Electronic Supplementary Material (ESI) for Soft Matter

Confinement Induced Stochastic Sensing of Charged Coronene and Perylene Aggregates in α–Hemolysin Nanochannel

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ASSOCIATED CONTENT:

Table 1**: GAFF parameter set and partial atomic charges used for coronene tetra-carboxylate.**

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BOND
ca ca  478.40   1.387
ca ha  344.30   1.087
c  ca  349.70   1.487
c  o   648.00   1.214

ANGLE3
ca ca ca   67.180     119.970
ca ca ha   48.460     120.010
ca ca c    64.640     120.140
ca c  o    68.670     123.440
o  c  o    78.170     130.380

DIHEDRAL
X  ca ca X      3.625         2     180.0
X  c  ca X      3.625         2     180.0

IMPHI
X  X  ca ha     1.100         2     180.0
ca ca ca ca     1.100         2     180.0       ! Using default value
c  ca ca ca     1.100         2     180.0       ! Using default value
X  o  c  o      1.100         2     180.0

!         ϵ         Rmin/2
!       (kcal/mol)     (Å)
ca        0.0860    1.9080
ha        0.0150    1.4590
 c        0.0860    1.9080
 o        0.2100    1.6612
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Partial Atomic charges of Coronene

ATOM C1	ca	-0.131898
ATOM C2	ca	-0.049736
ATOM C3	ca	0.014321
ATOM C4	ca	0.049326
ATOM C5	ca	0.038684
ATOM C6	ca	-0.275297
ATOM C7	ca	0.014321
ATOM C8	ca	0.014321
ATOM C9	ca	0.014321
ATOM C10	ca	0.049326
ATOM C11	ca	-0.049736
ATOM C12	ca	-0.101625
ATOM C13	ca	-0.101625
ATOM C14	ca	-0.049736
ATOM C15	ca	-0.131898
ATOM C16	ca	-0.275297
ATOM H1	ha	0.116147
ATOM H2	ha	0.140814
ATOM H3	ha	0.140814
ATOM H4	ha	0.116147
ATOM C17	ca	-0.101625
ATOM C18	ca	-0.101625
ATOM C19	ca	-0.049736
ATOM C20	ca	-0.131898
ATOM C21	ca	-0.275297
ATOM C22	ca	0.038684
ATOM H5	ha	0.140814
ATOM H6	ha	0.116147
ATOM C23	ca	-0.131898
ATOM H7	ha	0.140814
ATOM C24	ca	-0.275297
ATOM H8	ha	0.116147
ATOM C25	c	1.069969
ATOM C26	c	1.069969
ATOM C27	c	1.069969
ATOM C28	c	1.069969
ATOM O1	o	-0.913351
ATOM O2	o	-0.913351
ATOM O3	o	-0.913351
ATOM O4	o	-0.913351
ATOM O5	o	-0.913351
ATOM O6	o	-0.913351
ATOM O7	o	-0.913351
ATOM O8	o	-0.913351

c : carbon atom of the carbonyl group

ca : carbon atom of the benzene ring

FIGURES:

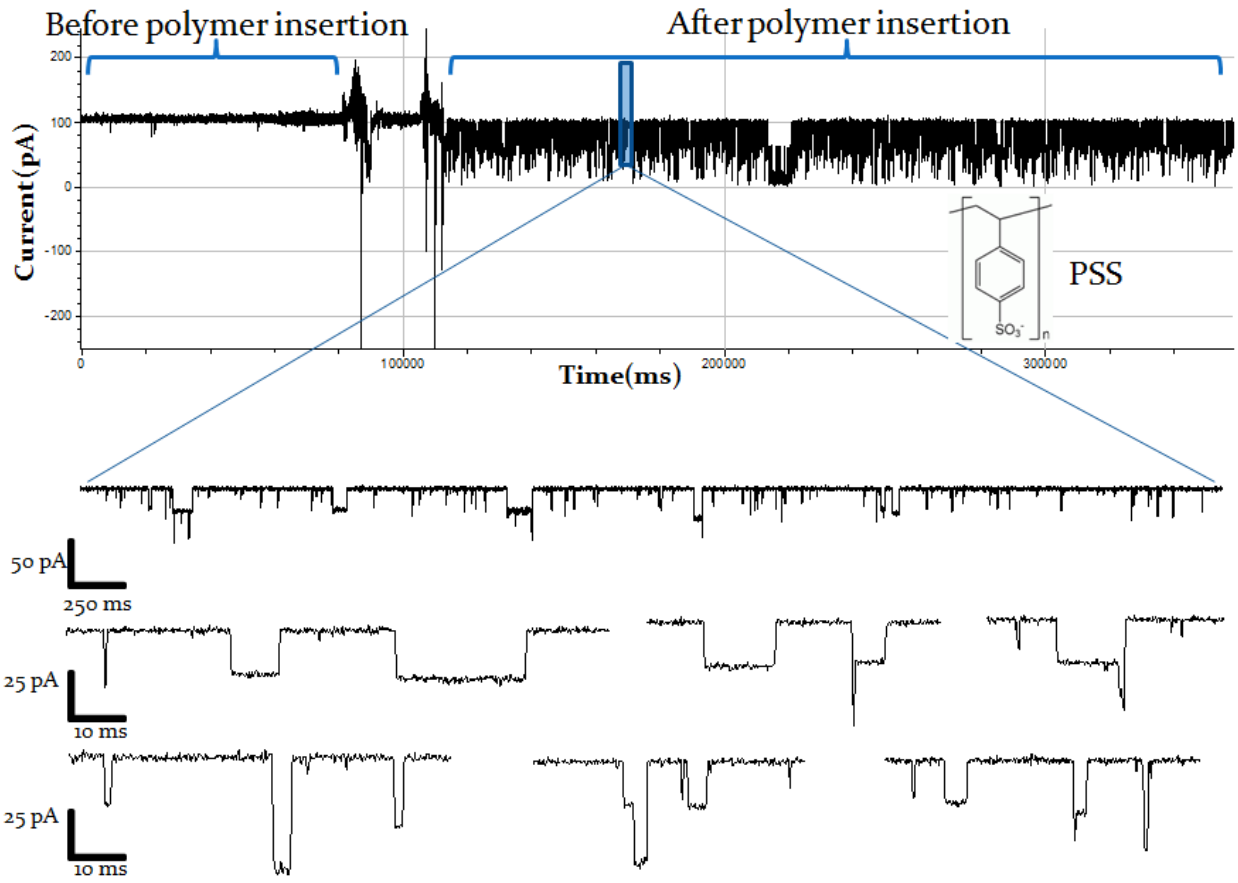

Figure S1: Translocation of polyelectrolyte sodium polystyrene sulfonate(PSS), Molecular Weight ≈ 70000, through alpha hemolysin single channel showing different kinds of blocking events.

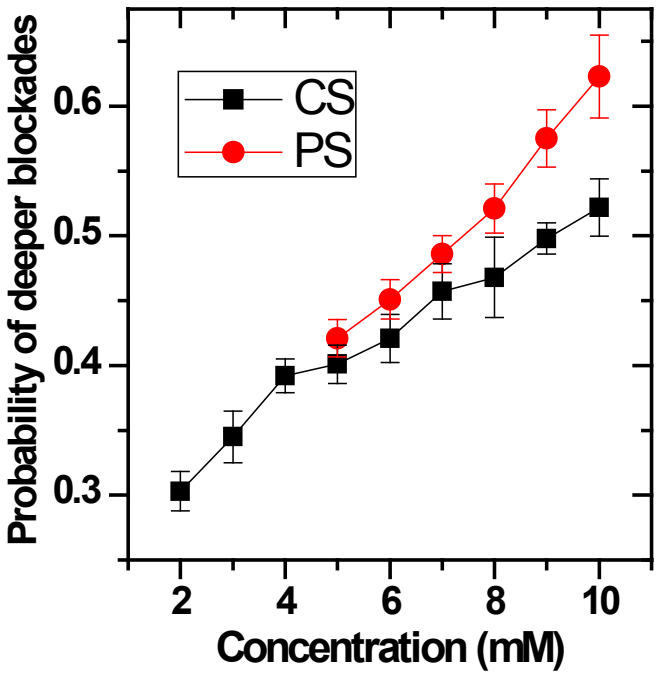

Figure S2: Probability of deeper blockade with respect to concentration for a bias of 100 mV across the pore.

