Supporting information

Alkaline earth metal ion coordination increases radical scavenging efficiency of kaempferol

Ling-Ling Qian†, Yao Lu†, Yi Xu†, Zhi-Yin Yang†, Jing Yang†, Yi-Ming Zhou†, Rui-Min Han†,, Jian-Ping Zhang†, Leif H. Skibsted‡*

†Department of Chemistry, Renmin University of China, Beijing, 100872

‡Department of Food Science, University of Copenhagen, Rolighedsvej 30, DK-1958 Frederiksberg C, Denmark

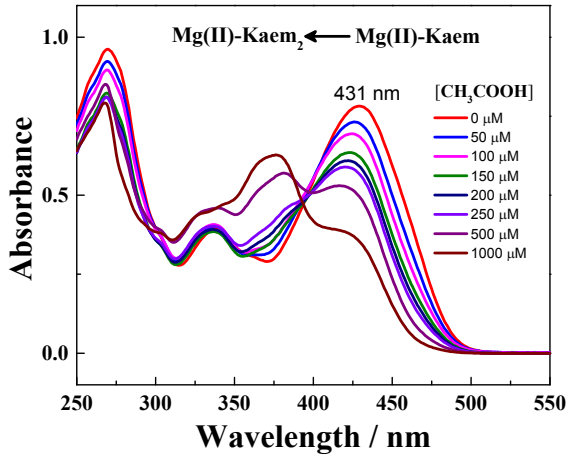

Figure S1. Absorption spectra of 50 μM Kaem in the presence of 500 μM $Mg(CH_3COO)_2$ with addition of 50, 100, 150, 200, 250, 500 and 1000 μM CH_3COOH.

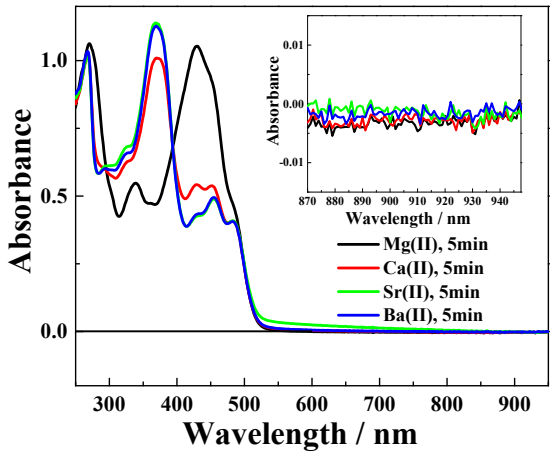

Figure S2. Absorption spectra of 5 μM *β*-Car with 50 μM Kaem and 500 μM Mg/Ca/Sr/Ba(II) after 532 nm laser radiation (10 Hz, 4 mJ/pulse) for 5 min. Inset: enlarged view of spectra at 870~950 nm.

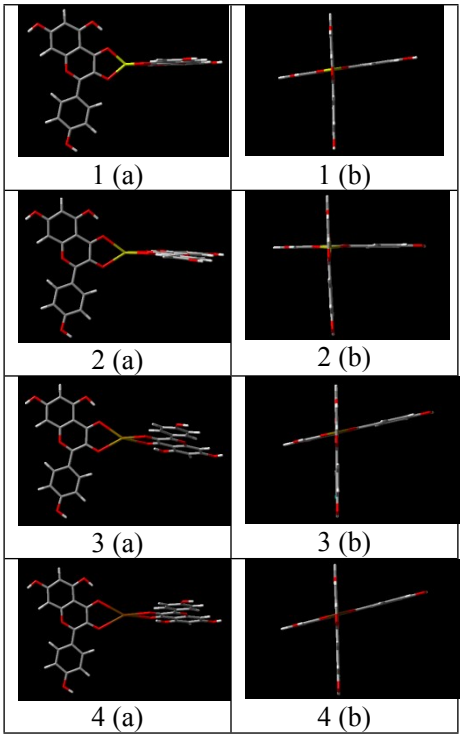

Figure S3. Optimized structures of (1) Mg(II)-Kaem$_2$, (2) Ca(II)-Kaem$_2$, (3) Sr(II)-Kaem$_2$, (4) Ba(II)-Kaem$_2$ complexes viewed from (a) perpendicular to the plane of one Kaem ligand and parallel to the other Kaem , and from (b) parallel to the two planes of the two Kaem ligands.

Table S1. IR spectra peak (cm^{-1}) for 1.0 mM Kaem/Api, and solids prepared by removing solvent from ethanol solutions of Kaem/Api and M(CH_3COO)$_2$ with ratios of 1:10. M= Mg(II), Ca(II), Sr(II), Ba(II).

