Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B.

Crystal structure dependent *in vitro* antioxidant activity of biocompatible calcium gallate MOFs

Tania Hidalgo,[a#] Lucy Cooper,[a#] Martin Gorman,[a] Tamara Lozano-Fernández,[b] Rosana Simón-Vázquez,[b] Georges Mouchaham,[a] Jérome Marrot,[a] Nathalie Guillou,[a] Christian Serre,[a,c] Pierre Fertey,[d] África González-Fernández,[b] Thomas Devic[a,e*] and Patricia Horcajada[a,f*]

[a]Institut Lavoisier, UMR 8180 CNRS Université de Versailles Saint-Quentin-en-Yvelines, 45 avenue des Etats-Unis, 78035 Versailles cedex, France.

[b] Immunology, Biomedical Research Center (CINBIO) and Institute of Biomedical Research of Vigo (IBIV), Universidad de Vigo, Campus Lagoas Marcosende, 36310 Vigo, Pontevedra. Spain.

[c] Institut des Matériaux Poreux de Paris, FRE 2000 CNRS Ecole Normale Supérieure - Ecole Supérieure de Physique et de Chimie Industrielles de Paris, Paris Research University, Paris, France.

[d] Synchrotron Soleil, beamline Cristal, L'Orme des Merisiers, Saint-Aubin, 91192 Gif-sur-Yvette cedex, France.

[e] Current address :.Institut des Matériaux Jean Rouxel, UMR 6502 CNRS Université de Nantes,2 rue de la Houssinière, 44322 Nantes cedex 3, France.

[f] Current address: IMDEA Energy. Av. Ramón de la Sagra 3, 28935 Móstoles, Madrid, Spain

# equally contributing authors

*Correspondence - E-mail: thomas.devic@cnrs-imn.fr, patricia.horcajada@imdea.org

Note that the data from Mg(H_2gal), displayed here, were already reported in Cooper *et al, Chem.Comm*, 2015, **51**, 5848.