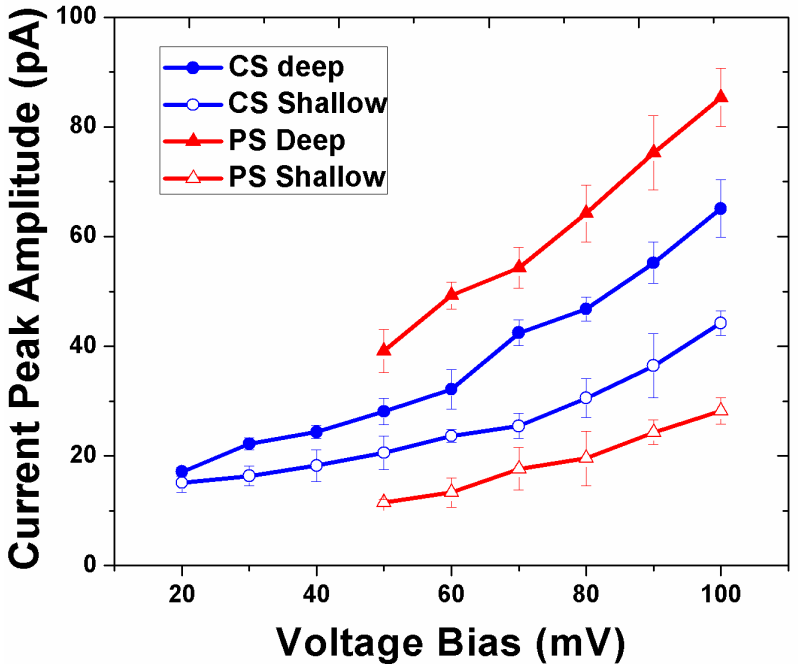

Figure S3. Linear variation of both deeper and shallower current peak amplitude with applied bias for 2 mM of CS and 7 mM of PS. (standard deviation error bars).

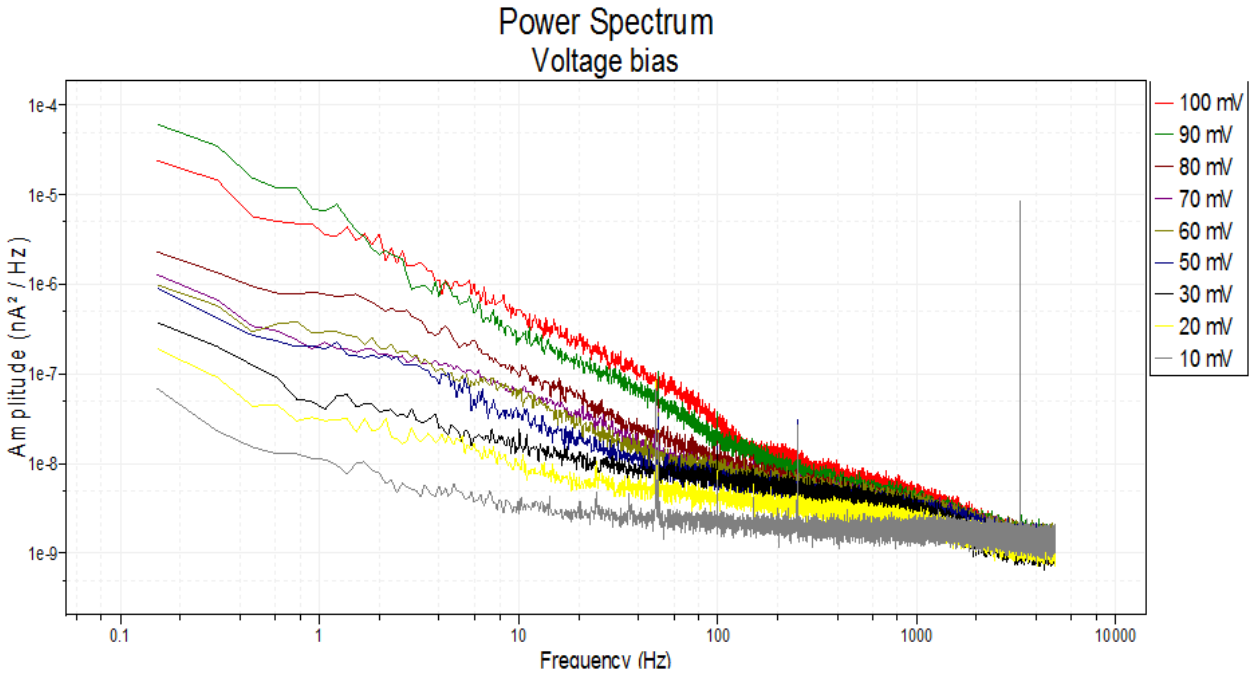

Figure S4: Voltage dependence on the power spectral density of *I(t)* of single pore with 2 mM concentration of coronene salt in cis compartment. Showing $1/f^{\alpha}$ behavior, where α increases from 0.5 – 2 with increasing voltage. Data acquisition was carried out with 1 kHz low-pass analog filter and digitized at 10 kHz sampling rate for a time series of 400 seconds.

