0	2,53740	35,345	25,1
2	0	0	2	2,39500	37,523	27,8
3	1	0	1	2,24230	40,184	100,0
4	1	0	2	1,74170	52,497	13,0
5	1	1	0	1,46500	63,445	12,5
6	1	0	3	1,35140	69,501	13,3
7	2	0	0	1,26870	74,768	1,7
8	1	1	2	1,24970	76,106	12,5
9	2	0	1	1,22640	77,820	8,6
10	0	0	4	1,19750	80,070	1,7
11	2	0	2	1,12110	86,801	1,9
12	1	0	4	1,08300	90,676	1,7
13	2	0	3	0,99330	101,700	3,7
14	2	1	0	0,95910	106,864	1,1

AgO	Cu	<u>bic</u>				
No.	h	k		d [A] 2	Theta[deg	]   [%]
1	1	1	1	2,78050	32,167	100,0
2	2	0	0	2,40800	37,313	33,5
3	2	2	0	1,70270	53,795	32,4
4	3	1	1	1,45210	64,075	26,5
5	2	2	2	1,39030	67,291	5,6
6	4	0	0	1,20400	79,551	3,5
7	3	3	1	1,10490	88,400	7,9
8	4	2	0	1,07690	91,335	5,7
9	4	2	2	0,98310	103,172	6,2

# AgO tétragonal

No.	h	k		d [A] 2	Theta[deg	]   [%]
1	1	0	1	5,46880	16,194	0,5
2	2	0	0	3,41650	26,060	0,2
3	1	1	2	3,31670	26,859	0,1
4	1	2	1	2,89760	30,834	1,2
5	1	0	3	2,77800	32,197	0,7
6	2	0	2	2,73440	32,724	100,0
7	2	2	0	2,41580	37,188	48,8
8	0	0	4	2,28050	39,483	20,3
9	3	0	1	2,20980	40,801	0,1
10	2	1	3	2,15540	41,879	0,5
11	2	2	2	2,13480	42,302	0,1
12	1	1	4	2,06230	43,865	0,1
13	1	3	2	1,95270	46,467	0,2
14	2	0	4	1,89680	47,921	0,1
15	2	3	1	1,85550	49,057	0,2

Ag2	ос	ubi	с			
No.	h	k		d [A] 2	Theta[deg	]   [%]
1	1	1	0	3.34200	26.652	2.0
2	1	1	1	2.72900	32.791	100.0
3	2	0	0	2.36200	38.067	28.0
4	2	1	1	1.92910	47.070	1.0
5	2	2	0	1.67090	54.904	13.0
6	3	1	1	1.42500	65.444	8.0
7	2	2	2	1.36420	68.756	2.0
8	4	0	0	1.18150	81.380	1.0
9	3	3	1	1.08430	90.537	1.0
10	4	2	0	1.05680	93.588	1.0
11	4	2	2	0.96460	105.987	1.0
12	5	1	1	0.90950	115.763	1.0

Ag2	Ag2O2 monoclinic					
No.	h	k		d [A] 2	Theta[deg	]   [%]
1	1	0	0	5.58160	15.865	1.0
2	1	1	0	2.95440	30.227	2.0
3	0	1	1	2.90120	30.795	1.0
4	2	0	0	2.79050	32.048	58.0
5	-1	1	1	2.76900	32.304	100.0
6	-1	0	2	2.70710	33.064	2.0
7	0	0	2	2.62080	34.185	35.0
8	1	1	1	2.41480	37.204	90.0
9	-2	0	2	2.28380	39.424	31.0
10	2	1	0	2.17800	41.424	1.0
11	-1	1	2	2.13680	42.261	1.0
12	0	1	2	2.09360	43.176	1.0
13	-2	1	2	1.91050	47.556	1.0
14	3	0	0	1.86110	48.899	1.0
15	1	1	2	1.82230	50.011	1.0
16	-3	0	2	1.79340	50.874	1.0
17	0	2	0	1.74140	52.507	7.0
18	-3	1	1	1.70030	53.877	20.0
19	2	0	2	1.67570	54.734	10.0
20	0	2	1	1.65240	55.572	1.0
21	3	1	0	1.64120	55.984	1.0
22	-1	1	3	1.62140	56.730	17.0
23	-2	2	1	1.48530	62.479	1.0
24	2	2	0	1.47760	62.841	10.0
25	3	1	1	1.45990	63.692	9.0
26	0	2	2	1.45050	64.154	8.0
27	-4	0	2	1.42230	65.584	3.0
28	1	1	3	1.40900	66.282	5.0
29	4	0	0	1.39550	67.007	11.0
30	-2	2	2	1.38490	67.589	6.0
31	-2	0	4	1.35320	69.395	3.0
32	1	2	2	1.35010	69.577	1.0
33	0	0	4	1.31050	72.001	3.0
34	-1	2	3	1.26190	75.241	5.0
35	2	2	2	1.20740	79.283	3.0
36	-4	0	4	1.14210	84.824	1.0
37	-1	3	1	1.12510	86.416	2.0
38	-5	1	1	1.10560	88.330	3.0
39	-4	2	2	1.10170	88.724	3.0

