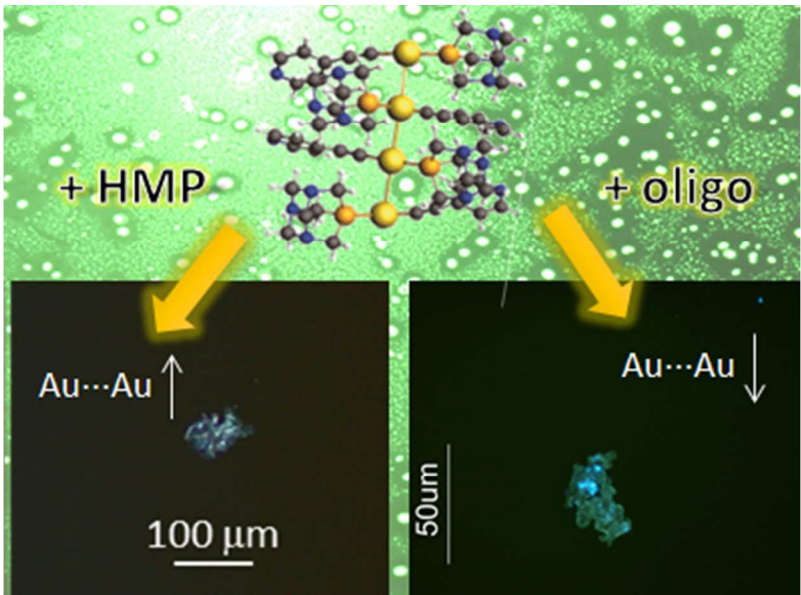


Modulation of supramolecular gold(I) aggregates by anion's interaction

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Modulation of supramolecular gold(I) aggregates by anion's interaction

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Abstract

The gold complexes [Au(4-pyridylethynyl)(PTA)] and [Au(4-pyridylethynyl)(DAPTA)] (PTA = 1,3,5-triaza-7-phosphaadamantane; DAPTA = 3,7-diacetyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane) were used as host in molecular recognition processes of sodium hexametaphosphate (HMP) and a single stranded 24-long oligonucleotide. Experiments were performed by absorption titrations and looking at the resulting host:guest adducts by polarized optical, fluorescence and scanning electron microscopy. The resulting information indicates that different type of interactions are present with the two different guest molecules. In the case of HMP, the compounds aggregate giving rise to larger structures, favoring exciton splitting coupling and the formation of head to tail interactions. In the case of oligonucleotide studies, the formation of smaller supramolecular structures is observed, with less contribution of aurophilic contacts and organized in a parallel way (head to head interactions organized by the presence of the oligonucleotide).

Keywords: molecular recognition; gold(I); oligonucleotides; spectroscopy; microscopy; DLS

Introduction

In nature, supramolecular self-assembly is ubiquitous. Numerous examples exist whereby weak interactions, such as hydrogen-bonding, van der Waals, π - π stacking, dipole-dipole, and metal coordination, direct the organization of multiple components into discrete, complex architectures that, in most cases, have vital functions. Owing to the weakness of the forces involved, supramolecular self-assembly presents significant synthetic challenges. Following nature's lead,(1,2) chemists, over the past 50 years or thereabouts, have begun to develop effective strategies for creating complex yet stable supramolecular assemblies with diverse potential applications.(3-6)

Since the early days of supramolecular sciences, chemists have devoted great efforts to design molecular receptors capable of specific recognition of a wide variety of targets ranging from small inorganic ions to large biomolecules.(7) These molecular receptors have been widely used to produce (nano)-materials with selective molecular recognition properties.(8) Supramolecular chemistry of anion recognition is one of the most promising sub-areas for the development of various useful selective and sensitive anion sensors.(9,10) Among all anions, detection of phosphates is relevant since they are known to be present in natural water as orthophosphates (H_3PO_4 , H_2PO_4^- , HPO_4^{2-} and PO_4^{3-}) (11-15) and other forms of soluble phosphates including organic phosphates and polyphosphates. Polyphosphates are particularly interesting because they can act as a scaffold for the supramolecular organization of the sensor and allow to explore optical changes related to the sensor aggregation (e.g. excimer formation, exciton splitting, aurophilicity) induced by the presence of the polyphosphate template, a field where there is still a lot to explore, and finds inspiration of the self-assembly of viral proteins around nucleic acids.(16-18)

Gold(I) complexes are excellent candidates to be used in "modulating supramolecular chemistry" due to the presence of additional weak interactions ($\text{Au}\cdots\text{Au}$ aurophilic contacts) that are observed to play a key role in the formation of very large assemblies.(19,20) In the last years, we have developed in our research groups, water soluble gold(I) complexes that give rise to the formation of very large supramolecular structures.(21-24) The resulting assemblies are necessarily being affected by modifications on the chemical structures, such as the introduction of positive or negative charge in the molecule and change of counterion.(24,25)

Taking into consideration all these data, in this work, we have used two gold(I) complexes (Chart 1) that have been observed to give rise to the formation of very large fibers in water, as hosts in molecular recognition of two different biological/environmental relevant anions (hexametaphosphate and a 24-long oligonucleotide with sequence 5'-TTTGGATCCTGGTCACTGAGGCAC-3'). The influence of the different topology of the selected guests on the resulting host:guest species are carefully analyzed.

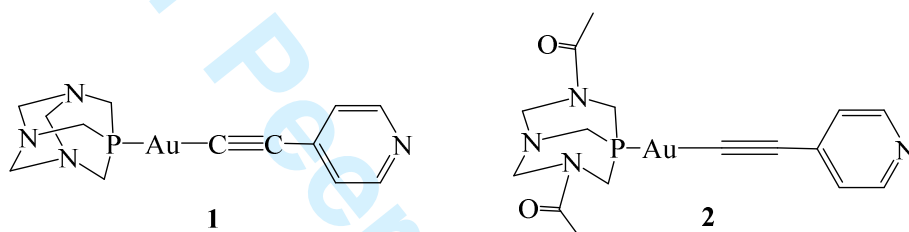


Chart 1. Gold(I) complexes used as hosts in this work.

Results and Discussion

[Au(4-pyridylethynyl)(PTA)] (**1**) and [Au(4-pyridylethynyl)(DAPTA)] (**2**) gold(I) complexes were used as candidates for molecular recognition studies of biological relevant species. Two kind of guest molecules were chosen: the cyclic hexametaphosphate anion and a single stranded 24-units oligonucleotide (Figure 1).