Compound	ν(C=O)	ν(C=C)	ν(C-OH)	ν(C-O-C)	ν(M-O)
Kaem	1657	1613	1372	1243	-
Kaem-Mg(II)	1648	1602	1367	1226	609
Kaem-Ca(II)	1650	1615	1365	1223	582
Kaem-Sr(II)	1653	1608	1367	1221	463
Kaem-Ba(II)	1654	1607	1370	1224	644
Api	1659	1605	1357	1243	
Api-Mg(II)	1640	1595	1357	1248	605
Api-Ca(II)	1659	1605	1377	1243	
Api-Sr(II)	1659	1605	1364	1243	
Api-Ba(II)	1659	1605	1367	1243	

Table S2. Experimental (Exp.) and calculated (Cal.) ESI mass spectra (m/z) for solids prepared by removing solvent from ethanol solutions of 1000 μM Kaem/Api and $M(CH_3COO)_2$ with ratios of 1:0.5 and 1:1, M= Mg(II), Ca(II),Sr(II), Ba(II).

Exp. (m/z)	Cal. (m/z)	Kaem:M(II) =1:0.5	Exp. (m/z)	Cal. (m/z)	Kaem/Api:M(II)=1:1
595	595/596/597	Mg-(Kaem−H)$_2$+H$^+$	363/364/365	363/364/365	Mg-(Kaem−2H) +Na$^+$+CH_3OH
613/614/615	613/614/615	Mg-(Kaem−H)$_2$+H$^+$+H_2O	379/380/381	379/380/381	Mg-(Kaem−2H)+ K$^+$+CH_3OH
617	617/618/619	Mg-(Kaem−H)$_2$+Na$^+$	147/148	147/148/148	[Mg-(Api−H)]$^+$+H$^+$
627	627/628/629	Mg-(Kaem−H)$_2$+CH_3OH+H$^+$	198	198/199/199	[Mg-(Api−H)]$^+$+K$^+$+2CH_3OH
665/667	665/666/667	Mg-(Kaem−H)$_2$+CH_3OH+K$^+$	217	217/217/218	2[Mg-(Api−H)]$^+$+H$^+$+2CH_3OH
667	665/666/667	Ca-(Kaem−H)$_2$+CH_3OH+Na$^+$	339/340/341	339/340/341	[Mg-(Api−H)]$^+$+ C_2H_5OH
649	649/650/651	Ca-(Kaem−H)$_2$+ K$^+$	325/326/327	325/326/327	[Mg-(Api−H)]$^+$+ CH_3OH
633	633/634/635	Ca-(Kaem−H)$_2$+Na$^+$			
657/658/659	657/658/659	Ca-(Kaem−H)$_2$+H$^+$+C_2H_5OH			
652/653	651/652/653	Ca-(Kaem−H)$_2$+Na$^+$+H_2O			
659/657	659/660/657	Sr-(Kaem−H)$_2$+H$^+$			
681	681/682/679	Sr-(Kaem−H)$_2$+Na$^+$			
709/710/708	709/710/708	Ba-(Kaem−H)$_2$+H$^+$			
745	745/746/744	Ba-(Kaem−H)$_2$ +2H_2O+H$^+$			
759/760/758	759/760/758	Ba-(Kaem−H)$_2$+H_2O+CH_3OH +H$^+$			
763/764/762	763/764/762	Ba-(Kaem−H)$_2$+CH_3OH +Na$^+$			

Table S3. Fractions (*F*, %) of Kaem and AEM(II)-kaempferol complexes in ethanol and in ethanol:chloroform (7/3) at indicated varying ratios.

ratio	F(%) in ethanol *F(%) in ethanol:chloroform (7/3)*			
	Kaem/Mg-Kaem$_2$/ Mg-Kaem	***Kaem/ Ca-Kaem$_2$***	***Kaem/ Sr-Kaem$_2$***	***Kaem/Ba-Kaem$_2$***
1:0.2	0.64/0.34/0.02 *(0.70/0.28/0.02)*	0.66/0.34 *(0.65/0.35)*	0.62/0.38 *(0.65/0.35)*	0.63/0.37 *(0.66/0.34)*
1:0.5	0.28/0.62/0.1 *(0.42//0.51/0.07)*	0.37/0.63 *(0.34/0.66)*	0.23/0.77 *(0.34/0.66)*	0.29/0.71 *(0.36/0.64)*
1:1	0.12/0.64/0.24 *(0.26/0.60/0.14)*	0.23/0.77 *(0.20/0.80)*	0.12/0.88 *(0.20/0.80)*	0.16/0.84 *(0.21/0.79)*
1:2	0.07/0.55/0.38 *(0.16/0.62/0.22)*	0.15/0.85 *(0.13/0.87)*	0.07/0.93 *(0.13/0.87)*	0.10/0.90 *(0.14/0.86)*
1:5	0.03/0.39/0.58 *(0.09/0.55/0.36)*	0.09/0.91 *(0.08/0.92)*	0.04/0.96 *(0.08/0.92)*	0.06/0.94 *(0.08/0.92)*
1:10	0.02/0.27/0.71 *(0.05/0.46/0.49)*	0.06/0.94 *(0.06/0.94)*	0.03/0.97 *(0.05/0.95)*	0.04/0.96 *(0.06/0.94)*
1:20	0.01/0.17/0.82 *(0.03/0.35/0.62)*	0.04/0.96 *(0.04/0.96)*	0.02/0.98 *(0.04/0.96)*	0.03/0.97 *(0.04/0.96)*