Ag2O3 orthorhombic						
No.	h	k		d [A] 2	Theta[deg	[]   [%]
1	2	2	0	4.06810	21.830	5.0
2	1	1	1	3.34200	26.652	100.0
3	4	0	0	3.21890	27.691	10.0
4	4	2	0	2.74150	32.637	90.0
5	3	1	1	2.69410	33.228	30.0
6	0	4	0	2.62330	34.152	30.0
7	1	3	1	2.48160	36.167	60.0
8	3	3	1	2.17830	41.418	50.0
9	5	1	1	2.06530	43.798	30.0
10	4	4	0	2.03270	44.538	10.0
11	6	2	0	1.98580	45.648	5.0
12	5	3	1	1.80420	50.548	20.0
13	2	0	2	1.76120	51.873	20.0
14	3	5	1	1.67570	54.734	25.0
15	2	2	2	1.67020	54.929	20.0
16	7	1	1	1.62340	56.653	15.0
17	8	0	0	1.60860	57.222	10.0
18	8	2	0	1.53670	60.168	30.0
19	7	3	1	1.48620	62.437	25.0
20	2	4	2	1.46260	63.561	30.0
21	1	7	1	1.37920	67.906	10.0
22	8	4	0	1.37120	68.357	5.0
23	6	2	2	1.34630	69.802	30.0
24	9	1	1	1.32090	71.347	10.0
25	0	8	0	1.31100	71.969	5.0
26	7	5	1	1.29390	73.073	5.0

Ag2O	Hexagonal

No.	h	k	ĭ	d [A] 21	Theta[deg	]   [%]	
1	0	0	1	4.95100	17.901	2.8	
2	1	0	0	4.60550	19.257	1.8	
3	1	0	1	3.37210	26.410	0.6	
4	1	1	0	2.65900	33.679	20.4	
5	0	0	2	2.47550	36.259	22.9	
6	-1	-1	1	2.34250	38.396	100.0	
7	2	0	0	2.30280	39.085	2.3	
8	1	0	2	2.18050	41.375	1.2	
9	2	0	1	2.08800	43.298	0.1	
10	-1	-1	2	1.81180	50.321	18.5	
11	2	1	0	1.74070	52.530	0.3	
12	2	0	2	1.68610	54.368	0.6	
13	0	0	3	1.65030	55.649	1.9	
14	-2	-1	1	1.64220	55.947	3.4	
15	3	0	0	1.53520	60.233	12.9	
16	3	0	1	1.46630	63.382	0.4	
17	-2	-1	2	1.42390	65.501	0.2	
18	-1	-1	3	1.40220	66.645	11.2	
19	2	0	3	1.34140	70.094	0.1	
20	2	2	0	1.32950	70.815	1.3	
21	3	0	2	1.30470	72.371	9.6	
22	-2	-2	1	1.28400	73.729	7.6	
23	3	1	0	1.27730	74.180	0.5	
24	-3	-1	1	1.23780	76.971	1.4	
25	-2	-1	3	1.19760	80.062	0.8	
26	1	0	4	1.19530	80.248	0.4	
27	-2	-2	2	1.17130	82.241	2.5	
28	4	0	0	1.15140	83.982	0.4	
29	-3	-1	2	1.13510	85.472	0.6	
30	3	0	3	1.12400	86.522	2.0	
31	-1	-1	4	1.12210	86.704	3.3	
32	2	0	4	1.09020	89.913	0.1	
33	3	2	0	1.05660	93.611	0.4	
34	4	0	2	1.04400	95.095	0.7	
35	-2	-2	3	1.03530	96.153	2.6	
36	-3	-2	1	1.03330	96.400	1.6	
37	-3	-1	3	1.01010	99.387	0.2	

