Supporting Information

Mixed-Valence Interactions in Triarylamine-Gold-Nanoparticle Conjugates

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Experimental

General. All reagents were obtained from commercial suppliers and were used without further purification. Diethylamine and tetrahydrofurane (thf) were freshly distilled and stored under nitrogen atmosphere. Thin-layer chromatography was carried out on Merck silica gel plates (60 F254). Merck silica gel 32-63 μ m was used for flash chromatography. The NMR spectra were recorded on a Bruker AVANCE 400 FT-NMR (400MHz) instrument. ESI pos. high resolution mass spectroscopy was performed on a Bruker Daltonik micrOTOF focus spectrometer. IR Spectroscopy was carried out on a Jasco 410 FT-IR Spectrometer. Absorption band maxima are given in cm⁻¹ and intensities are denoted as *s* (strong) and *w* (weak).

OSWV. The Osteryoung square wave voltammograms were recorded on an electrochemical workstation BAS CV-50 W including software version 2.0. The square-wave amplitude was 25 mV, the frequency was 15 Hz and the potential step height for base staircase wave form was 4 mV. The electrochemical experiments were performed in dry, argon-saturated dichloromethane with 0.15 M tetrabutylammonium hexafluorophosphate (TBAH) as the supporting electrolyte using a conventional three-electrode set-up with a platinum disk electrode (0.12 cm²). The potentials are referenced against ferrocene (Fc/Fc⁺). The reversibility of the redox process was checked by multi-cycle thin layer cyclovoltammetry. For measurements under thin-layer conditions the working electrode was placed onto a mobile glass hemisphere.¹

Spectroelectrochemistry. The solutions of the voltammetry experiments were transferred by a syringe into a spectroelectrochemical optical transparent thin-layer cell (optical path length of 100 μ m with a gold minigrid working electrode) described by Salbeck.² UV/vis/NIR spectra were recorded with a JASCO V-570 UV/vis/NIR spectrometer while applying a constant potential (EG & G potentiostat/galvanostat model 363) to the solution in the thin-layer arrangement referenced against a Pt electrode. The potential was increased in 50 mV steps. Spectra were recorded until the first oxidative process was fully covered. Back reduction was also performed in order to prove reversibility of the whole process in all cases.

Polarised steady-state fluorescence spectroscopy: Fluorescence-anisotropy measurements were carried out in a sucrose octaacetate (SOA) matrix at room temperature. Two Glan–Thompson polarisers from Photon Technology International were used in an L-format setup. SOA was purchased from Acros Organics and recrystalised twice from ethanol. Sample preparation was done according to a procedure reported in literature.³ Compound **Ref** and SOA were dissolved in dichloromethane (Merck, Uvasol). The solution was filtered through a 0.1 μ m filter in order to remove any traces of lint and dust and purged with dry and oxygen-free argon for 10 min. Dichloromethane was partially removed in vacuo until a viscous oil resulted, which was filled into a 1 cm fluorescence quartz cuvette. The cuvette was then kept in an oven at 100 °C for about 1 h and at 130 °C for 5 h to remove the remaining dichloromethane.

STEM measurements: The pictures were recorded using a FEI Helios Nanolab equipped with an insertable multi-segment solid-state detector. An acceleration voltage of 30 kV and a beam current of 170 pA were used. Samples for STEM analysis were prepared from a 20 μ g/ml solution of the nanoparticles in dichloromethane. A single drop was transferred on a carbon coated copper grid. The solvent was evaporated at room temperature. The typical images and the histograms of the size distribution of the MPCs are shown in S2 and S3.

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X-ray photoelectron spectroscopy (XPS): The X-ray photoelectron spectroscopic measurements for chemical analysis of the Au nanoparticles have been performed with a Scienta R4000 electron analyser using a monochromatic Al K α light source.⁴. Molybdenum substrates have been coated with a solution of **Au-Tara** in thf and were transferred in to the UHV measuring chamber (p = 10⁻¹⁰ mbar). Since the samples are mainly dominated by carbon and oxygen from both the residua of the solvent and the organic shell of the Au nanoparticles we slightly sputtered the samples by Ar⁺-ion bombardment. This process permitted a reduction of the amount of light elements like carbon and oxygen without destroying the metal core of the nanocluster. Figure S5 shows the photoemission results of **Au-TaraS** and **Au-TaraL**, respectively.

