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Layer-by-layer functionalization of gold nanorods by polyelectrolytes to control surface spacer and precisely tune the surface plasmon resonance position

Céline Jégat and Guillaume Laurent*

Université Paris-Saclay, ENS Paris-Saclay, CNRS, PPSM, 91190 Gif-sur-Yvette, France

E-mail: guillaume.laurent@ens-cachan.fr

1 We present a layer-by-layer functionalization of gold
2 nanorods (GNRs) by polyelectrolytes in order to control
3 precisely the spacer surrounding the metallic nanoparticles
4 but also to modulate its plasmonic properties. Alternate
5 functionalization with negatively and positively charged
6 polyelectrolytes ensures a 2 nm step control of the spacer
7 from 0 nm up to 10 nm, depending on the number of layers.
8 Such process changes the local refractive index and thus
9 induces a red shift of the surface plasmon resonance. Both
10 solution and solid samples were studied.

11 **Keywords:** gold nanoparticles functionalization,
12 polyelectrolytes layers, spacer thickness control,
13 plasmonic properties modulation

14 The enhancement of the metallic nanoparticles
15 synthesis protocols impacts since many years the field of
16 materials science.¹⁻³ In fact, controlling precisely the size,
17 shape and the core metal gives access to specific plasmonic
18 properties. Numerous studies describe them and their
19 various applications in designing new meta-materials,
20 sensing and biomedicine⁴⁻⁸ each underlying that the control
21 of the direct environment of the metallic nanoparticle is
22 mandatory whatever we consider inter-particles coupling or
23 targeted organic compound functionalized on the metallic
24 nanoparticles.⁹ Different methods experienced the change of
25 their initial surfactant coating by other appropriate spacer.
26 Two of the most commonly used are the DNA linker¹⁰ and
27 the silica shell coating.¹¹ The first one shows the advantage
28 of having a precise length for the linker and allows
29 designing either hybrid organic / metallic system or dimer
30 nanoparticles. Despite it is quite easy to use; DNA linker is
31 still expensive and does not allow a good surface coverage
32 in case of organic functionalization. Moreover, the stability
33 of the hybrid system is not optimized. On the other hand,
34 silica shell surrounding metallic nanoparticles increases the
35 stability of the system and exhibits a potentially high surface
36 coverage with further functionalization with organic
37 compound using click chemistry. However, it is hard to
38 control the shell thickness for value bellow 10 nm; which is
39 a huge drawback because the value of the enhanced
40 electromagnetic field for plasmonic nanoparticles decreases
41 as the inverse of the cube distance from the surface,
42 enforcing a spacer thickness smaller than 10 nm.¹²

43 Considering the different drawbacks of the previous
44 spacers, using polyelectrolytes could represent a new way in
45 the functionalization of metallic nanoparticles. In fact, as
46 polyelectrolytes are organic polymers where the initial
47 monomer is positively or negatively charged, specific
48 electrostatic interactions afford an easy control of the spacer
49 thickness and at the same time increase the colloidal
50 stability of the system.¹³⁻¹⁶ Moreover, controlling the direct

51 environment of the metallic nanoparticles means controlling
52 the local refractive index and thus enables the modulation of
53 the localized surface plasmon resonance (LSPR).¹⁷⁻¹⁹

54 In this paper, negative and positive polyelectrolytes are
55 sequentially used to functionalize GNRs. Using such layer-
56 by-layer process ensures a perfect control of the spacer
57 surrounding the metallic nanoparticles, an increase of its
58 colloidal stability and a higher density when deposited on
59 glass substrate. Zetametry measurements are performed to
60 characterize the layer-by-layer deposition and the evolution
61 of the colloidal stability over the process. Extinction
62 spectroscopy is used to show the spectral shift observed
63 over the LSPR bands during the layer-by-layer process.

