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Spectroscopic evidence for hydration and dehydration of lipid bilayers upon interaction with metal ions: a new physical insight

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Supporting Information

SI-Table 1: Time resolved data for the PRODAN and PRODAN in different lipid bilayers at 440 nm.[#]

	$\chi 2$	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	a_1 (%)	a_2 (%)	a_3 (%)
PRODAN	1.1	1.80	0.60		0.26	0.74	
DPPC-PRODAN	1.008	1.83	0.58	4.28	0.46	0.22	0.32
DMPC-PRODAN	0.99	1.68	0.37	3.89	0.42	0.13	0.45
POPC-PRODAN	1.19	1.05	0.10	2.89	0.43	0.31	0.27

 # Expt. error in the measurement is around 5-10%

SI-Table 2(a): Time resolved data for the DPPC-PRODAN at 440 nm upon increasing concentration of Ca^{+2} at fixed lipid concentration (0.6mM).[#]

DPPC	$\chi 2$	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	a_1 (%)	a_2 (%)	a_3 (%)
0 mM Ca^{+2}	1.008	1.83	0.58	4.28	0.46	0.22	0.32
1 mM Ca^{+2}	1.00	1.23	0.416	2.93	0.43	0.22	0.35
2 mM Ca^{+2}	1.04	1.12	0.33	2.84	0.46	0.21	0.33
3 mM Ca^{+2}	1.08	1.09	0.31	2.78	0.47	0.17	0.36
5 mM Ca^{+2}	1.11	1.05	0.32	2.77	0.48	0.17	0.35
7 mM Ca^{+2}	1.11	1.05	0.336	2.77	0.47	0.13	0.40
10 mM Ca^{+2}	1.00	1.15	0.384	2.79	0.44	0.18	0.38
15 mM Ca^{+2}	1.06	1.11	0.43	2.79	0.44	0.17	0.39
20 mM Ca^{+2}	1.18	1.10	0.35	2.84	0.46	0.13	0.41
30 mM Ca^{+2}	1.12	1.13	0.384	2.90	0.44	0.16	0.40
40 mM Ca^{+2}	1.03	1.16	0.39	2.97	0.44	0.15	0.41

 # Expt. error in the measurement is around 5-10%

SI-Table 2(b): Time resolved data for the DMPC-PRODAN at 440 nm upon increasing concentration of Ca^{+2} at fixed lipid concentration (0.6mM).#

DMPC	$\chi 2$	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	a_1 (%)	a_2 (%)	a_3 (%)
0 mM Ca^{+2}	0.99	1.68	0.37	3.89	0.42	0.13	0.45
1mM Ca^{+2}	1.04	1.50	0.54	3.49	0.40	0.19	0.41
2 mM Ca^{+2}	1.01	1.41	0.48	3.32	0.42	0.18	0.40
3 mM Ca^{+2}	1.095	1.57	0.52	3.26	0.44	0.18	0.38
4 mM Ca^{+2}	1.04	1.34	0.36	3.10	0.43	0.13	0.44
5 mM Ca^{+2}	1.06	1.33	0.40	3.05	0.43	0.11	0.46
7 mM Ca^{+2}	1.08	1.31	0.39	3.07	0.43	0.11	0.46
10 mM Ca^{+2}	1.09	1.36	0.40	3.12	0.42	0.10	0.48
15 mM Ca^{+2}	1.13	1.25	0.41	3.20	0.41	0.09	0.50
20 mM Ca^{+2}	1.12	1.39	0.39	3.37	0.42	0.13	0.45
30 mM Ca^{+2}	1.14	1.27	0.36	3.30	0.41	0.10	0.49
40 mM Ca^{+2}	1.12	1.36	0.35	3.38	0.42	0.15	0.44
50 mM Ca^{+2}	1.21	1.24	0.24	3.45	0.40	0.11	0.48

 # Expt. error in the measurement is around 5-10%

SI-Table 2(c): Time resolved data for the POPC-PRODAN at 440 nm upon increasing concentration of Ca^{+2} at fixed lipid concentration (0.6mM).#

