

Zn²⁺-Regulated Self-Sorting and Mixing of Phosphates and Carboxylates on the Surface of Functionalized Gold Nanoparticles**

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Abstract: Herein, we describe the self-sorting of phosphate- and carboxylate-containing molecules on the surface of monolayer-protected gold nanoparticles. Self-sorting is driven by selective interactions between the phosphate probe and Zn²⁺ complexes in one monolayer; these interactions force the carboxylate probe to move to a second type of nanoparticle. This process effectively separates the probes and causes their localization in well-defined spaces surrounding the nanoparticles. The removal/addition of Zn²⁺ metal ions from the system is used to convert the system from an ordered to a disordered state and vice versa. The possibility to control the location and transport of populations of molecules in a complex mixture creates new perspectives for the development of innovative complex catalytic systems that mimic nature.

Nature strictly relies on self-assembly for the formation of functional molecular structures.^[1] Inspired by nature, chemists have learned over the past decades to master the process of self-assembly up to the level that highly complex molecular structures can now be readily prepared.^[2] In this process, the storage of chemical information in the building blocks is of fundamental importance, as it determines their location in the assembly. The reliability of this approach emerged in a striking manner from studies by Isaacs and co-workers that demonstrated how a complex mixture of building blocks could undergo spontaneous sorting into well-defined molecular architectures according to the embedded chemical information.^[3,4] Also, these studies provided clear evidence that multiple dynamic assemblies can coexist, thus offering the important perspective of creating complex synthetic systems that resemble natural systems.^[5,6] For example, it has recently been shown that narcissistic self-sorting (i.e. the self-recognition of building blocks) can indeed drive the spontaneous formation of homodomains in rodlike micellar aggregates.^[7] Eventually, this approach may lead towards the spontaneous formation of different compartments in synthetic systems in a similar manner as happens in a cell.^[8–10] In the field of nanotechnology, the self-sorting of small molecules on solid 2D surfaces is drawing much attention, as it provides an attractive way of surface patterning.^[11,12] Herein, we describe the self-sorting of carboxylate and phosphate molecules on the surface of two different monolayer-protected gold nano-

particles (Au MPCs). In this case, self-sorting regards the topological location of populations of molecules on the surface of different nanoparticles, rather than the formation of well-defined supramolecular architectures. It is shown that Zn²⁺ metal ions can be used as regulators to cycle the system between a self-sorted state in which the two types of molecules reside on different surfaces and a “mixed state” in which both molecules are present on both surfaces.

Previously, we studied the self-assembly of small anionic molecules, such as nucleotides and peptides, on the monolayer surface of Au MPC **1**·Zn²⁺ (*d* = 1.8 ± 0.4 nm) for applications in catalysis and sensing.^[13,14] It was found that such molecules bound to the surface under saturation conditions even at low micromolar concentrations in an aqueous buffer.^[15,16] These studies revealed further that the presence of the Zn²⁺ metal ion in the monolayer of Au MPC **1**·Zn²⁺ caused an increase in the surface-saturation concentration (SSC) of the probes on the surface as compared to that of the analogous Au MPC system **1** without Zn²⁺. Also, Zn²⁺ caused a higher affinity of phosphate probes as compared to carboxylate probes. In particular, the latter observation made us postulate that the metal ion would be able to induce the selective assembly of a phosphate probe on the surface of Au MPC **1**·Zn²⁺ in the presence of a carboxylate probe. A second, nonselective nanosystem (e.g. Au MPC **2**^[15,17,18] with quaternary ammonium head groups) could then act as a scavenger of the carboxylate probe. This process would effectively result in the self-sorting of two probes on two different surfaces (Figure 1).

To explore this possibility, we selected phosphate probe **A** and carboxylate probe **B** on the basis of previous studies.^[19] Both probes are equipped with a fluorogenic moiety (a methylamino anthranilic ester in **A**, coumarin 343 in **B**) so that the binding of the probes to the nanoparticles could be studied by means of fluorescence-quenching titrations. The distinct excitation and emission wavelengths for **A** (λ_{ex} = 355 nm, λ_{em} = 448 nm) and **B** (λ_{ex} = 445 nm, λ_{em} = 493 nm) enable the simultaneous study of both probes in a mixture.^[20] Importantly, both probes bind to the surface of either Au MPC **1**·Zn²⁺ or Au MPC **2** under saturation conditions even at low micromolar concentrations in water, thus implying that it is possible to operate at probe concentrations at which effectively all probe molecules are bound. The SSCs of both probes on the surfaces of Au MPC **1**·Zn²⁺ and Au MPC **2** were determined by means of fluorescence-quenching titrations (see the Supporting Information). The respective concentrations of Au MPC **1**·Zn²⁺ and Au MPC **2** were regulated such that both nanosystems would be able to bind approximately the same amount of the probes (3.4 μM for **A** and 2.7 μM for **B**).

