Supplementary Information

Approach to Anionic Alkaline Earth Metal-Methanesulfonates Bearing Photo-responsive Methylviologen

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Table S1. Crystallographic data of **1–4**.

	1	**2**	**3**	**4**
Empirical formula	$C_{18}H_{40}Mg_2N_2O_{22}S_6$	$C_{18}H_{40}Ca_2N_2O_{22}S_6$	$C_9H_{24}MgNO_{13}S_3$	$C_7H_{21}CaNO_{10}S_3$
CCDC no.	2358180	2362824	2358181	2362825
Formula weight	877.50	909.04	474.78	415.51
Temperature (k)	298(2)	298(2)	294(2)	296(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	P_{21}/c
a [Å]	5.7456(8)	5.8064(6)	5.7797(4)	5.80060(10)
b [Å]	9.3568(12)	9.5980(11)	9.7473(7)	31.3766(9)
c [Å]	16.623(2)	16.929(2)	17.7172(12)	9.1840(3)
α [°]	88.264(4)	88.105(4)	96.331(2)	90
β [°]	85.531(4)	84.771(4)	93.814(2)	93.5180(10)
γ [°]	79.245(4)	79.178(4)	100.767(2)	90
V [Å^3]	875.2(2)	922.67(18)	970.69(12)	1668.37(8)
Z	1	1	2	4
$d_{calcd.}$ [Mg/m^3]	1.665	1.636	1.624	1.654
μ [mm^{-1}]	0.515	0.732	0.478	0.797
F (000)	458	474	498	872
Crystal size [mm^3]	0.063 x 0.061 x 0.058	0.072 x 0.069 x 0.066	0.078 x 0.075 x 0.071	0.073 x 0.071 x 0.068
Theta range for data collection (°)	2.216 to 28.314	2.161 to 28.356	2.144 to 28.318	2.315 to 28.272
Reflections collected	33995	33514	33196	39524
Independent reflections	4350 [R(int) = 0.0482]	4603 [R(int) = 0.0381]	4827 [R(int) = 0.0493]	4130 [R(int) = 0.1301]
Goodness-of-fit on F^2	1.042	1.055	1.568	1.006
Completeness to theta = 25.242° (%)	100.0	100	100	100
Max. and min. transmission	0.6973 and 0.7457	0.7100 and 0.7457	0.6873 and 0.7457	0.6369 and 0.7457
Data / restraints / parameters	4350 / 0 / 246	4603 / 0 / 246	4827 / 0 / 281	4103 / 0 / 213
Final R indices [I>2sigma(I)]	R1 = 0.0334, wR2 = 0.0778	R1 = 0.0346, wR2 = 0.0938	R1 = 0.0563, wR2 = 0.1423	R1 = 0.0499, wR2 = 0.1333
R indices (all data)	R1 = 0.0452, wR2 = 0.0841	R1 = 0.0374, wR2 = 0.0956	R1 = 0.0579, wR2 = 0.1439	R1 = 0.0516, wR2 = 0.1355
Largest diff. peak and hole (e.Å^{-3})	0.341 and -0.373	0.493 and -0.722	1.103 and 0.963	0.957 and -0.812

Table S2. Selected bond lengths [Å] and angles [°] for **1.**

Bond lengths [Å]		Bond angles [°]	
Mg(1)-O(1)	2.0812(14)	O(1)-Mg(1)-O(5)#1	89.22(6)
Mg(1)-O(4)	2.0648(15)	O(4)-Mg(1)-O(1)	175.32(7)
Mg(1)-O(5)	2.0936(16)	O(4)-Mg(1)-O(7)	94.09(7)
Mg(1)-O(7)	2.0671(15)	O(7)-Mg(1)-O(1)	85.24(6)
Mg(1)-O(10)	2.0438(16)	O(7)-Mg(1)-O(5)#1	173.40(7)
Mg(1)-O(11)	2.0542(16)	O(10)-Mg(1)-O(1)	95.75(7)
		O(10)-Mg(1)-O(4)	88.88(7)
		O(10)-Mg(1)-O(11)	172.19(7)
		O(11)-Mg(1)-O(1)	90.95(6)
		O(11)-Mg(1)-O(4)	84.48(7)

Selected Hydrogen bond lengths [Å] and angles [°].

D-H…A	d(D-H)	d(H..A)	<DHA	d(D..A)
O10-H10B…O6	0.741	2.16	166.53	2.886
O10-H10A…O9	0.812	1.938	166.6	2.735
O11-H11A…O3	0.794	1.962	166.99	2.741
O11-H11B…O6	0.829	2.256	159.87	3.047
C5-H5…O8	0.93	2.352	170.61	3.273
C7-H7…O8	0.93	2.3	172.85	3.225
C4-H4…O2	0.93	2.248	159.62	3.136

