Mixed-valence interactions in triarylamine-gold-nanoparticle conjugates[†]

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Optical and electrochemical investigations of triarylamine redox centres attached to gold nanoparticles *via* a π -conjugated bridge show intervalence charge-transfer bands which prove to be surprisingly strong interchromophore interactions.

Gold nanoparticle-chromophore conjugates have a high potential for biomedical,^{1,2} photoelectrochemical, catalytic and sensing applications.³ In the advent of nanoparticle research gold particles with aliphatic ligand shells were synthesised and investigated. In recent years these aliphatic ligands were functionalised with chromophores such as pyrenes⁴ or porphyrins.^{5,6} While in most studies concerning nanoparticle-chromophore conjugates fluorescence properties are in focus,^{1-3,5} in this study, we are interested in the optical absorption properties of gold nanoparticles that are covered by a π -conjugated bridging unit which is terminated by an organic redox centre, *i.e.* a triarylamine. While in a recent study, we were addressing the electron-transfer interactions between triarylamine redox centres attached to solid gold electrodes,⁷ in the present communication our goal is to elucidate how the optical properties of triarylamine-gold-nanoparticle conjugates depend on interactions between the triarylamine redox centre via the conjugated bridge and the gold core, and on interactions between two different triarylamines. That is, we use the gold core as a template to bring many triarylamine units in close contact. We use triarylamine redox centres as they can be used as reversibly oxidisable redox catalysts⁸ and they are used as hole transport components in many optoelectronic applications.9 Furthermore, they are used as redox centres in organic mixedvalence compounds that serve as model systems for basic electron-transfer studies.^{10–13}

The first step to synthesise triarylamine-functionalised gold nanoparticles (**Au-Tara**) was to generate the precursor **Au-Pre** by reduction of HAuCl₄ with LiBH₄ in the presence of 4-bromothiophenol.¹⁴ Extraction of the crude product with dichloromethane (dcm) only or with both dcm and thf yields

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^b Conrad Wilhelm Röntgen Center for Complex Material Systems, Würzburg, Germany. Fax: +49 931 888 4606; Tel: +49 931 888 5318 particles of different size (Au-PreS and Au-PreL, respectively). The two fractions with different particle size and the terminal alkyne 1 were then transformed *via* a Hagihara–Sonogashira coupling reaction into the desired products Au-TaraS and Au-TaraL.¹⁵ For comparison, the reference compound **Ref** was synthesised *via* a palladium-catalysed reaction starting from compound 1 (Scheme 1).

The gold core diameter distribution of the nanoparticles was measured using dark-field scanning transmission electron microscopy. **Au-TaraS** has an average diameter of 2.24 (± 0.48) nm and **Au-TaraL** of 2.71 (± 0.56) nm. Thus, in **Au-TaraS** each gold core is covered by *ca*. 25 chromophores (for details see ESI†). The composition and stability of the gold core structure of the **Au-Tara** particles after Sonogashira coupling was checked by UV/Vis/NIR- and X-ray photoelectron-spectroscopy (XPS) (see Fig. S4 and S5†).

The surface plasmon band (SPB) is a characteristic feature in the absorption spectrum of metallic nanoparticles. In the case of spherical particles with the same organic layer, the energy and the intensity of the SPB depend on the size of the gold core.³ In agreement with this fact the larger particle **Au-TaraL** shows an intense SPB at 19000 cm⁻¹ which is practically absent in the smaller particle **Au-TaraS** (Fig. 1 and Fig. S4[†] for the precursor particles).

The absorption spectrum of the reference compound **Ref** displays two intense bands at 27 600 cm⁻¹ (polarised along the molecular axis) and 34 500 cm⁻¹ (polarised perpendicularly, see, Fig. S6†). The higher energy band is also seen with a slight red shift in the spectrum of **Au-TaraS** but has a very weak intensity in the case of **Au-TaraL**. Much in contrast, the second characteristic band of **Ref** at 27 600 cm⁻¹ is hardly detectable in the spectra of **Au-TaraL** and **Au-TaraS**.

The strong damping of the band at 27 600 cm⁻¹ and the red shift of the band at 34 500 cm⁻¹ are caused by an interaction between the gold core and the chromophore.^{4,6,16} The different degree of damping between the 27 600 cm⁻¹ band and the



Scheme 1 Synthesis of the nanoparticles Au-Pre and Au-Tara (S small, L large nanoparticle) and the chromophore Ref.

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Fig. 1 Absorption spectra of the triarylamine-functionalised particles Au-TaraS (black line) and Au-TaraL (red line) and the reference compound **Ref** (blue line) in dcm.

34 500 cm⁻¹ band might be due to the different relative orientation of the chromophore transition dipole to the surface normal of the gold particle.¹⁷ In fact, it is likely that the orientation of the arylthiol units deviates strongly from the gold surface normal.¹⁸

Osteryoung square wave voltammetry (OSWV) of Ref in tetrabutylammonium hexafluorophosphate (TBAH) dcm solution shows two peaks ($E_{(Ox1)} = 280 \text{ mV}$, $E_{(Ox2)} = 950 \text{ mV}$) which can be assigned to the first and second oxidation of the triarylamine centres (Fig. 2). Only the first oxidation peak is reversible. The OSWV of Au-TaraS and Au-TaraL reveals a splitting of the first triarylamine oxidation into two reversible oxidation processes. A fit of the voltammogram with two Voigt-functions (see Fig. S8[†]) reveals a separation (seen as a shoulder) of about 130 mV for Au-TaraS and 140 mV for Au-TaraL (Table 1). This splitting is caused by a very strong coupling between neighbouring triarylamine centres (the statistical value for two non-interacting redox centres is 35.6 mV). Such a splitting of the first oxidation is often seen in bis(triarylamine) systems^{10–13,19} and is also seen for ferrocenes attached to a ruthenium particle via a vinylene unit.20

