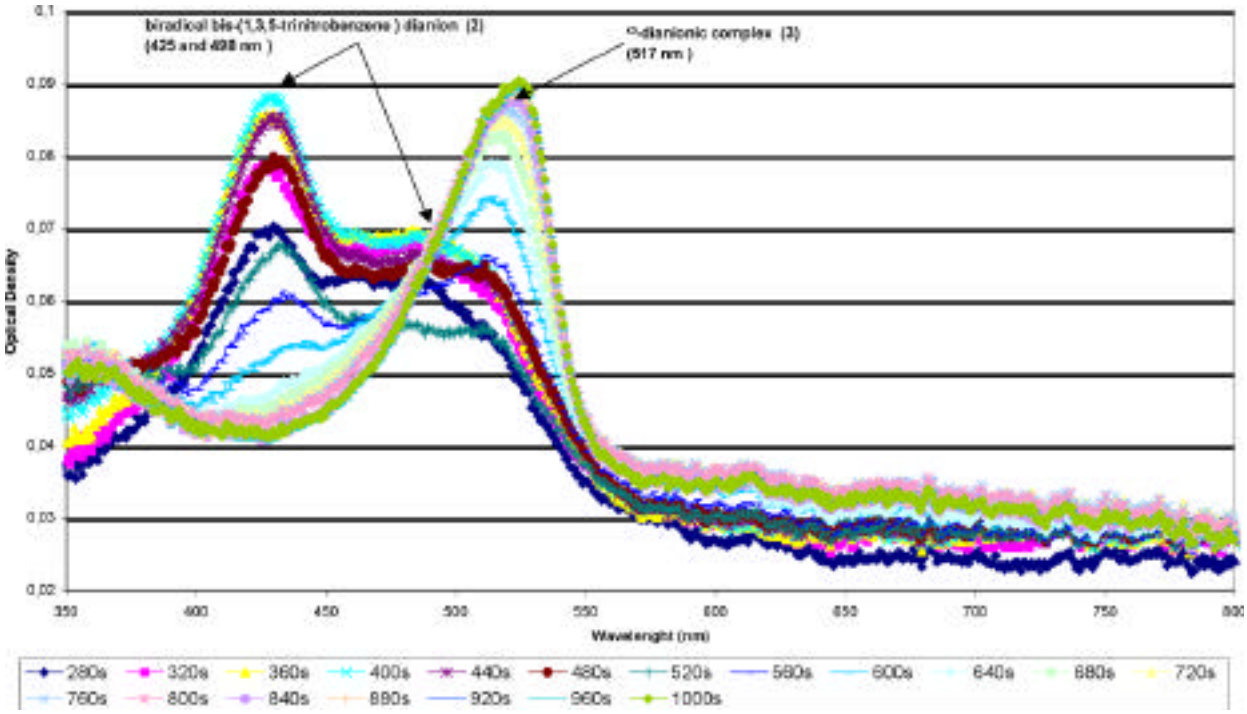

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[23]This oxidation wave appears only after a first reduction scan.
[24] a)The ESR spectrum reported by Marshall [24b] for stable radical anion of **1** exactly corresponds to the ESR if product **2** described here. These authors analyzed the spectrum and assigned the hfcs as corresponding to a doubled radical anion, with three equivalent nitrogen and three equivalent hydrogen atoms. Glarum and Marshall, assumed that the similitude of trinitrobenzene with other nitrocompounds erroneously presupposed the existence of one stable radical anion for produc **1,** b)S.H.Glarum and J.H.Marshall; *J.Chem.Phys*. **1964**, *41*, 2182.
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[28]a) A.Neudeck and L.Dunsch;*J.Electroanal.Chem.***1995**,*386*,135, b)A.,Neudeck and L.Kress; *J.Electroanal.Chem.***1997**,*437*,141
[29] In DMF (Scheme1), $k_3 = 1.2x10^{-3}s^{-1}$
[30]a) Molecular Modeling(AMI, Hyperchemã)show that the structure proposed for product 2 (Scheme 2, Figure 6) is a minimum in the potential energy surface[30 b]. B)P.Calle and C.Sieiro, unpublished results.