Synthesis of 4-[(4-*tert*-butylthiophenyl)ethynyl]-*N*,*N*-bis(4-methoxyphenyl)benzene-amine Ref. The alkyne 1 (400 mg, 1.21 mmol), *tert*-butyl protected thiophenol 5 (426 mg, 1.74 mmol), Pd(PhCN)₂Cl₂ (23.3 mg, 60.7 μ mol), CuI (9.25 mg, 48.6 μ mol) and P(¹Bu)₃ (97.2 μ L, 1.0 M in toluene, 97.2 μ mol) were dissolved in diethylamine and degassed. The reaction mixture was stirred for 12 h under a nitrogen atmosphere at reflux in the dark. The solvent was removed *in vacuo*, and the residue was dissolved in dichloromethane and washed with water. The crude product was purified by flash chromatography on silica gel (petroleum ether / dichloromethane 3:1 \rightarrow 2:1) to obtain 140 mg (284 μ mol, 23 %) of an orange solid. ¹H NMR (400 MHz, acetone-d₆, 295 K): δ / ppm = 7.55 (AA', 2H, SCCHCHC or SCCHCHC), 7.50 (BB', 2H, SCCHCHC or SCCHCHC), 7.35 (AA', 2H, NCCHCHCC or NCCHCHCC), 7.13 (AA', 4H, OCCHCHC or OCCHCHC), 6.96 (BB', 4H, OCCHCHC or OCCHCHC), 6.80 (BB', 2H, NCCHCHCC or NCCHCHCC), 3.82 (s, 6H, OCH₃), 1.30 (s, 9H, SCCH₃). ¹³C NMR (101 MHz, acetone-d₆, 295 K): δ / ppm = 157.1 (quart.), 149.6 (quart.), 140.4 (quart.), 137.6 (SCCHCHC or SCCHCHC), 133.1 (quart.), 132.7 (NCCHCHCC or NCCHCHCC), 115.2 (OCCHCHC or SCCHCHC), 113.6 (quart.), 92.0 (quart.), 87.8 (quart.), 55.8 (OCH₃), 46.7 ((SCCH₃), 31.1 (SCCH₃). IR (KBr)): ν / cm⁻¹ = 2960 (w), 2205 (w), 1600 (w), 1590 (w), 1500 (s), 1230 (s), 1030 (s), 820 (s). MS (ESI pos, high resolution): *m*/z found: 493.20732 calculated: 493.20700 (Δ ppm = 0.65).

Synthesis of 4-bromothiophenol protected gold nanoparticle Au-Pre

Au-PreS

Tetrachloroauric acid trihydrate (140 mg, 355 μ mol) and 4-bromothiophenol (134 mg, 711 μ mol) were dissolved in dry thf (14 ml). This solution and a LiBH₄-solution (14.2 ml, 0.1 M in thf, 1.42 μ mol) were simultaneous added to stirred dry thf (8 ml) via a syringe pump (2.5 ml/min). Immediately after addition the solution was concentrated to 4 ml and filtered through a glass frit (pore 3) to purify the product from agglomerated nanoparticles. The filter residue was extracted with dichloromethane (20 ml) and the combined organic phases were washed with water. The organic solution was concentrated to 4 ml and added to *n*-hexane (30 ml). This mixture was centrifuged and the black residue was washed with *n*-hexane. The yield was 60 mg of a black solid.

Au-PreL

Tetrachloroauric acid trihydrate (144 mg, 366 μ mol) and 4-bromothiophenol (138 mg, 731 μ mol) were dissolved in dry thf (14.4 ml). This solution and a LiBH₄-solution (14.6 ml, 0.1 M in thf, 1.46 μ mol) were simultaneous add to stirred dry thf (8 ml) via a syringe pump (2.5 ml/min). Immediately after addition the solution was concentrated to 4 ml and filtered through a glass frit (pore 3) to purify the product from agglomerated nanoparticles. The filter residue was extracted with dichloromethane (20 ml) and thf (20 ml). The combined organic phases were washed with water. The organic solution was concentrated to 4 ml and 30 ml *n*-hexane added. This mixture was centrifuged and the black residue was washed with *n*-hexane. The yield was 59 mg of a black solid.