POPC	$\chi 2$	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	a_1 (%)	a_2 (%)	a_3 (%)
0 mM Ca^{+2}	1.19	1.05	0.10	2.89	0.43	0.31	0.27
1 mM Ca^{+2}	1.06	1.17	0.33	2.82	0.48	0.19	0.33
2 mM Ca^{+2}	1.09	1.13	0.28	2.90	0.49	0.20	0.31
3 mM Ca^{+2}	1.07	1.20	0.35	2.95	0.48	0.17	0.34
5 mM Ca^{+2}	1.01	1.16	0.26	2.91	0.48	0.19	0.33
7 mM Ca^{+2}	1.13	1.13	0.36	2.81	0.48	0.20	0.32
10 mM Ca^{+2}	1.04	1.12	0.30	2.81	0.49	0.19	0.32
15 mM Ca^{+2}	1.08	1.21	0.27	2.80	0.50	0.18	0.32
20 mM Ca^{+2}	1.10	1.15	0.27	2.86	0.47	0.23	0.30
30 mM Ca^{+2}	1.11	1.08	0.29	2.84	0.50	0.20	0.30
40 mM Ca^{+2}	1.11	1.15	0.29	2.80	0.49	0.19	0.32

 # Expt. error in the measurement is around 5-10%

SI-Table 3(a): Time resolved data for the DPPC-PRODAN at 440 nm upon increasing concentration of Mg^{+2} at fixed lipid concentration (0.6mM).#

DPPC	$\chi 2$	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	a_1 (%)	a_2 (%)	a_3 (%)
0 mM Mg^{+2}	1.008	1.83	0.58	4.28	0.46	0.22	0.32
1 mM Mg^{+2}	1.02	1.44	0.44	3.46	0.41	0.21	0.39
2 mM Mg^{+2}	0.973	1.13	0.33	2.81	0.45	0.25	0.30
3 mM Mg^{+2}	1.17	1.08	0.30	2.74	0.47	0.24	0.29
5 mM Mg^{+2}	1.11	0.96	0.22	2.47	0.45	0.26	0.29
7 mM Mg^{+2}	1.03	0.88	0.195	2.40	0.43	0.35	0.22
10 mM Mg^{+2}	0.98	0.84	0.186	2.34	0.37	0.45	0.18
15 mM Mg^{+2}	1.18	0.77	0.153	2.23	0.33	0.50	0.17
20 mM Mg^{+2}	1.16	0.67	0.14	2.07	0.32	0.51	0.17
30 mM Mg^{+2}	1.07	0.66	0.15	2.04	0.32	0.52	0.16
40 mM Mg^{+2}	1.05	0.68	0.157	1.99	0.30	0.54	0.15

 # Expt. error in the measurement is around 5-10%

SI-Table 3(b): Time resolved data for the DMPC-PRODAN at 440 nm upon increasing concentration of Mg^{+2} at fixed lipid concentration (0.6mM).#