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1 #2 -x+1,-y+2,-z+2

Table S3. Selected bond lengths [Å] and angles [°] for **2.**

Bond lengths [Å]		Bond angles [°]	
Ca(1)-O(1)	2.3245(11)	O(1)-Ca(1)-O(5)#1	87.73(5)
Ca(1)-O(4)	2.2989(12)	O(1)-Ca(1)-O(10)	98.20(6)
Ca(1)-O(5)#1	2.3321(15)	O(1)-Ca(1)-O(11)	89.23(5)
Ca(1)-O(7)	2.2940(13)	O(4)-Ca(1)-O(1)	84.15(5)
Ca(1)-O(10)	2.3253(14)	O(4)-Ca(1)-O(5)#1	94.88(6)
Ca(1)-O(11)	2.3355(14)	O(4)-Ca(1)-O(10)	88.20(5)
		O(4)-Ca(1)-O(11)	95.82(6)
		O(7)-Ca(1)-O(1)	174.66(5)
		O(7)-Ca(1)-O(4)	93.51(6)
		O(7)-Ca(1)-O(10)	86.50(6)
		O(7)-Ca(1)-O(11)	86.22(6)
		O(10)-Ca(1)-O(11)	171.89(6)

Hydrogen bond lengths [Å] and angles [°] for **2.**

D-H…A	d(D-H)	d(H..A)	<DHA	d(D..A)
O10-H10B…O6	0.933	1.959	173.58	2.888
O10-H10A…O9	0.767	2.001	166.93	2.754
O11-H11A…O3	0.872	1.893	175.9	2.764
O11-H11B…O6	0.782	2.391	159.86	3.137
C4-H4…O2	0.93	2.269	161.65	3.165
C5-HA…O8	0.93	2.309	171.7	3.232
C7-H7…O8	0.93	2.374	176.93	3.303

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+1,-z+1 #2 -x,-y+2,-z+2

Table S4. Selected bond lengths [Å] and angles [°] for **3.**

Bond lengths [Å]		Bond angles [°]	
Mg(1)-O(1)	2.0551(13)	O(1)-Mg(1)-O(6)	88.79(5)
Mg(1)-O(6)	2.0656(12)	O(1)-Mg(1)-O(10)	89.84(6)
Mg(1)-O(10)	2.0759(12)	O(1)-Mg(1)-O(11)	94.19(6)
Mg(1)-O(11)	2.0740(13)	O(1)-Mg(1)-O(12)	178.88(6)
Mg(1)-O(12)	2.0947(13)	O(6)-Mg(1)-O(10)	91.35(5)
Mg(1)-O(13)	2.0406(13)	O(6)-Mg(1)-O(11)	177.02(6)
		O(10)-Mg(1)-O(12)	91.20(6)
		O(11)-Mg(1)-O(10)	88.57(6)
		O(11)-Mg(1)-O(12)	85.43(6)
		O(13)-Mg(1)-O(10)	175.60(6)

Hydrogen bond lengths [Å] and angles [°].

D-H…A	d(D-H)	d(H..A)	<DHA	d(D..A)
O10-H10B…O3	0.829	1.933	167.92	2.749
O10-H10A…O7	0.76	2.011	166.76	2.756
O11-H11A…O7	0.751	2.033	176.25	2.782
O11-H11B…O8	0.737	2.123	155.02	2.808
O12-H12B…O8	0.743	2.138	162.20	2.855
O12-H12A…O9	0.769	2.061	176.08	2.829
O13-H13B…O5	0.847	1.911	159.77	2.722
O13-H13A…O10	0.79	2.089	161.64	2.85
C8-H8…O2	0.93	2.281	171.99	3.204

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+1,-z+1 #2 -x,-y+2,-z+2

Table S5. Selected bond lengths [Å] and angles [°] for **4.**

Bond lengths [Å]		Bond angles [°]	
Ca(1)-O(1)	2.3193(14)	O(1)-Ca(1)-O(2)#1	88.96(6)
Ca(1)-O(2)#1	2.3307(14)	O(1)-Ca(1)-O(8)#2	94.61(6)
Ca(1)-O(4)	2.2905(16)	O(1)-Ca(1)-O(10)	83.05(6)
Ca(1)-O(7)	2.2979(15)	O(2)#1-Ca(1)-O(8)#2	85.26(6)
Ca(1)-O(8)#2	2.3327(14)	O(4)-Ca(1)-O(1)	89.17(6)
Ca(1)-O(10)	2.3688(16)	O(4)-Ca(1)-O(7)	88.32(7)
		O(4)-Ca(1)-O(8)#2	93.55(6)
		O(4)-Ca(1)-O(10)	96.99(7)
		O(7)-Ca(1)-O(1)	167.82(6)
		O(7)-Ca(1)-O(10)	85.42(7)
		O(7)-Ca(1)-O(8)#2	97.44(6)
		O(8)#2-Ca(1)-O(10)	169.16(6)

Hydrogen bond lengths [Å] and angles [°].

D-H…A	d(D-H)	d(H..A)	<DHA	d(D..A)
O10-H10A…O3	0.723	2.205	169.73	2.919
O10-H10B…O3	0.742	2.322	168.77	3.053

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+1,-z+1 #2 -x,-y+2,-z+2

Figure S1. Powder X-Ray Diffraction pattern of **1-4**: black(simulated), red (primitive sample).