Synthesis of the gold nanoparticle Au-TaraS via a *Hagihara-Sonogashira* reaction⁵:

Under a nitrogen atmosphere alkyne **1** (100 mg, 304 μ mol), P(*t*Bu)₃ (30 μ L, 1.0 M in toluene, 30 μ mol) and diisopropylamine (51 μ L, 364 μ mol) were added to a solution of nanoparticle **Au-PreS** (60 mg) in dry thf (6 ml). The mixture was degassed and Pd(PhCN)₂Cl₂ (9.3 mg, 24 μ mol) and CuI (2.9 mg, 15 μ mol) were added. The mixture was stirred for 12 h at room temperature. The solvent was removed *in vacuo*, and the residue was dissolved in dichloromethane and filtered (glass frit; pore 3). The solution was washed with a saturated aqueoüus solution of NaCl and water. The organic phase was concentrated to 4 ml and *n*-hexane (30 ml) was added. This mixture was centrifuged. The black residue was repeated at least seven times. The yield was 30 mg of a black solid. ¹H-NMR (400 MHz, dichloromethane-d₂, 295 K): δ / ppm = 8.50-5.50 (bm, 16H), 4.20-3.10 (bm, 6H). STEM: diameter 2.24 (± 0.48) nm. The density ρ of triarylamines per nanoparticle is about 25.*

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Synthesis of the gold nanoparticle Au-TaraL via a Hagihara-Sonogashira reaction⁵:

Under a nitrogen atmosphere alkyne **1** (39 mg, 118 μ mol), P(*t*Bu)₃ (12 μ L, 1.0 M in toluene, 12 μ mol) and diisopropylamine (20 μ L, 142 μ mol) were added to a solution of nanoparticle **Au-PreL** (59 mg) in dry thf (6 ml). The mixture was degassed and Pd(PhCN)₂Cl₂ (3.6 mg, 9.5 μ mol) and CuI (1.1 mg, 5.9 μ mol) were added. The mixture was stirred for 3 d at room temperature. The solvent was removed *in vacuo*, and the residue was dissolved in dichloromethane and filtered (glass frit; pore 3). The solution was washed with a saturated aqueous solution of NaCl and water. The organic phase was concentrated to 4 ml and *n*-hexane (30 ml) was added. This mixture was centrifuged. The black residue was dissolved in dichloromethane (4 ml) and dropped into *n*-hexane (30 ml) and again centrifuged. This purification step was repeated at least seven times. The yield was 35 mg of a black solid. ¹H-NMR (400 MHz, dichloromethane-d₂, 295 K): δ / ppm = 8.50-5.50 (bm, 16H), 4.20-3.10 (bm, 4H). STEM: diameter 2.71 (± 0.56) nm.



Fig. S1¹H-NMR (400 MHz) of nanoparticle Au-TaraS (A) and Au-TaraL (B) in dichloromethane-d₂.

*The density ρ of triarylamines per nanoparticle was calculated with eqn (1):

$$\rho = \frac{\varepsilon_{Au225}^{600nm}}{A_{Au-TaraS}^{600nm}} \times \frac{A_{Au-TaraS}^{7/0nm}}{\varepsilon_{Ref}^{770nm}}$$
(1)

where $\varepsilon_{Au225}^{600nm}$ is the extinction coefficient of a Au₂₂₅(SC₆H₁₃)₅₇ nanoparticle (diameter 2.0 nm)⁶ at 600 nm, $A_{Au-TaraS}^{600nm}$ is the absorbance of **Au-TaraS** at 600 nm, $A_{Au-TaraS}^{770nm}$ is the corrected absorbance of the monoradical cation band at 770 nm of the oxidised species of **Au-TaraS** (eqn (2)) and $\varepsilon_{\text{Ref}^{00nm}}^{770nm}$ is the extinction coefficient of the monoradical cation band at 770 nm of the oxidised species of **Ref**.

$$A_{Au-TaraS^{OX}}^{770nm} = A_{Au-TaraS}^{770nm} - A_{Au-TaraS^{OX}}^{770nm*}$$
(2)

where $A_{Au-TaraS}^{770nm}$ is the absorbance of the unoxidised species of **Au-TaraS** at 770 nm and $A_{Au-TaraS}^{770nm^*}$ is the absorbance of the oxidised species at 770 nm.