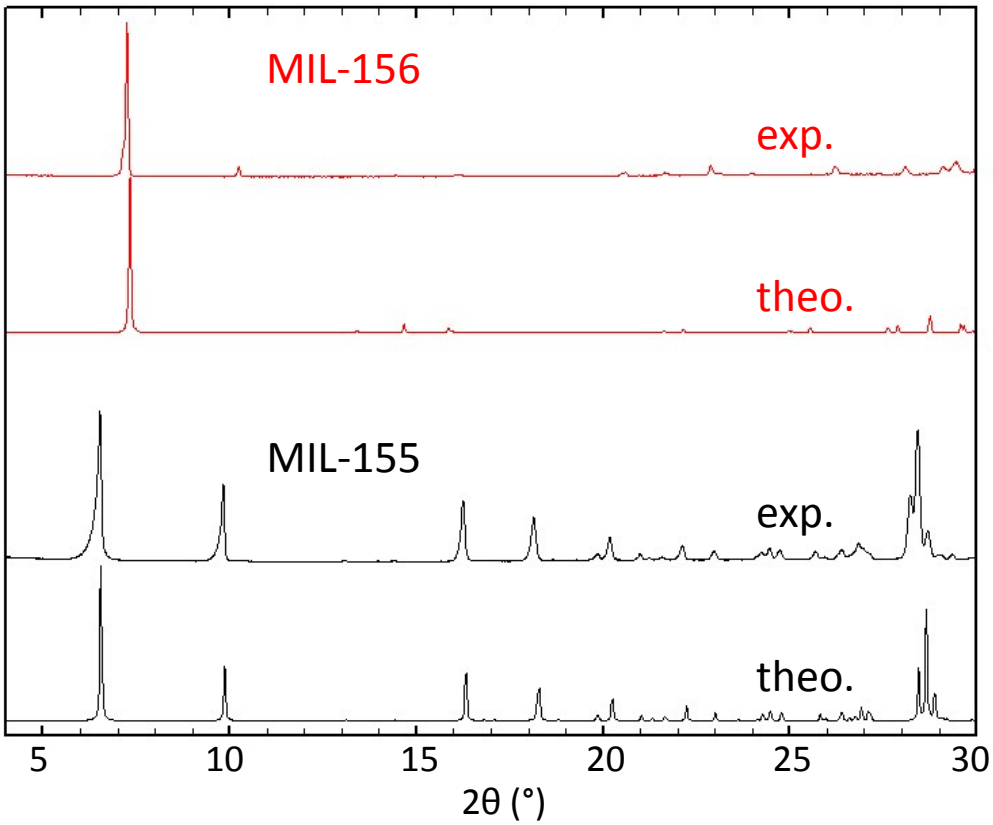

Figure S1. Experimental and calculated X-ray diffraction patterns of MIL-155 and MIL-156 (λ = 1.5406 Å).

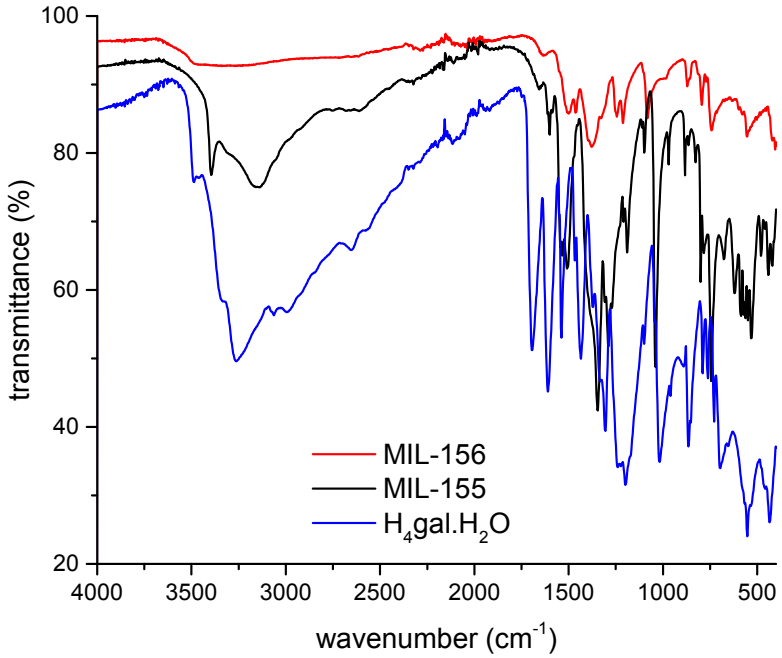

Figure S2. IR spectra for MIL-155 (black) and MIL-156 (red) and gallic acid monohydrate (blue).

Table S1. Crystallographic data and refinement parameters for MIL-155 and MIL-156.

	MIL-155 or $[Ca_2(H_2O)(H_2gal)_2]\bullet 2H_2O$	*MIL-156 or* $[Ca_3K_2(H_2O)_2(gal)_2]\bullet nH_2O$ *(n = 5)*
Empirical formula	$Ca_2O_{13}C_{14}H_{14}$	$Ca_{1.5}KO_{8.5}C_7H_9$
Formula weight	470.42 g·mol^{-1}	328.36 g·mol^{-1}
Temperature	100(2) K	297(2) K
Wavelength	0.96650 Å	0.71073 Å
Crystal system, space group	triclinic, *P*-1	orthorhombic, *P*ccn
Unit cell dimensions	*a* =6.4362(3) Å *b* =9.2435(4) Å *c* = 14.2581(13) Å *α* =102.463(3)° *β* =103.033(4)° *γ* =93.745(5)°	*a* = 17.3088(16 Å *b* = 17.4277(15) Å *c* = 7.8949(7) Å
Volume (Å^3)	801.12(9) Å^3	2381.5(4) Å^3
Z, calculated density	2,1.9502(2) g·cm^3	8,1.832 g·cm^3
Adsorption coefficient	0.792 mm^{-1}	1.124 mm^{-1}
F(000)	484	1344
Crystal size	0.02 x 0.02 x 0.004 mm	0.2 x 0.08 x 0.04 mm
Theta range for data collection	4.084° - 32.403°	1.658° - 25.025°
Limiting indices	$-5 \le h \le 6$, $-10 \le k \le 9$, $-15 \le l \le 15$	$-20 \le h \le 20$, $-20 \le k \le 20$, $-9 \le l \le 9$
Reflections collected / unique	4438/1977 [R(int) = 0.0654]	32186/2107 [R(int) = 0.0300]
Refinement method	full-matrix least squares	full-matrix least squares
Data/Restraints/Parameters	1977 /9/290	2107/0/168
Goodness of fit on F^2	1.089	1.076
Final R indices [I > 2σ(I)]	R1 = 0.0429, wR2 = 0.1184	R1 = 0.0665, wR2 = 0.2001
R indices (all data)	R1 = 0.0466, wR2 = 0.1402	R1 = 0.0754, wR2 = 0.2084
Largest diff peak and hole (e·Å^{-3})	0.491 and -0.458	1.964 and -0.516

