ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

Unprecedented *Ipso* Aromatic Nucleophilic Substitution Upon Oxidative Decarboxylation of Tris-(*p*-carboxyltetrathiaaryl)methyl (TAM) Radicals: A New Access to Diversely Substituted TAM Radicals

Christophe Decroos,[a] Thierry Prangé,[b] Daniel Mansuy,[a] Jean-Luc Boucher, [a] and Yun Li,*[a]

[a]*Laboratoire de Chimie et Biochimie Pharmacologiques et Toxicologiques, Université Paris Descartes, UMR 8601 CNRS, 45 Rue des Saints Pères, 75270 Paris cedex 06, France.*
[b]*Laboratoire de Cristallographie et RMN Biologiques, Université Paris Descartes, UMR 8015 CNRS, 4 Av de l'Observatoire, 75270 Paris cedex 06, France.*

Experimental Section

General procedure for TAM-Nu (4-7) synthesis: To a solution of TAM **1** in distilled water (~ 1 mL per mg of TAM **1**) under magnetic stirring was added 2 equiv. of $K_2Ir(IV)Cl_6$ (20 mM solution freshly prepared from distilled water). After 1 min at room temperature, 50 equiv. of nucleophile were added to the reaction mixture. If not soluble in water, the nucleophile was dissolved in a minimum of an organic solvent such as THF or methanol. When *N*-acetylcysteine methyl ester was used as a nucleophile, NaOH (50 equiv. of a 0.1 M solution) was mixed with the thiol before adding to TAM $\mathbf{1}^+$. After 10 min at room temperature, the mixture was analyzed by HPLC-MS. Solvents were removed and products were purified by semi-preparative HPLC with a reversed-phase Hypersil ODS column (250 × 7.8 mm) and a water / acetonitrile gradient was used.

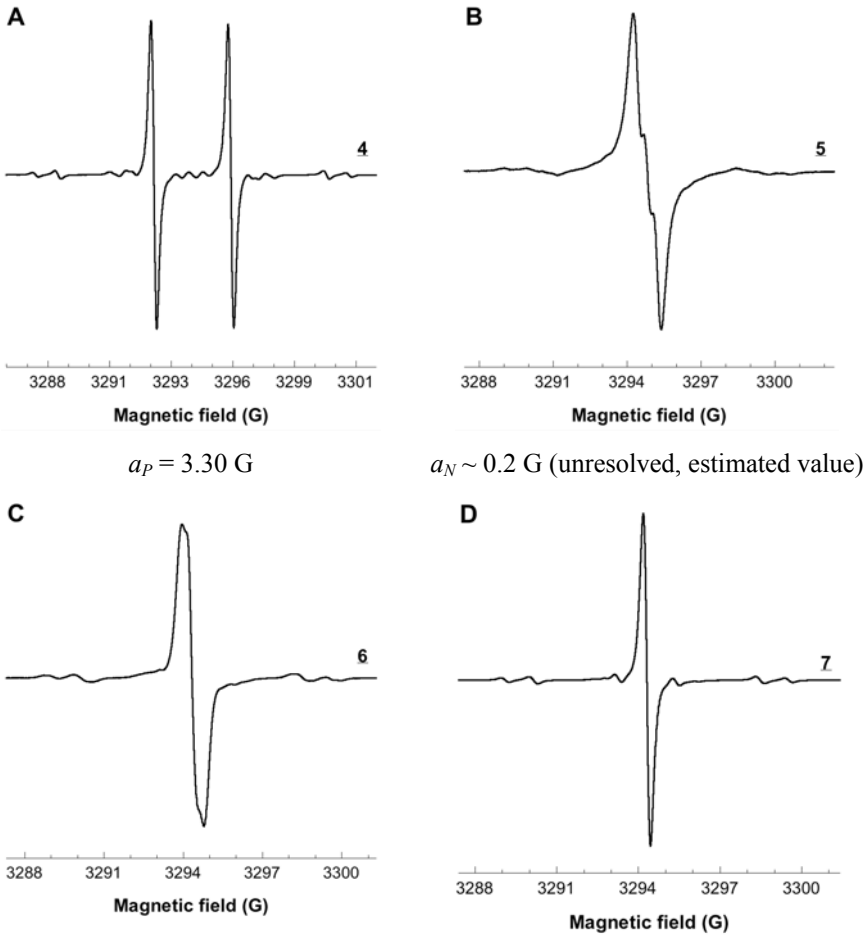
Radical **11** was synthesized according to the same procedure (50 equiv. $NaNO_2$) except for the use of 12 equiv. of $K_2Ir(IV)Cl_6$. Product was purified by precipitation and isolated in a 74% yield. Slow diffusion of pentane into a solution of **11** in chloroform at room temperature for about 2 weeks allowed the isolation of single crystals suitable for X-ray diffraction.[15]