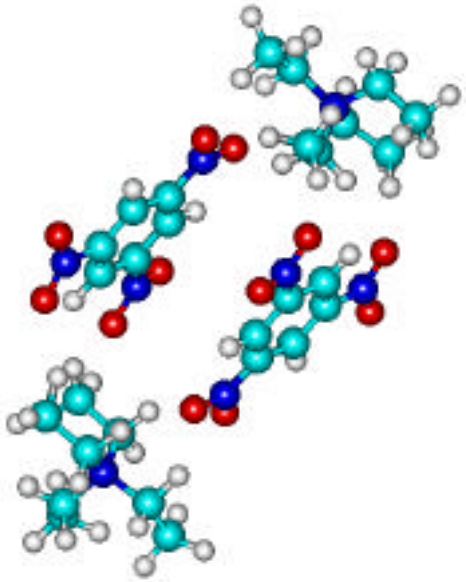

Figure 6. Molecular Modeling (AMI, Hyperchem©) for product **2**.

[**] We greatefully acknowledge financial support from the DGI and DGESIC through projects BQU2000-0336 and PB.98-109 and from the "Generalitat de Catalunya" through project 1999SGR00090 and from CAM through project 07N/0007/1999
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SUPPORTING MATERIAL

Figure 1

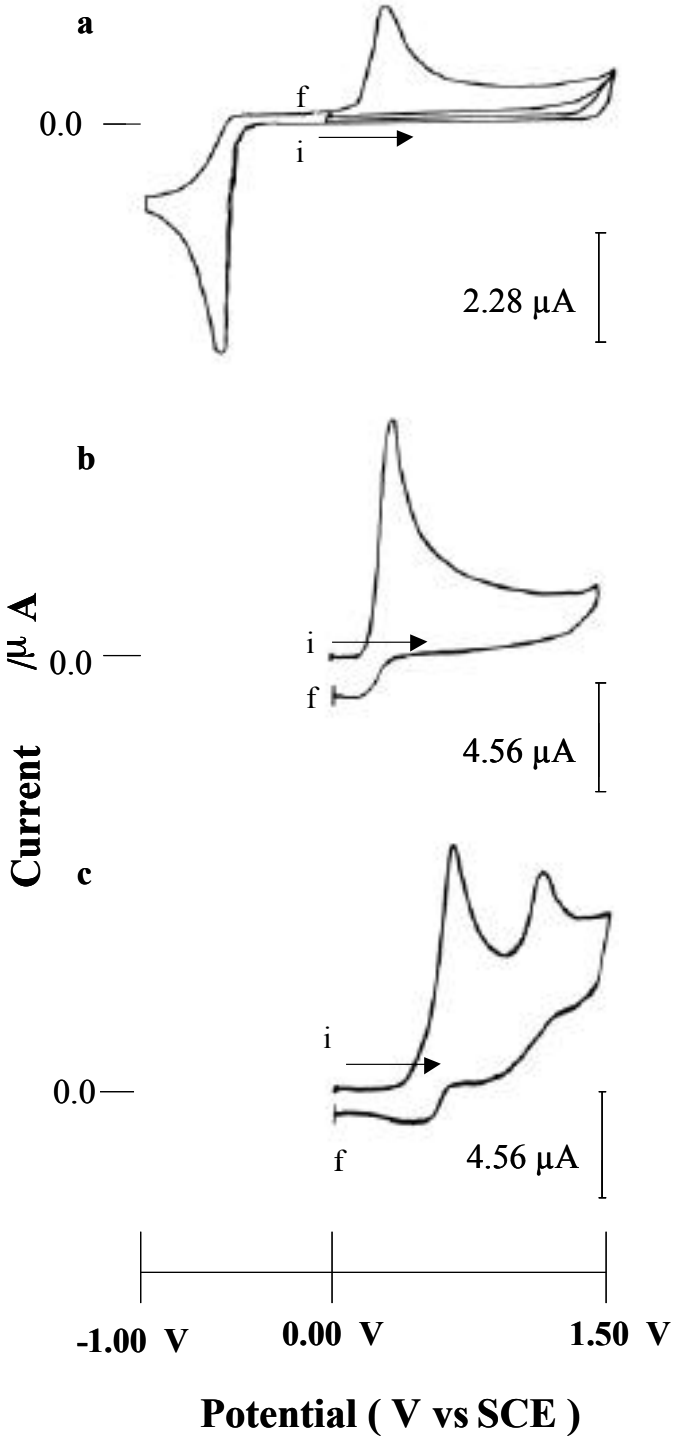

Figure 1. a) Cyclic voltammetry of **1** (6.0 mM) in DMF + 0.1M nBu_4NBF_4 at 10ºC. Scan rate 1.0 V/s, glassy carbon disk electrode (0.05 mm diameter). The scan is in the potential range: 0.00/1.50/-1.00/0.00 V (2cycles) **b)** Cyclic voltammetry of **2** (6.0 mM) in DMF + 0.1M nBu_4NBF_4 at 10ºC. Scan rate 1.0 V/s, glassy carbon disk electrode (0.05 mm diameter). The scan is in the potential range: 0.00/1.50/0.00 V **c)** Cyclic voltammetry