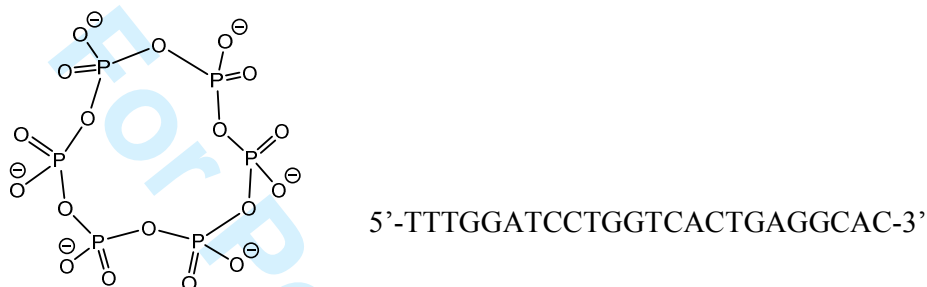


Figure 1. Scheme of the guest molecules used in this work.

Compounds **1** and **2** present a vibronically structured absorption band at *ca.* 270 nm, corresponding to the 4-pyridylethynyl unit. It was previously observed that this band decreases on intensity and becomes broader when the compound aggregates in water and, at the same time, a low energy absorption band above 350 nm increases on intensity (Figure 2).^(21,22) The analysis of the absorption spectra of these bands is a key point to retrieve important information about the aggregation processes.⁽²⁶⁾

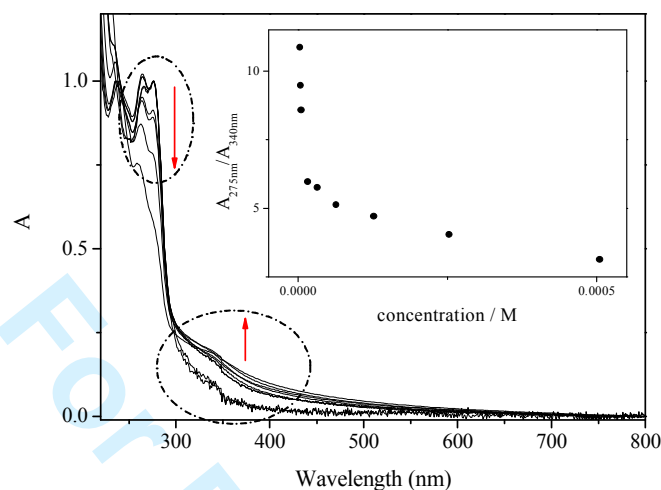


Figure 2. Normalized absorption spectra of **1** recorded in water at different concentrations (from $5 \cdot 10^{-6}$ M to $5 \cdot 10^{-4}$ M). **Inset:** Absorption variations of $A_{275\text{nm}}/A_{340\text{nm}}$ versus concentration.

Interaction with hexametaphosphate

Titration of **1** and **2** with sodium hexametaphosphate (HMP) were carried out by subsequent additions of an aqueous solution of the anion to a $1.5 \cdot 10^{-5}$ M aqueous solution of the gold(I) complexes (freshly prepared). Absorption spectra were collected after each addition and the results are shown in Figures 3 and S1.

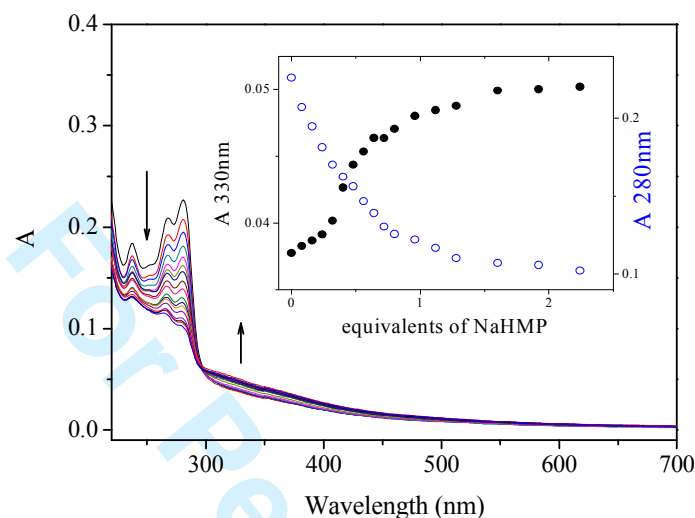


Figure 3. Absorption spectra of **1** after addition of several amounts of HMP. Inset: Absorption variations of the bands at 330 nm (solid circles) and 280 nm (open circles) with respect to the number of equivalents of HMP added to the solution.

The recorded variations are indicative of different facts. Firstly, changes of the absorption at 280 nm give rise to a less resolved band with lower intensity being indicative of the formation of aggregates with π - π stacking contribution (exciton splitting).(27) These interactions, in the presence of HMP anion, seem to be more favored in complex **1** (more pronounced broadening in absorption bands). This is probably due to the lower water solubility of the hydrophilic end of the molecule (phosphane moiety) in **1** than in **2**. The broadening is due to the establishment of π - π interactions between pyridyl moieties, minimizing contact with water. At the same time, the band at 330 nm increases on intensity in agreement with the establishment of Au...Au interactions in the resulting adducts. The resulting variations of these bands with respect to the number of equivalents of anion added to the solution let us detect to different variations. Firstly, after addition of 0.3 equivalents of HMP, there is a change on the recorded variations at 330 nm. Then, a plateau is observed after addition of 1 equivalent of the anion. This may indicate the preliminary formation of a 3:1 complex, where three units of the gold complex are interacting with the anion and then, it evolves

to the formation of a 1:1 adduct. Additionally, the presence of the band above 300 nm is indicative that the interaction with HMP organizes the new structures favoring the establishment of aurophilic interactions, together with other possible π - π / $\text{Au}\cdots\pi$ interactions that induce exciton splitting with head-to tail disposition of the gold(I) complexes (J aggregates).(28)

Dynamic Light Scattering (DLS) measurements were carried out for 1:1 mixtures of complexes **1** and **2** in the presence of HMP at the same concentrations of the performed titrations. As can be seen in Figure 4, the formation of large aggregates with *ca.* 300 nm and 800 nm size for **1** and **2** adducts respectively were detected. Taking into consideration that solutions at similar concentrations of **1** and **2** in water give rise to 100-150 nm size structures,(29) this is a direct evidence about the size of the resulting species obtained from the interaction of the complexes with HMP. Additionally, this is also in agreement with the results recorded by absorption spectra that indicate the aggregation process (see above).