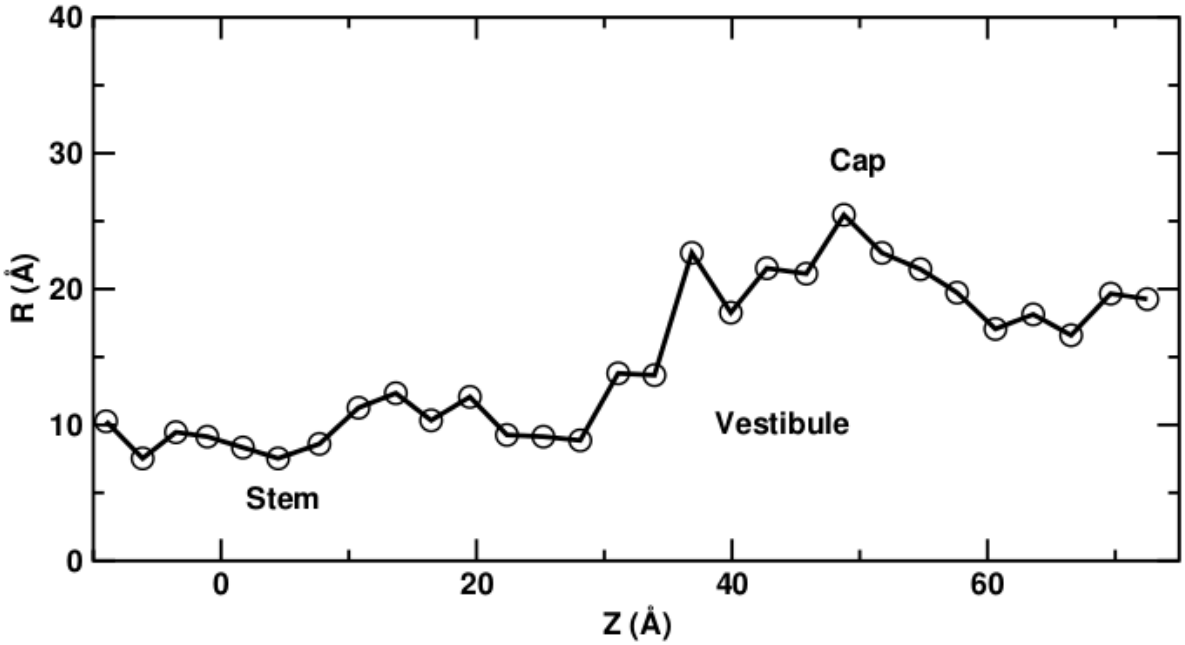

Figure S5: Average radial profile of the transmembrane pore after equilibration. The average was taken from 1ns MD trajectory.

Method to calculate radius profile:

We have calculated radius profile of the protein pore from the waters inside the transmembrane pore. We have divided the interior of the protein pore in disc segment of radius of 5 Å. Then evaluated the number of waters in this region and increased the radius by 1 Å gradually until the ratio of waters to nonwaters atoms in the shell between the two successive disc fall below 20%. In this process, interior of the whole channel was sampled after every 3 Å apart.This method was used to find out the radius of the pore as the number of waters fall sharply at the

boundary of the interior part of the transmembrane pore.