64 Gold nanorods with specific aspect ratio were prepared
65 by a modified “seed mediated growth method” using binary
66 surfactant mixtures.²⁰ In this synthesis procedure, sodium
67 oleate (NaOL) is combined with CTAB and thus achieves a
68 greater tunability of GNRs dimensions. This anionic
69 surfactant has a double bond that allows the reduction of the
70 gold salt in the absence of other reducers, in this case
71 ascorbic acid (AA), so a lower molar ratio of gold:AA is
72 used compared to the original method. The mixture of
73 CTAB and NaOL also enables the use of lower
74 concentration of surfactant in the reaction.¹⁵

75 The reaction has two steps. First, a small quantity of
76 gold salt is reduced using sodium borohydride as a strong
77 reducing agent in order to create small gold nanospheres
78 called “seeds”, which will be used as cores of the gold
79 nanorods. Secondly, a growth solution provides the gold salt
80 and the other reactants for the growth of these seeds with the
81 desired size and shape. These reactions are prepared as
82 follows.

83 **Seed Solution:** 5 mL of 0.5 mM HAuCl₄ is mixed with
84 5 mL of 0.2 M CTAB solution in a beaker. 0.6 mL of fresh
85 NaBH₄ is diluted to 1 mL with water and then injected to the
86 Au(III)-CTAB solution under vigorous stirring. The solution
87 color changes from yellow to brownish yellow and the
88 stirring is stopped after 2 min. The seed solution is aged at
89 room temperature for (at least) 30 min before use.

90 **Growth solution:** 3.5 g of CTAB and 0.617 g of NaOL
91 are dissolved in 125 mL of water in a 0.5 L Erlenmeyer
92 flask. 12 mL of AgNO₃ solution (4 mM) is added. The
93 mixture is kept undisturbed at 30°C for 15 min after which
94 125 mL of 1 mM HAuCl₄ solution is added. The solution
95 becomes colorless after 90 min of stirring (700 rpm) and 2
96 mL of HCl (37 wt. % in water, 12.1 M) is then introduced to
97 adjust the pH. After another 15 min of slow stirring (400
98 rpm), 0.625 mL of 0.064 M AA is added and the solution is
99 vigorously stirred for 30 s. Finally, 0.2 mL of the seed
100 solution is injected into the growth solution. The resultant

1 mixture is stirred for 30 s and left undisturbed at 30°C for
2 12-15 h for GNRs growth.

3 The synthesized GNRs were characterized using
4 extinction spectroscopy and scanning electron microscopy
5 (SEM) (Figure 1). They show two different LSPR bands:
6 the transversal one is located at 525 nm and the longitudinal
7 one at 881 nm. The spectrum is related to the original
8 synthesized solution, within the GNRs are surrounded by a
9 double layer of surfactant (mainly CTAB) and the solvent
10 which contains an excess of surfactant. The size distribution
11 of the GNRs was measured thanks to the SEM images over
12 one thousand nanoparticles. The average values are 97 nm
13 for the long axis and 21 nm for the short one, which gives
14 an aspect ratio around 4.6.

15 In order to use gold nanoparticles for enhanced
16 spectroscopies, the control of the distance between the
17 metallic surface and the molecules under interest is
18 mandatory. To achieve this goal, polyelectrolytes are under
19 great interest due to the layer-by-layer process which
20 ensures a precise control of the functionalization. Before
21 deposition of the polyelectrolytes, surfactants surrounding
22 the GNRs (CTAB and NaOL) need to be removed. So 10

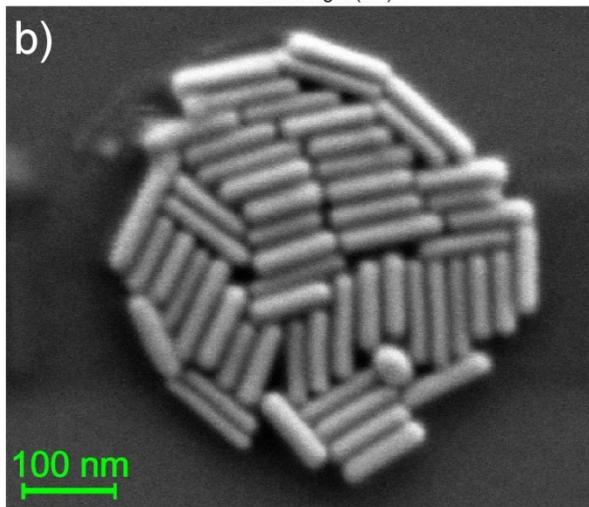
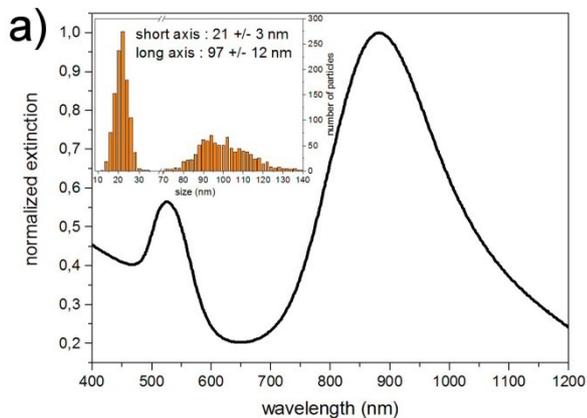