Table S2. Bond valence calculations[1] for MIL-155 or $[Ca_2(H_2O)(H_2gal)_2]\cdot 2H_2O$ (see Figure 2c for the atom labelling).). * Total charge (-1) delocalized on the carboxylate group (O1 and O2).

Fragment	*Atomic pair*	*Distance (Å)*	*Valence*	*Proposed charge*
H_2gal A	O1-Ca1	2.384	0.32	
	O1-Ca2	2.381	0.33	
		total O1	**0.65**	**-0.5***
	O2-Ca1	2.420	0.29	
	O2-Ca2	2.411	0.30	
		total O2	**0.60**	**-0.5***
	O3-Ca2	2.498	0.24	
		total O3	**0.24**	**0**
	O4-Ca1	2.355	0.35	
	O4-Ca2	2.341	0.36	
		total O4	**0.71**	**-1**
	O5-Ca1	2.452	0.27	
		total O5	**0.27**	**0**
H_2gal B	O12-Ca1	2.420	0.29	
		total O12	**0.29**	**-0.5***
	O14-Ca1	2.355	0.35	
	O14-Ca2	2.417	0.30	
		total O14	**0.65**	**-1**
	O15-Ca2	2.430	0.29	0
		total O15	**0.29**	**0**
Ow1(H_2)	Ow1-Ca1	2.600	0.18	
	Ow1-Ca2	2.470	0.26	
		total Ow1	**0.44**	**0**

Table S3. Comparison of C-O bond lengths (Å) for MIL-155 and $[Ni(H_2gal)]\cdot 2H_2O$ (see Figure 2c for the atom labelling).

functional group	*MIL-155*				*$[Ni(H_2gal)]\cdot 2H_2O$*	
	H_2galA		H_2galB			
carboxylate	C1 - O1	1.281(4)	C11 - O11	1.293(4)	C3-O2	1.264
	C1 - O2	1.269(4)	C11 – O12	1.270(5)		
meta-phenol(ate)	C4 – O3	1.381(4)	C14 – O13	1.376(4)	C4 – O1	1.369
	C6 – O5	1.389(4)	C16 – O15	1.391(4)		
para-phenol(ate)	C5 – O4	1.334(4)	C15 – O14	1.332(4)	C1 – O3	1.323

Table S4. Hydrogen-bond distances and angles in MIL-155 (D = donor, A= acceptor).

