COMMUNICATIONS

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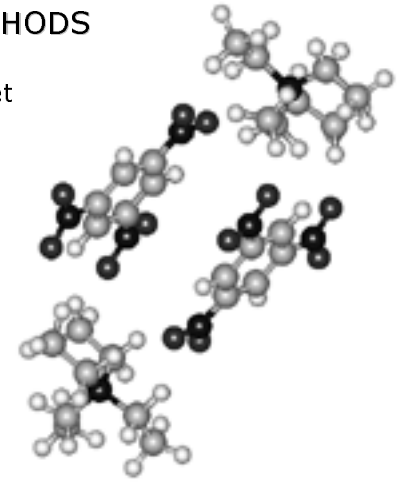

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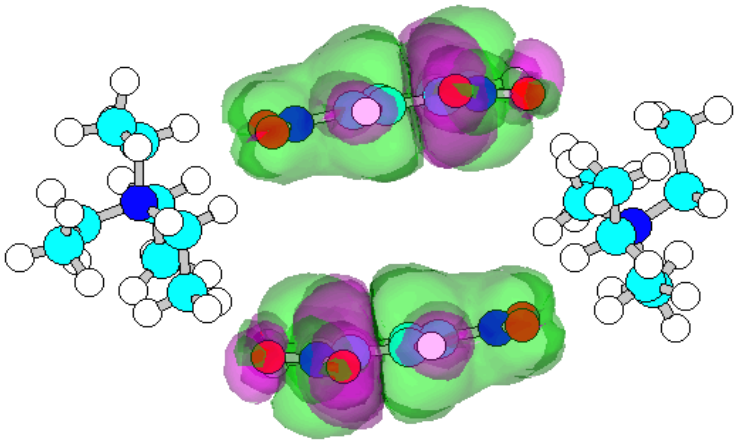
Supporting Information Available: Cyclic voltammograms and determination of the rate constant, k_3, by spectroelectrochemistry (4 pages).

Digital Abstract



Molecular Modeling (AMI, Hyperchem©)

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Addition compounds, resulting from coupling between two radical-anions [1-5] or two radical-cations [6,7] are common outcoming in electrochemical reactions. The final product is a doubly charged dimer (σ-complex). It is also well known that the S_NAr mechanism involves addition compounds (σ-complexes) as intermediates. [8-12] In this mechanism, the existence of precursor-complexes (also called π-complexes) formed prior to the σ-complexes has been shown by UV and NMR spectroscopies. [13-17] Terrier [18] achieved the first isolation of a π-complex (precursor-complex), in a σ-complex formation process between 1,3,5-trinitrobenzene and indole-3-carboxilate ion.

In this report, we present evidence of the isolation and characterization, for the first time [19] to our knowledge, of the biradical *bis*(1,3,5-trinitrobenzene) dianion, a precursor-complex formed in the electrochemical reduction of 1,3,5-trinitrobenzene **1**, prior to the appearance of the corresponding σ^H-complex.

The electrochemical behavior of 1,3,5-trinitrobenzene **1** is definitively different from that of nitrobenzene or dinitrobenzenes. [20] In DMF,0.1M nBu_4NBF_4 (10ºC) at low scan rates, one chemically irreversible reduction wave appears at –0.56V. [21] This wave becomes reversible at scan rates higher than 400 $V.s^{-1}$ (Eº = -0.58V). Analysis of the peak potential, at low and high scan rates, indicates a one-electron process. The shape of the voltammograms (peak width) suggests a fast electron transfer with kinetic control by chemical reaction. [22] In the 2-10mM range, the peak potential is concentration-dependent (22.5 mV by unit log concentration) and the variation of peak potential with the scan rate is 23 mV by unit log scan rate. We can therefore conclude that the initially produced radical anion reacts following a slow second order reaction pathway, the EC_2 mechanism, [22] forming a dimeric structure. The estimated value for the dimerisation rate constant is $3.00\pm0.05 \times 10^5$ $l.mol^{-1}.s^{-1}$. The product of this reaction, **2**, is responsible for an oxidation wave that appears at 0.27 V. [23] After 10 minutes, new oxidation peaks at 0.59 and 1.00V appear and the height of the 0.27 V peak has been reduced to around in 50% of the initial value. After about one hour, the peak at 0.27 V is no longer visible, and only the peaks at 0.59 and 1.00 V remain. These new peaks are assigned to a new product **3** (Scheme 1).