Figure 1. a) Extinction spectrum of synthesized gold nanorods. Insert shows the size distribution measured on 1034 nanoparticles; b) SEM image of the corresponding gold nanorods. Scale bar represents 100 nm.

23 mL of GNRs solution are centrifugated at 6 000 rpm during
24 20 min (relative centrifugal force RCF = 3 461 g) and then
25 the pellet is dispersed in 10 mL of milliQ water. This cycle
26 is done two more times.

27 Assuming that naked GNRs are slightly positively
28 charged, the first layer needs to be a negatively charged
29 polyelectrolyte; we choose sodium polystyrene sulfonate
30 (PSS, M = 70 000 g/mol), purchased from Sigma-Aldrich
31 and used without further purification. So 10 mL of naked
32 GNRs solution is mixed with 3 mL of PSS solution (10
33 mg/mL in water) under 2 min of gentle stirring. The mixed
34 solution is kept undisturbed for 45 min to allow the
35 electrostatic interactions between the GNRs and the
36 polyelectrolytes thanks to the natural Brownian motion. To
37 remove the excess of polyelectrolytes, centrifugation is
38 performed at 12 000 rpm during 10 min (RCF = 15 455 g)
39 and the pellet is dispersed in 10 mL of NaCl solution (0.5
40 mM) to prevent the flocculation of the hybrid nanoparticles
41 (gold nanorods with one layer, GNRs-1L). The addition of
42 NaCl increases the ionic strength of the solution which
43 stabilizes the polyelectrolyte layer in water. Without NaCl,
44 the functionalized GNRs precipitate within few hours.

45 To set the second polyelectrolyte layer, we choose the
46 poly(diallyldimethylammonium chloride) (PDADMAC, M
47 < 100 000 g/mol) which is positively charged. The same
48 process is used for the second layer. Briefly, 10 mL of
49 GNRs-1L are mixed with 3 mL of PDADMAC solution
50 (purchased from Sigma-Aldrich and used without further
51 purification or dilution). After 2 min of gentle stirring and
52 45 min at rest, the same centrifugation parameters are used.
53 The final pellet is dispersed in 10 mL of NaCl solution. The
54 use of NaCl solution instead of milliQ water is very
55 important to prevent the flocculation of the gold nanorods
56 with two layers of polyelectrolytes (GNRs-2L).

57 We can continue the layer-by-layer process deposition
58 by alternating between PSS and PDADMAC
59 polyelectrolytes, depending on the main charged surface of
60 the hybrids. Because the centrifugation step is more and
61 more critical as the number of layer increases, the rotation
62 speed (or even the RCF) needs to be adjusted in

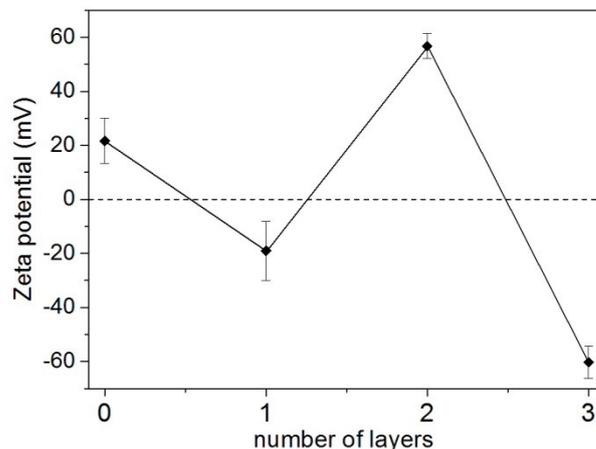


Figure 2. Evolution of the zeta potential of hybrid nanoparticles, starting from naked GNRs (0 layer) to three layers of polyelectrolytes.