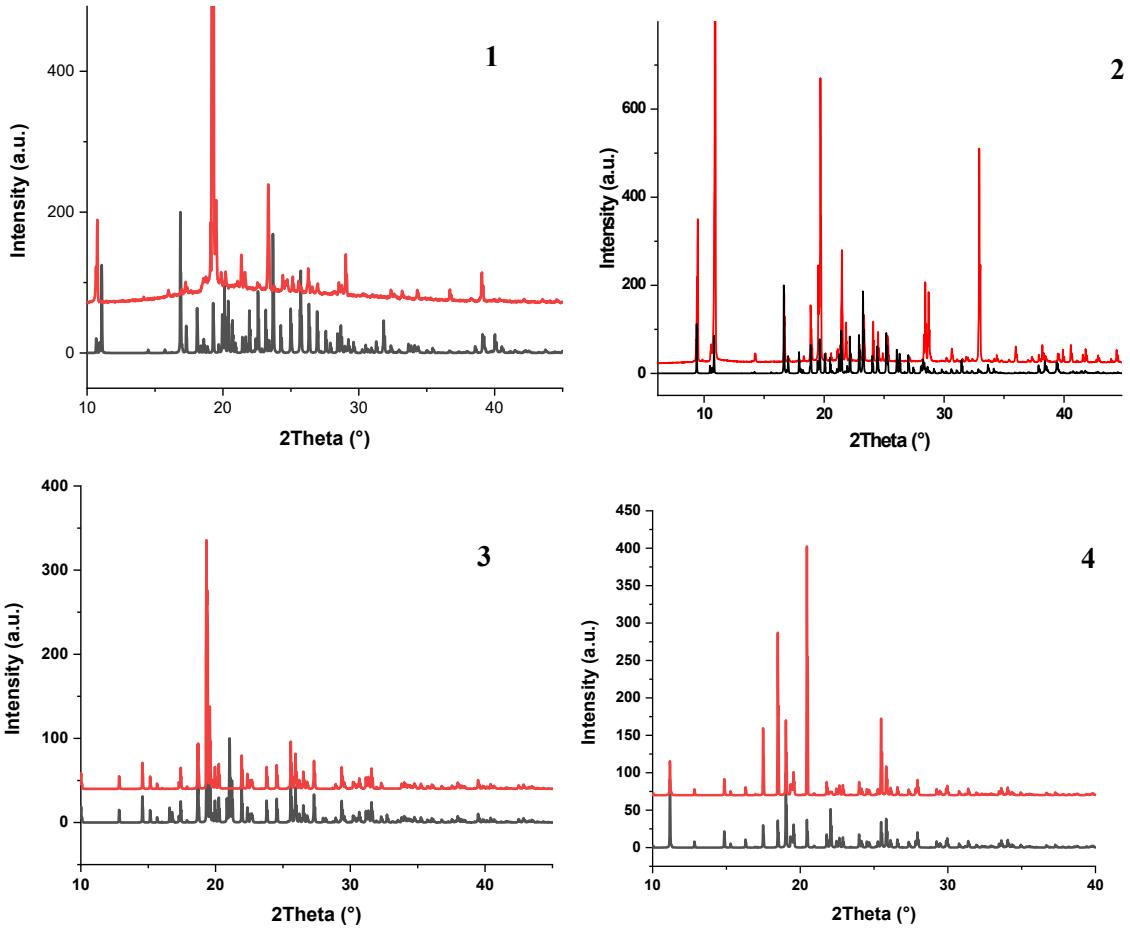


Figure S2. ^{1}H NMR spectrum of $[MV\{Mg(OSO_2Me)_3(H_2O)_2\}_2]$ (**1**) in D_2O**.**

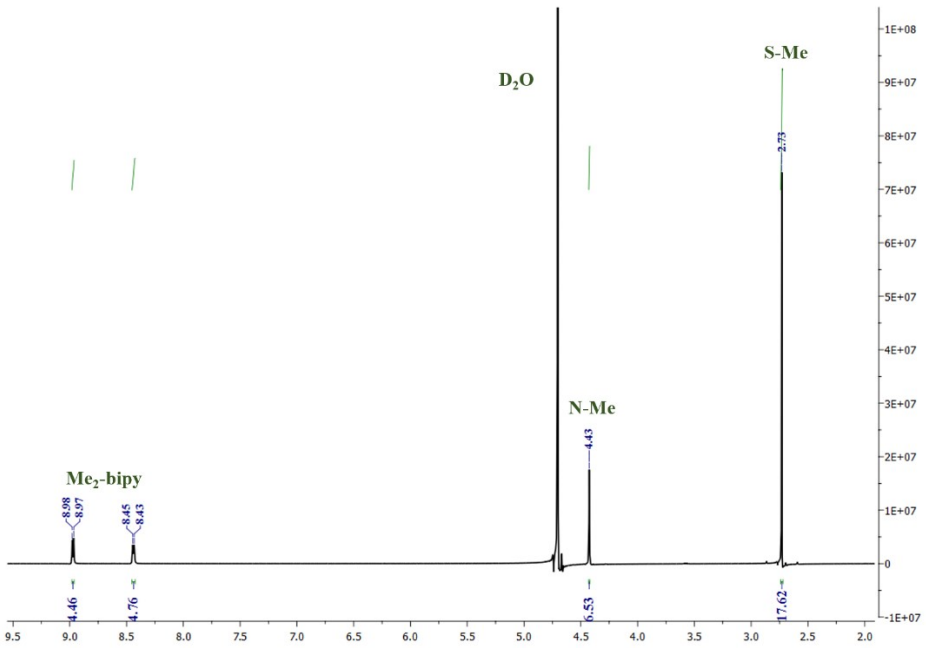


Figure S3. ^{1}H NMR spectrum of [MV{Ca(OSO$_2$Me)$_3$(H$_2$O)$_2$}$_2$] (**2**) in D$_2$O**.**