D-H···A	*H···A distance (Å)*	*D···A distance (Å)*	*D-H···A angle (°)*
Ow1-Hw1B···O12	1.96	2.65	142
Ow1-Hw1A···Ow3	1.88(3)	2.703(4)	170(4)
Ow2-Hw2A···O13	1.88(3)	2.683(4)	163(5)
Ow2-Hw2B···Ow3	1.98(2)	2.802(4)	177(6)
Ow3-Hw3A···Ow2	2.00(3)	2.819(5)	171(4)
O3-H3A···O11	1.92(3)	2.723(4)	171(4)
Ow3-Hw3B···O11	1.88(3)	2.716(4)	175(4)
O5-H5A···O11	1.86(3)	2.658(4)	164(4)
O13-H13A ···O5	2.12	2.791(4)	139
O15-H15A···Ow2	1.84(3)	2.646(4)	164(4)

Table S5. Bond valence calculations1 for MIL-156 or $[Ca_3K_2(H_2O)_2(gal)_2]\bullet nH_2O$, n ~5 (see Figure 3c for the atom labelling).* Total charge (-1) delocalized on the carboxylate group (O1 and O2).

Fragment	*Atomic pair*	*Distance (Å)*	*Valence*	*Proposed charge*
gal	O2-Ca1	2.322	0.38	
		total O2	**0.38**	**-0.5***
	O3-Ca1	2.268	0.44	
	O3-Ca2	2.554	0.20	
	O3-K1	2.821	0.10	
		total O3	**0.75**	-1
	O4-Ca1	2.314	0.39	
	O4-Ca2	2.405	0.31	
	O4-Ca2	2.415	0.30	
		total O4	**1**	**-1**
	O5-Ca1	2.268	0.44	
	O5-Ca2	2.529	0.22	
	O5-K1	2.880	0.08	
		total O5	**0.75**	**-1**
Ow1(H_2)	Ow1-Ca1	2.510	0.23	
	Ow1-Ca1	2.540	0.21	
		total Ow1	0.44	**0**

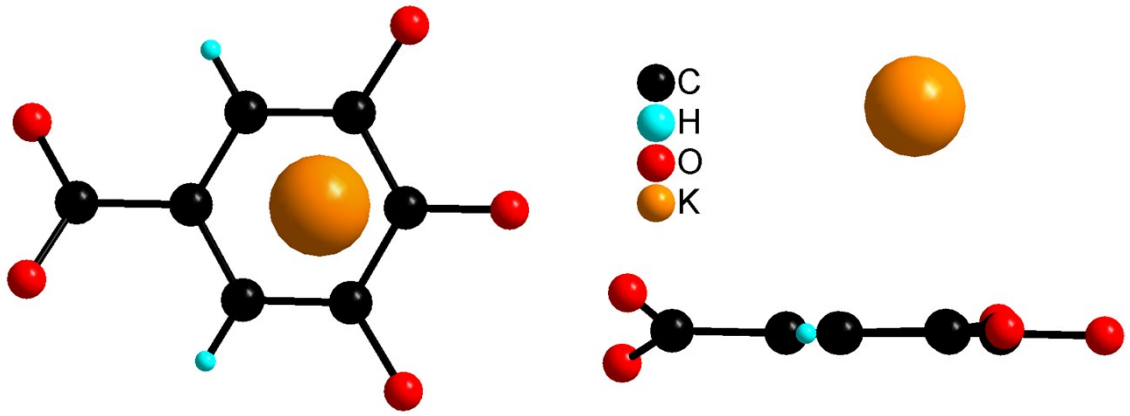

Figure S3. Top (left) and side (right) view of the short K^+-π contact in MIL-156.

Table S6. Donor (D) – Acceptor (A) hydrogen-bond distances in MIL-156 (H atoms were not located).

D(-H)···A	*D···A distance (Å)*
Ow1···O1	2.625(5)
Ow2 ···O1	2.800(6)
Ow1 ···Ow2 (or reverse)	2.849(6)
Ow3 ···Ow4 (or reverse)	2.81(2)

