Remarkable Effect of the Dithiafulvene Structures on their Capacity as Reducing Agents: Influence of Conjugated Thiocarbonyl Group

Anabel E. Lanterna,^{a,c,†} María F. Torresan,^{b,c} Rodrigo A. Iglesias,^{b,c} Eduardo A. Coronado,^{b,c} Alejandro M. Granados^{a,c,*}

^a Universidad Nacional de Córdoba. Facultad de Ciencias Químicas. Departamento de Química Orgánica. Córdoba, Argentina

^b Universidad Nacional de Córdoba. Facultad de Ciencias Químicas. Departamento de Fisicoquímica. Córdoba, Argentina.

^c Consejo Nacional de Investigaciones Científicas y Técnicas, CONICET. Instituto de Investigaciones en Fisicoquímica de Córdoba, INFIQC. Córdoba, Argentina.

ABSTRACT: The use of dithiafulvene (DTF) derivative compounds having strong electron donating properties as reducing agents to obtain noble metal nanoparticles (PdNP, AgNP, AuNP) is demonstrated. The resulting oxidized DTF product was characterized by spectroelectrochemistry. The stability of the colloidal dispersions are explained considering that the oxidized DTF layer have a delocalized positive charge providing both steric and electrostatic stabilization, which allows that the generated nanoparticles remain in a colloidal state for six months or more. Our results suggest that the presence of a thiocarbonyl group in DTF moiety increases the stability of the oxidized DTF (radical cation DTF 2⁺), avoiding the formation of the tetrathiafulvene (TTF) as occurs with other derivatives reported in literature, which do not have a conjugated thiocarbonyl group in their structure. It has also been shown that the capacity as a reductive agent of DTF strongly depends on the substitution pattern of the base structure.

KEYWORDS: Dithiafulvene, nanoparticle, reducing agents, gold, silver, palladium

1. INTRODUCTION

The dithiafulvene unit (1,3-dithiole-2-ylidene group) is a good electron donor present in the design and synthesis of new organic materials, especially in the search for extended tetrathiafulvalene derivatives.^{1,2} Push–pull donor–acceptor dyads can also be formed by dithiafulvene units showing unprecedented non-linear optical and redox-controlled characteristics.^{3,4} Although dithiafulvene compounds (DTF) were discovered a long time ago,⁵ it is quite difficult to find literature about their capacity as reducing agents, or their metal affinity. The major data set are referred to the use of tetrathiafulvene (TTF) derivatives as substrates for the synthesis of novel materials.^{3,6} Additionally, it has been recently demonstrated by Zhou et al. that π -conjugated polymer containing the strong electron-donating (DTF) unit in the main chain, led to gold nanoparticles (AuNPs) with the resulting oxidized conjugated polymer protecting their surface producing in this way a stable colloidal dispersion.^{7,8} Even when DTF moieties (TTF “half-unit”) do also possess electron-donor capabilities, some authors consider that they are harder to oxidize.⁹ We have shown recently the ability of butyl 2-(4-phenyl-1,3-dithiol-2-ylidene)ethanedithioate (Scheme 1, DTF 2: R₁= H, R₂= butyl, DTFBu) to reduce Au(III) producing as result capped AuNPs.¹⁰ Likewise, Adows and Zhao have also reported the ability of 5-((4,5-bis(decylthio)-1,3-dithiol-2-ylidene)methyl)isophthalic acid, carboxylated DTF 1 and TTF derivative (Scheme 1) as reducing agents of Au (III).¹¹ In the present work, we study different DTF 2 derivative compounds (scheme 1), synthesized in our group,¹² as reducing agents not only of Au (III) but also of other metals cations such as Ag(I) and Pd (II), giving as product metal NPs (MNPs) capped with oxidized DTF. The oxidized DTFBu, was produced and characterized by spectroelectrochemistry (SE) in the absence of the metal precursors and the spectral data of this species fits very well with those observed in the chemical redox reaction

reported. Contrary to what is reported for DTF 1,¹¹ our results suggest that the presence of a thiocarbonyl group (DFT 2) increases the stability of the oxidized DTF, avoiding the formation of the TTF.

Scheme 1. Carboxylated DTF 1 and TTF structures studied by Zhao et al.¹¹ for the reduction of Au(III) in organic solvents. DTF 2 derivative compounds studied in the present work.