of **3** (6.0 mM) in DMF + 0.1M nBu_4NBF_4 at 10ºC. Scan rate 1.0 V/s, glassy carbon disk electrode (0.05 mm diameter). The scan is in the potential range: 0.00/1.50/0.00 V

d

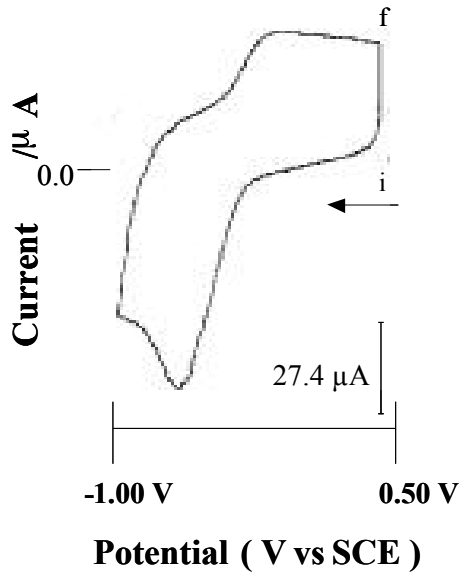

Figure 1d. Cyclic voltammetry of **1** (6.0 mM) in DMF + 0.1M nBu_4NBF_4 at 10ºC. Scan rate 400 V/s, glassy carbon disk electrode (0.05 mm diameter). The scan is in the potential range: 0.50/-1.00/0.50 V

Figure 2

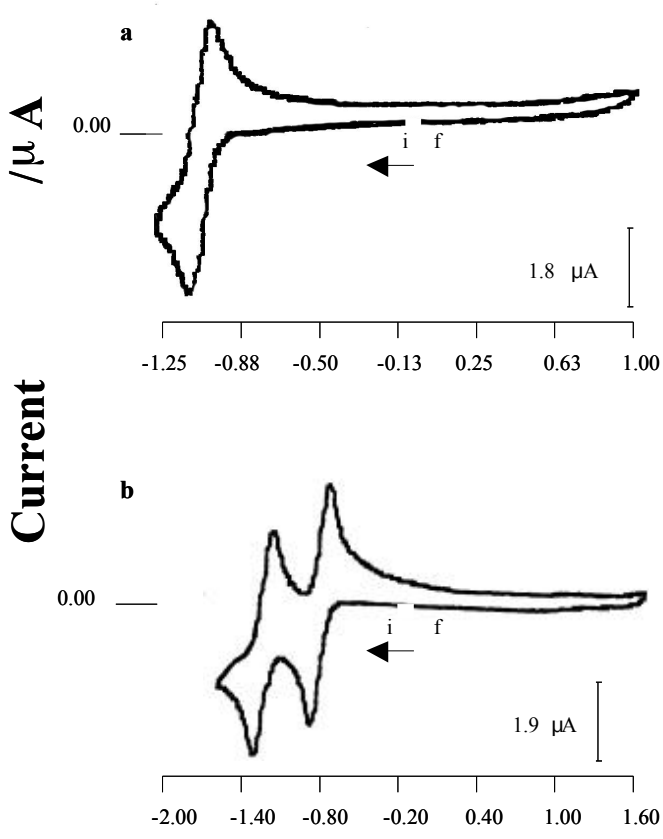

Figure 2. a) Cyclic voltammetry of nitrobenzene (6.0 mM) in DMF + 0.1M nBu_4NBF_4 at 10ºC. Scan rate 1.0 V/s, glassy carbon disk electrode (0.05 mm diameter). The scan is in the potential range: 0.00/-1.25/1.00/0.00 V **b)** Cyclic voltammetry of 1,3-dinitrobenzene (6.0 mM) in DMF + 0.1M nBu_4NBF_4 at 10ºC. Scan rate 1.0 V/s, glassy carbon disk electrode (0.05 mm diameter). The scan is in the potential range: 0.00/-2.00/1.50/0.00 V