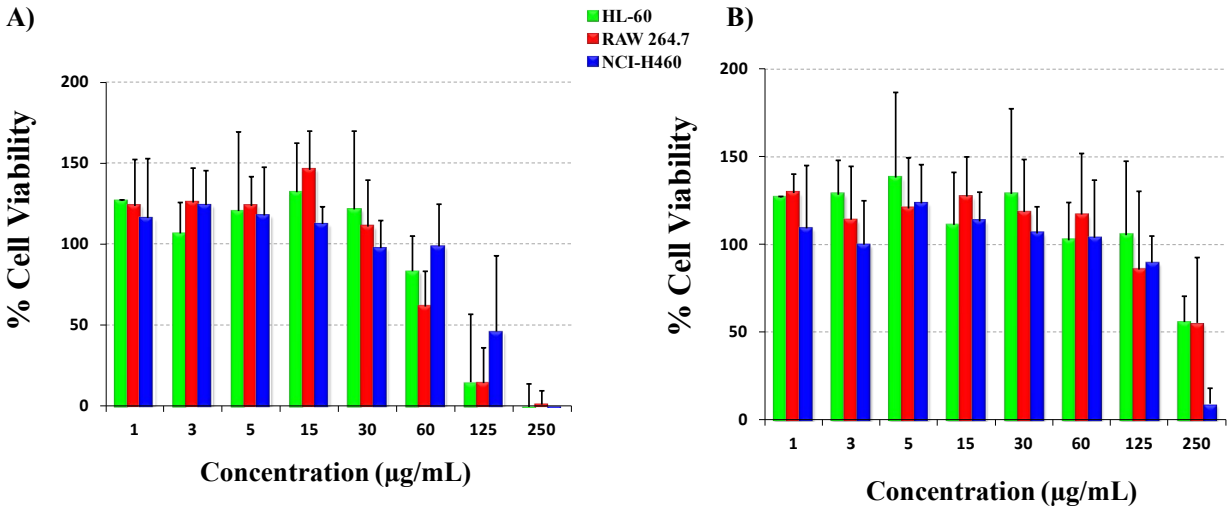

Figure S4. Cell viability of HL-60, RAW 264.7 and NCI-H460 macrophages after 24 h in contact with A) MIL-155 or B) MIL-156. Note that the data shown in each concentration correspond to the average of the quadruplicate replicate obtained in three independent experiments (n =12). The vertical error bars drawn in the diagram indicate the range of fluctuations from which the standard deviations were calculated.