$$\mathbf{1} + 1\,e^- \rightleftharpoons \mathbf{1}^{-\bullet} \qquad E^o = -0.58\ V$$

$$2\ \mathbf{1}^{-\bullet} \xrightarrow{k_2} \mathbf{2} \qquad k_2 = 3 \cdot 10^5\ mol \cdot l \cdot s^{-1}$$

$$\mathbf{2} \xrightarrow{k_3} \mathbf{3} \qquad k_3 = 1.2 \cdot 10^{-3}\ s^{-1} \quad [29]$$

Scheme 1

It is possible to isolate product **2** as stable paramagnetic crystalline pure solid. A potential controlled electrolysis at -0.60 V *vs*. SCE of **1** (20 mM, in ACN, , using 0.1 M of $TEABF_4$ as supporting electrolyte under **argon** atmosphere) give rises quantitatively **2**, on a graphite working electrode after passage of 1F . This black solid is isolated as tetraethylammonium salt.

The product **2,** formed during the electrolysis process, was self-assembled on the Carbon-Graphite electrode surface. This product **2** grows on the surface electrode following a needle crystalline structure (figure 1).

This paramagnetic solid **2** has been characterized as follows. Elemental analysis for **2** was carried out. Calculated for a dimeric structure ($C_{28}H_{46}N_8O_{12}$): 16.37% N, 48.98% C, 6.71% H. Found: 15.94% N, 48.60% C, 6.72% H. The UV-VIS spectrum contains new bands of low intensity at 425 and 498 nm not present in the spectrum of **1** (a single band at 268

nm). A biradical character has been demonstrated by ESR spectroscopy. The ESR spectrum, for the solution of **2** in DMF/N_2, shows 13 lines corresponding to a triplet biradical with $J<<A_o$ (a_N=2.08G and a_H=4.16G) [24] (Figure 2). In the case of ^{1}HNMR, a substantial shift ($\Delta\delta$=0.76 ppm) to high field (when compared with product **1**) without broadening of the peaks, was observed[25] (Scheme 2, Table 1). In conclusion, **2** can be formulated as the tetraethylammonium salt of biradical *bis*-(1,3,5-trinitrobenzene) dianion .

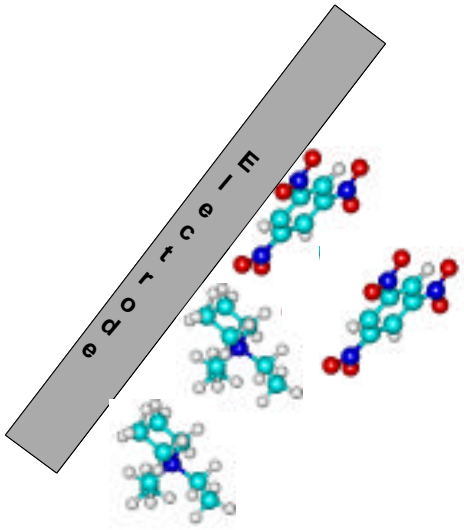
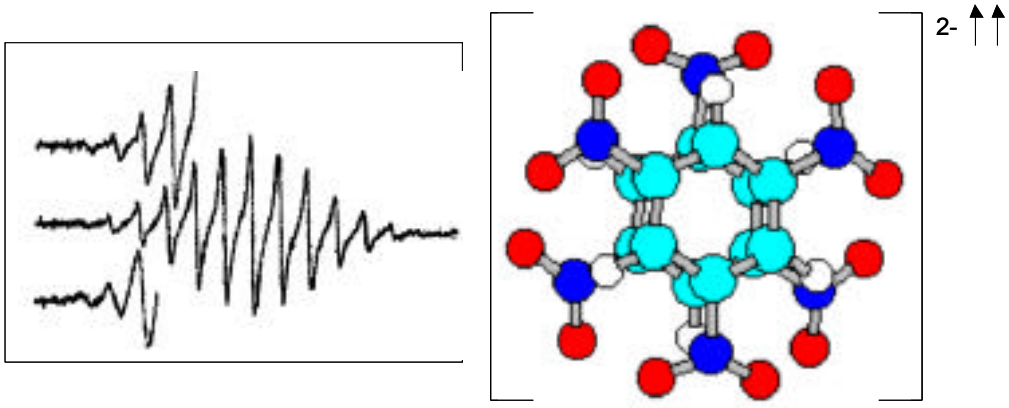


