Electronic Supplementary Material (ESI) for RSC Advances.

Electronic supplementary information

Quantum chemical studies on nucleophilic sites in calcium ion bound Zwitterionic calmodulin loops

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Supplementary Information:

Supplementary Tables S1-S5

Supplementary Figure S1 and S2

Table S1. Significant contributions of atoms; D22 $O1$ (Loop 1); D58 $O1$ and $O2$ (Loop 2); Y99 O_h (Loop 3); Y138 O_h (Loop 4) to HOMO$^-$ of different loops, showing predominant 2p character.

	$2p_x$	$2p_y$	$2p_z$
$C^{(2)}_{III,D22,O2}$	0.006	0.029	0.124
$C^{(2)}_{III,D58,O1}$	0.023	0.034	0.016
$C^{(2)}_{III,D58,O2}$	0.009	0.038	0.020
$C^{(2)}_{VII,Y99,Oh}$	0.010	0.082	0.005
$C^{(2)}_{X,Y138,Oh}$	0.011	0.036	0.027

Table S2. Significant contributions of atoms; N60 $O1$ (Loop 2); S101 C (Loop 3) and N137 $O1$ (Loop 4) to LUMO$^+$ of different loops indicating 2p character.

	$2p_x$	$2p_y$	$2p_z$
$C^{(2)}_{V,N60,O1}$	0.014	0.064	0.004
$C^{(2)}_{IX,S101,C}$	0.014	0.082	0.069
$C^{(2)}_{IX,N137,O1}$	0.001	0.000	0.025

Table S3. Nucleophilic index, f_k^- of atoms contributing to HOMO$^-$ of different loops.

ATOMS	$f_k^- \times 10^3$
D22, $O1$ (loop 1)	-7
D22, $O2$ (loop 1)	9
D58, $O1$ (loop 2)	1
D58, $O2$ (loop 2)	-2
Y99, O_h (loop 3)	-55
Y138, O_h (loop 4)	-0.8

Table S4. Electrophilic index, f_k^+ of atoms contributing to LUMO$^+$ of different loops.

ATOMS	$f_k^+ \times 10^3$
T26, O_γ (loop 1)	-1
N60, $O1$ (loop 2)	2
Y99, $C_{\delta 1}$ (loop 3)	-95
Y99, $C_{\varepsilon 1}$ (loop 3)	-78
Y99, $C_{\delta 2}$ (loop 3)	-92
Y138, $C_{\delta 1}$ (loop 4)	-56
Y138, C_γ (loop 4)	-73

Table S5. HOMO$^-$ (E^-), LUMO$^+$ (E^+) and corresponding energy gap Δ (in eV) of a different conformation of Ca^{2+} bound loop 3 and loop 4 generated from MD simulation.

loop	E^- (eV)	E^+ (eV)	Δ (eV)
3	-5.90	0.48	6.38
4	-5.73	0.24	5.97

Supplementary Figure Captions:

Fig. S1. Exponential decay of terminal capping contributions with decay constants: (a) $\xi_{C-ter}^{(L2)} = 0.3\,\text{eV}$, (b) $\xi_{N-ter}^{(L2)} = 0.01\,\text{eV}$ for loop 2. (c) $\xi_{C-ter}^{(L3)} = 0.5$ eV, (d) $\xi_{N-ter}^{(L3)} = 0.01\,\text{eV}$ for loop 3. (e) $\xi_{C-ter}^{(L4)} = 0.01\,\text{eV}$ and (f) $\xi_{N-ter}^{(L4)} = 0.03\,\text{eV}$ for loop 4.

Fig. S2. Zwitterionic terminal capping contributions, $C_{N-ter}^{(2)}$ (black) and $C_{C-ter}^{(2)}$ (gray) of (a) Ca^{2+}-loop 3 and (b) Ca^{2+}-loop 4 with respect to the HOMO-LUMO levels of neutral capped systems (red) indicating closing of HOMO-LUMO gap.