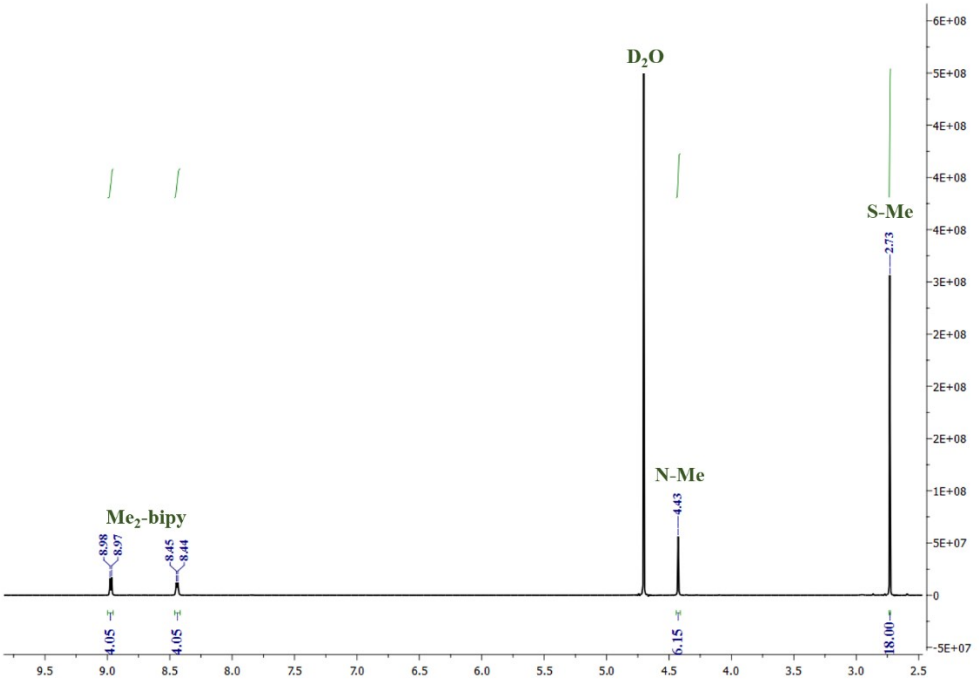


Figure S4. ^{1}H NMR spectrum of [{Mg(OSO$_2$Me)$_2$(H$_2$O)$_4$}MV·2OSO$_2$Me] (**3**) in D$_2$O**.**

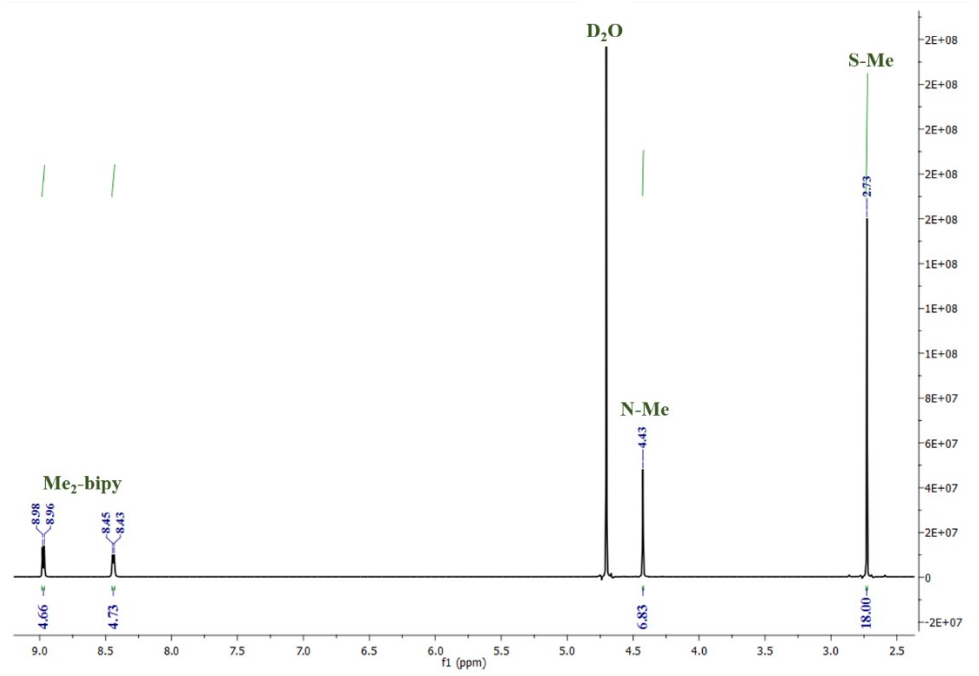


Figure S5. ^{1}H NMR spectrum of $[Me_4\text{-pip}\{Ca_2(OSO_2Me)_6(H_2O)_2\}]_n$ **(4)** in D_2O**.**