2. EXPERIMENTAL SECTION

2.1. Instrumentation.

Transmission electron microscopy images (TEM) were obtained using a JEOL JEM EX 1220 transmission electron microscope operating at an accelerating voltage of 80 kV. Several drops of the MeCN solutions of the samples were placed on a 200 mesh copper grid covered with a Formvar film. Excess solutions were removed with tissue paper. The UV-Vis spectra of the samples were recorded on a double beam spectrophotometer. Cyclic voltammetry (CV) and spectroelectrochemical (SE) analysis were performed using a potentiostat (Autolab, PGSTAT-

101), a photodiode array spectrometer (Ocean Optics HR2000+) and a 150W Xenon lamp, attenuated with neutral density filters, as UV-Vis light source.

2.2. Experimental Procedure.

Synthesis of DTF compounds. DTF were synthesized by the regioselective cycloaddition of dithiolethiones and alkynyl Fischer carbene Complexes, which has been previously reported in detail.¹²

Synthesis of capped metal colloids. In a typical preparation of oxidized DTF-MNP, a solution of DTF in AcN (6.1 μ M) was mixed together with the metal precursor salt solution to reach different M/DTF ratios. The reaction mixture was kept under dark conditions for 24 h before analysis by UV-Vis spectroscopy.

Cyclic voltammetry (CV) and spectroelectrochemical (SE) analysis. Cyclic voltammograms of DTF solutions (1 mM) in AcN or CH₂Cl₂ were measured employing tetrabutylammonium perchlorate (5mM) as supporting electrolyte. The lab-made electrochemical cell uses a glassy carbon working electrode, a Pt wire counterelectrode and Ag|AgCl (3M KCl) as reference electrode. SE analysis was performed by measuring differential absorption spectra of DTF solutions (1 mM) in AcN or CH₂Cl₂ at different time intervals during a linear potential scan from 0 to 2.5 V at a sweep rate of 10mV/s. Tetrabutylammonium perchlorate (5×10^{-3} M) was used as supporting electrolyte. The photoelectrochemical cell was set up in a conventional spectrophotometric cuvette fitting an ITO glass as the working electrode, a Pt wire counterelectrode and Ag|AgCl (3M KCl) as reference electrode. Polychromatic light from the light source was collimated to a 4mm diameter spot onto the ITO surface and the light transmitted was collected by the photodiode array spectrometer.

3. RESULTS AND DISCUSSION

The synthesis of the dithiafulvene units, **DTF 2**, showed in Scheme 1, has been reported previously by our group,¹² as a regioselective cycloaddition of 1,2-dithiole-3-thiones rings to an alkynyl Fischer carbene complex. Specifically, in the present work we extend the use of DTF as reducing agent for the preparation of oxidized DTF-AgNPs and PdNPs, employing DTfBut as a proof of concept example. The metal NPs obtained were characterized by TEM and UV-vis spectroscopy (*vide infra*). The influence of changing the R1 and R2 moieties of **DTF 2** derivatives (shown in scheme 1) on the efficiency for reducing Au(III) was also evaluated. As a general feature, **DTF 2** derivatives have two absorption peaks (Figure S1), the first one around $\lambda=350$ nm ($\lambda=320$ nm for R1=H, $\lambda=350$ nm for R1= (CO)₅WCOCH₃, WDTfPcIPh or R1= (CO)₅CrCOCH₃, CrDTfDod) assigned to the π - π^* transition, and the second one at 450 nm corresponding to the n - π^* transition of the non shared electron pair of S atoms in the DTF moiety. Upon addition of the metal ion salt precursor (HAuCl₄, PdCl₂ or AgNO₃), a redshift of the absorption band around $\lambda=450$ nm is observed for Pd(II) while for the cases of Au(III) and Ag(I), a new band around 580 nm is also detected, as expected for the localized plasmon resonance band of Au and AgNPs (Figure 1). Particularly for the case of silver this band at 580 nm could be an indication of the presence of nano-structures with some degree of anisotropy in their growth.^{13,14} TEM images further confirmed the presence of NPs (*vide infra*).