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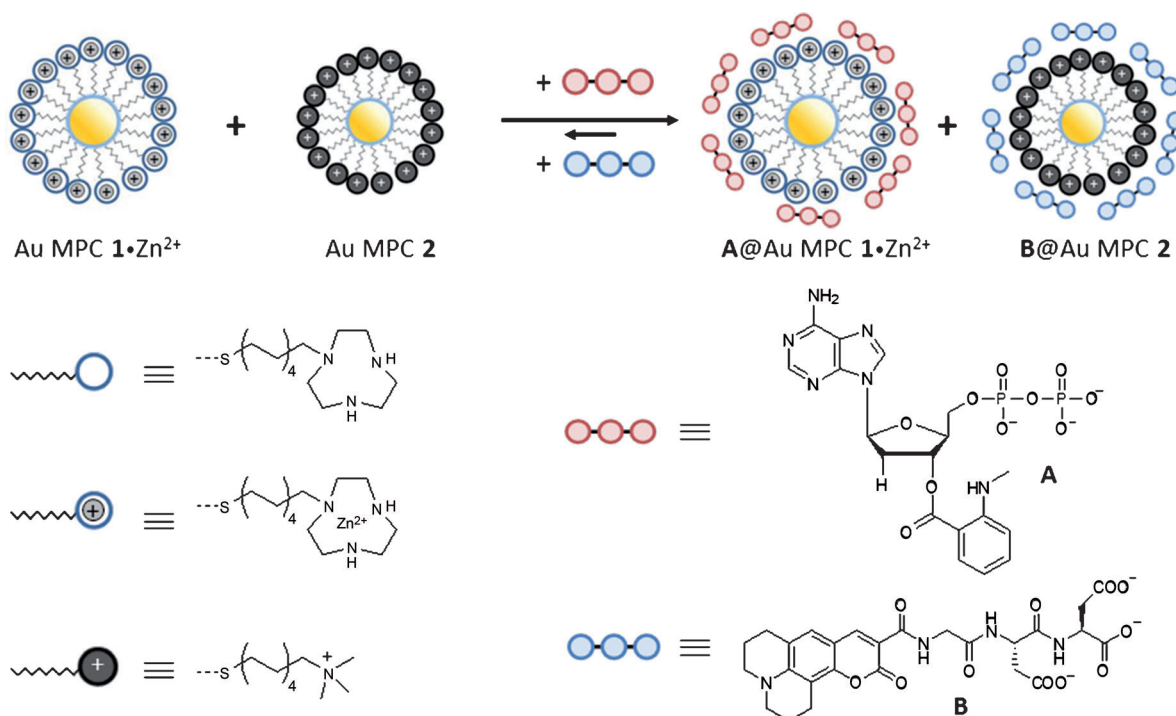


Figure 1. Schematic representation of the self-sorting of probes **A** and **B** on Au MPCs **1**·Zn²⁺ and **2**.

For self-sorting to occur, two requirements must be fulfilled. The first is that Au MPC **1**·Zn²⁺ must have a preference to bind probe **A** over probe **B**, and the second is that Au MPC **1**·Zn²⁺ must in general have a higher affinity for either probe as compared to Au MPC **2**. Only in that case, preferential probe binding to Au MPC **2** is not necessary, since the distribution of the probes on the two available surfaces will be determined by the preference imposed by Au MPC **1**·Zn²⁺. Both prerequisites were studied in a series of experiments.