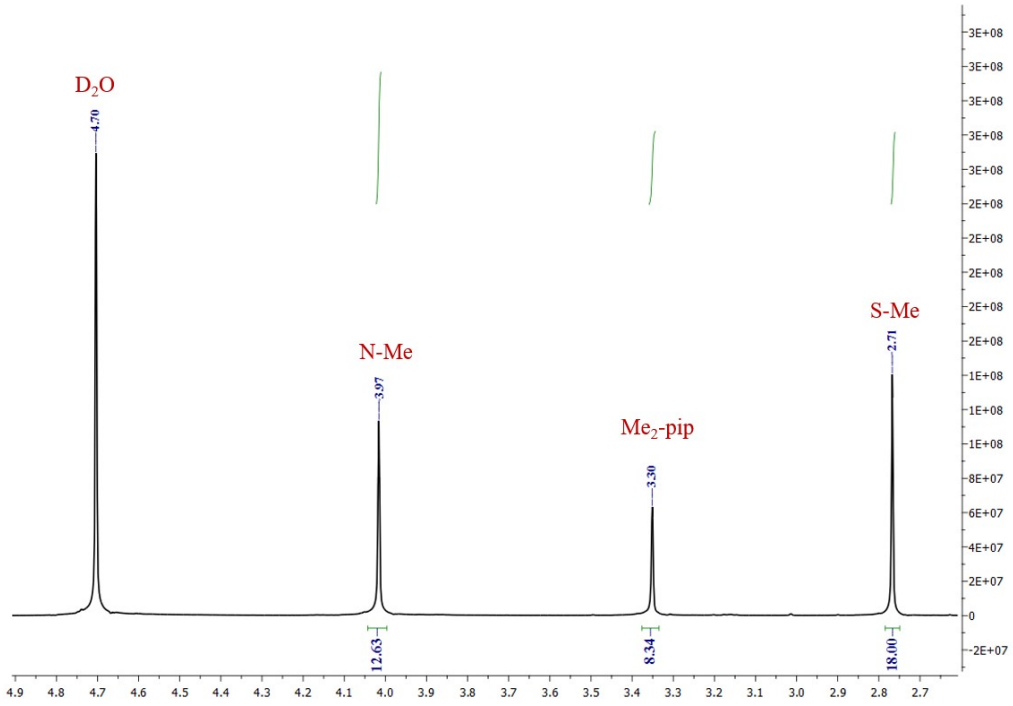
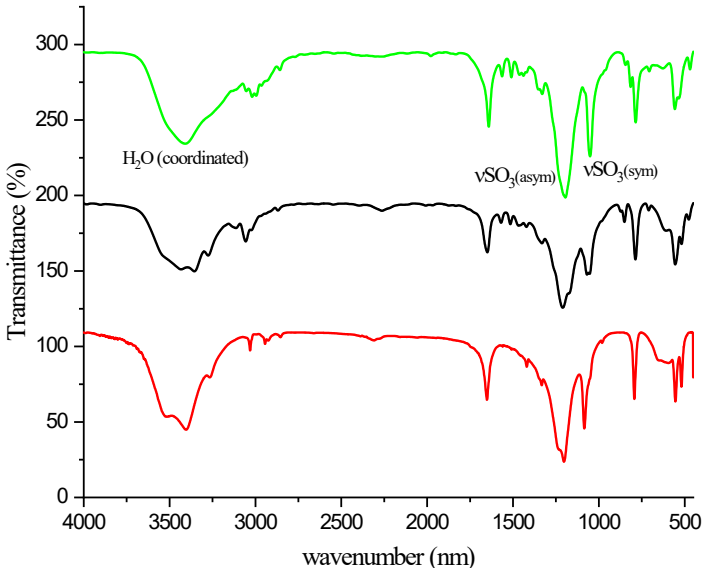
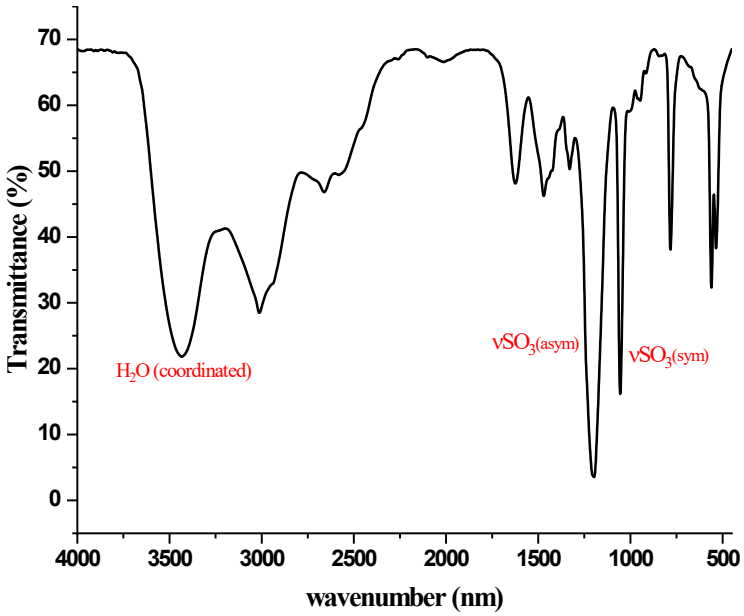


Figure S6. FT-IR spectrum of **1-4.**



FT-IR spectrum of 1(red), 2(black) and 3(green).



FT-IR spectrum of **4**.