Figure 1. Image of the electrode surface during the electrolysis process



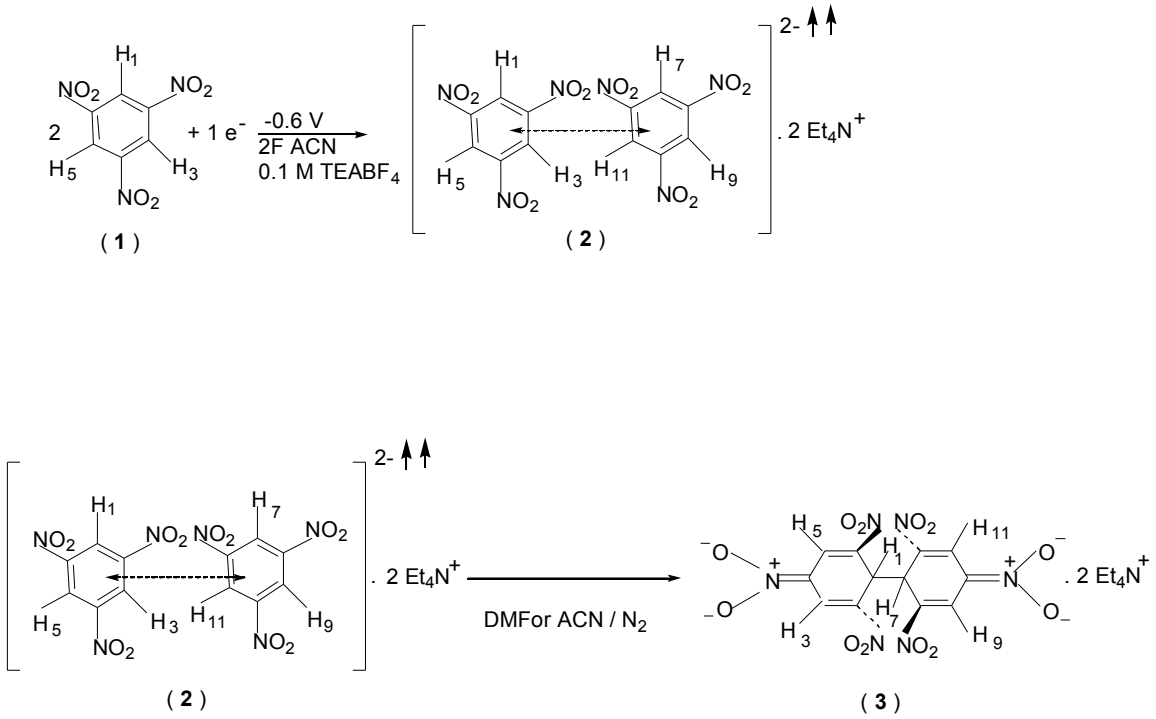
Compound 2

(S=1 with $J<<A_0$)

a_N= 2.08 G
a_H= 4.16 G

13 lines
(1:3:9:16:27:33:38:33:27:16:9:3:1)

Figure 2. EPR analysis**.** Experimental conditions: Varian E12 spectrometer with 100 kHz field modulation. Gain= 1.6 .10^3, SR= 400; MA= 0.5 G; ST= 8 min; Microwave Power= 20 mW.



Scheme 2

Table 1. NMR parameters for the **1**, **2** and **3**

Compound	H1	H3	H5	H7	H9	H11
1	9.22	9.22	9.22	-	-	-
2	8.44/*8.46*[a]	8.44/*8.46*[a]	8.44/*8.46*[a]	8.44/*8.46*[a]	8.44/*8.46*[a]	8.44/*8.46*[a]
3	5.53/*5.84*[a]	8.15/*8.22*[a]	8.15/*8.22*[a]	5.53/*5.84*[a]	8.15/*8.22*[a]	8.15/*8.22*[a]