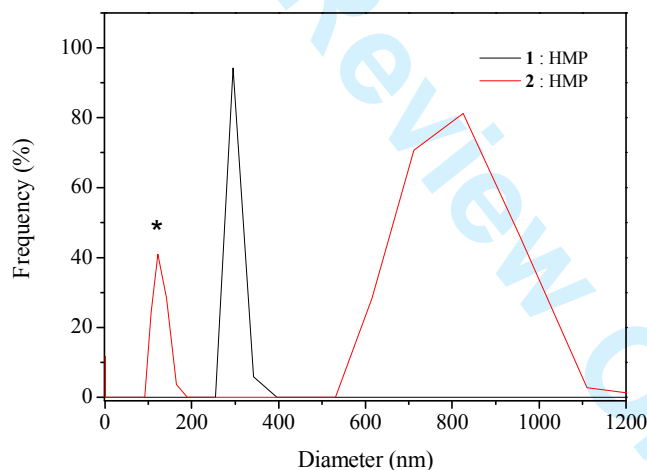


Figure 4. DLS size distributions for fresh aqueous solutions of **1** and **2** (2×10^{-5} M) in the presence of 1 equivalent of Na_6HMP . * Residual uncomplexed **2**.

Dried samples of 1:1 adducts were also observed under optical and fluorescence microscopy and the formation of well-organized structures, with very large size (*ca.* 50 μm) were detected. Samples also contain smaller aggregates that should be those previously observed in solution by DLS (Figures 5 and S2-S3).

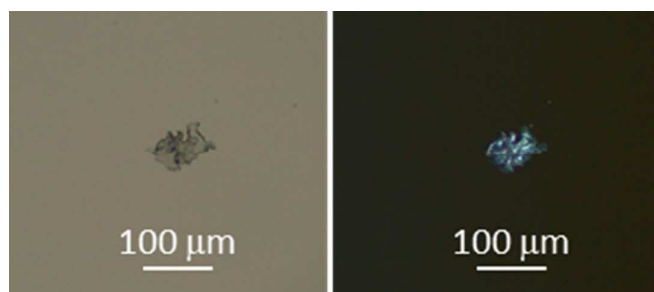


Figure 5. Optical microscopy image of **2**:HMP adduct without polarization (left) and between cross-polarizers (right).

Interaction with an oligonucleotide

Analogous experiments were performed with an oligonucleotide in order to analyze how the aggregation/disaggregation process can be affected by using a biological relevant species with longer and linear sequence. The oligonucleotide used is a single stranded deoxyoligonucleotide, 24 nucleotides long and with the sequence 5'-TTTGGATCCTGGTCACTGAGGCAC-3'. Taking into consideration that the oligonucleotide absorbs at 260 nm, some differences on the experiments should be performed in order to retrieve rigorous data about the host:guest interaction. The absorption of a $5 \cdot 10^{-5}$ M solutions of **1** and **2** were performed after addition of different amounts of the oligonucleotide, following the same procedure used for HMP titrations. On the other hand, titrations were also performed with water (without gold(I) complex, only increasing the amount of oligonucleotide) and the resulting absorptions were subtracted providing a way to analyze the net effect of the interaction between them.

Upon the first addition of oligonucleotide (0.25 equivalents), it is noticeable that the absorption has slightly diminished. The addition of increasing amounts of the oligonucleotide does not induce significant changes; only further a very small progressive decrease in absorption together with the formation of small precipitates (responsible for the decrease in absorbance, i.e., decrease in concentration of the solution, Figure S4). The corresponding absorption of the oligonucleotide has to be subtracted from the spectra in order to avoid the interference in the resulting host:guest absorption pattern. The interaction with the oligonucleotide is much slower than previously observed with HMP and the effect of the oligonucleotide on the absorption

of fresh solutions of gold complexes is small. We decided to follow the interaction with oligonucleotides over a wider period of time, i.e., on aged samples. Due to the high absorption of the oligonucleotide, differential absorption spectroscopy (Figure 6) was chosen as an efficient method for these experiments. The resulting variations indicate a global increase of the absorption band at 260 nm with a simultaneous decrease of the band at 305 nm with increasing amounts of oligonucleotide. This effect increases with time (Figure 7). Noticeable, this is a strikingly different spectroscopic behavior from the previously observed with HMP anion, being indicative of different aggregation arrangements in the presence of the different guests. The recorded blue-shift is more compatible with the formation of head to head aggregates (H- aggregates) induced by the interaction with the linear anion that may organize the gold(I) complexes in a parallel way.

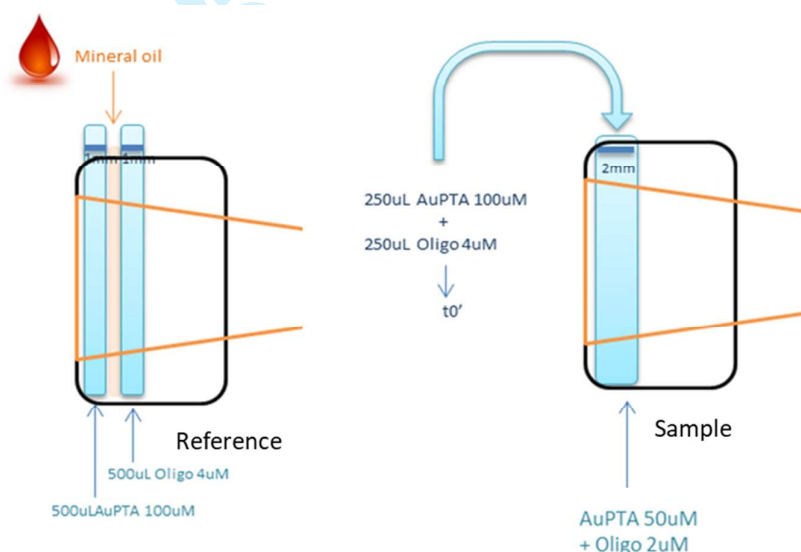


Figure 6. Schematic representation of the differential absorption experiments.