Fig. S2 Dark field STEM images of Au-TaraS and the associated histogram.



Fig. S3 Dark field STEM images of Au-TaraL and the associated histogram.

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Fig. S4 Absorption spectra of the triarylamine functionalised particles Au-TaraS (black line) and Au-TaraL (red line) and the corresponding precursors Au-PreS (dashed black line) and Au-PreL (dashed red line).

UV/Vis/NIR absorption spectra of **Au-TaraS** and **Au-TaraL:** As can be seen from figure S4 the characteristic surface plasmon bands of the gold core at ca. 18000 cm⁻¹ have similar intensities for the **Au-Pre** particles and the corresponding **Au-Tara** particles. Additionally, in the spectra of **Au-Pre** a band at 39500 cm⁻¹ is seen. This band can be attributed to the 4-bromothiophenol ligand and is absent in the spectra of the **Au-Tara** particles. This analysis points out that the Sonogashira reaction does not affect the particle size but it does manipulate the organic layer.



Fig. S5 XPS of Au-TaraS (A) and Au-TaraL (B).

XPS analysis of **Au-TaraS** (A) and **Au-TaraL** (B): As can be seen from figure S5 the features of C1s and O1s and several peaks of the molybdenum substrate as well as the core levels of the Au nanoparticles are clearly visible. In order to verify the absence of the Pd catalyst we performed detailed measurements in a binding energy range of about 560 eV (see insets of Fig. S5) where the 3p3/2 level is expected. Within the typical accuracy for the determination of the chemical compositions by core level spectroscopy (~1%) we obtain no evidence for Pd in both the **Au-TaraS** and **Au-TaraL** samples. Thus, the palladium catalysed reaction does not affect the composition of the gold core.

Polarised steady-state fluorescence spectroscopy: In theory a maximum anisotropy value of r = 0.40 is obtained for a parallel orientation of the absorption and the emission transition moments and a minimum value of r = -0.20 for a perpendicular orientation.⁷ The excitation and emission-anisotropy spectrum of **Ref** is shown in figure S6. The excitation-anisotropy for the low-energy transition at 27700 cm⁻¹ is ca. 0.3. Thus, this transition has a parallel orientated transition moment to the emission moment. The deviation from the theoretical maximum value of 0.40 indicates that there is a small

contribution from higher energy transitions due to band overlap. For the high-energy transition at 34700 cm^{-1} the anisotropy is at circa 0.1. Because of the strong decrease in the anisotropy we assume that transition moments of the absorption and emission for this transition may be oriented perpendicularly. The fact that the anisotropy does not reach the theoretical value of -0.20 is caused by contributions from overlap with lower and higher transitions.

As the absorption transition moment of the 27700 cm^{-1} band is parallel and that of the 34700 cm^{-1} band is perpendicularly oriented to the emission transition moment we conclude that the two transition moments of the two absorptions are approximately oriented perpendicularly to each other.



Fig. S6 Anisotropy of the excitation (emission wave number 22800 cm⁻¹; green) and the emission (excitation wave number 27700 cm⁻¹ and 34700 cm⁻¹; red and blue) of **Ref** in a sucrose octaacetate (SOA) matrix at room temperature. The corresponding nonpolarised absorption (solid line) and emission (dashed line) spectra of **Ref** in *n*-Bu₂O are added for comparison.



Fig. S7 Spectroelectrochemistry of Ref in dcm/TBAH.



Fig. S8 Fit (circles) of the OSWV of Au-TaraS (A) and Au-TaraL (B) with two Voigt-functions (dashed green lines) after baseline (capacitive background current) correction with an exponential function.

Notes and references

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