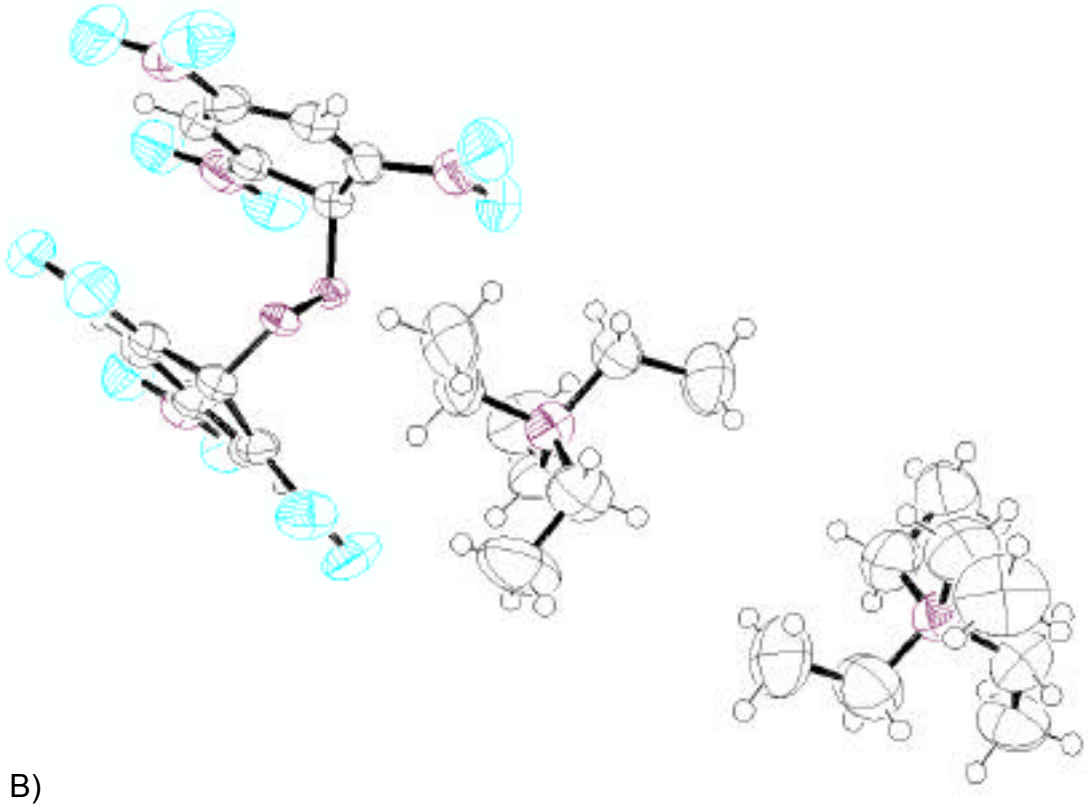
Solvent: (CD_3CN); internal reference Me_4Si. [a] *Solvent: (N,N-Dimethylformamide-d_7);* internal reference Me_4Si. ^{13}C NMR of **2** in N,N-Dimethylformamide-d_7 : $C_{1,3,5,7,9,11}$, 128.86 ; internal reference Me_4Si

X-Ray analysis of self–assembled samples synthesized under **argon** atmosphere in order to characterized **2,** was carried out. The resolution of the cell parameters was achieved, but unfortunately the small size of the single crystal and its shape, did not allow us to resolve structure.

By theoretical modeling, the distance between the two aromatic rings in compound **2** can be calculated. Thus, 3 Å is the minimum distance between the two rings without collapsing into compound **3**. Therefore, the insertion of a molecule of appropriate size, between the two rings, would stabilize the compound, allowing the determination of its X-ray structure. Indeed, a sample of solid **2**, self-assembled on carbon-graphite electrode surface under **argon** was kept under **nitrogen**, before to perform the X-ray analysis. In this way, resolution of the X-ray structure was possible and the result is depicted in figure 3. The X-ray structure shows the insertion of a molecule of nitrogen

between the two aromatic rings, and this is a very strong support for the assignment of **2** to the tetraethylammonium salt of **BIRADICAL BIS (1,3,5-TRINITROBENZENE)DIANION**.

A)



B)

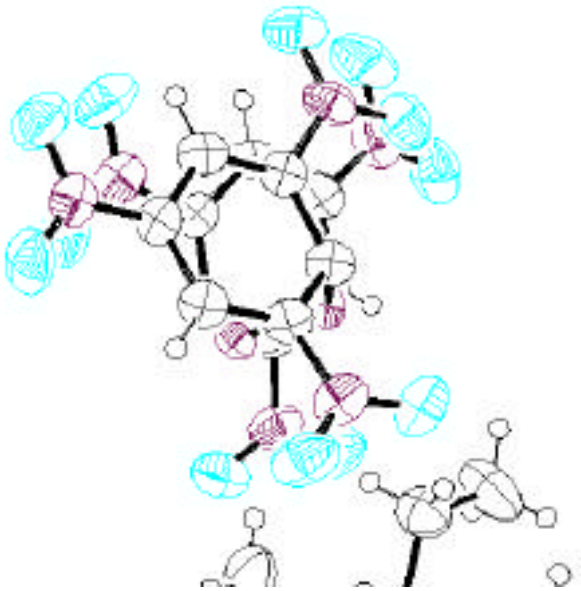


Figure 3. X-Ray Structure of **2** related compound a) and b) two different perspectives