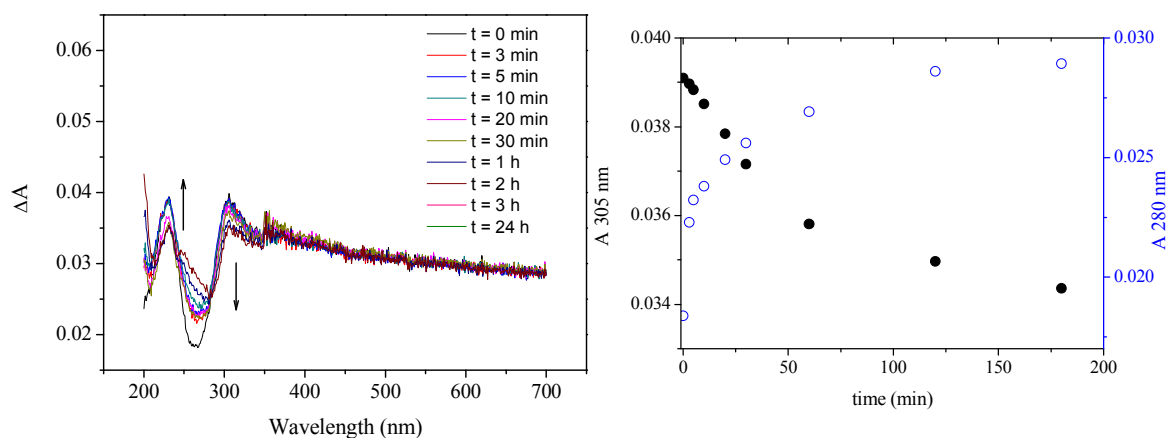


Figure 7. Differential absorption spectra of **1** : oligonucleotide (1:1) with time (left); Absorption variations at 280 nm (open circles) and 305 nm (solid circles) maxima with time (right).

Analogous experiments were carried out only with compound **1** in water following spectral variations in time (in the absence of the oligonucleotide). In this case much smaller spectral variations are observed in the same time window (200 min), with no monotonic behavior (Figure S5). That means that the presence of the oligonucleotide is essential for the observed variations recorded by absorption spectroscopy in aged solutions. Similar behavior, although in much longer time scales, is displayed with **2**, where some weeks were needed to observe the disappearance of the aurophilic absorption band in the presence of oligonucleotide (Figure S6). This is compatible with the higher solubility in water of the complex and with the fact that all aggregation/disaggregation processes have been previously detected to require more time.⁽²⁴⁾ Additionally, the global changes of the band at 265 nm do not reflect an increase on absorption, due to the precipitation of some fibrillary structures in the medium (thus decreasing the concentration of the complex in solution), but it is noticeable that the vibronically structured band assigned to the chromophore is affected (Figure S7). As previously observed with **1**, variations of the absorption spectra of **2** alone along time in the same time range do not show significative changes in the ratio between bands at 265/275 nm, but only a decrease resulting from the formation of fibers that precipitated from the solution, reducing the concentration of **2** (Figure S8).

DLS experiments were not feasible to be performed in these cases due to the high dispersion of light caused by the oligonucleotide.

As we previously reported, complexes **1** and **2** give rise to the formation of structures detectable by fluorescence microscopy as greenish luminescent fibers upon aggregation(21,22) (Figure 8A). Observation of the samples, in the presence of **1** equivalent of oligonucleotide, after four weeks evolution, supports previous studies carried out by absorption spectroscopy. As it is displayed in Figure 8B-E, the global view of the sample displays globules of greenish material containing blue fluorescent dots. The aggregates display in general smaller sizes with respect to the original fibers and the greenish emission from the gold(I) complex is diminished in the presence of the oligonucleotide.

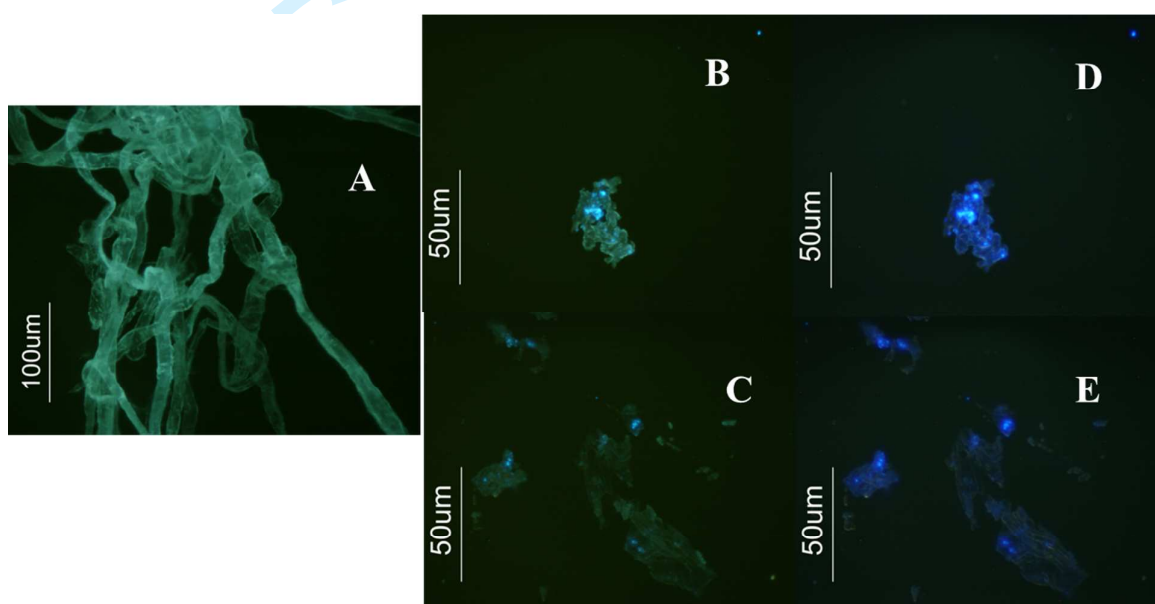


Figure 8. Fluorescence microscopy images of 4 weeks old aqueous solution of **2** (A); **2** in the presence of oligonucleotides with Filter 395-440 nm (B and C) and Filter 300-400 nm (D and E).