Figure S7. TGA profiles of **1-4.**

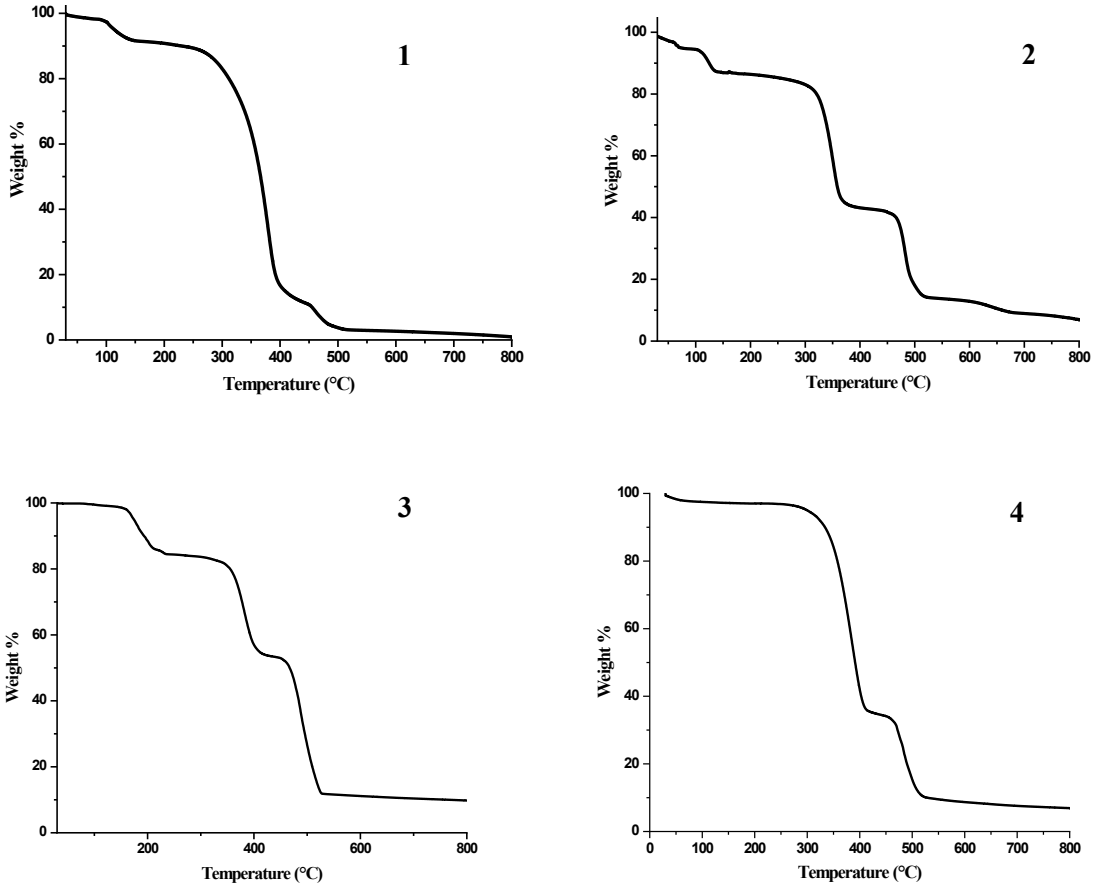


Figure S8. Cyclic Voltammogram of **1**-**3** showing repeated cycles.