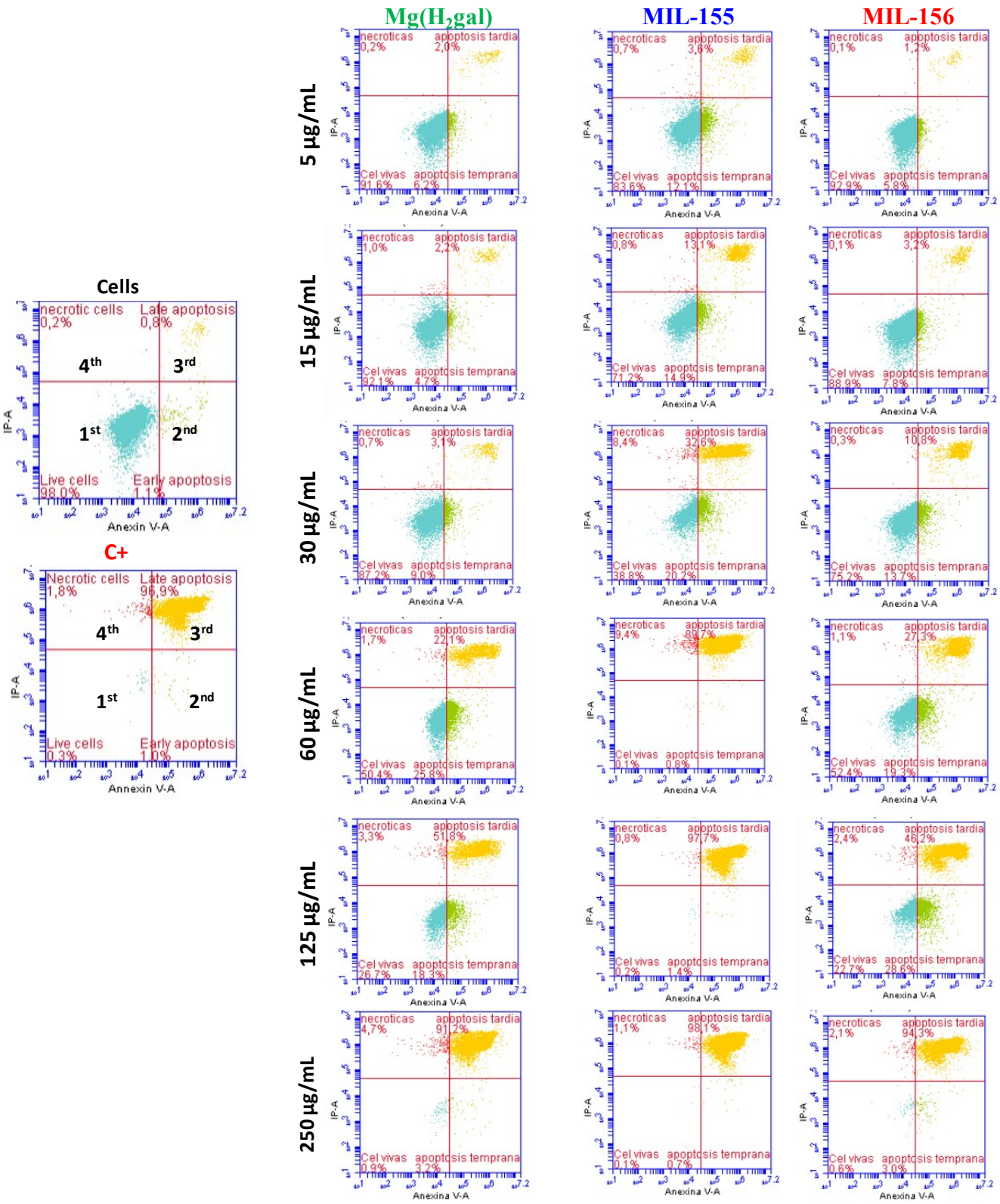

Figure S5. Annexin-V analysis of HL-60 cell line after 24 h in contact with different concentration (5, 15, 30, 60, 125 and 250 µg·mL^{-1}) of Mg(H_2gal)•2H_2O, MIL-155 and MIL-156. Negative and positive controls (C+) were considered as cells alone and cells in the presence of H_2O_2, respectively. From the 1st to 4th quadrant are represented different cell states as live, early apoptotic, late apoptotic and necrotic cells, respectively. Note that these data, corresponding to one of the triplicates obtained in three independent experiments (n = 9), are totally representative from the whole results.

