Electronic Supplementary Material for PCCP

SUPPORTING INFORMATION

Oxygen Carriers Based on Electrochemically Reduced Trinitroarenes

Iluminada Gallardo* and Gonzalo Guirado

[*]Prof. I.Gallardo, Dr. G.Guirado

Departament de Química, Universitat Autònoma de Barcelona

08193-Bellaterra (Barcelona). Spain

Phone: 00 34 9358121 37 ; Fax: 00 34 935812920

e-mail: Iluminada.Gallardo@uab.es

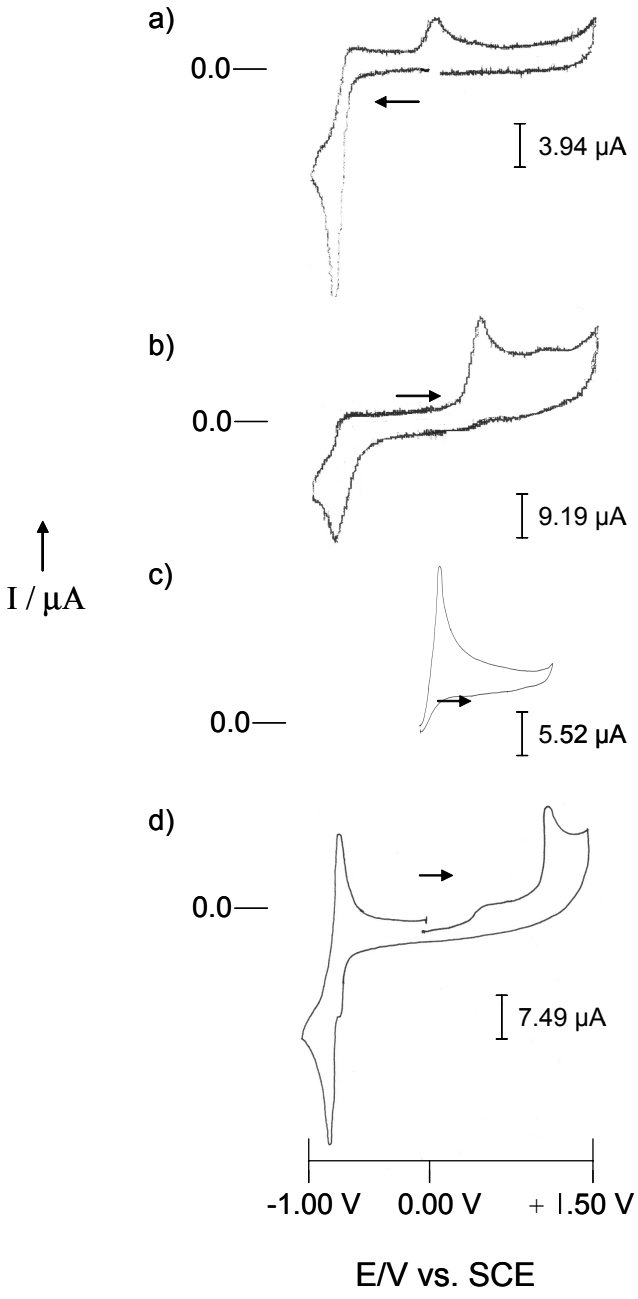


Figure S1. Cyclic voltammetry (CV) 4.0 mM in DMF + 0.1M nBu_4NBF_4 at 10ºC. Scan rate 1.0 V/s, glassy carbon disk electrode (0.05 mm diameter). a) of **TNT** solution *under Ar atmosphere* b) of a **TNT** electrolyzed solution at -0.75 V after 1F *under Ar atmosphere* (σ^H-dimer) c) of a **TNT** solution after the addition of equimolecular amount of **TDAE** (π-dimer, π-$(TNA)^{2-}$ $[TDAE]^{2+}$) under argon atmosphere d) of a $\boldsymbol{\sigma^H_{o\text{-}o}}$**-adduct(TNT)** solution *under atmosphere argon atmosphere* ($\sigma^H_{o\text{-}o}$-adduct, (**TNT**) $[TDAE]^{2+}$, formed by a oxygen purged solution of π-(TNT)$[TDAE]^{2+}$) in the potential range: 0.00/1.50/-1.00/0.00 V.