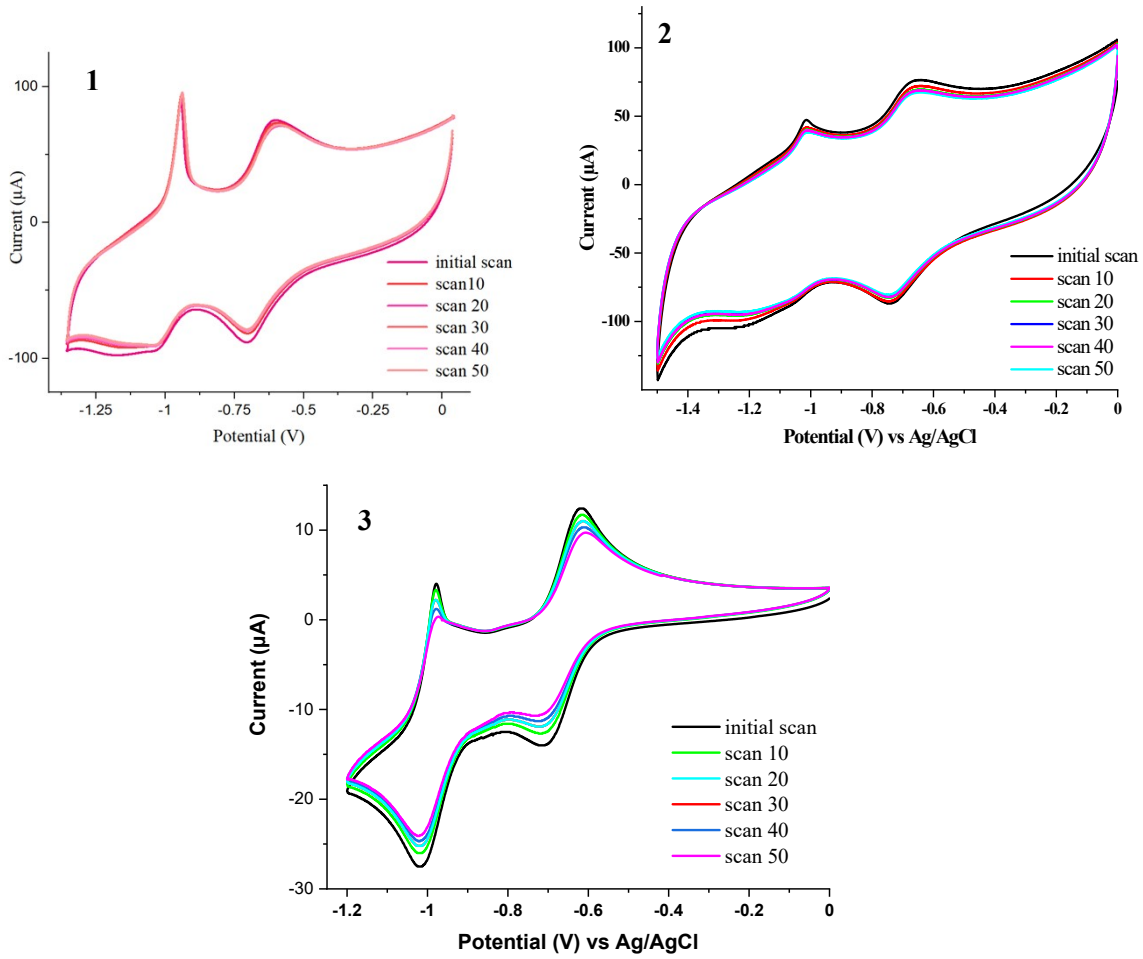
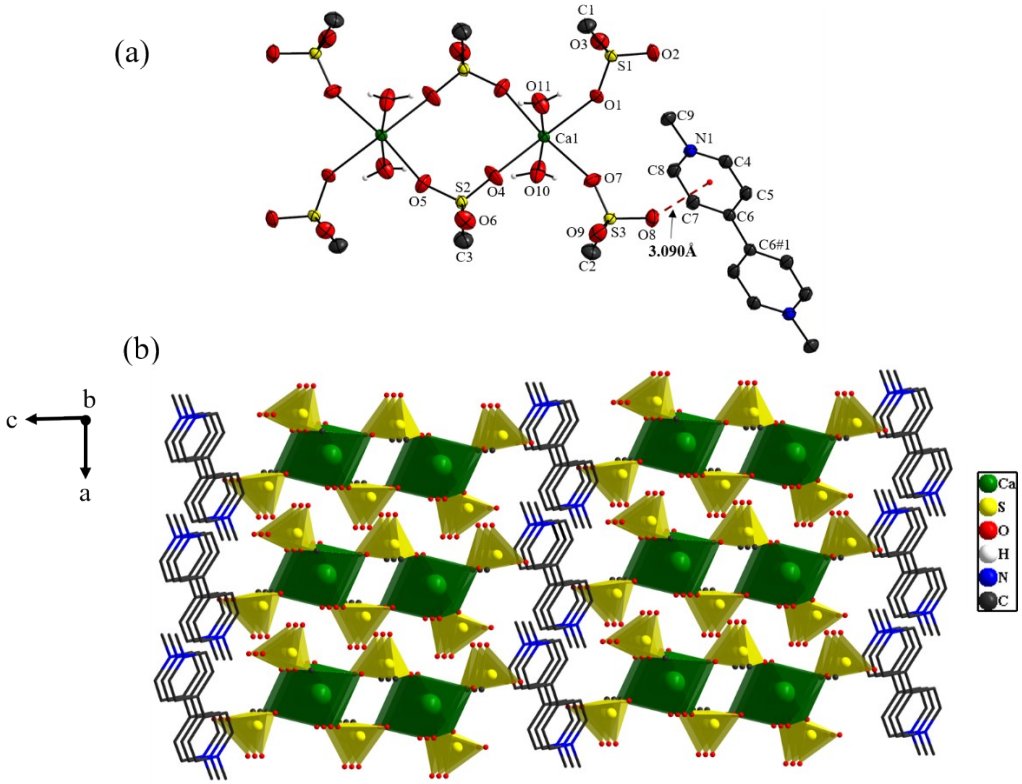


Figure S9. Perspective ORTEP and extended structure of **2**.



All hydrogen atoms except for water are omitted for clarity.

Figure S10. Extended structure of **4** along the *bc*-plane.