We performed competition experiments between probes **A** and **B** to determine their relative affinities for Au MPC **1**·Zn²⁺ and Au MPC **2**. In these experiments, increasing amounts of probe **A** were added to a solution containing either Au MPC **1**·Zn²⁺ or Au MPC **2** together with probe **B** at a fixed concentration of 2.7 μM . After each addition, the fluorescence emission of both **A** and **B** was measured. The strong difference between Au MPC **1**·Zn²⁺ and Au MPC **2** becomes immediately evident from a glance at the displacement curves (Figure 2). The initial additions of **A** to **B**@Au MPC **1**·Zn²⁺ resulted in a quantitative displacement of **B** by **A**, as indicated by the linear increase in the fluorescence intensity of **B** and the complete quenching of **A** (Figure 2a). On the other hand, the addition of **A** to **B**@Au MPC **2** led to only a partial displacement of **B** (Figure 2b). Quantitative analysis revealed the surface composition of each nanosystem after the addition of **A** (3.4 μM): **A**/**B** 90:10 for Au MPC **1**·Zn²⁺ and 45:55 for Au MPC **2** (see the Supporting Information). These experiments show that Au MPC **1**·Zn²⁺ binds **A** with a much higher affinity as

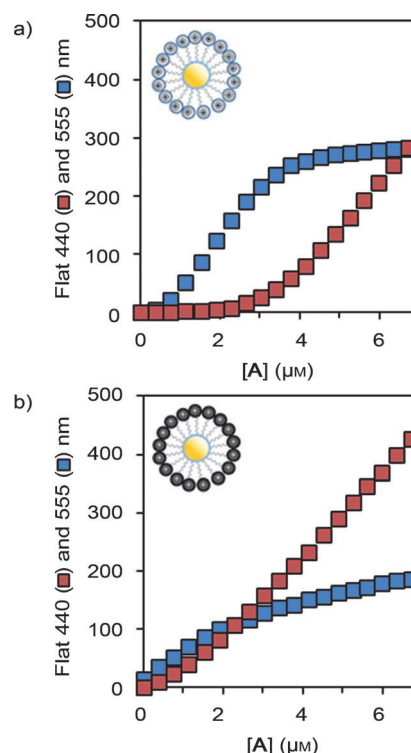


Figure 2. Fluorescence intensity of probes **A** (red squares) and **B** (blue squares) as a function of the amount of **A** added to a) **B**@Au MPC **1**·Zn²⁺ and b) **B**@Au MPC **2**. Experimental conditions: [Au MPC **1**·Zn²⁺] = 8 μM , [Au MPC **2**] $\approx$ 20 μM , [**B**] = 2.7 μM , [HEPES] = 10 mM, pH 7.0, 37°C. HEPES = 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid.

compared to **B**, whereas Au MPC **2** does not have a marked preference.

Proof that Au MPC **1**·Zn²⁺ has a higher-affinity surface as compared to that of Au MPC **2** was obtained by studying the affinities of probes **A** and **B** for either surface in the presence of increasing amounts of tetraethylammonium chloride (TEACl). The increase in ionic strength in the solution weakens the interaction between the two anionic probes and the monolayer surfaces. The displacement of surface-bound probes **A** and **B** was studied independently for each nanosystem (Figure 3; see also the Supporting Information). The

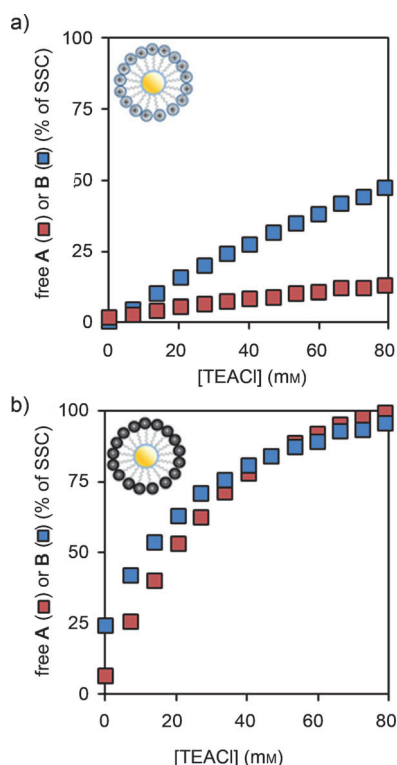


Figure 3. Amount of displaced **A** (red squares) and **B** (blue squares) as a function of the amount of TEACl added to a) either **A**@Au MPC **1**·Zn²⁺ or **B**@Au MPC **1**·Zn²⁺, and b) either **A**@Au MPC **2** or **B**@Au MPC **2**. Experimental conditions: [Au MPC **1**·Zn²⁺] = 8 μ M, [Au MPC **2**] $\approx$ 20 μ M, [A] = 3.4 μ M, [B] = 2.7 μ M, [HEPES] = 10 mM, pH 7.0, 37°C. See the Supporting Information for the conversion of the measured fluorescence intensities into concentrations of **A** and **B**.