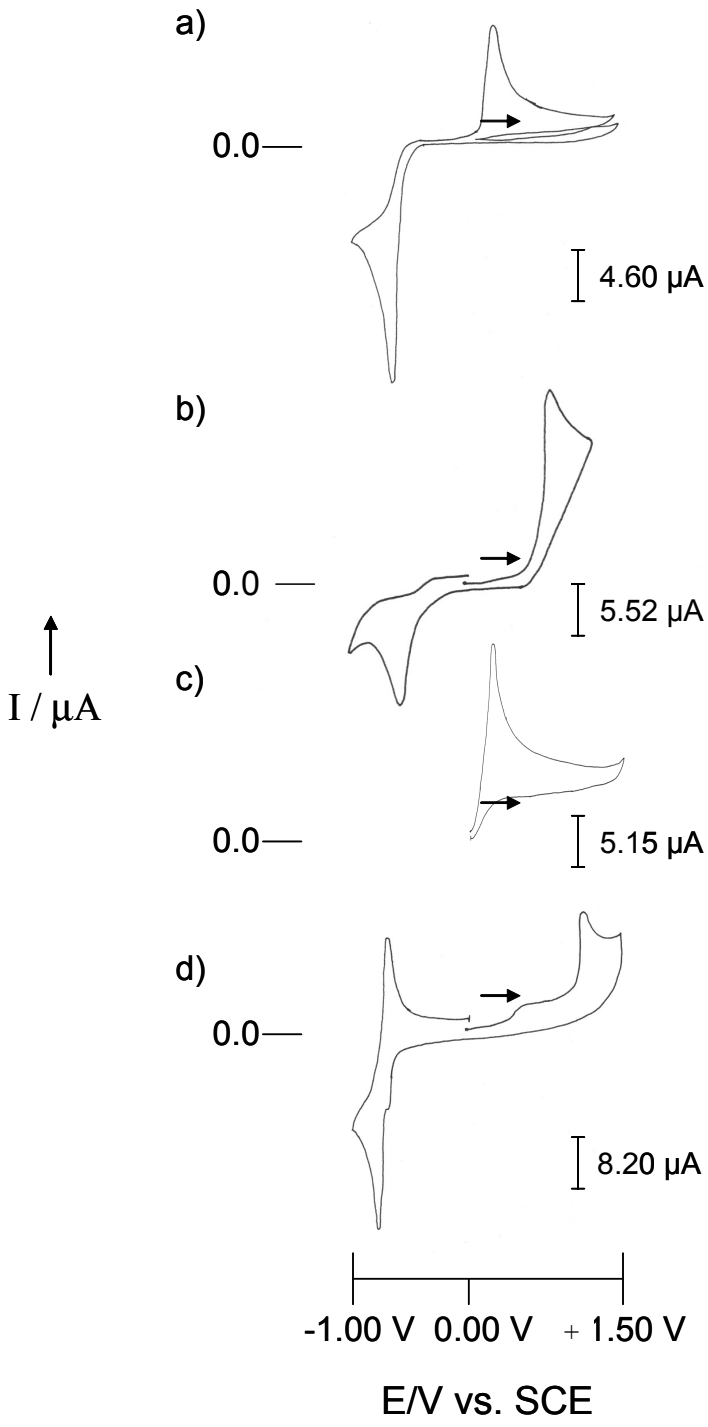


Figure S2. Cyclic voltammetry (CV) 4.0 mM in DMF + 0.1M nBu_4NBF_4 at 10ºC. Scan rate 1.0 V/s, glassy carbon disk electrode (0.05 mm diameter). a) of **TNA** solution *under Ar atmosphere* b) of a **TNA** electrolyzed solution at -0.75 V after 1F *under Ar atmosphere* (σ^H-dimer) c) of a **TNA** solution after the addition of equimolecular amount of **TDAE** (π-dimer, π-$(TNA)^{2-}$ $[TDAE]^{2+}$) *under argon atmosphere* d) of a **$\sigma^H_{o\text{-}o}$-adduct(TNA)** solution under *atmosphere argon atmosphere* ($\sigma^H_{o\text{-}o}$-adduct (**TNA**)$[TDAE]^{2+}$ formed by a oxygen purged solution of π-$(TNA)[TDAE]^{2+}$) in the potential range: 0.00/1.50/-1.00/0.00 V

.

