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Metal−Metal and π−π Interactions Directed End-to-End Assembly of Gold Nanorods

Frankie Chi-Ming Leung, Sammual Yu-Lut Leung, Clive Yik-Sham Chung, and Vivian Wing-Wah Yam*

Institute of Molecular Functional Materials (Areas of Excellence Scheme, University Grants Committee (Hong Kong)) and Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong SAR, P. R. China

S *Supporting Information*

ABSTRACT: The end-to-end aggregation of gold nano-rods (GNRs) has been demonstrated to be directed by a thioacetate-containing alkynylplatinum(II) terpyridine complex. The *in situ* deprotected complex is preferentially attached at the ends of the gold nanorods (GNRs) and induce the aggregation of GNRs in an "end-to-end" manner by Pt···Pt and π−π interactions, which have been characterized by electron microscopy, energy dispersed X-ray (EDX) analysis, and UV−vis absorption spectroscopy. The assembly of the nanorods into chain-like nanostructures can be controlled by the concentration of the Pt(II) complexes.

Nanomaterials have attracted tremendous attention in various fields of research.[1−4] Gold nanorods (GNRs) have gained considerable attention due to their strong optical absorption in the visible and near-infrared regions, which can be tuned by the manipulation of the aggregation of GNRs.[5] The anisotropic functionalization has enabled GNRs to be assembled in an "end-to-end" fashion, with a strong effect on the longitudinal surface plasmon resonance (LSPR).[6] The ends of the GNRs are found to be selectively functionalized with organosulfides containing either a thiol or a disulfide functional group. Through the end-functionalization of the GNRs, various covalent bonding or noncovalent interactions have been exploited to drive the assembly process.[7−9] Different linkage methods could be applied for inducing the end-to-end assembly of GNRs, such as by using hydrogen bonding of organic ligands with terminal carboxylic and/or amino groups,[10] solvent-mediated hydrophobic interactions of the mercaptocarboxylic acids,[11] formation of covalent bonds between short dithiol linker molecules and GNRs,[12] coordination bond formation of transition metal complexes with terpyridine-functionalized GNRs,[13] streptavidin-mediated linkage using disulfide modified biotin molecules,[14] disulfide modified antibody−antigen interactions,[15] and Hg^{2+} ion-induced dimerization of thymine oligonucleotide functionalized GNRs.[16] Conversely, the exploitation of metal complexes, particularly those capable of formation of metal−metal interactions, for the end-to-end assembly of GNRs has essentially been unexplored.

Square-planar d[8] platinum(II) polypyridine complexes have been extensively studied in the past few decades because of their propensity to form noncovalent metal−metal interactions as well as their rich spectroscopic properties associated with Pt···Pt and π−π stacking interactions upon aggregation.[18−25]

The water-soluble alkynylplatinum(II) terpyridine complexes are found to show intermolecular self-assembly in aqueous media and result in drastic spectroscopic changes.[26−29] With the strong tendency toward the formation of Pt···Pt and π−π stacking interactions, it is believed that these complexes could provide the driving force through such interactions to direct the end-to-end assembly of GNRs. In this work, we first demonstrate the introduction of Pt···Pt and π−π stacking interactions for directing the end-to-end assembly of GNRs. Such exploration is believed to open up a new strategy for the design of hybrid materials through the incorporation of supramolecular assembly motifs and the conjugation of nanomaterials.