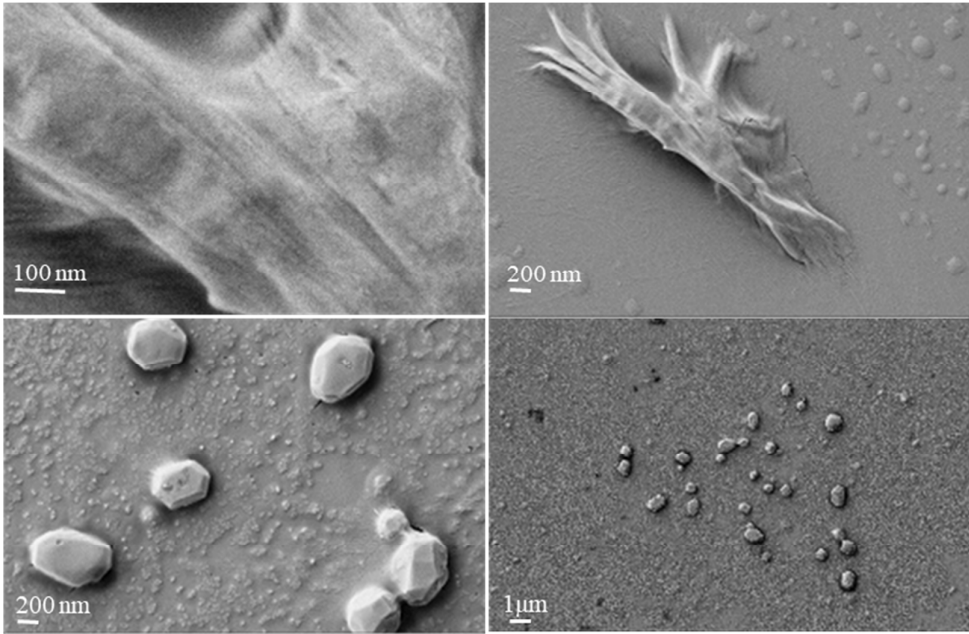


Figure 9. Scanning Electron Microscopy images of **2** (above) and **2** + 1 equivalent of oligonucleotide (below).

Inspection of the same samples, dried from the solution, under Scanning Electron Microscopy images let us observe in more detail the resulting morphology of the gold(I) complexes : oligonucleotide adducts, with a icosahedral-like shape (Figure 9). These smaller structures should present lower contribution of aurophilic contacts in agreement with previous absorption spectroscopy experiments. Moreover, inspection of the SEM images resulting from the same concentration of oligonucleotides in the absence of gold(I) complexes is also in agreement with these interactions, since the large dendritic structures of the oligonucleotides disappear (Figure S9).

These studies open a new way of research regarding water soluble supramolecular gold(I) complexes. The interaction of supramolecular gold(I) aggregates with different guest molecules should induce to the formation of species with different topologies and luminescent properties.

Conclusions

The interaction of [Au(4-pyridylethynyl)(PTA)] and [Au(4-pyridylethynyl)(DAPTA)] complexes with two different species have been observed to depend on the structure of the guest molecule. Gold(I) complexes aggregates in water giving rise to the formation of very long fibers starting from small spherical structures in fresh solutions. In the presence of sodium hexametaphosphate, these initial spherical aggregates become larger. Absorption spectroscopy indicates the increase on the band assigned to aurophilic contacts together with a decrease on intensity of the band assigned to the 4-pyridylethynyl chromophore, as usually observed in aggregation processes due to the additional contribution of some π - π stacking. Analysis of the samples by DLS also indicates the formation of larger aggregates (500 – 800 nm) in the presence of hexametaphosphate, in agreement with the observation of the resulting adducts under optical microscopy.

The interactions with an oligonucleotide should be performed removing the high absorption contribution of the guest and with aged samples. In this way, differential absorption spectroscopy indicates that, in these cases, the formation of smaller structures are obtained in the presence of the oligonucleotides, with less contribution of Au...Au interactions. Additionally, fluorescence microscopy images display the interaction between host and guest molecules leading to smaller structures and diminishing of the green emission of the complexes.

Both gold complexes behave in the same way, although the compound containing DAPTA phosphine needs more time to evolve due to the higher solubility in water of this phosphine.

Thus, we can modulate the formation of larger or smaller host: adducts by the correct choice of the guest molecule.

Experimental Section

General Procedures. Synthesis of [Au(4-pyridylethynyl)(PTA)](21) and [Au(4-pyridylethynyl)(DAPTA)](22) complexes were reported elsewhere. Sodium hexametaphosphate (Aldrich, 96%) and ssDNA oligonucleotide 24 nucleotides long with the sequence 5' TTTGGATCCTGGTCACTGAGGCAC 3' (STAB Vida, Portugal) were used as received. Solutions were prepared with Millipore water.

Physical Measurements.

Absorption spectra were acquired on a Varian Cary 100 Bio spectrophotometer. Fluorescence microscopy was recorded on an Axioplan 2ie Zeiss imaging microscope equipped with a NikonDXM1200F digital camera. Excitation light for fluorescence imaging was selected using filters in the range 395-440 nm. Optical microscopy images have been acquired on a Leica ICC50 W. 5 μ L of each sample was dropped on a microscopy glass slide and a cover slide was placed on top.

Scanning electron microscopy (SEM) was carried out at 2 kV using a Carl Zeiss Auriga crossbeam (SEM-FIB) work-station instrument equipped with an Oxford energy-dispersive X-ray spectrometer. The acquisition of the data was performed using an accelerating voltage of 2kV and aperture size of 30 μ m or 5 kV with 5.6–7.2 mm as working distance.

Dynamic Light Scattering measurements were carried out by using ZS 100 Nanoparticle Analyzer at 173° scattering angle at 25 °C.

Absorption titrations with sodium hexametaphosphate. The experiments were performed by preparation of standard solution of the gold complexes in water ($2 \cdot 10^{-5}$ M) and subsequent addition of small amounts of a solution of the guest prepared at higher concentrations to minimize dilution effects. Absorption spectra were recorded at each point.

Similar experiments have been performed with the solutions of the gold(I) complexes in the absence of guest. A solution of the gold complexes in water ($2 \cdot 10^{-5}$ M) has been prepared and the corresponding absorption spectra was recorded at different times.

Absorption titrations with oligonucleotide. A solution of **1-2** was made, in water, at the concentration of 100 μM , in a 25mL flask.

After 45 days in the dark, 500 μL of this solution were collected and a given amount of oligonucleotide solution (in water at 100 μM) was added in order to obtain a final concentration of the oligonucleotide of 2 μM . UV-Visible absorption spectra were recorded before the addition, right after oligonucleotide addition, and along time. These spectra were recorded using the corresponding oligonucleotide reference, i.e., the spectra were performed using 500 μL of water as reference and the same amount of oligonucleotide was also added to the reference when it was added to the sample.