obtained displacement curves showed that probes **A** and **B** were both displaced quantitatively from Au MPC **2** upon the addition of TEACl (80 mM; Figure 3b). In agreement with previous studies,^[15] the nearly superimposable curves obtained for probes **A** and **B** indicate that the chemical nature of the anionic group is irrelevant for binding, which explains the lack of selectivity for probe binding to Au MPC **2**. On the other hand, the same experiment performed with Au MPC **1**·Zn²⁺ resulted in the displacement of just 15% of **A** and 50% of **B** (Figure 3a). These experiments illustrate three important features. First, the much lower displacement levels demonstrate that Au MPC **1**·Zn²⁺ binds both probes more strongly than Au MPC **2**. Second, they confirm the selectivity

of Au MPC **1**·Zn²⁺ for **A** over **B**, and third, they show that the interaction between **A** and Au MPC **1**·Zn²⁺ is the only interaction that is hardly affected by an increase in ionic strength.

Two final titration experiments confirmed that the observed probe selectivities and affinities are maintained also in a complex system composed of both nanosystems and probes (see the Supporting Information). In the first experiment, a solution containing the two nanosystems Au MPC **1**·Zn²⁺ and Au MPC **2**, probe **B**, and TEACl (80 mM) was titrated with probe **A**. In the absence of **A**, a lower amount of **B** was bound (1.1 μ M), in agreement with the SSC of **B**@Au MPC **1**·Zn²⁺ under these conditions. The addition of **A** up to a concentration of around 2.8 μ M resulted in the binding of **A** and the complete displacement of **B**. This result confirms that the selectivity of Au MPC **1**·Zn²⁺ for **A** is maintained in the full-component mixture. Alternatively, the titration of **B** into a solution of Au MPC **1**·Zn²⁺, Au MPC **2**, probe **A**, and TEACl (80 mM) showed no binding of **B** at all, thus confirming the higher affinity of **A** also in the full-component mixture.

Having established that Au MPC **1**·Zn²⁺ binds **A** selectively over **B** and that Au MPC **1**·Zn²⁺ binds both probes **A** and **B** with a higher affinity as compared to Au MPC **2**, we then proceeded with the self-sorting experiment by adding Au MPC **1**·Zn²⁺ and Au MPC **2** sequentially to a solution of probes **A** and **B** (Figure 4). After each step, the fluorescence intensity of each probe was measured and used to calculate the amount of free probe in solution (see the Supporting Information). The addition of Au MPC **1**·Zn²⁺ resulted in the near-quantitative capture of **A**, whereas only a marginal amount of **B** was captured. The respective amounts of captured probe (88% for **A** and 12% for **B**) correspond very nicely to those obtained from the displacement studies (Figure 2a). The successive addition of Au MPC **2** caused the complete capture of all remaining probes **A** and **B** that were still free in solution, thus resulting in a situation in which effectively all probes were surface-bound. On the basis of the experiments described above, we could conclude that **A** resided almost exclusively on Au MPC **1**·Zn²⁺, whereas **B** was localized on Au MPC **2**. This hypothesis was confirmed by the observation that the addition of TEACl (80 mM) to the self-sorted system caused the release of **A** to only a modest extent (17%), which is consistent with the amount of **A** that is released from Au MPC **1**·Zn²⁺ upon adding TEACl. On the other hand, probe **B** was nearly quantitatively (96%) released at the same time, which is consistent with its localization on Au MPC **2**.