Table S1. ESI-HRMS molecular ion of TAM-Nu **4**, **5**, **6**, **7** and **11**

TAM-Nu	ESI-HRMS
4	1156.1316 (calculated for $C_{51}H_{65}O_4PS_{12}$ 1156.1269)
5	1071.9973 (calculated for $C_{46}H_{44}N_2O_4S_{12}$ 1071.9950)
6	1038.0272 (calculated for $C_{44}H_{48}NO_4S_{12}$ 1038.0232)
7	1152.9716 (calculated for $C_{45}H_{48}NO_7NaS_{13}$ 1152.9698)
11	1001.9272 (calculated for $C_{37}H_{36}N_3O_6S_{12}$ 1001.9253)

EPR spectroscopy

EPR spectra were recorded at 20°C using a Bruker Elexsys 500 EPR spectrometer operating at X-band (9.85 GHz) with a SHQ cavity and an AquaX quartz cell, under the following conditions: modulation frequency, 100 kHz; modulation amplitude, 0.1 G; time constant, 40.96 ms; conversion time, 40.96 ms; and microwave power, 1 mW.



a_P = 3.30 G

a_N ~ 0.2 G (unresolved, estimated value)

a_N = 0.38 G

Figure S1. EPR spectra of TAM-Nu **4** (A), **5** (B), **5** (C), and **7** (D) (in degassed MeOH)

UV-Visible Spectroscopy

UV-Visible spectra were recorded at room temperature on a Cary 300 spectrophotometer (Varian, Les Ulis, France).