In our previous report,¹⁰ we have been able to follow the formation of AuNPs simply by the optical changes of the DTF moiety, this behavior can be compared to the use of citrate as a reducing agent.¹⁵ Therefore, we concluded that the formation of AuNPs can be performed without the addition of any other reducing agent and that the resulting colloidal solution remains stable for more than six months thanks to the passivation of the metal NP surface with the

resulting oxidized DTF. We postulated a minimum mechanism that consists of two steps: 1) electron transfer from DTFBut to Au(III), giving an intermediate complex (oxidized DTF-Au(I)) as product, 2) disproportionation of this intermediate complex to Au(0) and Au(III) possibly promoted by the oxidized DTF species. Indeed, Zhao and Adows have shown that **DTF 1** in the presence of Au(III) produces **TTF²⁺** in AcN, but their work did not report the formation of AuNPs in these conditions.¹¹ This observation suggests that although there are structural similarities between the carboxylated **DTF 1** and the **DTF 2** studied here, the redox capability of these derivatives is strongly associated to their substitutions. In order to prove that **DTF 2** derivatives can undergo oxidation without the concomitant formation of the corresponding **TTF²⁺** cations, the electrochemical behaviour of DTFBut was characterized by both cyclic voltammetry (CV) and SE. The CV scan for DTFBut depicts an oxidation peak at +1.65V in AcN (+1.67V in CH₂Cl₂) (see Figure S2). Although these oxidation potentials are higher than the ones reported for **DTF 1** derivatives,¹¹ all **DTF 2** derivatives tested here were able to produce AuNPs in AcN. Also, here we show that **DTF 2** is not only able to reduce Au(III) to form the AuNPs but also Ag(I) and Pd(II) and produce the concomitant MNPs. Additionally, we study the electrochemical behaviour of the **DTF 2** derivatives in order to give more insights on the oxidized DTF species formed during the redox process. No evidences of the formation of the associated tetrathiafulvene derivatives (strong absorption around 600-800 nm)¹¹ were found upon oxidation in the presence of any of the noble metal cations. The differences found could be explained by the nature of the **DTF 2** radical cation (DTF 2⁺) formed during the redox process (Scheme 2). Sulfur-centered radicals are intrinsically more stable^{16,17} and prone to interact with metal surfaces.¹⁸⁻²¹ In order to prove this hypothesis, spectroelectrochemical experiments were performed with DTFBut in the absence of Au, Ag or Pd ions. As can be seen in figure 2 the

differential spectra recorded at different applied potentials only show a decrease of the DTFBu concentration on the electrode surface (decrease in the absorption band at 454 nm) leading to the formation of oxidized species, DTF_{ox} , which show absorption bands at around 400 and 485 nm. No further changes are observed above 530 nm suggesting the absence of TTF^{2+} species.¹¹ Interestingly, the same trend is found if the differential spectral is recorded versus time after addition of the metal precursor, as shown in Figure 3. As can be noticed, in the presence of Au^{3+} ions (Figure 3 *top*) as the reduction process takes place there is a simultaneous decrease of the absorption bands corresponding to DTFBu (band c) and Au (III) (band a). The oxidized DTF species can be recognized by the formation of the new bands b and d. Band e accounts for the formation of AuNPs. Similarly, Figure 3 *bottom* shows the spectral changes when DTFBu is mixed with PdCl_2 . In this case, it is important to note that band d is not only more intense but also broader. This could account for the absorption of PdNPs as discussed below. Remarkably, the isosbestic point found during SE experiments coincides with the isosbestic points found when a metal precursor is added to the DTFBu solution, supporting our hypothesis.

Additionally, the reactivity of each derivative compound can be qualitative tested by comparing the absorbance at the maximum LSPR band obtained during the synthesis of oxidized DTF-AuNPs (see Table 1). Thus, the alkyl substituents in R_2 favour the NPs formation in comparison with aromatic substituent (*cf.* entries *i*, *ii* and *iii*). When R_1 is a Fischer carbene moiety (W or Cr) the NPs formation is diminished. Although we have recently shown that Fischer carbenes anchored on glass surfaces are able to reduce Au(III) and produce AuNPs,²² the reactivity of **DTF 2** derivatives in solution is decreased by the presence of the carbene moiety. Hence, the carbene group seems to act as an electron-withdrawing group, discouraging the electron transfer to the metal precursor in the redox process (*cf.* entries *ii-v*).