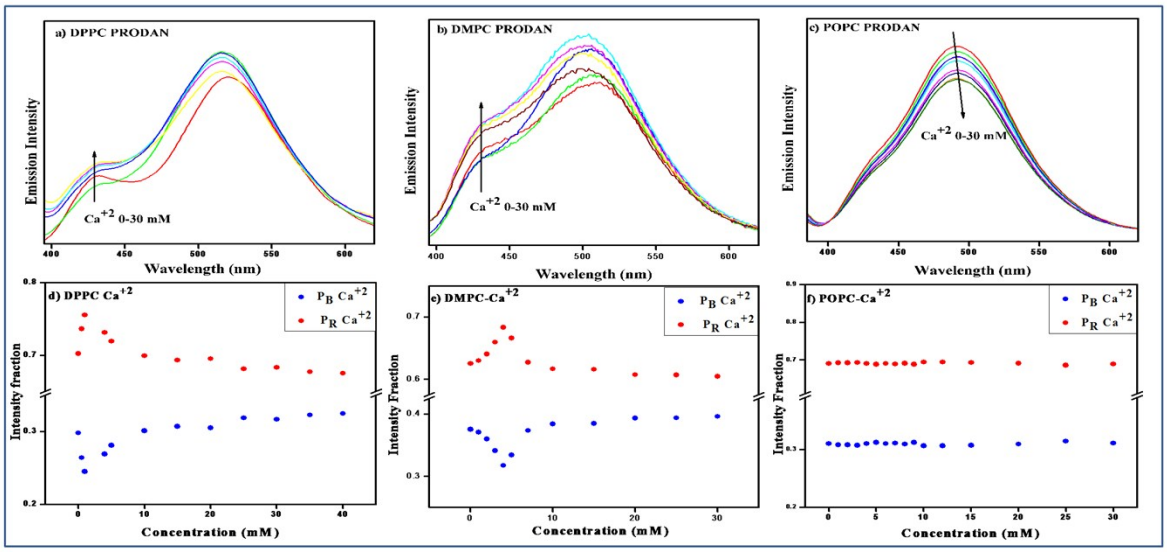
DMPC	$\chi 2$	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	a_1 (%)	a_2 (%)	a_3 (%)
0 mM Mg^{+2}	0.99	1.68	0.37	3.89	0.42	0.13	0.45
1 mM Mg^{+2}	1.14	1.42	0.41	3.32	0.45	0.23	0.31
2 mM Mg^{+2}	1.08	1.31	0.35	3.22	0.48	0.21	0.32
3 mM Mg^{+2}	1.07	1.21	0.33	3.06	0.47	0.22	0.31
4 mM Mg^{+2}	1.07	1.20	0.32	2.99	0.42	0.24	0.29
5 mM Mg^{+2}	1.02	1.19	0.33	2.98	0.47	0.25	0.28
7 mM Mg^{+2}	1.11	1.01	0.23	2.74	0.45	0.30	0.24
10 mM Mg^{+2}	1.11	0.96	0.24	2.71	0.42	0.38	0.19
15 mM Mg^{+2}	1.15	0.77	0.15	2.54	0.36	0.51	0.13
20 mM Mg^{+2}	1.06	0.76	0.16	2.54	0.34	0.56	0.10
30 mM Mg^{+2}	1.11	0.72	0.15	2.45	0.33	0.58	0.10
40 mM Mg^{+2}	1.10	0.77	0.16	2.40	0.33	0.58	0.10

 # Expt. error in the measurement is around 5-10%

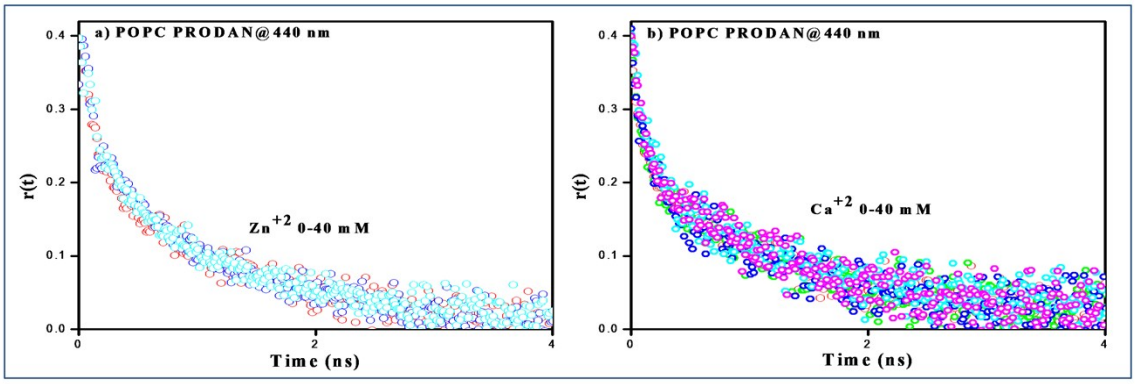
SI-Table 3(c): Time resolved data for the POPC-PRODAN at 440 nm upon increasing concentration of Mg^{+2} at fixed lipid concentration (0.6mM).#

POPC	$\chi 2$	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	a_1 (%)	a_2 (%)	a_3 (%)
0 mM Mg^{+2}	1.19	1.05	0.10	2.89	0.43	0.31	0.27
1 mM Mg^{+2}	1.07	1.23	0.349	2.97	0.48	0.18	0.34
2 mM Mg^{+2}	1.11	1.10	0.23	2.90	0.50	0.17	0.33
3 mM Mg^{+2}	1.04	1.25	0.37	3.04	0.49	0.21	0.30
5 mM Mg^{+2}	1.18	1.17	0.25	2.98	0.48	0.17	0.34
7 mM Mg^{+2}	1.04	1.21	0.36	2.96	0.48	0.20	0.32
10 mM Mg^{+2}	1.01	1.19	0.31	2.96	0.49	0.19	0.32
15 mM Mg^{+2}	1.09	1.17	0.23	2.99	0.50	0.18	0.32
20 mM Mg^{+2}	1.10	1.14	0.25	2.94	0.50	0.18	0.32
30 mM Mg^{+2}	1.09	1.04	0.26	2.80	0.47	0.23	0.30
40 mM Mg^{+2}	1.11	1.20	0.29	2.95	0.49	0.19	0.32