#### Ag3O4 Monoclinic

No.hkl	d [A] 2Theta	[deg]   [%]
1011	4.68860 18.93	12 2.0
2020	4.60080 19.22	77 10.0
3021	3.51800 25.29	96 10.0
4 1 0 0	3.43660 25.90	05 5.0
5110	3.21850 27.69	95 60.0
611-1	3.15570 28.2	57 25.0
7120	2.75430 32.48	81 10.0
8002	2.72750 32.80	09 40.0
912-1	2.71540 32.9	60 40.0
10 0 3 1	2.67550 33.4	66 100.0
11 0 1 2	2.61450 34.2	70 5.0
12 1 1 1	2.50390 35.8	34 60.0
13 1 1 -2	2.41530 37.1	96 30.0
14 0 2 2	2.34690 38.3	22 5.0
15 0 4 0	2.30410 39.0	62 5.0
16 1 3 0	2.29000 39.3	12 10.0
17 1 3 -1	2.26450 39.7	74 50.0
18 1 2 -2	2.19790 41.0	32 20.0
19 0 4 1	2.12010 42.6	10 5.0
20 0 3 2	2.03850 44.4	04 2.0
21 1 3 -2	1.93900 46.8	315 5.0
22 1 4 0	1.91280 47.4	95 10.0
23 1 4 -1	1.89900 47.8	362 5.0
24 1 1 2	1.85630 49.0	34 5.0
25 2 1 -1	1.75530 52.0	60 20.0
26 1 2 2	1.75260 52.1	46 10.0
27 0 5 1	1.74480 52.3	97 10.0
28 1 4 1	1.72360 53.0	92 1.0
29 1 2 -3	1.70150 53.8	36 10.0
30 0 2 3	1.69060 54.2	12 10.0
31 2 0 -2	1.67970 54.5	93 4.0
32 1 5 0	1.62320 56.6	61 15.0
33 1 5 -1	1.61410 57.0	010 4.0
34 1 3 2	1.61260 57.0	67 2.0
35 2 2 0	1.61000 57.1	.68 5.0
36 2 2 -2	1.57840 58.4	22 5.0
37 1 3 -3	1.57240 58.6	66 20.0
38 0 3 3	1.56380 59.0	21 20.0
39 0 6 0	1.53500 60.2	42 10.0
40 0 5 2	1.52600 60.6	34 5.0
41 1 5 1	1.50300 61.6	62 15.0
42 1 5 -2	1.48300 62.5	87 10.0
43 1 4 2	1.46330 63.5	27 15.0
44 2 1 -3	1.45100 64.1	29 10.0
45 2 2 1	1.44560 64.3	98 5.0
46 1 1 3	1.43160 65.1	05 10.0
47 1 0 -4	1.40890 66.2	287 10.0
48 1 6 -1	1.39620 66.9	69 10.0
49 2 4 0	1.37730 68.0	12 20.0
50 0 0 4	1.36350 68.7	97 5.0