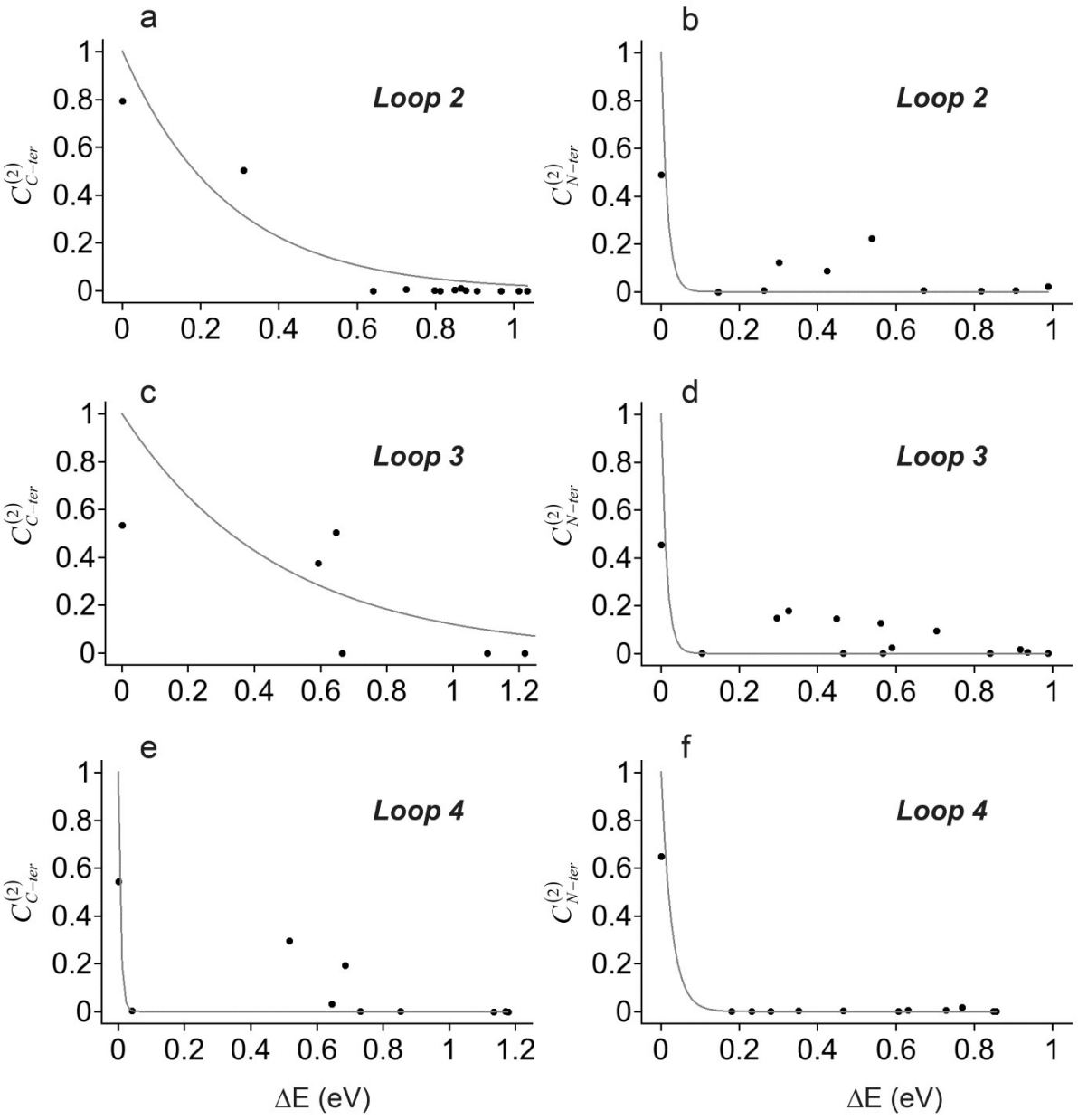
a
Loop 2
b
Loop 2
c
Loop 3
d
Loop 3
e
Loop 4
f
Loop 4
$C^{(2)}_{C-ter}$
$C^{(2)}_{N-ter}$
ΔE (eV)
ΔE (eV)

Fig. S1

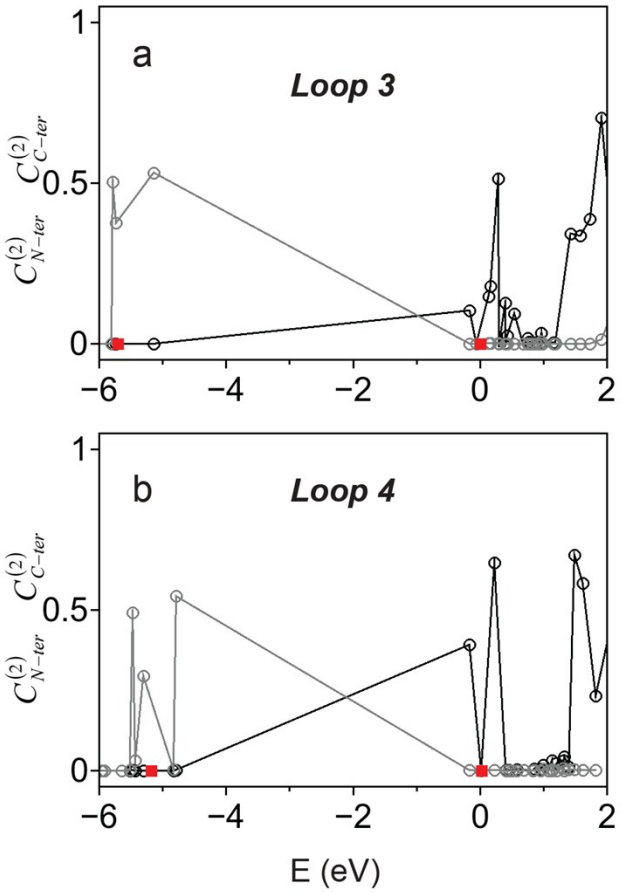

Fig. S2