Acknowledgements

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Supporting Information

Absorption spectra of **2** in the presence of increasing amounts of Na_6HMP (Figure S1); Optical microscopy image of **1**:HMP adduct without polarization (left) and between cross-polarizers (right) (Figure S2); Fluorescence microscopy image of **1**:HMP adduct (left) and **2**:HMP adducts (right) with excitation band pass: 450-490 nm (Figure S3); Absorption spectra of **1** ($5 \cdot 10^{-6}$ M) in the presence of increasing amounts of oligonucleotide in water (Figure S4); Differential absorption spectra of **1** with time

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(Figure S5); Absorption spectra of **2** in the presence of oligonucleotide along time (Figure S6); Normalized absorption spectra of **2** in the presence of oligonucleotide along time (Figure S7); Absorption spectra of **2** in water at different times (Figure S8); SEM images of dried samples of 2μM solution of oligonucleotide (Figure S9).

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References

- (1) Lehn, J.-M. *Angew. Chem., Int. Ed.* **1988**, 27, 89.
- (2) Pedersen, C.J. *Angew. Chem.* **1988**, 100, 1053.
- (3) Ward, M.D.; Raithby, P.R. *Chem. Soc. Rev.* **2013**, 42, 1619.
- (4) Yoshizawa, M.; Klosterman, J.K.; Fujita, M. *Angew. Chem., Int. Ed.* **2009**, 48, 3418.
- (5) Bilbeisi, R.A.; Olsen, J.-C.; Charbonnière, L.J.; Trabolsi, A. *Inorg. Chim. Acta* **2014**, 417, 79.
- (6) Nishino, T.; Shiigi, H.; Kiguchi, M.; Nagaoka, T. *Chem. Commun.* **2017**, 53, 5212.
- (7) Gale, P.A.; Steed, J.W.: *Supramolecular chemistry: from molecules to nanomaterials*. John Wiley & Sons, Chichester (**2012**).
- (8) Ariga, K.; Ito, H.; Hill, J.P.; Tsukube, H. *Chem. Soc. Rev.* **2012**, 41, 5800.
- (9) Gale, P.A. *Coord. Chem. Rev.* **2000**, 199, 181.
- (10) Gale, P.A.; Quesada, R. *Coord. Chem. Rev.* **2006**, 250, 3219.
- (11) Rodríguez, L.; Lima, J.C.; Parola, A.J.; Pina, F.; Meitz, R.; Aucejo, R.; García-España, E.; Llinares, J.M.; Soriano, C.; Alarcón, J. *Inorg. Chem.* **2008**, 47, 6173.
- (12) Cano, M.; Rodríguez, L.; Lima, J.C.; Pina, F.; Dalla Cort, A.; Pasquini, C.; Schiaffino, L. *Inorg. Chem.* **2009**, 48, 6229.
- (13) Sabaté, F.; Giannicchi, I.; Acón, L.; Dalla Cort, A.; Rodríguez, L. *Inorg. Chim. Acta* **2015**, 434, 1.
- (14) Gale, P.A.; Busschaert, N.; Haynes, C.J.E.; Karagiannidis, L.E.; Kirby, I.L. *Chem. Soc. Rev.*, **2014**, 43, 205.
- (15) Albelda, M.T.; Frías, J.C.; García-España, E.; Schneider, H.-J. *Chem. Soc. Rev.* **2012**, 41, 3859.
- (16) Whitesides, G.; Mathias, J.; Seto, C. *Science*, **1991**, 254, 1312.
- (17) Klug, A. *Angew. Chem. Int. Ed.* **1983**, 22, 565.
- (18) Sun, H.; Luo, Q.; Hou, C.; Liu, J. *Nano Today* **2017**, 14, 16.
- (19) Lima, J.C. Rodríguez, L. *Chem. Soc. Rev.*, **2011**, 40, 5442.
- (20) Lima, J.C.; Rodríguez, L. *Inorganics* **2015**, 3, 1.
- (21) Gavara, R.; Llorca, J.; Lima, J. C.; Rodríguez, L. *Chem. Commun.*, **2013**, 49, 72.
- (22) Aguiló, E.; Gavara, R.; Lima, J. C.; Llorca, J.; Rodríguez, L. *J. Mat. Chem. C*, **2013**, 1, 5538.
- (23) Moro, A.J.; Rome, B.; Aguiló, E.; Arcau, J.; Puttreddy, R.; Rissanen, K.; Lima, J.C.; Rodríguez, L. *Org. Biomol. Chem.* **2015**, 13, 2026.

- (24) Aguiló, E.; Gavara, R.; Baucells, C.; Guitart, M.; Lima, J.C.; Llorca, J.; Rodríguez, L. *Dalton Trans.* **2016**, 45, 7328.
- (25) Gavara, R.; Aguiló, E.; Schur, J.; Llorca, J.; Ott, I.; Rodríguez, L. *Inorg. Chim. Acta* **2016**, 446, 189.
- (26) Gavara, R.; Lima, J.C.; Rodríguez, L. *Photochem. Photobiol. Sci.* **2016**, 15, 635.
- (27) Ferrer, M.; Gutiérrez, A.; Rodríguez, L.; Rossell, O.; Lima, J.C.; Font-Bardía, M.; Solans, X. *Eur. J. Inorg. Chem.* **2008**, 2899.
- (28) Würthner, R.; Kaiser, T.E.; Saha-Müller, C.R. *Angew. Chem. Int. Ed.* **2011**, 50, 3376.
- (29) Gavara, R.; Aguiló, E.; Fonseca Guerra, C.; Rodríguez, L.; Lima, J.C. *Inorg. Chem.*, **2015**, 54, 5195.