Additional evidence for the localization of **A** on Au MPC **1**·Zn²⁺ came from the subsequent addition of the *N,N,N',N'*-tetrakis(2-pyridylmethyl)ethylenediamine (TPEN) ligand, which is a scavenger for the Zn²⁺ ions present in the monolayer of Au MPC **1**·Zn²⁺.^[16,19] An independent titration showed that the removal of Zn²⁺ from Au MPC **1**·Zn²⁺ resulted in a decrease of the SSC of **A** from 3.4 to 1.7 μ M, in line with previous observations (see the Supporting Information).^[16] Indeed, the addition of TPEN to the nanoparticle mixture caused a partial release of probe **A** to a final value of around 65% (*t* = 60 min; Figure 4). The remaining 35%

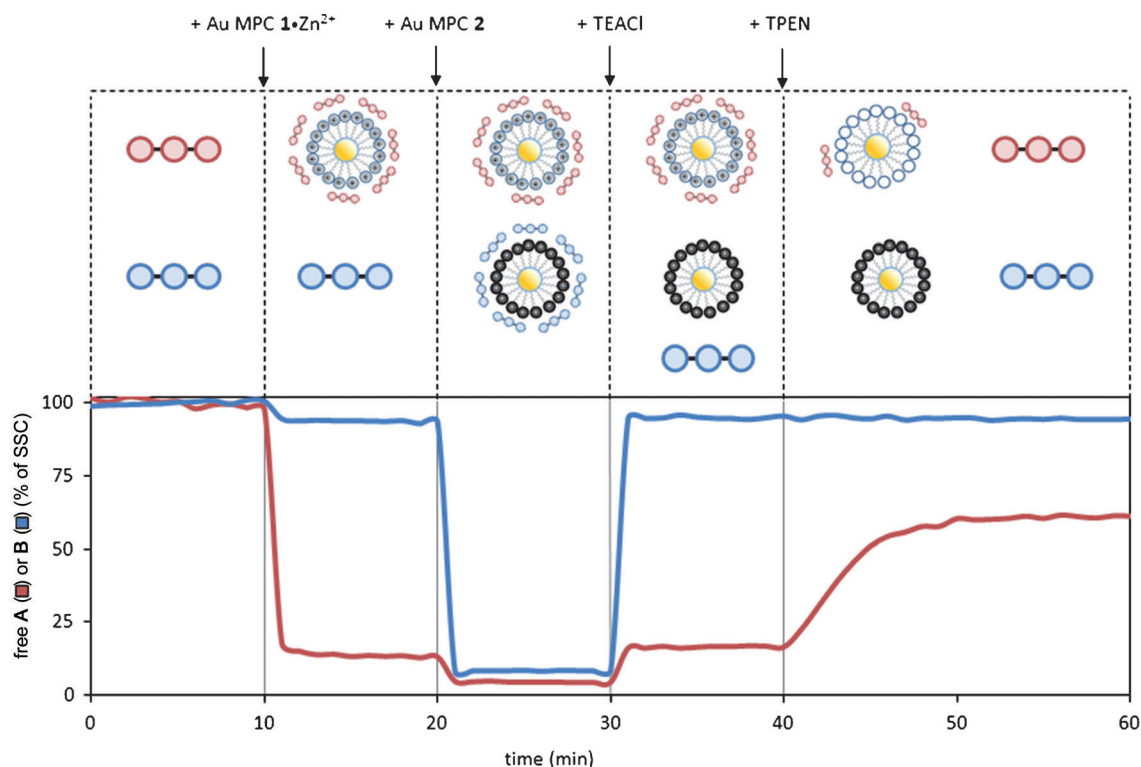


Figure 4. Self-sorting experiment. The addition of Au MPC 1·Zn²⁺ to a mixture of **A** (red) and **B** (blue; $t = 10$ min) resulted in the nearly quantitative capture of **A**. Probe **B** was captured upon the addition of Au MPC 2 ($t = 20$ min). The addition of TEACl (80 mM; $t = 30$ min) resulted in the quantitative release of **B** and the release of just a minor fraction of **A**. The final addition of the Zn²⁺-chelator TPEN to the mixture resulted in the partial release of **A**. The amount of **A** released was consistent with the expected amount based on the SSC of **A** on Au MPC 1 in the presence of TEACl. Experimental conditions: [Au MPC 1·Zn²⁺] = 8 μ M, [Au MPC 2] $\approx$ 20 μ M, [TEACl] = 80 mM, [TPEN] = 20 μ M, [**A**] = 3.4 μ M, [**B**] = 2.7 μ M, [HEPES] = 10 mM, pH 7.0, 37 °C. See the Supporting Information for the conversion of the measured fluorescence intensities into concentrations of **A** and **B**.

corresponds to a concentration of 1.1 μ M of probe **A** still bound to the surface of Au MPC 1 and is consistent with the SSC of probe **A** under these conditions (i.e. in the presence of TEACl (80 mM); see the Supporting Information). Importantly, the probe-displacement curves observed after the sequential addition of TEACl and TPEN are identical to those of a control experiment in which the displacement experiments with TEACl and TPEN were performed separately on **A**@Au MPC 1·Zn²⁺ and **B**@Au MPC 2 (see the Supporting Information).