Water-soluble thioacetate-containing platinum(II) complexes **1** and **2** are synthesized, and their chemical structures are shown in Figure 1. *In situ* deprotection of the thioacetate group by a base, such as sodium methoxide or pyrrolidine,[30−32] gave
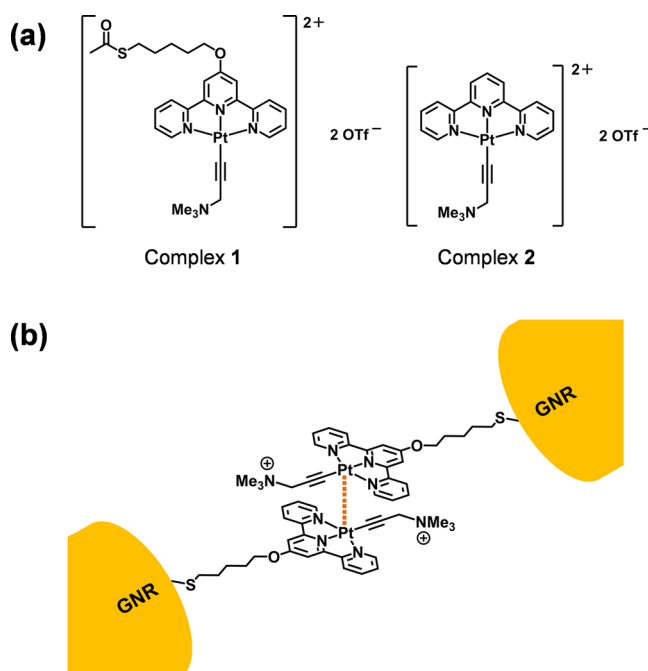

Figure 1. (a) Chemical structures of complexes **1** and **2**. (b) Schematic diagram of the proposed end-to-end assembly of GNRs induced by Pt···Pt and π−π stacking interactions.

the thiol-containing platinum(II) complex, which has been characterized by ESI mass spectroscopy (Figure S1). The self-assembly properties of complex **1** have been monitored using UV−vis absorption spectroscopy. In the UV−vis absorption spectrum, complex **1** in aqueous solution shows intense intraligand (IL) $[\pi \rightarrow \pi^*]$ transitions of the terpyridine and alkynyl ligands at ca. 271−329 nm, together with a low-energy absorption at ca. 375 nm, which is assigned as metal-to-ligand charge-transfer (MLCT) $[d\pi(Pt) \rightarrow \pi^*(tpy)]$ transitions with mixing of an alkynyl-to-terpyridine ligand-to-ligand charge transfer (LLCT) $[\pi(C\equiv CR) \rightarrow \pi^*(tpy)]$ character (Figure S2).[18−29] Concentration-dependent studies (Figure S2) of complex **1** in aqueous solution reveal that an increase in concentration of **1** leads to the growth of a low-energy absorption shoulder, which shows a deviation from Beer's Law (Figure S2, inset). With reference to previous spectroscopic work on alkynylplatinum(II) terpyridine complexes,[18−29,33−35] this low-energy absorption shoulder is tentatively assigned as a metal−metal-to-ligand charge transfer (MMLCT) transition, resulted from the self-assembly of platinum(II) complexes with the formation of Pt···Pt and $\pi−\pi$ stacking interactions. These, together with the self-assembly study of complex **2**,[35] suggest that the synthesized Pt(II) complexes would undergo ground-state aggregation or oligomerization in aqueous media, driven by Pt···Pt and $\pi−\pi$ interactions. To further confirm the ground state aggregation, variable-temperature UV−vis absorption spectroscopy has been studied (Figure S3). The low-energy absorption shoulder is found to decrease upon increasing the temperature. This indicates that the complexes could be deaggregated at elevated temperatures, leading to the disruption of Pt···Pt and $\pi−\pi$ stacking interactions.

A solution of CTAB-protected GNRs with an aspect ratio of 4 has been prepared according to the seed-mediated growth method reported in the literature.[36−39] The GNRs are well dispersed in 0.2 mM pyrrolidine solution as shown in Figure S4. The peak maxima of the transverse surface plasmon resonance (TSPR) and LSPR bands are found to be at ca. 505 and 730 nm, respectively.