Modulation of supramolecular gold(I) aggregates by anion's interaction

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Supporting Information

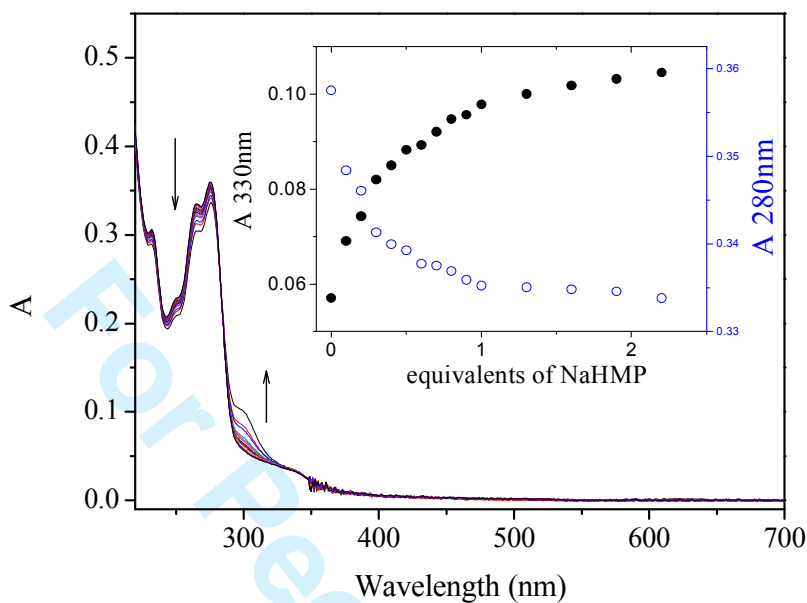


Figure S1. Absorption spectra of **2** in the presence of increasing amounts of Na₆HMP.

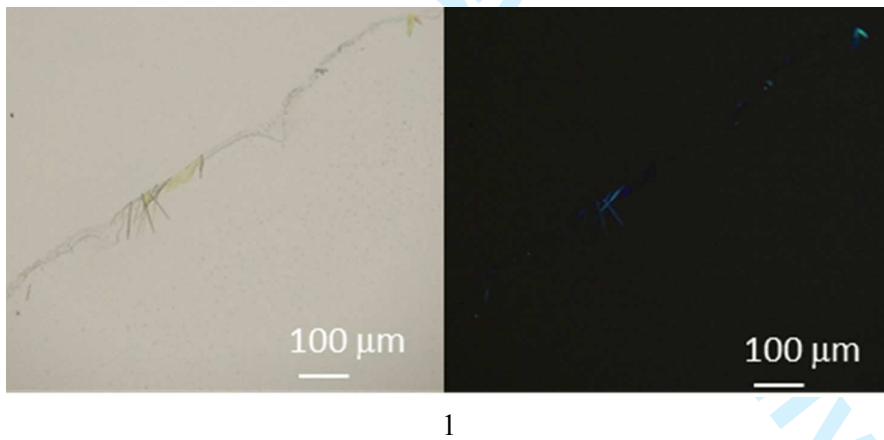


Figure S2. Optical microscopy image of **1**:HMP adduct without polarization (left) and between cross-polarizers (right).

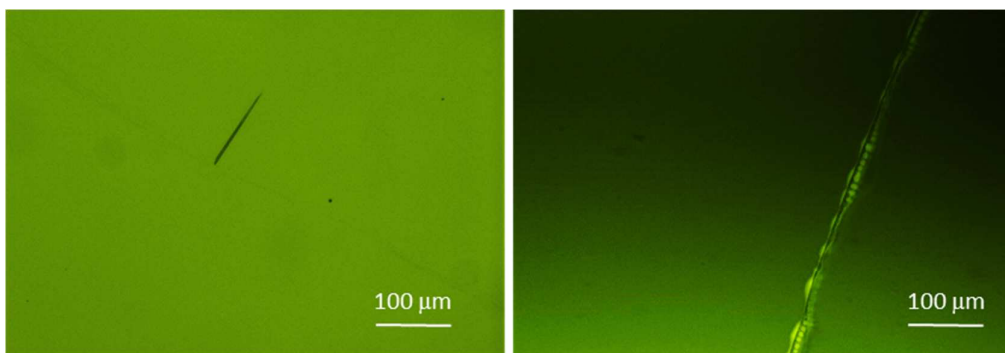


Figure S3. Fluorescence microscopy image of **1**:HMP adduct (left) and **2**:HMP adducts (right) with excitation band pass: 450-490 nm.

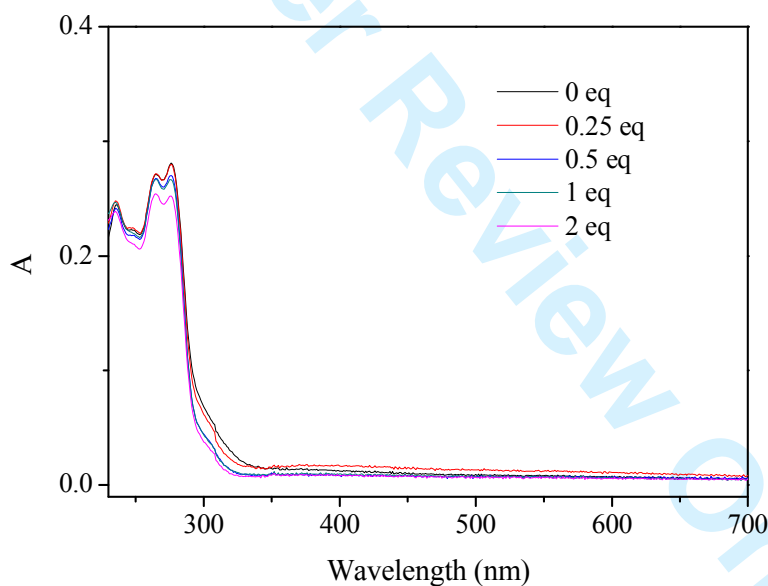


Figure S4. Absorption spectra of **1** ($1 \cdot 10^{-5}$ M) in the presence of increasing amounts of oligonucleotide in water.

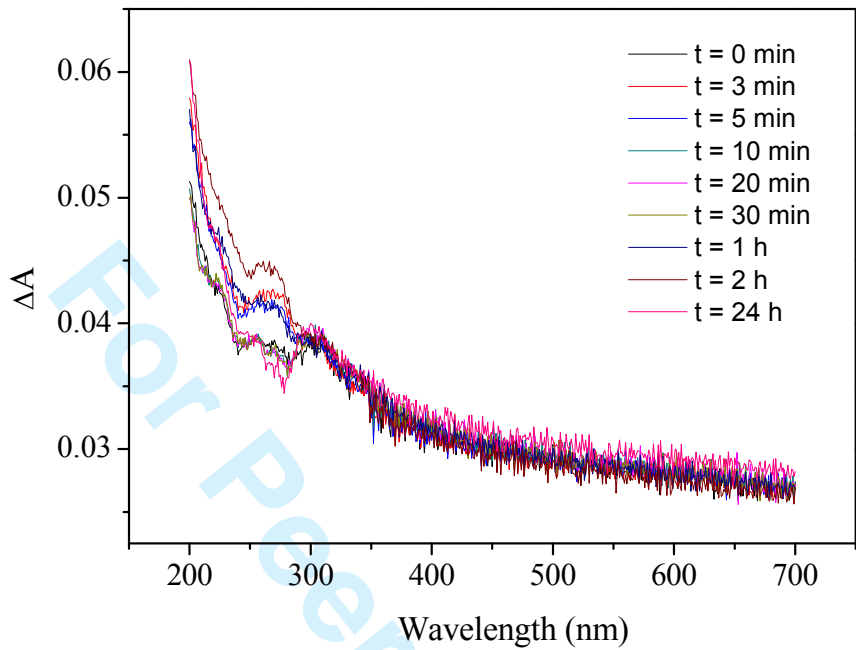


Figure S5. Differential absorption spectra of **1** with time.