We investigated the importance of Zn²⁺ in inducing self-sorting by performing analogous studies with Au MPC 1 instead of Au MPC 1·Zn²⁺. At the same concentration of TACN head groups, a drop in the SSC for both probes **A** and **B** was observed in the absence of Zn²⁺ (see the Supporting Information). Importantly, though, the absence of Zn²⁺ also reduced significantly the selectivity of the monolayer surface. This decrease in selectivity emerged in a clear manner from a displacement study performed by the addition of increasing amounts of **A** to **B**@Au MPC 1 (at a SSC of 1.3 μ M; Figure 5a). In particular, after the addition of **A** to a concentration of 1.7 μ M (equal to its SSC), the ratio of surface-bound probes **A** and **B** amounted to 65:35, as compared to 90:10 for Au MPC 1·Zn²⁺ and 45:55 for Au MPC 2. The fact that Au MPC 1 still maintains some preference for **A** presumably results from the formation of hydrogen bonds between the

TACN units and the phosphate groups,^[21] which is not possible for Au MPC 2.

A repetition of the self-sorting experiment with Au MPC 1 and Au MPC 2 indeed gave a very different result (Figure 5b). The addition of Au MPC 1 to a solution of **A** and **B** resulted in the partial capture of each, with **A** and **B** present on the surface in a 66:34 ratio, which corresponds to that found in the displacement studies. The subsequent addition of Au MPC 2 resulted in a near-quantitative quenching of the fluorescence of both probes, thus indicating that after the addition all probes are bound to a surface. Nonetheless, the absence of selective probe capture indicates that self-sorting does not occur (or occurs at least to a much lesser extent) in the absence of Zn²⁺. Indeed, the similarity of the two surfaces was further confirmed by the observation that in this case the addition of TEACl (80 mM) resulted in the immediate release of both probes **A** and **B**, and not just probe **B**. The extent of probe release is in agreement with the measured SSCs of **A** and **B** for Au MPC 1 in the presence of TEACl (80 mM; see the Supporting Information; in the presence of TEACl, no binding of either probe to Au MPC 2 was observed).

Considering the essential role of Zn²⁺ in the self-sorting process, we then argued that the removal of Zn²⁺ from the self-sorted system **A**@Au MPC 1·Zn²⁺/**B**@Au MPC 2 would drive the system to a less ordered state in which the probe molecules **A** and **B** are mixed on both surfaces (Figure 6a).