1 consequence to prevent full aggregation of the pellet (which
 2 makes it very difficult to disperse in NaCl solution).
 3 Furthermore, the molecular weight of the different
 4 polyelectrolytes were chosen depending on the size (and
 5 aspect ratio) of the gold nanorods. If their size increases,
 6 longer polyelectrolyte chains are needed.

7 During the layer-by-layer process, each step was
 8 controlled by zetametry. Measuring the GNRs zeta potential,
 9 formerly the electrokinetic potential, is an easy way to
 10 check if each layer is correctly deposited and at the same
 11 time to measure the stability of the hybrid system. Figure 2
 12 shows the variation of the zeta potential when the GNRs are
 13 functionalized with up to three layers of polyelectrolytes.
 14 First of all, we clearly see the sign alternation of the zeta
 15 potential as long as we increase the number of layers. It is
 16 positive for the naked GNRs, then negative for the first layer
 17 of PSS, positive again for the second layer of PDADMAC
 18 and then negative again for the third layer of PSS which is
 19 in accordance with the main charge of the last
 20 polyelectrolyte deposited. Secondly, as the number of layer
 21 increases, the absolute value of the zeta potential increases
 22 also, indicating that the stability behavior of the hybrid
 23 nanoparticles in solution is more efficient. It starts from 20
 24 mV for naked GNRs to increase to 60 mV for a three layers
 25 system. Considering that each polyelectrolyte layer
 26 thickness is around 2 nm,²¹ this layer-by-layer process
 27 allows to perfectly controlling the spacer between the
 28 surface of the metallic nanoparticle and the future studied
 29 organic compound to perform efficient enhanced
 30 spectroscopies. This layer-by-layer process is also a good
 31 way to prevent aggregation of the gold nanoparticles in
 32 solution.

33 Addition of polyelectrolytes layers around GNRs
 34 would also affect their optical plasmonic properties. In fact,
 35 LSPR bands are very sensitive to their direct environment,
 36 meaning the local refractive index in solution. Thus, putting
 37 more layers of polyelectrolytes surrounding the GNRs
 38 would change the average value of the refractive index,

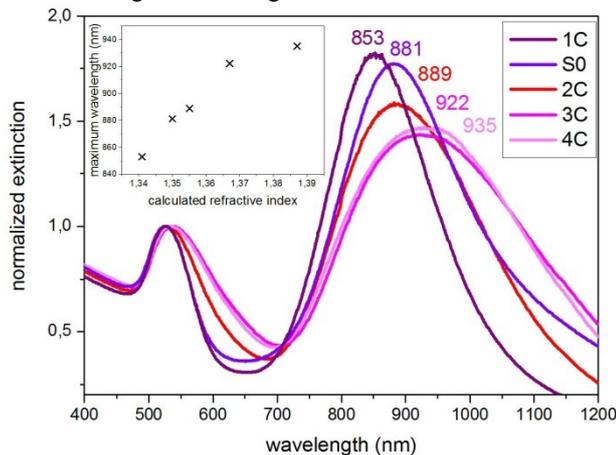


Figure 3. Extinction spectra of functionalized GNRs from 1 to 4 layers of polyelectrolytes. S0 is referred to the synthesized GNRs. Insert shows the evolution of the observed spectral shift with the estimated refractive index.

39 inducing LSPR bands spectral shifts. Figure 3 shows the
 40 evolution of the extinction spectra of the GNRs as long as
 41 we do the layer-by-layer process. We mainly observe a
 42 spectral red-shift of the LSPR bands which is small in the
 43 case of the transverse one but very important (up to 80 nm)
 44 for the longitudinal one. The way we estimate the average
 45 value of the local refractive index is based on the
 46 assumption that the surface plasmon effect is mainly
 47 efficient in the first 10 nm closed to the surface of the
 48 metallic nanoparticles.^{12, 22} Surfactants or polyelectrolytes
 49 layers are localized within this small area and need to be
 50 taken into account, in addition to the solvent, to estimate the
 51 relative value of the refractive index directly surrounding
 52 the GNRs. The complete calculation assumptions are
 53 described in the supporting information but simply the
 54 equation used is:

$$56 \quad RI = 1,33 \times \frac{V_{tot} - \sum_i V_{layer}}{V_{tot}} + \sum_i RI_{layer} \times \frac{V_{layer}}{V_{tot}} \quad (1)$$