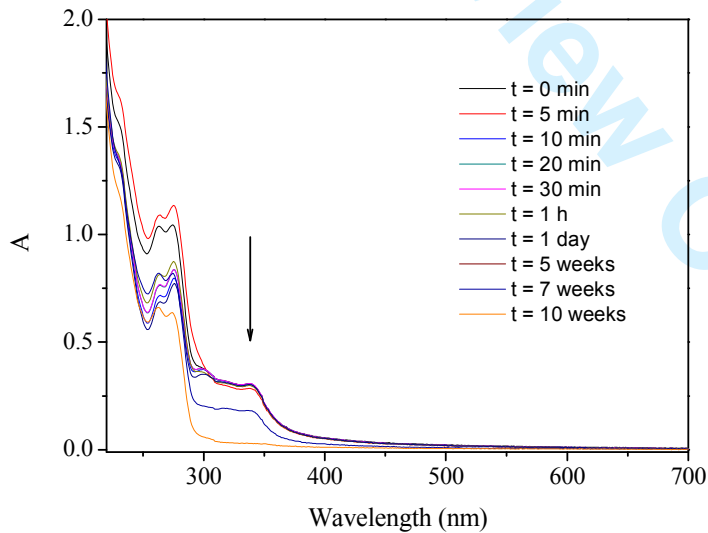


Figure S6. Absorption spectra of **2** in the presence of oligonucleotide along time.

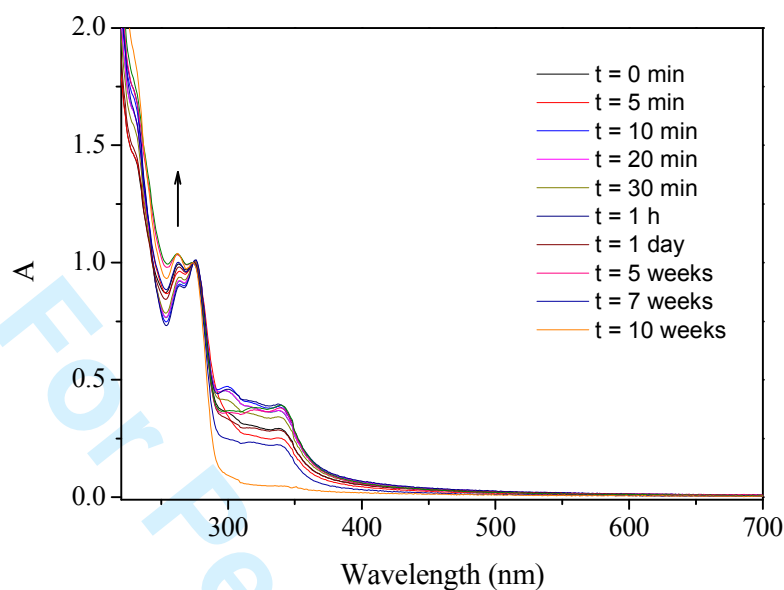


Figure S7. Normalized absorption spectra of **2** in the presence of oligonucleotide along time.

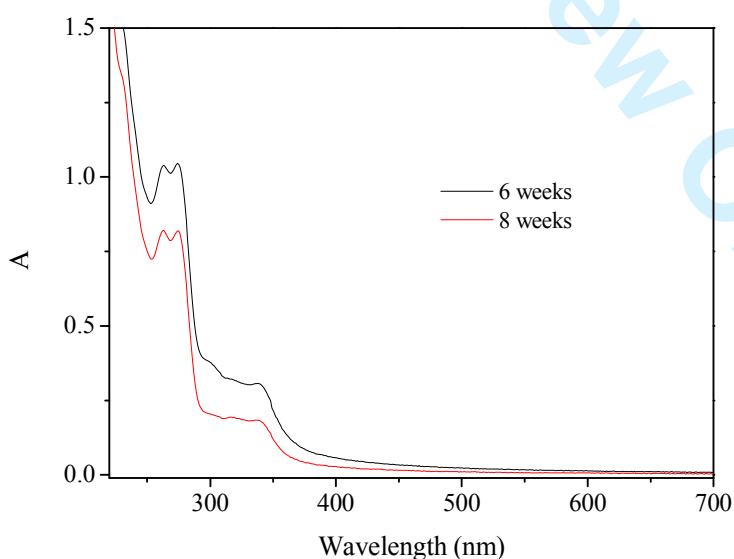


Figure S8. Absorption spectra of **2** in water at different times. The decrease of both chromophoric and aurophilic bands is in a similar degree and the ratio between the

bands at 265/275 nm is not modified.

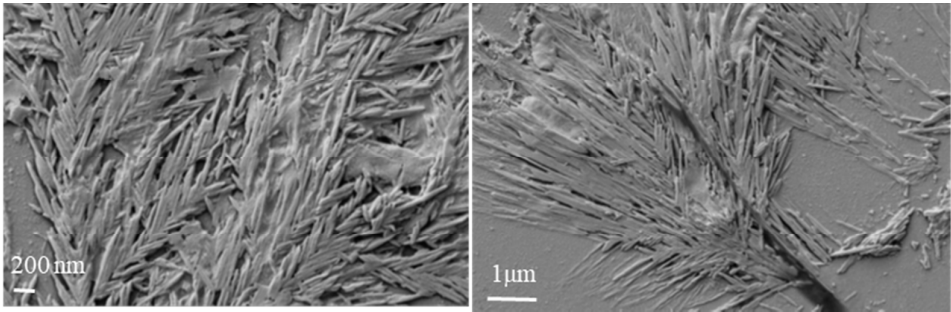


Figure S9. SEM images of dried samples of 2μM solution of oligonucleotide.