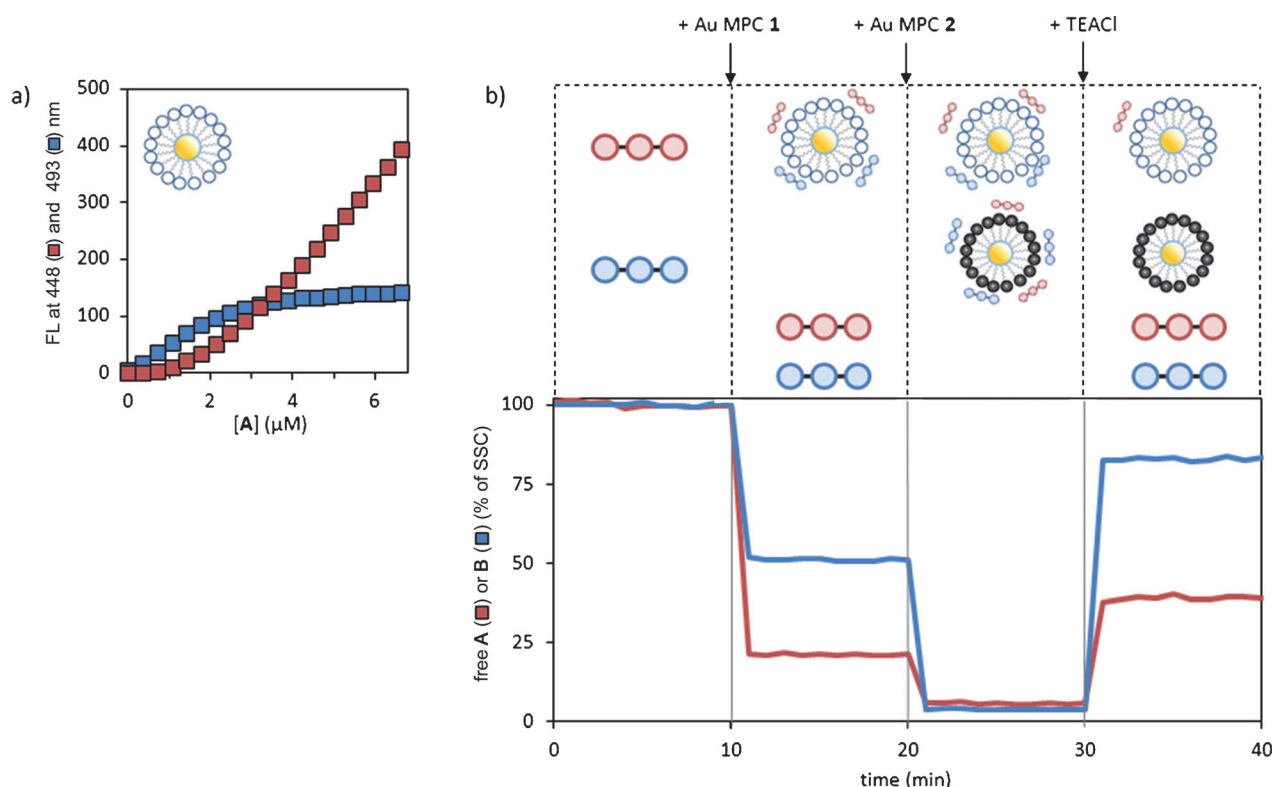


Figure 5. a) Fluorescence intensity of probes **A** (red squares) and **B** (blue squares) as a function of the amount of **A** added to **B**@Au MPC **1**. [Au MPC **1**]=8 μM, [Au MPC **2**] $\approx$ 20 μM, [**B**]=1.3 μM, [HEPES]=10 mM, pH 7.0, 37°C. b) Self-sorting experiment in the absence of Zn²⁺. The addition of Au MPC **1** to a mixture of **A** (red) and **B** (blue; t =10 min) resulted in the capture of both **A** and **B**. The subsequent addition of Au MPC **2** at t =20 min resulted in the quantitative capture of remaining **A** and **B**. The addition of TEACl (80 mM; t =30 min) resulted in the release of **A** and **B** to an extent consistent with the expected amount based on the respective SSCs of **A** and **B** on Au MPCs **1** and **2** in the presence of TEACl. Experimental conditions: [Au MPC **1**]=8 μM, [Au MPC **2**] $\approx$ 20 μM, [TEACl]=80 mM, [TPEN]=20 μM, [**A**]=1.7 μM, [**B**]=1.3 μM, [HEPES]=10 mM, pH 7.0, 37°C. See the Supporting Information for the conversion of the measured fluorescence intensities into concentrations of **A** and **B**. The difference in the end values from those obtained in the self-sorting experiment described in Figure 4 results from the different concentrations of **A** and **B**.

The addition of TPEN to a mixture of **A**@Au MPC **1**·Zn²⁺ and **B**@Au MPC **2** resulted in the gradual release of **A** from Au MPC **1**·Zn²⁺ owing to the lower SSC of **A** on Au MPC **1** (Figure 6b). As we have discussed elsewhere,^[16] the rate of this process is determined by the dissociation rate of Zn²⁺ from the TACN·Zn²⁺ complex. It takes around 20 min for free **A** to reach a constant concentration of 0.7 μM, which corresponds to a release of around 20% of surface-bound **A**. However, on the basis of the difference in the SSC between **A**@Au MPC **1**·Zn²⁺ and **A**@Au MPC **1**, a much higher amount (1.7 μM) was expected. The observed concentration implies that a proportion of the released probe **A** was transferred to the surface of Au MPC **2**. Since the surface of Au MPC **2** is saturated with **B**, this transfer induces the displacement of **B** from Au MPC **2**. Indeed, simultaneously with the release of **A**, the appearance of free probe **B** was observed. The identical kinetic profiles indicate that **A** and **B** exchange rapidly on the surface, in agreement with previous studies.^[15] The removal of Zn²⁺ from Au MPC **1**·Zn²⁺ also reduces the selectivity for the monolayer, and the result is a situation in which both probes are localized on either nanoparticle. The system can be reverted to the sorted state by the addition of Zn²⁺, which regenerates the TACN·Zn²⁺

complexes in the monolayer of Au MPC **1**. This process is very fast and again illustrates the rapid probe-exchange kinetics in the system. A second cycle demonstrated that it is possible to reversibly switch between the self-sorted and mixed states.