The electronic absorption spectral changes of a solution of GNRs in 0.2 mM pyrrolidine upon addition of complex **1** are studied and are shown in Figure 2. A drastic decrease of the 730 nm band with a concomitant growth of the broadened absorption band at >800 nm has been observed. Similar red shifts of the LSPR band have also been observed in other related "end-to-end" assembly of GNRs, attributed to the coupling effect of the LSPR of two neighboring GNRs.[5,10−16] It is believed that the "end-to-end" assembly of the GNRs is
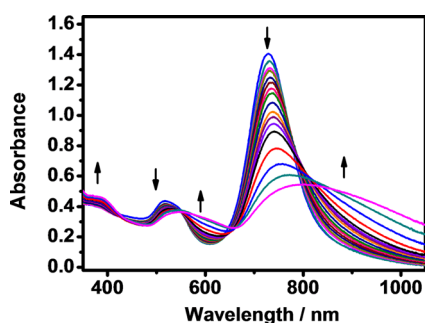
induced upon the addition of complex **1** as the *in situ* deprotected complex **1** would preferentially attach to the active ends of the GNRs due to the presence of the protective CTAB layer on the sides of the GNRs. The aggregation of the platinum(II) complexes is found to take place mainly at the ends of the GNRs such that the platinum(II) complexes would interact with those attached to the ends of the neighboring GNRs. In sharp contrast, no significant change has been observed upon addition of complex **2** that does not contain the thiol group (Figure S5), suggestive of the assembly and connection of the GNRs through supramolecular aggregation of the platinum(II) terpyridine moieties attached to the ends of the adjacent GNRs.

The end-to-end assembly of GNRs directed by complex **1** has been characterized by electron microscopic measurements. Initially, the GNRs are randomly aggregated with no dimensional features when the sample was dried in the absence of complex **1** (Figure S4). Interestingly, in the presence of complex **1**, the GNRs are found to form aggregates in an "end-to-end" manner, as shown in the TEM images (Figure 3a−3f). The extent of the assembly or aggregation, as reflected by the length of the aggregated GNR chain, is found to be increased by an increase in the concentration of complex **1**. It is believed that the deprotected complex **1** would undergo supramolecular assembly at the terminal ends of adjacent GNRs through

Figure 2. Electronic absorption spectra of GNRs dispersed in water with 0.2 mM of pyrrolidine in the presence of 0 to 90 μM of complex **1** with increments of 5 μM at 298 K.
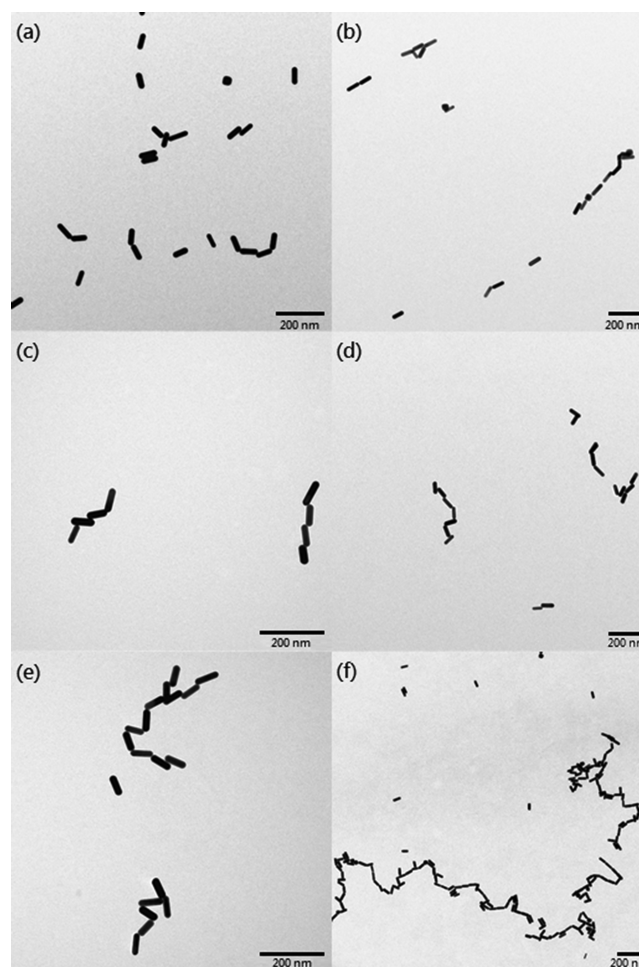
Figure 3. TEM images of mixtures of GNRs dispersed in water with 0.2 mM of pyrrolidine and (a) 44.4, (b) 54.1, (c) 63.7, (d) 78.1, (e) 87.5, and (f) 192 μM of complex **1**.