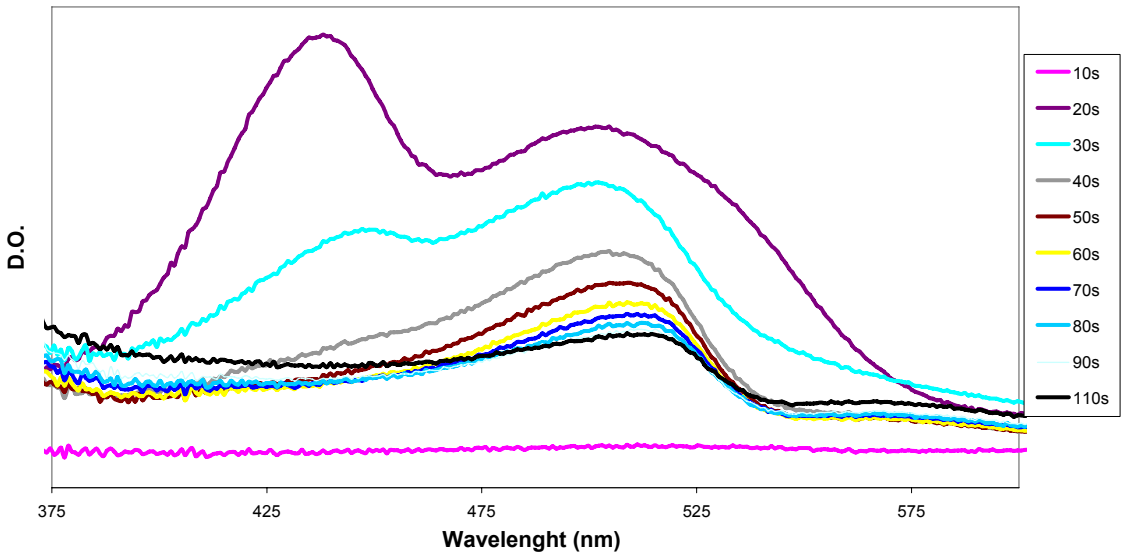


Figure S3. In situ UV/Vis spectra (Optical Density) O.D. vs. time (s) during a potential step experiment (E_1=0.00 V; E_2= -0.90 V; E_3= 0.00 V) of 5.10^{-4} M 2,4,6-trinitrotoluene (**TNT**) in 0.1 M $TBABF_4$ (acetonitrile, ACN) in the UV/Vis LIGA cell.