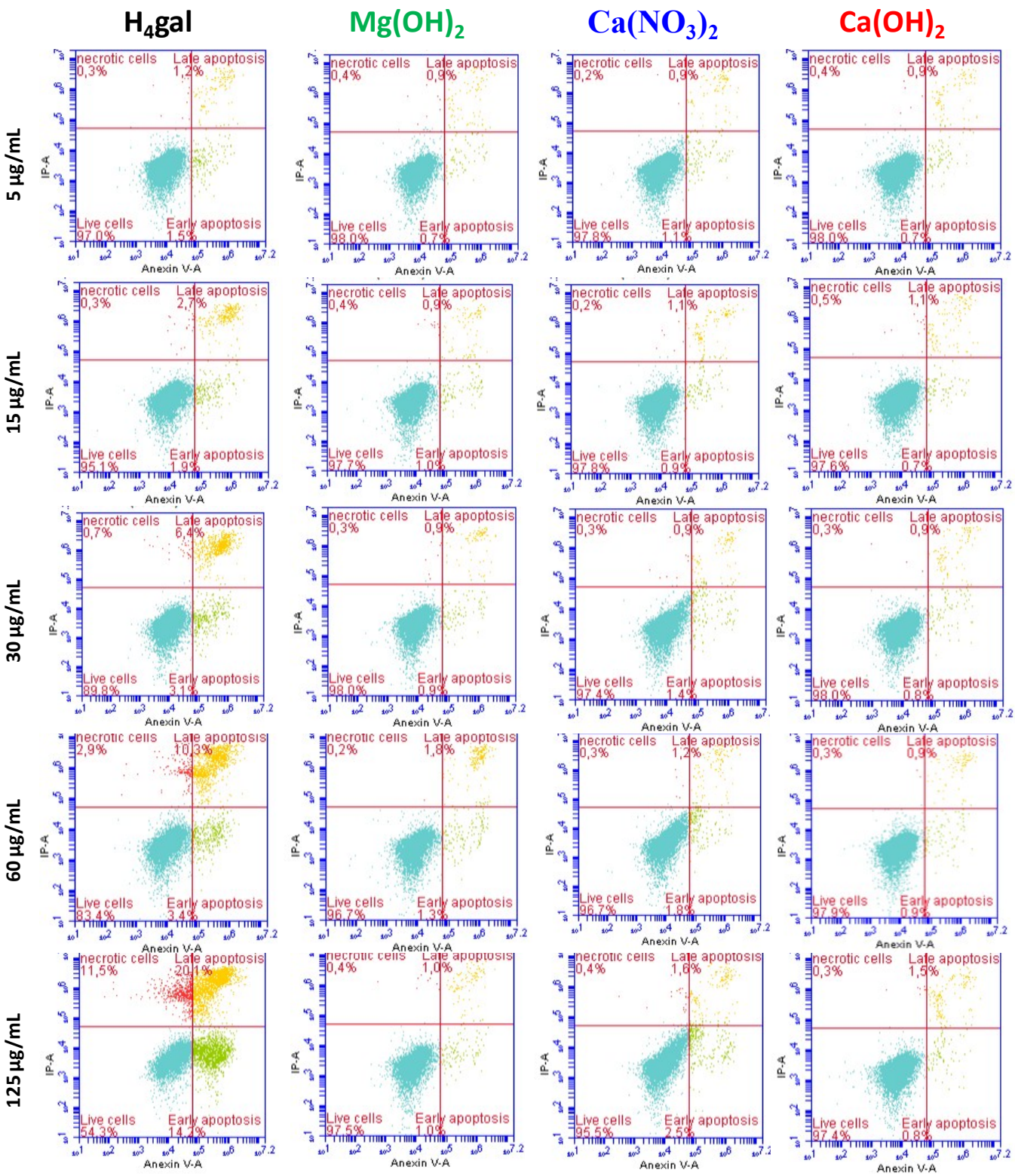

Figure S6. Annexin-V analysis of HL-60 cell line after 24 h in contact with different concentration (5, 15, 30, 60 and 125 µg.mL^{-1}) of each component of the different metal gallate precursors (H_4gal, $Mg(OH)_2$, $Ca(NO_3)_2$ and $Ca(OH)_2$). Negative and positive controls (C+) were considered as cells alone and cells in presence of H_2O_2, respectively (see Figure S5). From the 1st to 4th quadrant are represented different cell states as live, early apoptotic, late apoptotic and necrotic cells, respectively. Note that these data, corresponding to one of triplicates obtained in three independent experiments (n = 9), are totally representative from the whole results.