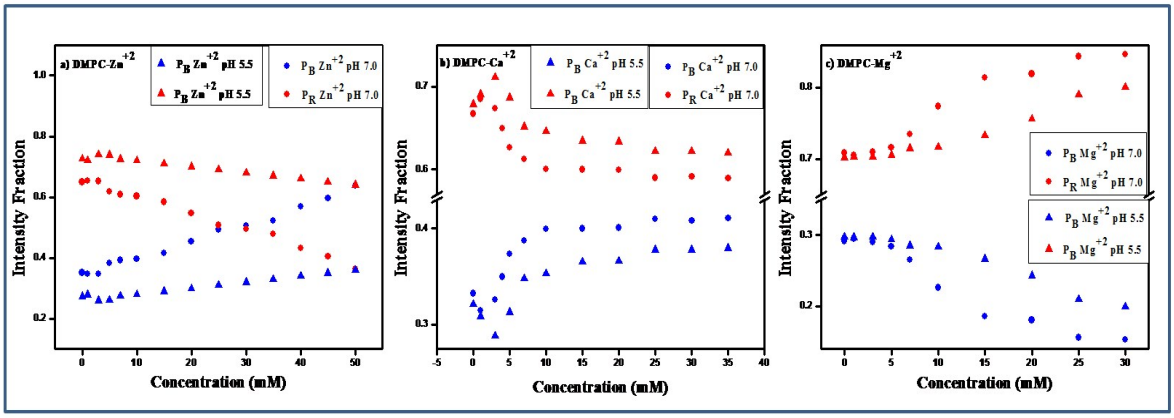
 # Expt. error in the measurement is around 5-10%



SI Figure 1: Emission spectra of PRODAN for addition of Ca^{+2} (0-40 mM) in a) DPPC b) DMPC and c) POPC. Estimated intensity fraction as a function of concentration of Ca^{+2} in d) DPPC, e) DMPC and f) POPC.



SI Figure 2: Time resolved decay curves of PRODAN in a) POPC-Zn^{+2} (0-40 mM) and b) POPC-Ca^{+2} (0-40 mM) at 440 nm.



SI Figure 3: Estimated intensity fraction as a function of metal ion concentration a) Zn^{+2}, b) Ca^{+2} and c) Mg^{+2} in DMPC lipid bilayers at pH~7.0 and pH~5.5.

SI-Table 4(a): Hydrodynamic diameter of DMPC lipid bilayers as obtained from DLS measurement in presence of different concentration of Metal salts (Zn^{+2}, Ca^{+2} and Mg^{+2}).

	Average Size at pH 7.0 (nm)	Average Size at pH 5.5 (nm)
DMPC	90.3	69.8
DMPC+ 1 mM Zn^{+2}	101.4	68.4
DMPC+ 5 mM Zn^{+2}	242.8	69.6
DMPC+ 7 mM Zn^{+2}	365.6	78.1
DMPC+ 10 mM Zn^{+2}	776.6	123.8
DMPC+ 15 mM Zn^{+2}	1605.3	208.4
	Average Size at pH 7.0 (nm)	Average Size at pH 5.5 (nm)
DMPC	90.3	69.8
DMPC+ 1 mM Ca^{+2}	95.6	72.4
DMPC+ 5 mM Ca^{+2}	242.9	85.5
DMPC+ 7 mM Ca^{+2}	349.7	87.6
DMPC+ 10 mM Ca^{+2}	426.7	95.0
DMPC+ 15 mM Ca^{+2}	733.1	95.5
	Average Size at pH 7.0 (nm)	Average Size at pH 5.5 (nm)
DMPC	90.0	69.8
DMPC+ 1 mM Mg^{+2}	93.6	75.6
DMPC+ 5 mM Mg^{+2}	90.3	82.3
DMPC+ 7 mM Mg^{+2}	224.9	85.5
DMPC+ 10 mM Mg^{+2}	332.8	87.6
DMPC+ 15 mM Mg^{+2}	461.8	85.4