Further information about the electronic coupling between the triarylamine centres on the particles was obtained by spectroelectrochemistry (SEC) at a transparent gold-minigrid electrode. Only the oxidation to the triarylamine radical cation is discussed because the oxidation to the dication is irreversible. The SEC of **Ref** shows that the typical triarylamine absorption

Table 1 Redox potentials of Ref, Au-TaraS and Au-TaraL vs. ferrocene (Fc/Fc^+) in dcm-TBAH

	Redox potential/mV	Redox potential/mV		
	$E_{(Ox1)}$	$E_{(Ox2)}$		
Ref Au-TaraS Au-TaraL	280^a 290^b , 420^b 280^b , 420^b	950^{a} 980^{a} 980^{a}		
^{<i>a</i>} Measured functions.	by OSWV. ^b Determined by a fit with two	Voigt-		

band at 27 600 cm⁻¹ decreases with increasing potential while at the same time the characteristic band for the monoradical cation at 13 000 cm⁻¹ and another band at 23 000 cm⁻¹ increase (see Fig. S7†). The band at 13 000 cm⁻¹ is associated with a π - π * transition of the dianisylphenylamine radical cation.¹⁰⁻¹³

For a better overview we divide the SEC of Au-TaraS into three sequential processes which are grouped according to isosbestic points (Fig. 3). The characteristics of the three processes are the increase of the triarylamine radical cation band at 13100 cm⁻¹ accompanied by a decrease of the band at 33 300 cm⁻¹. During this first process the weak bands at 24 900 cm⁻¹ and 27 900 cm⁻¹ decrease. Even more interesting is the observation of a weak band at about $10\,000 \text{ cm}^{-1}$ (ε ca. 2000 M⁻¹ cm⁻¹), which increases during the second process and then decreases during the third process (see inset in Fig. 3). This behaviour is indicative of an intervalence charge-transfer band (IVCT) which is associated with an optically induced hole transfer between an oxidised and a neutral neighbouring triarylamine. The IVCT band should be maximal at 50% oxidation of all triarylamine centres as indeed observed. IVCT bands of similar intensity are seen in many bis(triarylamine) radical cation systems^{10-13,19} and are also reported for ruthenium particles with attached ferrocenes.²⁰ In contrast to the mixed-valence bis(triarylamine) radical cations where hole transfer occurs over the conjugated bridges that connect the two triarylamine moieties, the hole in the partially oxidised triarylamine-gold-nanoparticle conjugates is transferred through space between the triarylamines.



Fig. 2 OSWV in dcm (TBAH) of Au-TaraS (black line), Au-TaraL (red line) and Ref (blue line).



Fig. 3 SEC of Au-TaraS (black line) in dcm–TBAH. The SEC is composed of three processes coloured yellow, red and blue.



Fig. 4 SEC of Au-TaraL (black line) in dcm–TBAH. The SEC is composed of three processes coloured yellow, red and blue. The coloured arrows symbolise the changes of the band intensities for each process.

The SEC of **Au-TaraL** can also be described by three sequential processes. (Fig. 4). Only the first process is fully reversible. Initial increasing of the potential (first process) leads to a dramatic decrease of all characteristic gold core band intensities. With further increase of the potential the triarylamine radical cation band at 13100 cm⁻¹ rises (second process) and the gold core bands gain more intensity. This process is associated with an increase in a band at ca. 10000 cm⁻¹. As the radical cation band at 10000 cm⁻¹ decreases (third process). Again, as in **Au-TaraS** the latter band is interpreted to be an IVCT band.

In the first process the gold core gets charged. Such a corecharging alters the electronic structure of the gold core and is known to affect some gold transitions within the gold nanoparticle.^{21,22} It might also be possible that the electrolyte (TBAH) mediates electrostatic interactions between the charged particles which causes an aggregation of particles. Chandrasekharan *et al.* found that aggregation of a gold nanoparticle coated with Rhodamine 6G was responsible for a damping and broadening of the SPB.²³ Whatever the reasons may be for this effect, oxidation of the triarylamine centres in the second step disturbs it strongly. In contrast, the smaller particle size of **Au-TaraS** and/or the superimposition with the more intense triarylamine bands could be the reasons that a damping of the gold core band intensities are not detectable in the SEC of **Au-TaraS**.

In summary, we present the first synthesis of triarylaminefunctionalised gold nanoparticles of two different sizes. The absorption properties of these two conjugates differ strongly both in the neutral state and in the ligand oxidised state. In the neutral state this is due to different electric fields emanating from the gold particle which interacts with the transition dipole of the ligands. In the ligand oxidised state, the OSWV and the SEC measurements of the nanoparticles revealed a strong coupling between neighbouring triarylamine units which is due to through space intervalence interactions²⁴ in these metal–organic mixed-valence conjugates. The SEC also showed for the larger particle that by charging the chromophore–nanoparticle system, the gold core transitions are damped. These multi-electron redox active nanoparticle systems may be interesting building blocks in the field of charge storage (electron sponge) as they can be loaded to a high degree at constant potential.

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