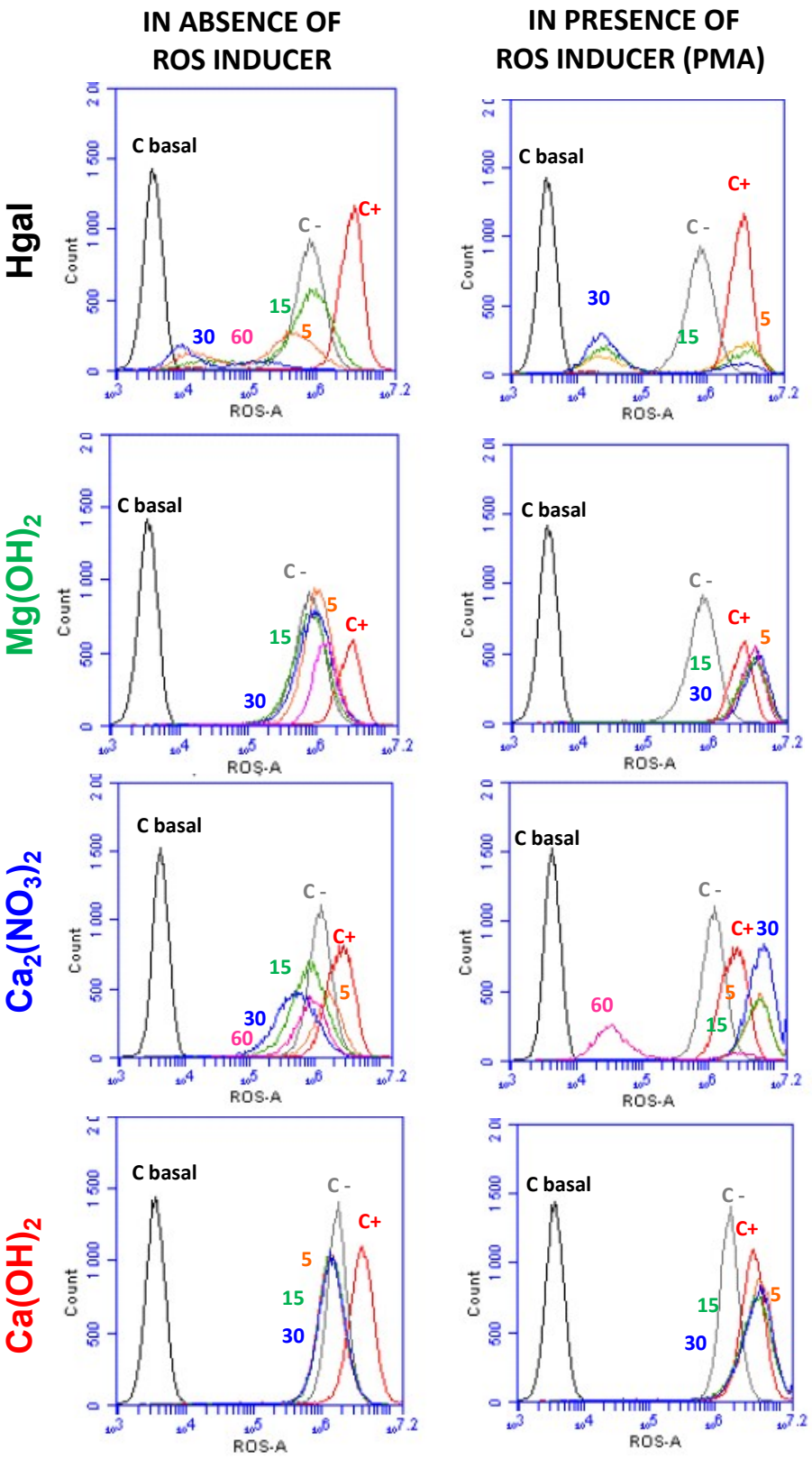

Figure S7. ROS production of HL-60 cells after 8 h in contact with the precursors H_4gal, $Mg(OH)_2$, $Ca(NO_3)_2$ and $Ca(OH)_2$). Negative (cells), basal (cells + DCFH-DA) and positive (cells + DCFH-DA + PMA) controls are disclosed as black, grey and red lines. Several concentrations (5, 15, 30 and 60 $\mu g \cdot mL^{-1}$) were tested, and are pictured in orange, green, blue and pink, respectively. Note that these data,

corresponding to one of the triplicates obtained in four independent experiments (n = 12), are totally representative from the whole results.

References

[1] N.E. Brese, M. O'Keeffe, *Acta Cryst.***,** 1991, **B47**, 192-197.