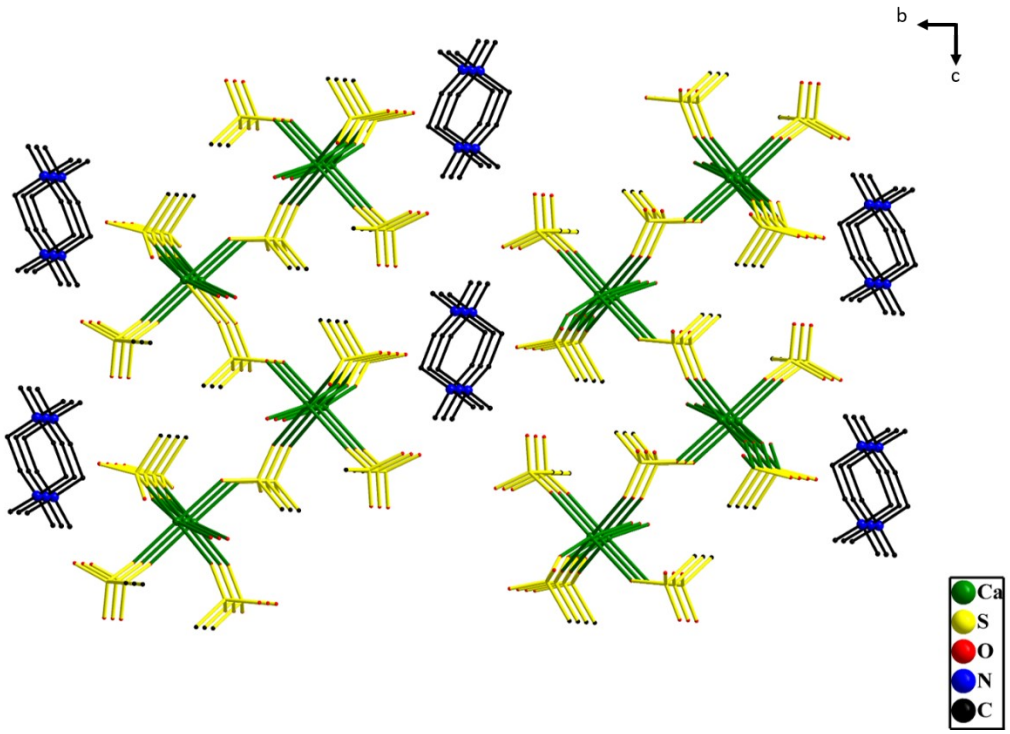


Figure S11. EPR Spectra of **2** and **3**.

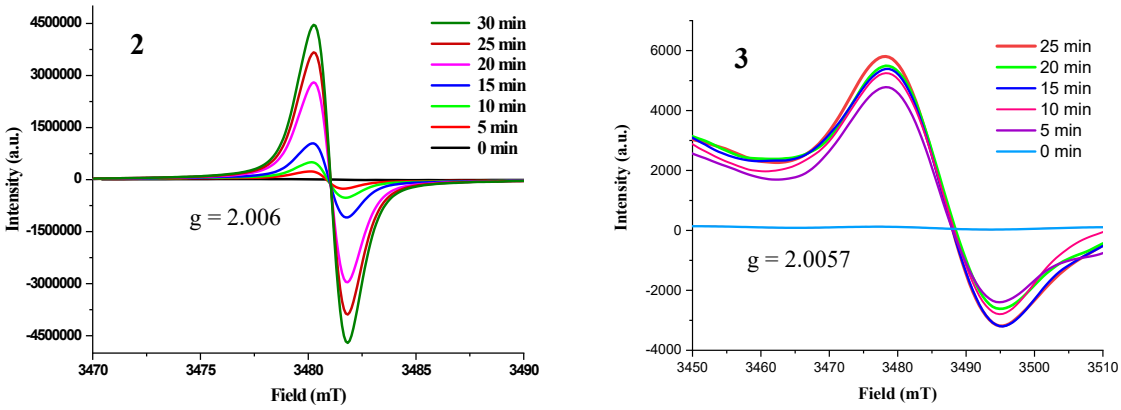


Figure S12. UV-vis diffused reflectance spectra of **2** and **3** under ambient light and Hg lamp.

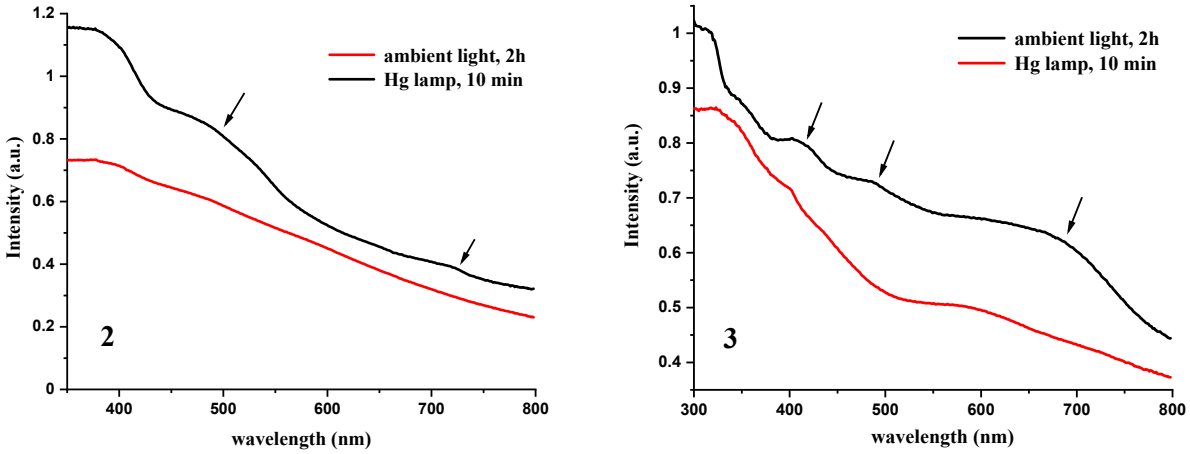


Figure S13. UV-vis spectrum of **2** in methanol**.**