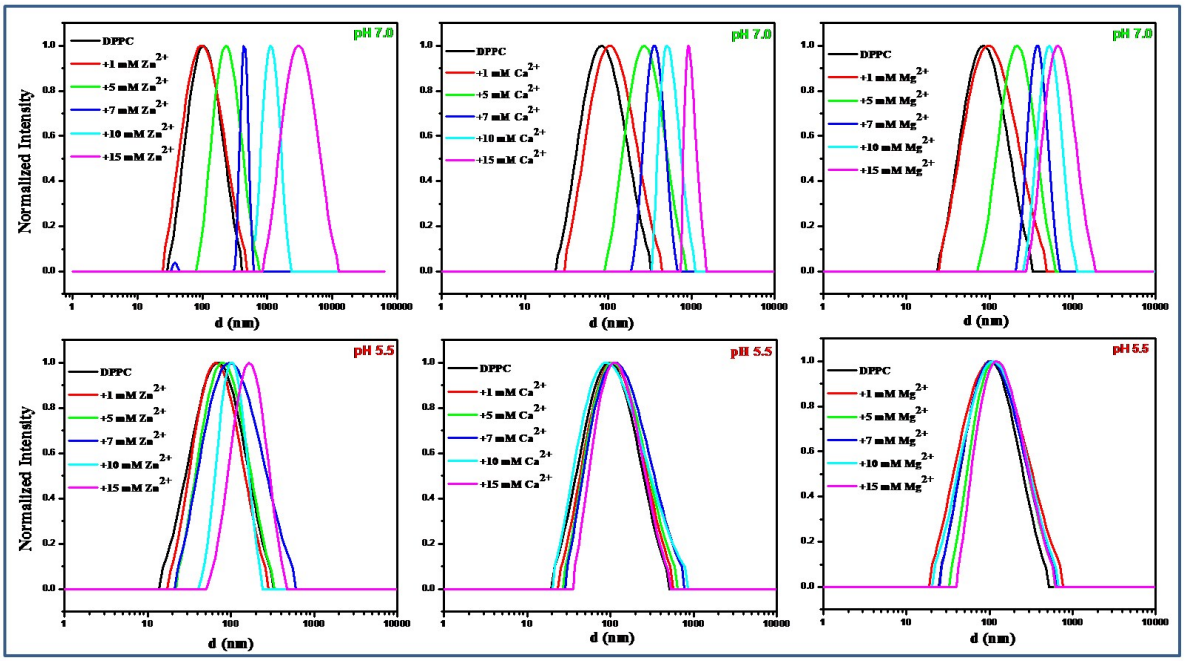
SI-Table 4(b): Hydrodynamic diameter of DPPC lipid bilayers as obtained from DLS measurement in presence of different concentration of Metal salts (Zn^{+2}, Ca^{+2} and Mg^{+2}).

	Average Size at pH 7.0 (nm)	Average Size at pH 5.5 (nm)
DPPC	94.3	84.4
DPPC+ 1 mM Zn^{+2}	98.2	85.1
DPPC+ 5 mM Zn^{+2}	307.6	89.8
DPPC+ 7 mM Zn^{+2}	430.9	97.3
DPPC+ 10 mM Zn^{+2}	982.6	129.5
DPPC+ 15 mM Zn^{+2}	2203.5	189.4