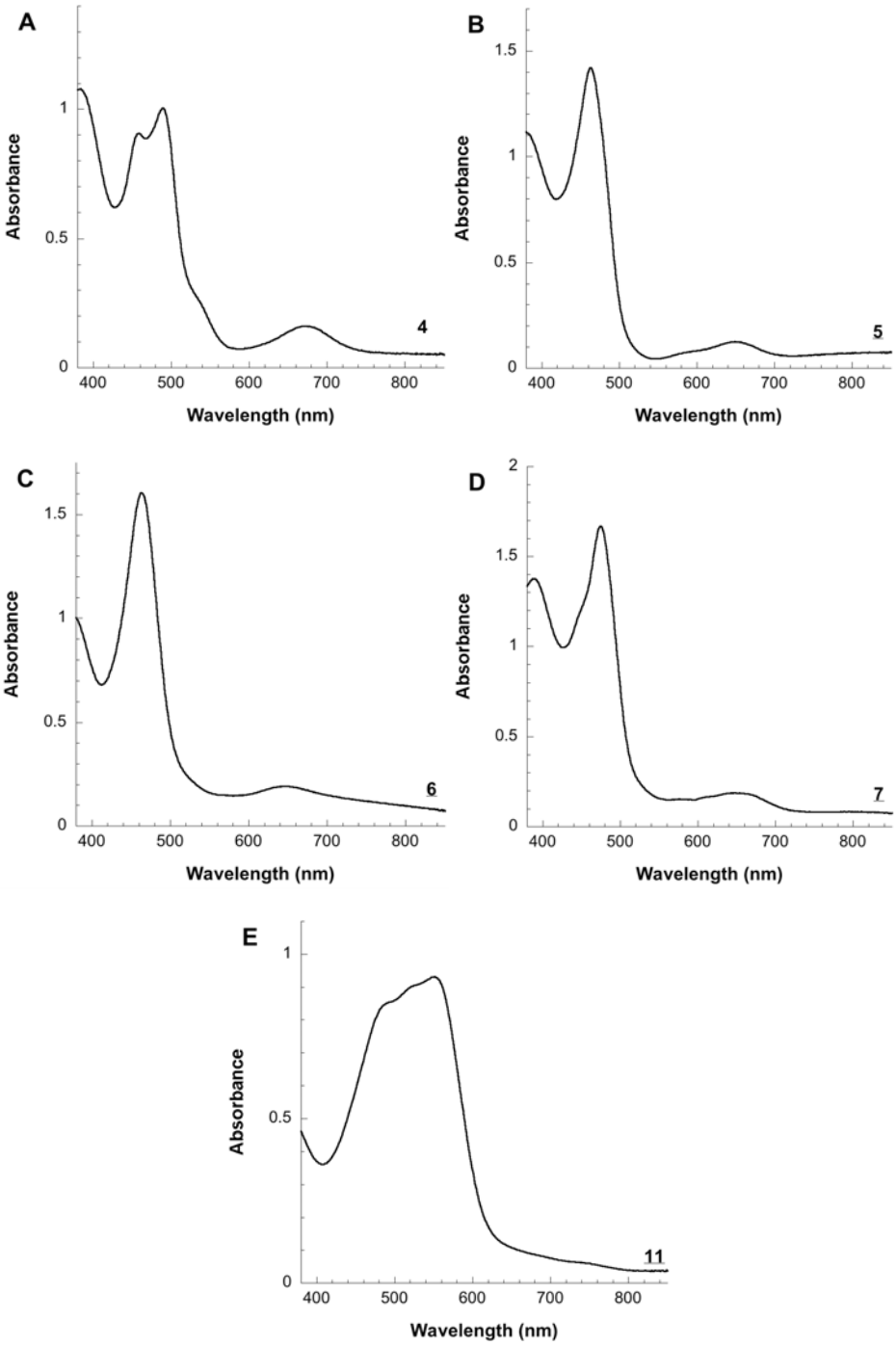


Figure S2. UV-Visible spectra of TAM-Nu **4** (A), **5** (B), **6** (C), **7** (D), and **11** (E) (in MeOH except for **11**: in CH_2Cl_2)

Table S2. Absorption maxima of the UV-visible spectra of TAM-Nu 4-7, 11 and 16-20 in the visible region

TAM-Nu	λ_{max} (nm)	TAM-Nu	λ_{max} (nm)
4	459, 490, and 671 [a]	**5**	463 and 648 [a]
6	463 and 648 [a]	**7**	475 and 643 [a]
11	494, 525, and 548 [b]		

[a] in MeOH; [b] in CH_2Cl_2.

Table S3. Crystallographic data for **11**.

Chemical formula	$C_{37}H_{36}N_3O_6S_{12}$
Formula weight	1003.53
Temperature (K)	110 (2)
Wavelength (Å)	0.92770
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions (in Å and °)	a = 11.770(1), α = 90 b = 23.106(1), β = 90.12(5) c = 16.200(1), γ = 90
Volume ($Å^3$)	4406.0(5)
Z	4
Density (mg/m^3, calculated90.12(5))	1.513
F(000)	2076
Crystal size (mm)	0.22 x 0.23 x 0.06
θ range for data collection–rotation method (°)	360
Index ranges	$0 < h < 12$; $0 < k < 26$; $-18 < l < +18$
No of reflections collected	11911
No of independent reflections	6231
Refinement method	full-matrix least-squares on F^2
Data / restraints / parameters	5631 / 0 / 526
Goodness-of-fit on F^2	1.015
Final R indexes [I>2σ(I)]	R1=0.0623, wR2=0.1715
R indexes (all data)	R1= 0.0637, wR2=0.1733
Largest diff. peak and hole ($eÅ^{-3}$)	+0.39 / -0.44