Figure 1. UV-Vis spectrum of the DTFBu in AcN (black) and UV-Vis spectra of DTF-protected Metal NPs (red) for the concentration ratios Au/DTF = 7 (A), Pd/DTF = 4 (B) and Ag/DTF = 8 (C); after one day of reaction.

Scheme 2. Resonance structures of a DTF 2 radical cation.

Figure 2. Differential spectra of DTFBT 1 mM in AcN obtained at different time intervals during a linear potential scan from 0 to 2.3 V at a sweep rate of 10 mV/s. Supporting electrolyte: tetrabutylammonium perchlorate 5 mM; working electrode: ITO; counter electrode: Pt wire; reference electrode: Ag/AgCl (3M KCl). Arrows shows the direction of change of the differential spectrum as the potential increases.

Figure 3. Differential spectra of DTFBut in AcN obtained at different time intervals after addition of the metal precursor. Top: HAuCl_4 (0.1 mM) added to DTFBut (0.04 mM) at 48 °C; bottom: PdCl_2 (0.26 mM) added to DTFBut (0.026 mM) at 27 °C.

Table 1. Absorbance at the maximum of the LSPR band for the synthesis of oxidized DTF-AuNPs using different DTF 2 derivatives as reducing agents in AcN at 48 °C.

Entry	DTF 2	Reaction time (h)	Abs @ 585 nm
i	DTFBut	2.5	0.345
ii	DTFDod	2.5	0.368
iii	DTFCIPh	2.5	0.135
iv	CrDTFDod	2.5	0.262
v	WDTFClPh	24	0.141

As mentioned, **DTF 2** can also reduce other metal cations, such as Ag(I) and Pd(II) (Figure 1). Due to the ease oxidation of metallic silver, the obtained AgNPs (see TEM images in the SI) are

not stable and they crash out of the solution after one day. In the case of Pd(II) reduction, the formation of NPs can be hard to determine using UV-vis spectroscopy. Although published discrete dipole approximation (DDA) based calculations indicates that PdNPs of around 100 nm should exhibit two thick extinction bands, one of them due to dipolar mode at 500 nm and the other at 320 nm corresponding to the quadrupolar mode,^{23,24} the optical properties of the DTF derivatives used here can make the detection of the PdNPs LSPR very difficult. As discussed above, the LSPR expected for these NPs seems to be hiding by the 500 nm band corresponding to the oxidized DTFBu (Figure 3 bottom). As can be seen in figure 4, two bands can be distinguished when the Pd/DTFBu ratio is lower than 3, one at 454 nm corresponding to the remained DTFBu, and the other at 504 nm attributed to the oxidized DTFBu derivative. In order to confirm the Pd NPs formation, TEM images were obtained for different concentrations of PdCl₂ (Figure 5). Different sizes of Pd NPs were found for each solution. When Pd concentration is high enough ($[Pd(II)]/[DTF] > 2$) spheroidal NPs with two populations of 5 and 17 nm diameters were found for $[Pd(II)]/[DTF]=3$, and two of 35 and 126 nm for $[Pd(II)]/[DTF]=5.4$. Further investigations using metal ions such as Ni(II), Cu(II), Cd(II) and Hg(II) were performed, but the changes in the UV-Vis region were negligible.

In summary, we probed that novel oxidized DTF-protected MNPs (M = Ag, Pd, Au) can be prepared via reduction of the metal ions by a DTF compound having strong electron-donating properties. The electron transfer from the DTFBu to the metal ions resulted in the formation of metal nanoparticles. Then, the oxidized DTF might possess a delocalized positive charge and provide both steric and electrostatic stabilization,⁷ protecting the metals as stable colloidal forms. The resulting AcN solutions of the protected Au and Pd NPs were stable without any precipitation for more than six months at room temperature under air. We demonstrated that the

Figure 4. UV-Vis spectra of DTFBuT after addition of different concentrations of PdCl_2 at 27 °C. Pd/DTFBuT: 0.5, 0.9, 1.3, 1.6, 2.1, 3.0, and 5.4 [DTFBuT] = 6 μM .

extended π -delocalization of polydithiafulvene is not necessary to get good results in terms of NPs synthesis. One DTF moiety is enough to lead a well stable colloid NP suspension. Finally, the fact that no evidence of TTF^{2+} formation has been found shows the effect of thiocarbonyl group on the stability of DTF_{ox} species.