intermolecular Pt···Pt and $\pi-\pi$ interactions, providing the driving force to connect the GNRs into chain-like nano-structured assemblies through the "end-to end" aggregation. In contrast, addition of complex **2** does not induce the oriented assembly. No morphological change has been observed in the TEM images of GNRs even with the addition of a large amount of complex **2** (Figure S6), indicating that the requirement for directing the "end-to-end" aggregation is the presence of thiol groups on the complexes that can anchor onto the GNRs. From the TEM images, "end-to-end" aggregation is found to predominate, with some "end-to-side" and "side-by-side" aggregations observed. Given the high activity and least protected nature of the terminal ends of the GNRs, the thiol groups should preferentially attach to the termini of the GNRs. It is possible that a small amount of thiol-containing Pt(II) complexes may attach to the side of the GNRs with defects on the protective layer, leading to assemblies other than those of the end-to-end fashion. In some cases, the GNRs not only are connected to each other one-by-one but also connect with two or more GNRs at one terminus. It becomes more serious when large amounts of complex **1** have been added. Probably several complexes at the ends of the GNRs would undergo supramolecular assembly via the noncovalent Pt···Pt and $\pi-\pi$ interactions in different directions that are not sterically demanding. The GNR chains would continue to grow, causing the formation of a complicated network, especially in the presence of large amounts of complex **1** (Figure S7). The "end-to-end" assembly of the GNRs has also been studied by DLS particle size measurements (Figure S8). The hydrodynamic diameter of the GNRs is found to increase dramatically upon increasing the concentration of complex **1**, further establishing the aggregation of the GNRs in the solution state upon the addition of complex **1**.

The magnified TEM image of the GNR chain is shown in Figure 4a. It can be clearly seen that there is a clear contrast
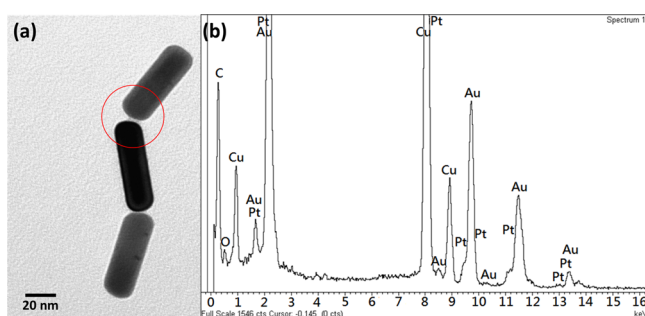

Figure 4. (a) TEM images of a mixture of GNRs dispersed in water with 0.2 mM of pyrrolidine and 54.1 μM of complex **1**. (b) The EDX spectrum of the red-circled area, showing the presence of Pt.

compared to the background in the gap between the two nanorods. A possible reason is the presence of the heavy platinum atom which can block the electron beam from the TEM to produce the contrast. For further confirmation, EDX analysis of the selected area has been conducted and the result is shown in Figure 4b. A small amount of platinum element is found to be present and is mainly located at the terminal end of the GNRs, while the content of the platinum element is negligible on the body of the GNRs (Figure S9). This further supports the preferential attachment of the Pt(II) complexes to the ends of the GNRs, which connect the GNRs together.

In conclusion, end-to-end assembly of the GNRs driven by metal−metal and $\pi-\pi$ interactions has been demonstrated. Further work to explore metal complex-induced "end-to-end" and "side-by-side" assembly of GNRs is in progress and may lead to interesting oriented assemblies. Moreover, the present work would open up many new opportunities and research dimensions on the exploration of other new types of nanomaterials for the fabrication of new classes of inorganic−organic hybrids for molecular recognition studies and various biomedical diagnostics and photonic applications.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b01382.

> Details of the synthesis, characterization and photo-physical studies of the platinum(II) complexes and GNRs, methods of physical measurements, data of the control experiments (PDF)

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: wwyam@hku.hk.

Notes
The authors declare no competing financial interest.

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