When **2** is kept in dimethylformamide solutions under nitrogen, it gives rise to the dianionic σ-complex **3** in about one hour (Scheme 2). This dark-brown solid **3** was isolated and characterized as previously described. [26] Elemental analysis of **3** was carried out. The UV-VIS spectrum contains two bands at 268 and 517 nm. The ^{1}H-NMR spectrum showed two singlet peaks at 8.22 ppm and 5.84 ppm, corresponding to the two different kinds of protons present in this dianionic σ-complex **3** (Scheme 2, Table 1). Product **3** give no signal in the ESR spectrum. Hence, **3** can be formulated as the tetraethylammonium salt of 1,1'-dihydride-bis(2,4,6-trinitrociclohexadienyl) dianion.

Strong support to characterization of **2** as a precursor-complex different from $\mathbf{1}^{\cdot -}$, and different from the σ-complex **3** was achieved by cyclic voltammetry and spectroelectrochemical experiments.

In cyclic voltammetry experiments, a fresh sample of **3,** in DMF,0.1M nBu_4NBF_4 (10ºC), shows two consecutive oxidation peaks at 0.59 and 1.00 V potentials which agrees with what is known for oxidation of σ-complexes. [27] On the other hand a fresh sample of **2,** in DMF,0.1M nBu_4NBF_4 (10ºC), shows one oxidation peak at 0.27 V, which not does correspond to a σ-complex, but rather to a more easily oxidizable product, such as a precursor-complex. Moreover, after exhaustive electrolysis of **2** (2F, at 0.4V) **1** is obtained (100% yield), while following exhaustive electrolysis of **3** (3F at 1.3V) **1** and 2,2',4,4',6,6'-hexanitrobiphenyle (90:10), are obtained.
Spectroelectrochemical experiments [28] allow us to detect the intermediates formed during the electrochemical experiments. All experiments were carried out in ACN, 0.1M nBu_4NBF_4, Figure 4 shows the UV/vis spectra during a cyclic voltammogram. It was possible to clearly detect the two first intermediates $\mathbf{1}^{\cdot -}$ and **2**. The $\mathbf{1}^{\cdot -}$ appears in the initial spectra, at 475 nm, and rapidly evolves to the precursor-complex **2** (425 and 492 nm) as a result of a dimerisation process (Scheme 1 and 2). A potential step experiment in the LIGA cell [28] facilitates the measuring of the disappearance of **2**, following the absorption wave at 425 nm. The appearance of **3** is linked with the disappearance of the **2**. We have established the value of the rate constant for the reaction between **2** and **3** as 0.12 s^{-1}. [29] In order to favor the presence of the final product **3**, we carried out an electrolysis on a Pt minigrid surface at –1.00V. Figure 5 shows the evolution of UV/Vis spectra of the compounds present in the mixture. The disappearance of **2** (425nm,498nm) and the appearance of **3** (517 nm) is evidently connected (figure 3.Supporting Material).

In conclusion, product **2**, the tetraethylammonium salt of biradical bis (1,3,5-trinitrobenzene) dianion, [30] has been isolated for the first time and characterized as a compound different to radical anion of 1,3,5-trinitrobenzene, and that evolves to **3**, the tetraethyl-ammonium salt of 1,1'-dihydride-bis(2,4,6-trinitrociclohexadienyl) dianion, in the electrochemical reduction of 1,3,5-trinitrobenzene**.**

Work currently in progress shows that the same behavior may be observed for other trinitrobenzene derivatives.