Taking into account the interesting properties of DTFs in terms of their ability to generate and stabilize nanostructures as well as the strong tendency to transfer electrons generating stable species, we are conducting studies to establish the influence of DTFs on the stability and optical properties of different semiconducting nanoparticles (quantum dots); the efficient withdrawal of holes, from these nanoparticles, using stable electron donors like DTFs will have relevance towards the development of materials with potential application in optoelectronic devices with improved efficiency..

Figure 5. TEM images of the solutions DTF-PdNPs. Pd/DTFBut: 1.3, 3.0, and 5.4 [DTFBut] = 6 μ M. Scale bar: top and middle: 200 nm, bottom: 2 μ m (50 nm inset).

ASSOCIATED CONTENT

Supporting Information. UV-Vis spectra of DTF 2 derivatives studied, cyclic voltammograms of DTFBu and transmission electron microscopy images of DTF-AuNP and DTF-AgNP.

AUTHOR INFORMATION

Corresponding Author

*A.M.G. ale@fcq.unc.edu.ar

Present Addresses

†Department of Chemistry and Biomolecular Sciences and Centre for Advanced Materials Research (CAMaR), University of Ottawa, 10 Marie Curie, Ottawa, Ontario K1N 6N5, Canada.

Author Contributions

All authors have given approval to the final version of the manuscript.

ACKNOWLEDGMENT

This research was supported in part by the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET); Agencia Nacional de Promoción Científica y Técnica ANPCyT, FONCYT, PME 2006-1544 and SECyT-Universidad Nacional de Córdoba, Argentina.

A.E.L. and M.F.T. were grateful recipients of a fellowship from CONICET.

REFERENCES

- [1] P. Frere, P. J. Skabara, Salts of extended tetrathiafulvalene analogues: relationships between molecular structure, electrochemical properties and solid state organisation, *Chem. Soc. Rev.* 34 (2005) 69-98.
- [2] H. Gopee, B. M. Petersen, A. D. Bond, J. O. Jeppesen, A bromine catalysed dimerisation of α,α' -dihalomonopyrrolo-TTF. *Chem. Commun.* 40 (2007) 4110-4112.
- [3] M. B. Nielsen, J. C. Petersen, N. Thorup, M. Jessing,; A. S. Andersson, A. S. Jepsen, J. P. Gisselbrecht, C. Boudon, M. Gross, Acetylenic dithiafulvene derived donor- π -acceptor dyads: synthesis, electrochemistry and non-linear optical properties, *J. Mater. Chem.* 15 (2005) 2599-2605.
- [4] J. K. Sorensen, M. Vestergaard, A. Kadziola, K. Kilsa, M. B. Nielsen, Synthesis of oligo(phenyleneethynylene)-tetrathiafulvalene cruciforms for molecular electronics, *Org. Lett.* 8 (2006) 1173-1176.
- [5] Greatly Enhanced Second-Order Nonlinear Optical Susceptibilities in Donor-Acceptor Organic Molecules, H. E. Katz, K. D. Singer, J. E. Sohn, C. W. Dirk, L. A. King, H. M. Gordon *J. Am. Chem. Soc.* 109 (1987) 6561-6563.
- [6] M. B. Nielsen, Molecular Scaffolding with Tetrathiafulvalene-Design and Synthesis of New Molecules for Molecular Electronics, *Phosphorus Sulfur* 186 (2011) 1055-1073.
- [7] Y. Zhou, H. Itoh, T. Uemura, K. Naka, Y. Chujo, Synthesis of novel stable nanometer-sized metal (M = Pd, Au, Pt) colloids protected by a π -conjugated polymer, *Langmuir* 18 (2002) 277-283.
- [8] Y. Zhou, H. Itoh, T. Uemura, K. Naka, Y. Chujo, Preparation of π -conjugated polymer-protected gold nanoparticles in stable colloidal form. *Chem. Commun.* (2001) 613-614.