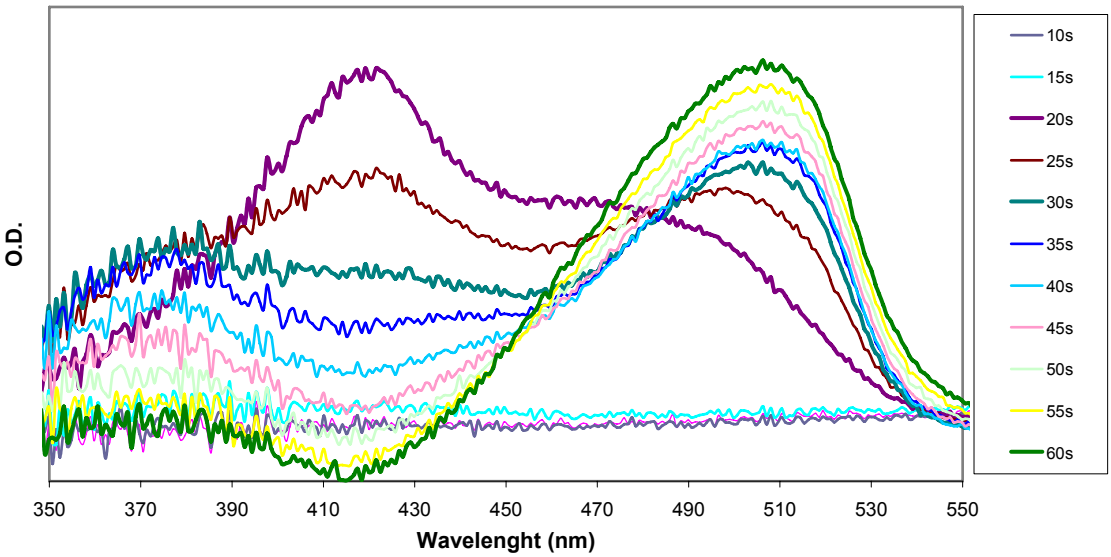


Figure S4. In situ UV/Vis spectra (Optical Density) O.D. vs. time (s) during a potential step experiment (E_1=0.00 V; E_2= -0.90 V; E_3= 0.00 V) of 5.10^{-4} M 2,4,6-trinitroanisole (**TNA**) in 0.1 M $TBABF_4$ (acetonitrile, ACN) in the UV/Vis LIGA cell.

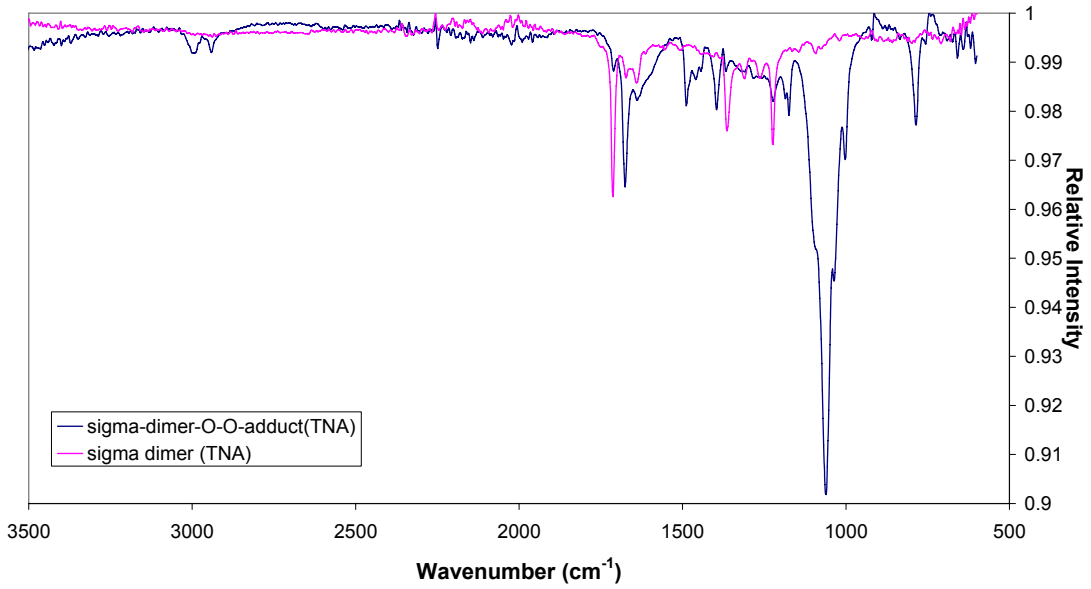


Figure S5. IR spectrum of **$\sigma^{H}_{O\text{-}O}$-adduct (TNA)** (dark blue line) and **σ^{H}-dimer (TNA)** (pink line).