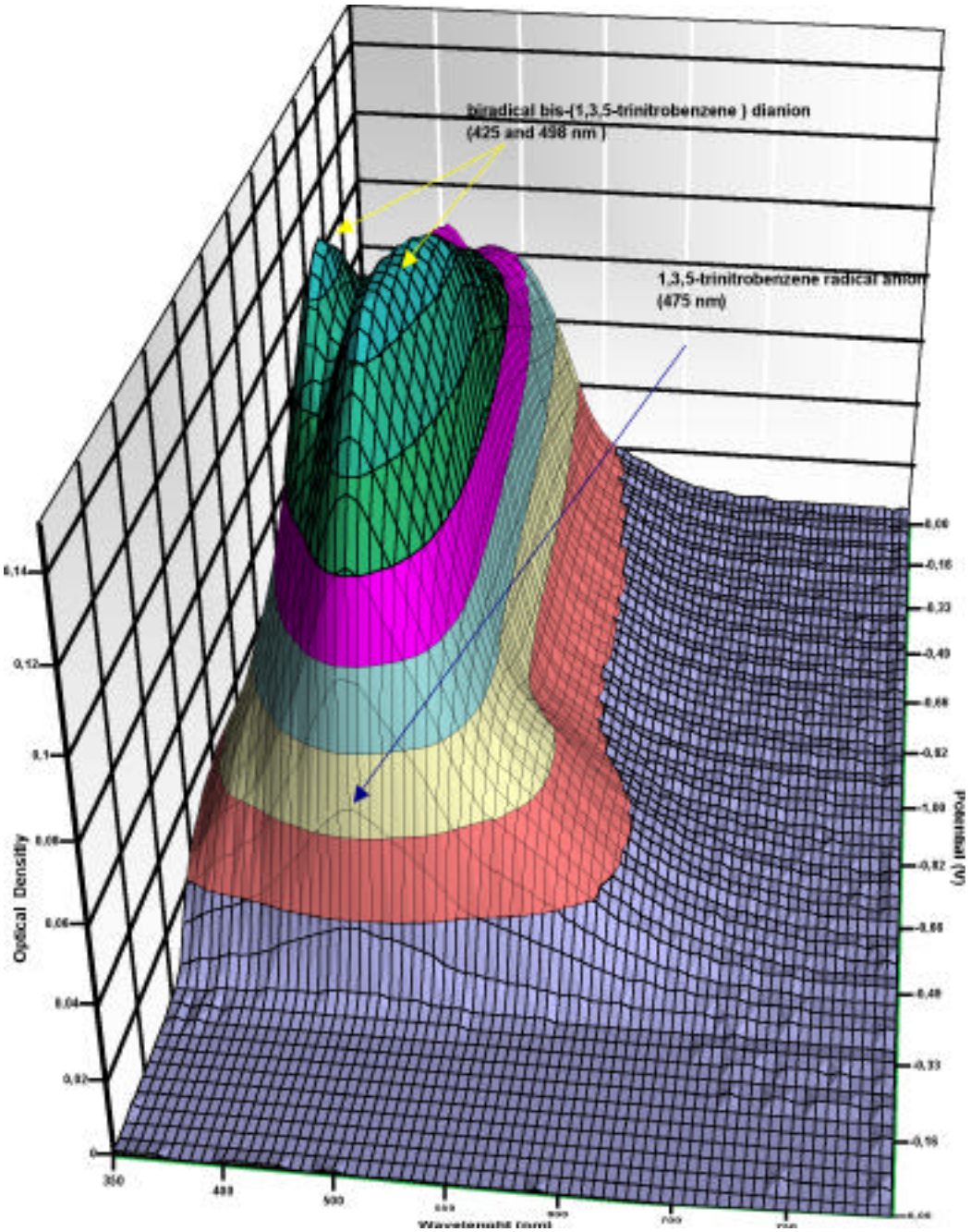


Figure 4. In situ UV/Vis spectra during cyclic voltammogram of 5.10 $^{-4}$ M 1,3,5-trinitrobenzene (**1**) in 0.1 m $TBABF_4$ (acetonitrile) with scan rate *v*= 0.1 $V.s^{-1}$ an initial potential E_{in}= 0.00V and switching potential E_{sw}=-1.00 V in the UV/Vis spectroelectrochemical LIGA cell with a honey combed Au-LIGA structure parameters: S_w=15 µm; S_b= 20 µm; S_h= 110 µm; d=2.2 mm

A_{LIGA}= 26.7 mm^2; (100%); $A_{honeycomb}$= 20.5 mm^2; (77%);

A_{stick}= 6.2 mm^2; A_{disk}=7.6mm^2; (28%).

(A disk is the top side area of the LIGA-structure including the opening of the honeycombs) and a capillary slilt of about 50 µm (between the LIGA structure and the quartz rods) [30a]