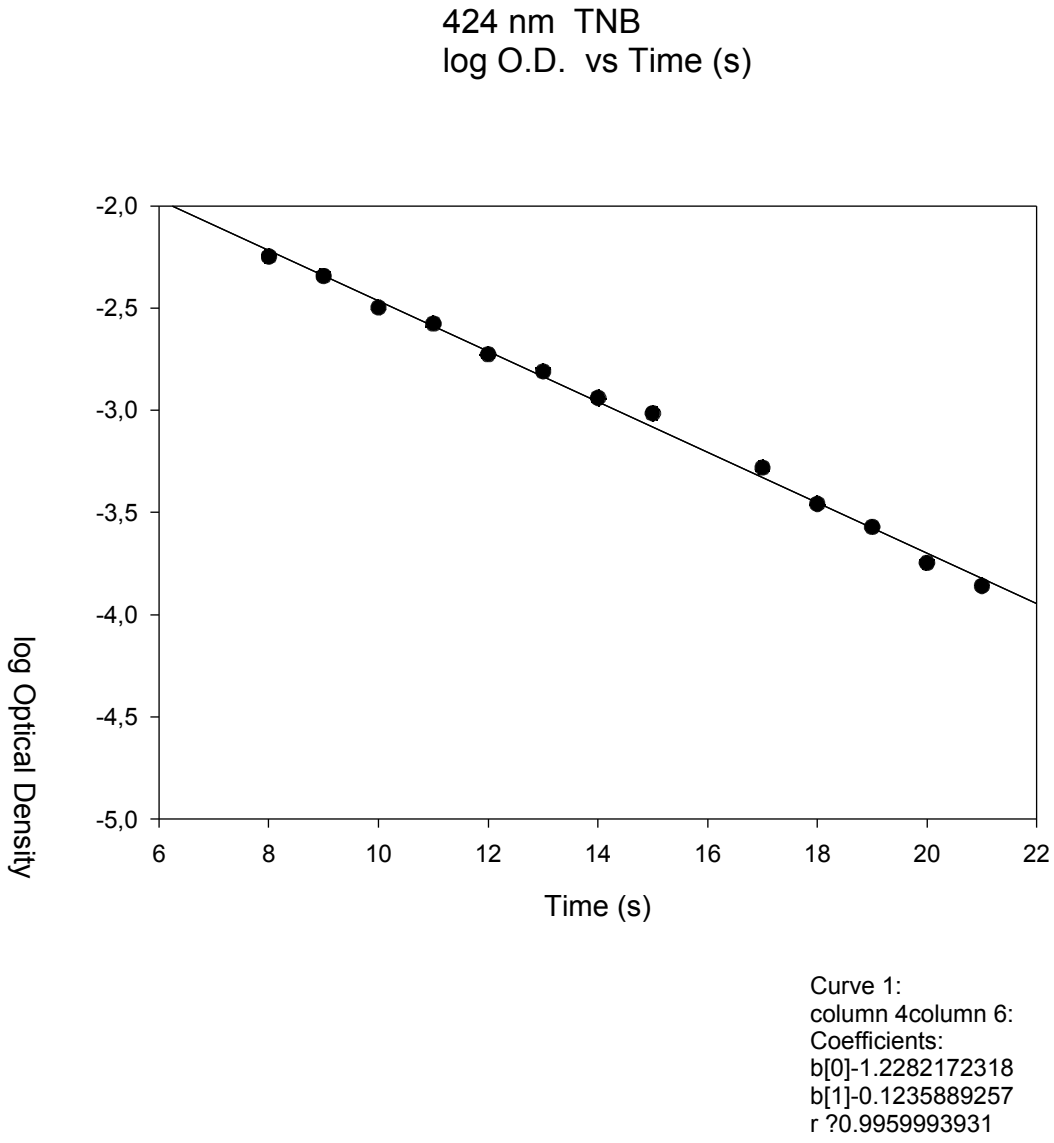

Figure 3. In situ UV/Vis spectra. Curve log Optical Density-time during a potential step experiment (E_1=0.00 V; E_2=-1.00 V; E_3= 0.00 V) of 5.10^{-4} M 1,3,5-trinitrobenzene (**1**) in 0.1 m $TBABF_4$ (acetonitrile) in the UV/Vis LIGA cell [30a,30b].