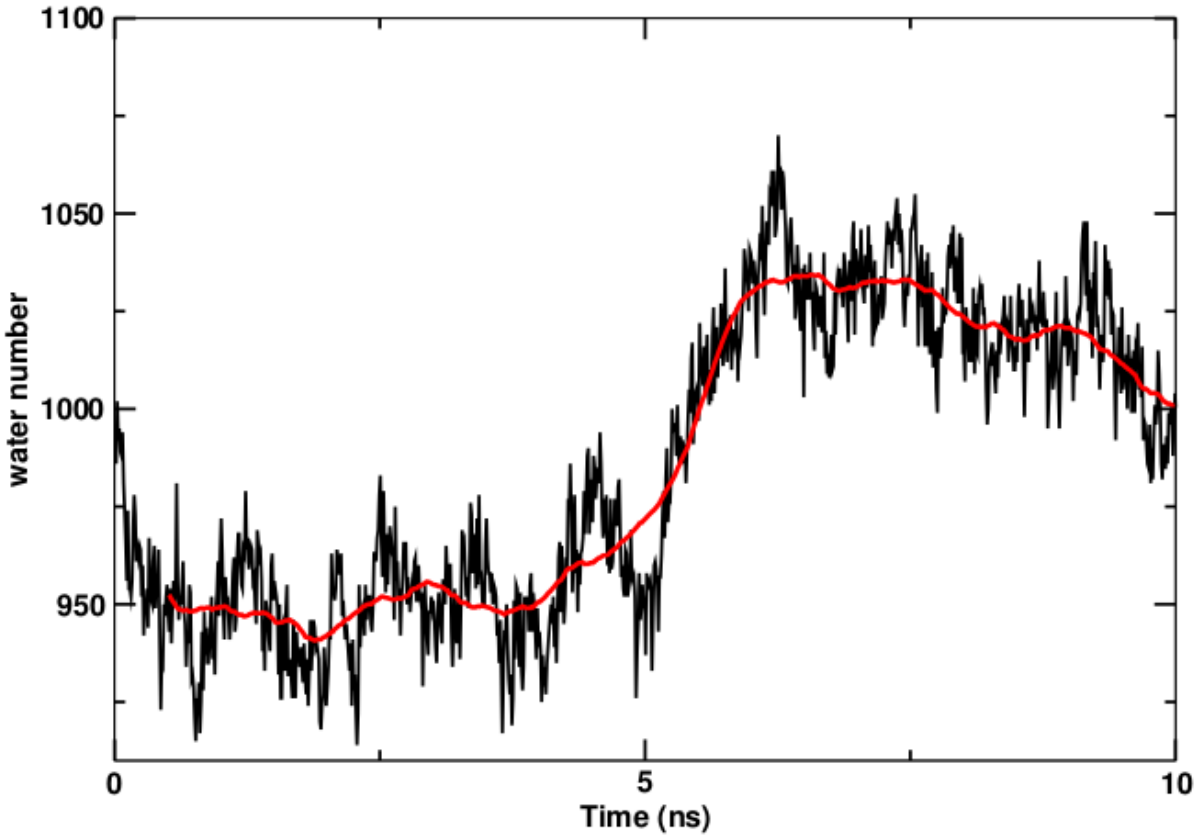

Figure S6: Number of waters inside the pore after equilibration.

As reported by literature,[1] the x-ray structure of the alpha- hemolysin channel contains 818 water molecules inside the protein pore.

Reference: 1) Aksimentiev et al , Biophysical Journal, 88, June 2005, 3745-3761

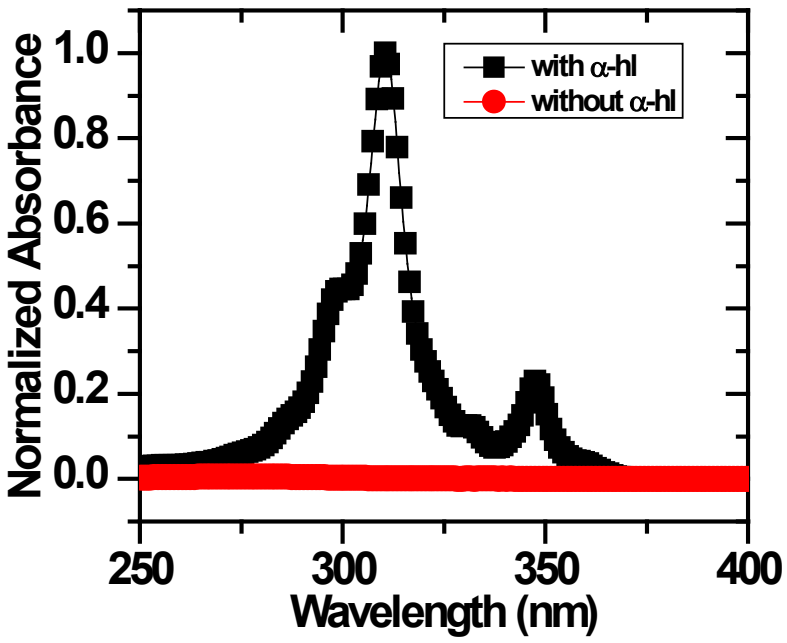

Figure S7: Absorption of solution from the trans chamber (CS was added in cis chamber). The black curve with square symbols correspond to normalized absorbance of collected solution from set of experiment with multiple pore running for more than 10,000 s. The red curve with circle symbols correspond to normalized absorbance of collected solution from measurement chamber running with only BLM without protein pore. The cis-chamber was filled with 3 mM CS and 100 mV bias was applied across the membrane for ~ 1 hr. The controlled background result did not show measurable absorbance.