- [9] M. A. Petersen, L. J. Zhu, S. H. Jensen, A. S. Andersson, A. Kadziola, K. Kilsa, M. B. Nielsen, Photoswitches containing a dithiafulvene electron donor, *Adv. Funct. Mater.* 17 (2007) 797-804.
- [10] A. E. Lanterna, E. A. Coronado, A. M. Granados, Synthesis of gold nanoparticles using electron-donating dithiafulvene units. *Tetrahedron Lett.*, 56 (2015) 4871-4876.
- [11] H. Adows, Y. M. Zhao, Redox interactions of Au(III) with carboxylated dithiafulvenes and tetrathiafulvalene analogues in polar organic media, *Chem. Commun.* (2016) 13101-13104.
- [12] A. M. Granados, A. M. Fracaroli, R. H. de Rossi, P. Fuertes, T. Torroba, Alkynyl Fischer carbene complex as a traceless directing group for the regioselective cycloaddition of dithiolethiones to arylacetylene: synthesis of E-dithiafulvene thione and dithioesters, *Chem. Commun.* (2008) 483-485.
- [13] Spontaneous Formation of Nanochains from Triangular Silver Nanoplates J. Zhao, M. Yang *Cryst. Res. Technol.* 53 (2018) 1800095.
- [14] Halide-Directed Synthesis of Square Prismatic Ag Nanocrystals by the Polyol Method S-W. Hsu, A. R. Tao *Chem. Mater.* 30 (2018) 4617–4623.
- [15] S. Kumar, K. S. Gandhi, R. Kumar, Modeling of formation of gold nanoparticles by citrate method, *Ind. Eng. Chem. Res.* 46 (2007) 3128-3136.
- [16] V. Nevalainen, P. Vainiotalo, Electron-Impact Induced Fragmentation of Dihydro-1,4-Dithiines - 2,3-Substituted 5,6-Dihydro-1,4-Dithiines, *Org. Mass Spectrom.* 22 (1987) 586-591.
- [17] A. M. Mak, R. Steudel, M. W. Wong, Homolytic S-S bond dissociation of 11 bis(thiocarbonyl)disulfides R-C(S)-S-S-C(S)R and prediction of a novel rubber vulcanization accelerator, *Chem-Asian J.* 3 (2008) 1026-1034.

- [18] Ligand and Solvation Effects on the Structural and Electronic Properties of Small Gold Clusters, F. Dufour, B. Fresch, O. Durupthy, C. Chaneac, F. Remacle, J. Phys. Chem. C 118 (2014) 4362–4376.
- [19] Nanoarray-Surfaces by Reconstitution of the Porin MspA into Stabilized Long-Chain-Lipid Monolayers at a Gold-Surface, M. Węrnier, S. Niebler, E. Gogritchiani, N. Egner, A. M. Braun, M. Niederweis, S. H. Bossmann, Electroanalysis 18 (2006) 1859 – 1870.
- [20] Effect of Ag containing (nano)particles on reactive adsorption of mustard gas surrogate on iron oxyhydroxide/graphite oxide composites under visible light irradiation, J. A. Arcibar-Orozco, D. A. Giannakoudakis, T. J. Bandosz, Chemical Engineering Journal 303 (2016) 123–136.
- [21] Novel radical tandem 1,6-enynes thioacylation/cyclization: Au-Pd nanoparticles catalysis versus thermal activation as a function of the substrate specificity, I. Notar Francesco, J. Giauffret, F. Fontaine-Vive, J. K. Edwards, C. J. Kiely, G. J. Hutchings, S. Antoniotti, Tetrahedron 70 (2014) 9635-9643.
- [22] M. C. Bertolino, A. M. Granados, Synthesis in situ of gold nanoparticles by a dialkynyl Fischer carbene complex anchored to glass surfaces, Appl. Surf. Sci. 383 (2016) 375-381.
- [23] K. M. Mayer, J. H. Hafner, Localized Surface Plasmon Resonance Sensors, Chem. Rev. 111 (2011) 3828-3857.
- [24] Y. J. Xiong, J. M. McLellan, Chen, J. Y.; Yin, Y. D.; Li, Z. Y.; Xia, Y. N. Kinetically controlled synthesis of triangular and hexagonal nanoplates of palladium and their SPR/SERS properties, J. Am. Chem. Soc. 127 (2005) 17118-17127.