57 where **RI** is the refractive index (1.33 is the value of the
 58 water solvent), V_{tot} the total volume considered, V_{layer} the
 59 volume of a considered layer and i the number of layers.
 60 Considering equation 1, we clearly observe a linear
 61 dependence between the optical shift of the LSPR bands and
 62 the value of the refractive index (insert of Figure 3). This
 63 allows at the same time a precise control of the layer-by-
 64 layer deposition process by spectroscopic measurements but
 65 also a fine modulation tuning of the LSPR bands. So a quick
 66 and simple prediction can be done on the modulation of the
 67 LSPR bands' position when considering further layers of
 68 polyelectrolytes. Therefore, using polyelectrolytes is an
 69 efficient way to both functionalize metallic nanoparticles
 70 and tune the LSPR bands position, which could be
 71 mandatory for enhanced spectroscopies when a good
 72 spectral overlap with other absorption band is needed.
 73

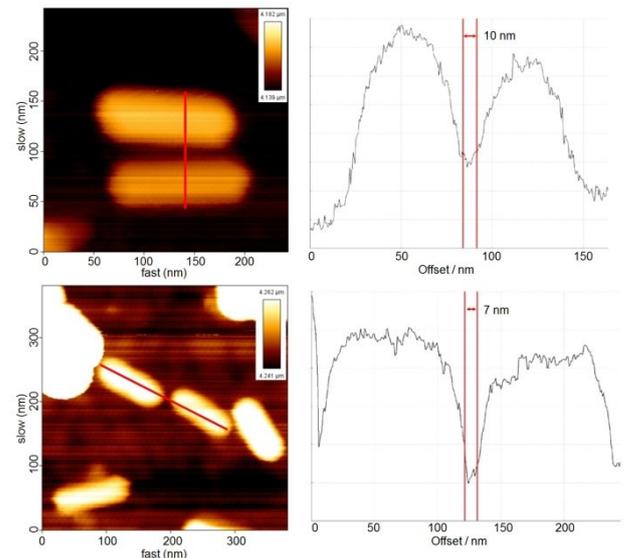


Figure 4. Left: AFM imaging of deposited GNRs-1L. Right: corresponding gap measurements between 2 GNRs-1L.

1 To go further than these results obtained in solution
 2 we considered solid substrates to see how polyelectrolytes
 3 can be used to ensure space between GNRs. So we prepared
 4 GNRs-1L and deposited a diluted solution by the droplet
 5 method on a silicon wafer to perform atomic force
 6 microscopy (AFM). Keep in mind that a single PSS layer is
 7 2 nm thickness. Figure 4 shows the distance measurement
 8 between side-by-side and head-to-head dimers. The average
 9 gap value between two GNRs is 8 nm which clearly
 10 indicates that the PSS layer induces repulsive forces
 11 between the nanoparticles. It means that polyelectrolytes
 12 functionalization prevents the aggregation in solution but
 13 also modulates the gap between deposited nanoparticles
 14 which is very important when dealing with inter-
 15 nanoparticles' coupling. AFM measurement with more than
 16 one layer was not possible due to the quantity of polymer
 17 surrounding the GNRs which pollutes the AFM tip and
 18 makes imaging complicated. Looking at the study of
 19 Mohwald and co-workers²¹, a single layer of polyelectrolyte
 20 is 2 nm thick, two layers are 4 nm thick and three layers are
 21 6 nm thick. Considering these layers thickness and the
 22 repulsive forces, we can estimate the distance between two
 23 GNRs-2L and two GNRs-3L to be over 8 and 12 nm
 24 respectively, when deposited on substrate.