# XRD patterns

#### Ag(0)Si2











# Ag(0)Si2

#### AH332-18h-x500000-020



# Ag(0)Si3

### AH355-x800000-021





# Ag(0)Si3 AH355-x600000-07



# Ag(0)Si3 AH355-x800000-15



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2085	83	23	82	1.2.4.12	11.35%	200	10.0	0,2382.0	m	21.1
1000	$\dot{e}2$	54	12	the to	0	,2518,0			March	18 M
1983 B	93	23	22	20,253	15.000			- 1965 A	1	8.33
2.35	30	22	86	1	S. 16.4	1996	5. SV 68	97 B 880	1.0110	1000
	32	22	53	9 a	10.00	161	絵の名言	10.00	ALC: N	1.54
1000	22	80	99		0,2274	ill -	10.00	200 C -	202.00	97.92
10.00	5R	98	53	10.44	100 100	985.5				2016
110	-16		λį,	11.42	10.00	140		1000		1
13.64	63	94.	83	10.55-74		1.8		A stays	18.75	A
6966	25	82	22	135356		1223		17.192	1.157	1000
2892	20	22	28)	5,5916	0.15%	6.98		100.24	E	100
Ag	Не	age	nal	2.2.3	14.24	107	17 mail			233
1510-0	h l	k 1		d [A] 2The	eta[deg] t	[%]	51. E. A		AC 73	361
1	1	0	0	2,53740	35,345	25,1	0.002	200412	25628	289
2	Ō	0	2	2,39500	37,523	27,8	200		an in the	2.5
3	1	0	1	2,24230	40,184	100,0	6.5.83		1.2.6	1832
4	1	ō	2	1,74170	52,497	13,0	1.0	1.1.1.1.1	62.63	199
5	1	1	0	1,46500	63,445	12,5	四世之	Stars	6-35	690
6	1	0	3	1,35140	69,501	13,3	2.1.1	意识时	同気用な	800
7	2	0	0	1,26870	74,768	1,7	Sec.	S125786	S-1223	189
8	1	1	2	1,24970	76,106	12,5	2111		25.5.6.4	7617
9	2	0	1	1,22640	77,820	8,6	では高い	知道会		
10	0	. 0	4	1,19750	80,070	1,7	125.8		242571	100
11	2	0	2	1,12110	86,801	1,9	C10215	Street,	NUMPER NO	0.04.7
12	1	0	4	1,08300	90,676	1,7				
13	2	0	3	0,99330	101,700	3,7				
14	2	1	0	0,95910	106,864	1,1				

# Ag(0)Si3 AH355-x600000-17













Ag(0)Si5 AH333-x600000-0012





# Ag(II)Si2 AH326B-1j-x800000-11

# Ag(II)Si2

#### AH326-14j-x800000-0017





Ag Cubic

h	k	1	d [4	A] 2Theta	a[deg]   [%	5]
1	1	1	1	2,35040	38,262	100,0
2	2	0	0	2,03550	44,473	45,1
3	2	2	0	1,43930	64,714	22,3
4	3	1	1	1,22740	77,745	22,1
5	2	2	2	1,17520	81,910	6,1
6	4	0	0	1,01780	98,371	2,6
7	3	3	1	0,93400	111,123	7,9

Ag(II)Si2

# AH326-14j-x600000-0014





-	-					
h	k	Ĩ.	d [/	A] 2Theta	a[deg]   [%	1
1	1	1	1	2,35040	38,262	100,0
2	2	0	0	2,03550	44,473	45,1
3	2	2	0	1,43930	64,714	22,3
4	3	1	1	1,22740	77,745	22,1
5	2	2	2	1,17520	81,910	6,1
6	4	0	0	1,01780	98,371	2,6
7	3	3	1	0,93400	111,123	7,9

#### Ag(II)Si2

#### AH326-14j-x600000-0015



AH324-14j-x500000-0015







# Ag(II)Si5

# AH324-14j-x500000-0015



### MIC picture for E. coli



Si-1 Si-2 Si-5 Si-2 Ag (0) Si-3 Ag (II) Si-5 Ag (0) Si-5 Ag (0) Dilutions 1/2 1/4 1/8 1/16 1/32 1/64 1/128 1/256 1/512 1/1024 1/2048 1/4096

CMB Escherichia coli O157:H7

# <u>MBC picture for E. coli</u>

CMI Escherichia coli O157:H7