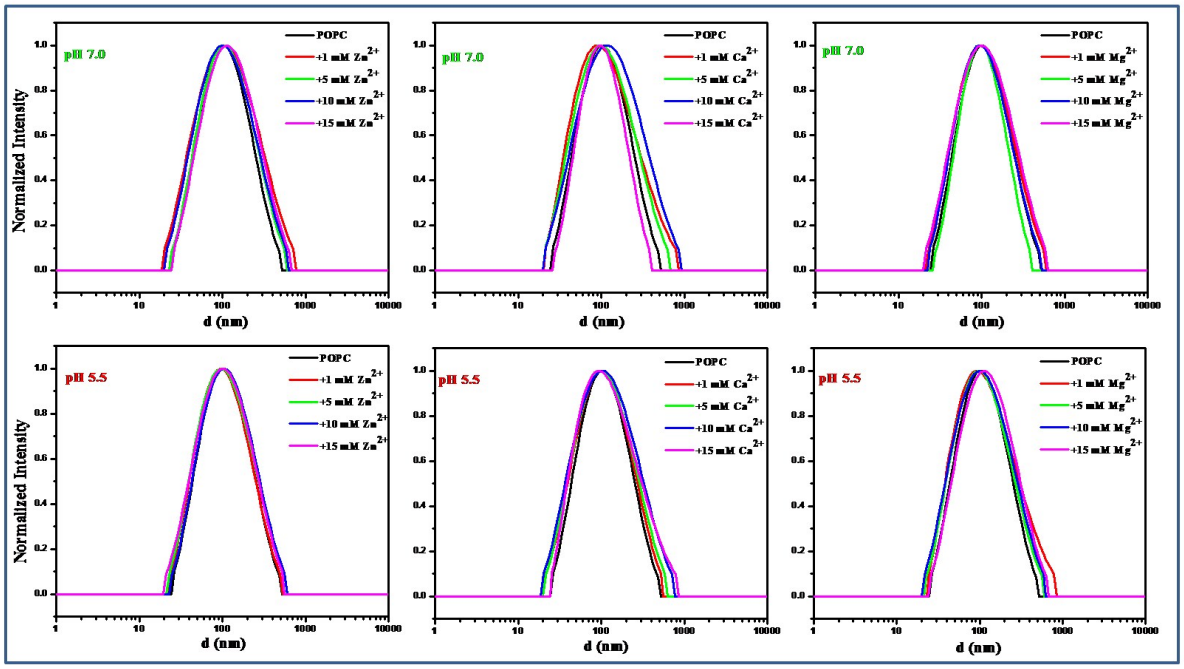
	Average Size at pH 7.0 (nm)	Average Size at pH 5.5 (nm)
DPPC	94.3	84.4
DPPC+ 1 mM Ca^{+2}	97.2	86.1
DPPC+ 5 mM Ca^{+2}	267.6	90.4
DPPC+ 7 mM Ca^{+2}	395.1	97.5
DPPC+ 10 mM Ca^{+2}	978.7	83.7
DPPC+ 15 mM Ca^{+2}	1407.8	101.5
	Average Size at pH 7.0 (nm)	Average Size at pH 5.5 (nm)
DPPC	94.3	84.4
DPPC+ 1 mM Mg^{+2}	97.7	83.8
DPPC+ 5 mM Mg^{+2}	276.1	99.5
DPPC+ 7 mM Mg^{+2}	360.9	86.5
DPPC+ 10 mM Mg^{+2}	513.1	87.1
DPPC+ 15 mM Mg^{+2}	687.5	98.1

SI-Table 4(C): Hydrodynamic diameter of POPC lipid bilayers as obtained from DLS measurement in presence of different concentration of Metal salts (Zn^{+2}, Ca^{+2} and Mg^{+2}).

	Average Size at pH 7.0 (nm)	Average Size at pH 5.5 (nm)
POPC	73.4	82.0
POPC+ 1 mM Zn^{+2}	78.2	86.9
POPC+ 5 mM Zn^{+2}	81.3	84.3
POPC+ 7 mM Zn^{+2}	93.5	87.9
POPC+ 10 mM Zn^{+2}	91.6	86.5
POPC+ 15 mM Zn^{+2}	97.2	81.0
	Average Size at pH 7.0 (nm)	Average Size at pH 5.5 (nm)
POPC	73.4	82.0
POPC+ 1 mM Ca^{+2}	87.3	96.7
POPC+ 5 mM Ca^{+2}	86.6	89.6
POPC+ 7 mM Ca^{+2}	94.4	93.5
POPC+ 10 mM Ca^{+2}	94.3	84.3
POPC+ 15 mM Ca^{+2}	91.5	87.6
	Average Size at pH 7.0 (nm)	Average Size at pH 5.5 (nm)
POPC	73.4	82.0
POPC+ 1 mM Mg^{+2}	89.3	83.6
POPC+ 5 mM Mg^{+2}	85.2	81.5
POPC+ 7 mM Mg^{+2}	85.9	81.4
POPC+ 10 mM Mg^{+2}	96.5	85.1
POPC+ 15 mM Mg^{+2}	95.6	84.9



SI-Figure 4: Normalized DLS spectra of DPPC lipid bilayers in presence of different concentration of metal ions at pH ~7.0 and pH~ 5.5.



SI-Figure 5: Normalized DLS spectra of POPC lipid bilayers in presence of different concentration of metal ions at pH ~7.0 and pH~ 5.5.