25 To go further, multi-layered GNRs were deposited on
 26 glass substrates to allow absorption measurements on solid
 27 sample. Prior to the deposition, the glass slide was washed
 28 using first ethanol and secondly oxygen plasma cleaner.
 29 Then we deposit 50 μ L of high concentrated solution of
 30 layered GNRs by the droplet method and we waited until
 31 the complete solvent evaporation. Figure 5 shows the
 32 absorption spectra obtained on different glass slides where
 33 GNRs from zero layer to four layers of polyelectrolytes
 34 were deposited. There are two main observations. First of all,
 35 we observed the same behavior as the solution samples. The
 36 longitudinal LSPR band is optically red-shifted as long as
 37 we increase the number of polyelectrolytes layers
 38 surrounding the GNRs, meaning as long as the local
 39 refractive index increases. In contrast with the solution

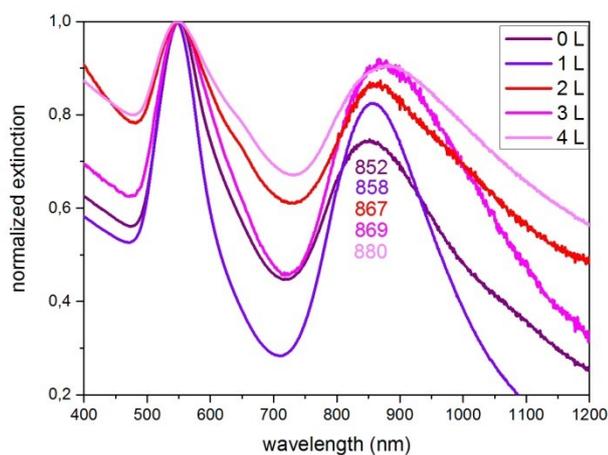


Figure 5. Extinction spectra of functionalized GNRs deposited on glass slides. Number of polyelectrolytes goes from 0 to 4 layers.

40 samples, it is rather difficult to estimate the value of the
 41 local refractive index on deposited sample. In fact, in
 42 solution you can consider each GNR individually so only
 43 the solvent and the layers have to be considered. When
 44 deposited on glass substrate, the direct environment of each
 45 GNR is composed of air, glass and other GNRs. So
 46 estimating an average value of the local refractive index
 47 cannot be efficiently achieved. The second observation is
 48 the broadening of both transverse and longitudinal LSPR
 49 bands for samples with higher number of layers. This
 50 observation is explained by the high density of GNRs that
 51 are deposited on the glass substrate. To characterize the
 52 GNRs' packing, SEM imaging was performed on GNRs-1L
 53 deposited on silicon wafer. Due to vacuum and electron gun
 54 source condition, an extra step of oxygen plasma cleaner
 55 was done to remove organic compounds like
 56 polyelectrolytes and possible rest of surfactant. The main
 57 advantage of this extra step is to increase the SEM imaging
 58 resolution. But the drawback is that destroying the
 59 polyelectrolyte layers changes the distance between the
 60 GNRs, especially for high number of layers or when GNRs
 61 are closely packed. That is why SEM measurements are
 62 only used to characterize the close packing and not the inter-
 63 particle distances. SEM imaging, in supporting information,
 64 clearly show wide areas of high density packing of GNRs.
 65 Regarding absorption spectroscopy, these closed packed
 66 nanorods induce the broadening of the LSPR bands but also
 67 a specific band that appears around 660 nm, due to
 68 transverse coupling between GNRs allowed by the short
 69 inter-particles distance.²³ Thus increasing the number of
 70 polyelectrolytes layers allows to tune the LSPR bands
 71 position but also to modulate the inter-particles coupling by
 72 controlling the distance between GNRs.

73 In conclusion, control of the distance between metallic
 74 nanoparticles and targeted organic dye is mandatory for
 75 enhanced spectroscopies. Different spacers can be used like
 76 silica shell or DNA but polyelectrolytes show many
 77 advantages. First of all, as it is a layer-by-layer process, you
 78 can control precisely the thickness of the spacer with a 2 nm
 79 single layer precision and also increase the colloidal
 80 stability of the functionalized gold nanoparticles. Then, as
 81 any modification of the GNRs' surface, putting some
 82 electrolytes modulates the position of the LSPR bands, but
 83 its linear dependence makes it easily predictable. Finally,
 84 for surface deposition, functionalized GNRs can grant
 85 access to selection of the gap between nanoparticles which
 86 govern the strength of inter-particles coupling and thus, the
 87 local field enhancement. To summarize, polyelectrolytes
 88 offer new possibilities in term of spacer control and further
 89 metallic nanoparticle's functionalization, especially with
 90 charged organic compounds.

91
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95 Supporting Information is available on
 96 http://dx.doi.org/10.1246/cl.*****
 97

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