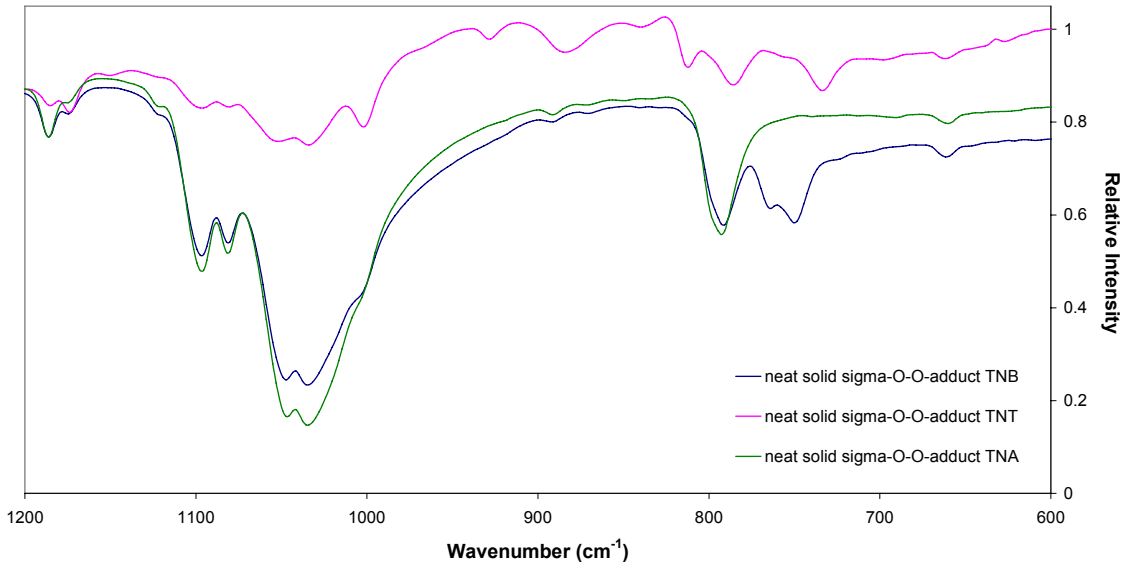
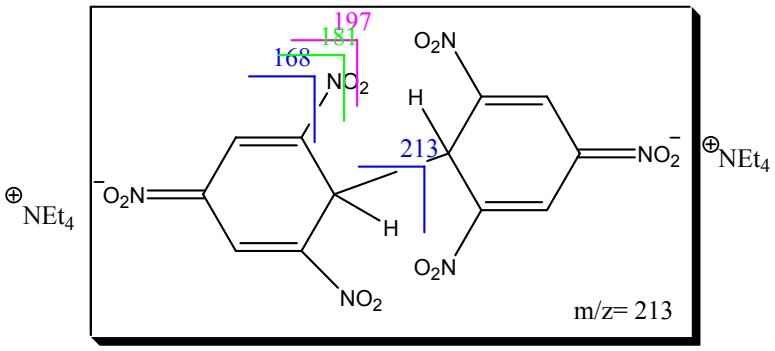


Figure S6. IR spectrum of: **$\sigma^{H}_{O\text{-}O}$-adduct (5)** (dark blue line), **$\sigma^{H}_{O\text{-}O}$-adduct (TNT)** (pink line) and **$\sigma^{H}_{O\text{-}O}$-adduct (TNA)** (dark green line).

Table ESI-1. Characterization of Compounds **3** ($\sigma^{H}_{C\text{-}C}$-adduct), **4** ($\sigma^{H}_{N=N}$ -adduct) and **5** ($\sigma^{H}_{O\text{-}O}$ -adduct) depicted in Scheme 1.