The importance of this experiment is that it shows that it is possible to control the distribution of the two probes in the system. The removal/addition of Zn²⁺ in one monolayer sets off a cascade of events that also affects the second, non-selective surface and ultimately leads to a very different state of the system (self-sorted or mixed). This behavior points to a role of Zn²⁺ as a regulator of mass transport between the surfaces.

In conclusion, we have shown that the concept of self-sorting can be used to spontaneously introduce order in a homogeneous system composed of nanoparticles and small molecules. Whereas self-sorting is most frequently associated with the formation of well-defined supramolecular architectures, in this case it regards the topological location of populations of molecules on the surface of different nanoparticles. An important role is played by the Zn²⁺ metal ions, which cause differentiation between the two surfaces and also serve as a regulatory element for switching the system

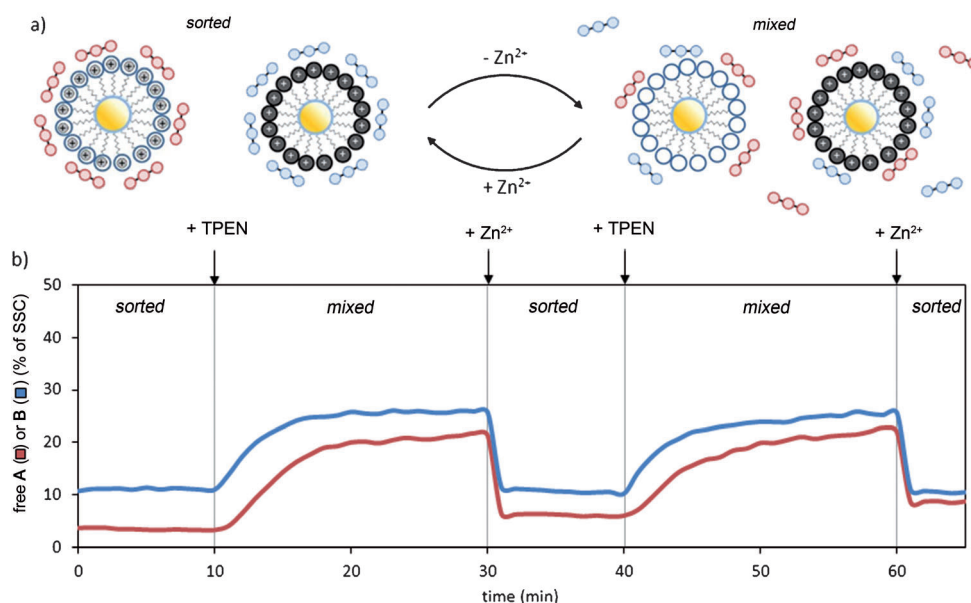


Figure 6. a) Zn^{2+} -regulated switching between a “self-sorted” and a “mixed” state. b) The addition of TPEN ($t=10$ min) to a self-sorted mixture of **A**@Au MPC 1· Zn^{2+} and **B**@Au MPC 2 resulted in the release of **A** from Au MPC 1. The excess **A** entered into competition with **B**@Au MPC 2, thus resulting in the release of **B**. The addition of Zn^{2+} to the system ($t=30$ min) restored the original situation. The complete cycle was repeated by the addition of TPEN and Zn^{2+} at $t=40$ and 60 min, respectively. Experimental conditions: [Au MPC 1· Zn^{2+}] = 8 μM , [Au MPC 2] $\approx$ 20 μM , [**A**] = 3.4 μM , [**B**] = 2.7 μM , [TPEN/ Zn^{2+}]_{cycled} = 20 μM , [HEPES] = 10 mM, pH 7.0, 37°C.

between a “sorted” and a “mixed” state. In view of the excellent catalytic activity of both Au MPC 1· Zn^{2+} ^[22] and Au MPC 2^[23] in hydrolyzing phosphodiester and carboxylate esters, respectively, these results create new perspectives for the development of complex catalytic systems that mimic nature.

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