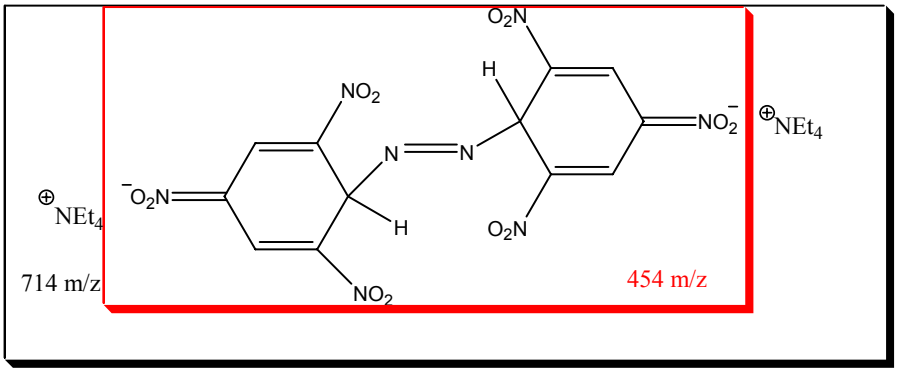
Physical data	**3** ($\sigma^{H}_{C\text{-}C}$-adduct)	**4** ($\sigma^{H}_{N=N}$ -adduct)	**5** ($\sigma^{H}_{O\text{-}O}$ -adduct)
^{1}H NMR (250 MHz, CD_3CN, r.t., TMS)	δ =8.15 (s) and 5.53(s) ppm (2:1)	δ =8.40 (s) and 6.41 (s) ppm (2:1)	δ =8.64 (s) and 6.72 (s) ppm (2:1)
Cyclic Voltammetry	0.56 V vs. SCE (irreversible) (In the reverse scan we obtain the reduction of the corresponding 1,3,5-trinitrobenzene)	1.09 V vs. SCE (pseudo reversible wave) (In the reverse scan we ONLY obtain the reduction of the corresponding 1,3,5-trinitrobenzene)	1.03 V vs. SCE (irreversible) (In the reverse scan, it is possible to detect the reduction wave from the liberated O_2 at -0.92 V vs. SCE as well as the corresponding to 1,3,5-trinitrobenzene)
IR	-	$\upsilon_{N=N}$ (1731 cm^{-1}) NEW band assigned to the azo group stretching mode	$\upsilon_{o\text{-}o}$ (1060 cm^{-1}) NEW band assigned to the O-O stretch vibration
Elemental Analysis (EA)	(C28H46N8O12): N 16.4, C 49.0, H 6.7 found: N 15.9, C 48.6, H 6.7	(C28H46N10O12): It has not been able to get enough quantity of highly pure nitrogenated samples. However the experimental nitrogen composition found when the EA was performed was higher than in compounds **3** and **5.**	(C28H46N8O14): Theoretical N 15.6, C 46.9, H 6.4 found: N 15.2,C 47.4,H 6.2.
ESI- (Main Peaks)	Compound **3** ($\sigma^{H}_{C\text{-}C}$-adduct)	m/z (I %)	
	$[(C_6H_3)_2]^{2-}$	213 (35%)	
	$[((C_6H_3)(NO_2)_2(NO) + 2H]^{-}$	199(61%)	
	$[(C_6H_3)(NO_2)_2(N) + 2H]^{-}$	183(100%)	
	$[(C_6H_3)(NO_2)_2 + H]^{-}$	168(5%)	

MW: 686.7



Compound **4** ($\sigma^{H}_{N=N}$ -adduct) m/z (I %)

MW: 714.7



$[((C_6H_3)(NO_2)_3N)_2 + 2NEt_4 - H]^-$ 713 (100%)

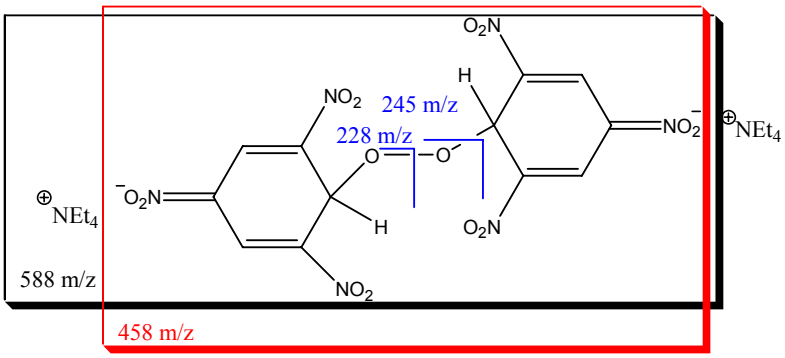
$[((C_6H_3)(NO_2)_3N)_2 + 2NEt_4 - H]^{2-}$ 357(99%)

$[((C_6H_3)(NO_2)_3N)_2]^-$ 454(6%)

$[(C_6H_3)(NO_2)_3N)_2 + 2H]^-$ 456(29%)

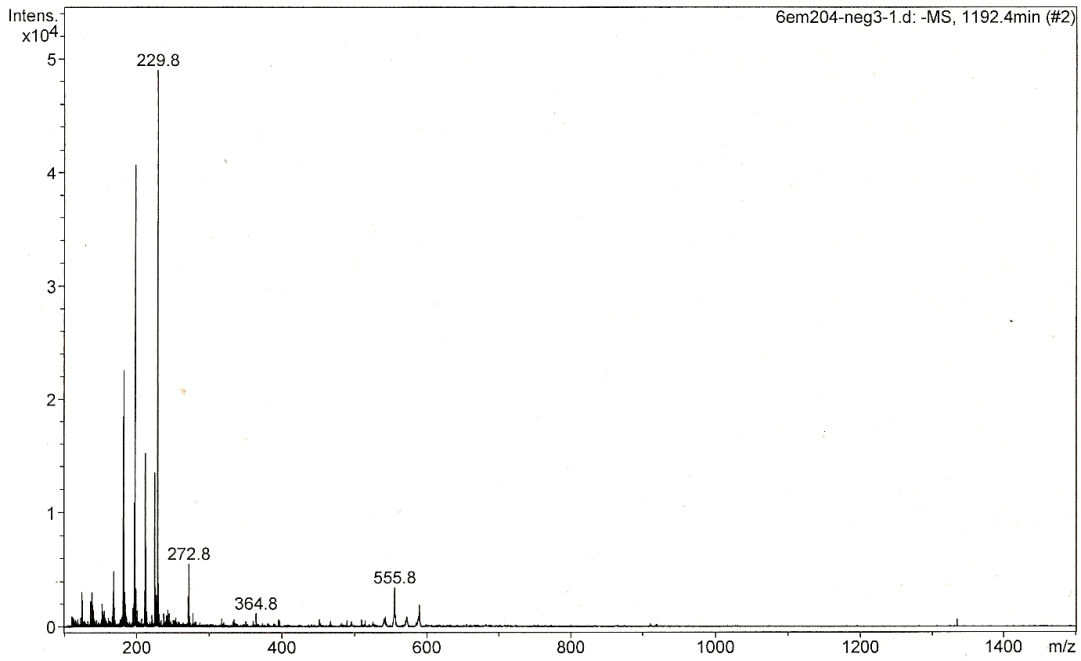
Compound **5** ($\sigma^{H}_{O\text{-}O}$-adduct) m/z (I %)

MW: 718.7



$[((C_6H_3)(NO_2)_3O)_2 + NEt_4 + H]^-$	589 (4%)
$[((C_6H_3)(NO_2)_3O)_2 - H]^-$	457(6%)
$[(C_6H_3)(NO_2)_3OH]^-$	230 (100%)
$[(C_6H_3)(NO_2)_3O_2]^-$	245(2%)
$[(C_6H_3)(NO_2)_2O]^-$	183(46%)
$[(C_6H_3)(NO_2)_2O_2]^-$	199(83%)

Compound 5 (ESI (-)/MS) : Fresh Solution. Color: Red



List of the Main Peaks:

m/z	I	I(%)
589.7	1912	4
555.6	3299	7
555.8	3492	7
556.8	1033	2
457.2	2815	6
225.9	13486	28
226.8	3471	7
227.8	2815	6
229.8	48969	100
230.8	3841	8
231.8	1134	2
212.8	15190	31
213.8	6997	14
214.8	1342	3
198.8	40643	83
199.8	3385	7
201.8	1444	3
182.8	22535	46
183.8	3069	6
184.8	2005	4
185.8	1263	3