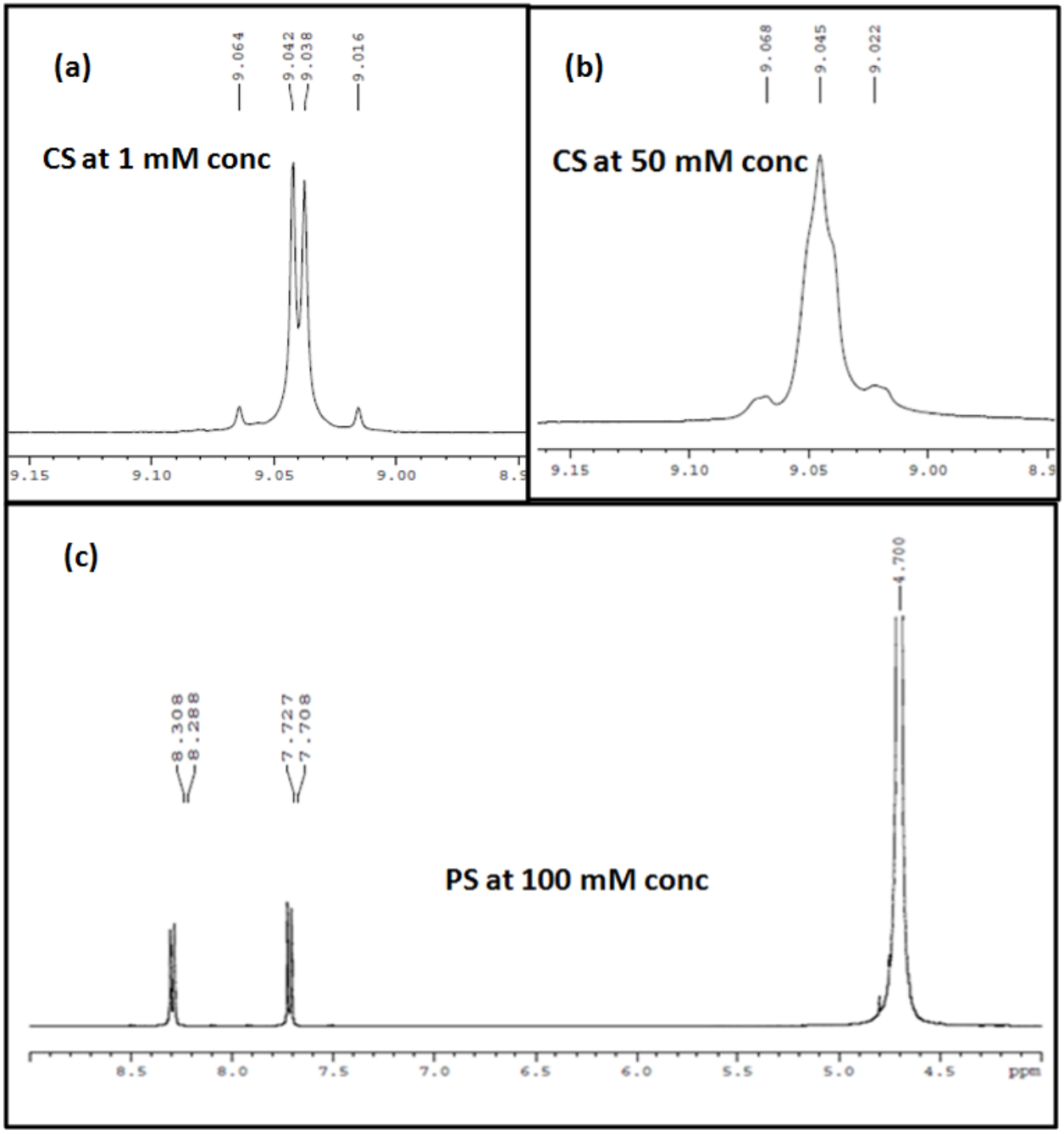

Figure S8. H-NMR of (a) CS at 1 mM concentration has four peaks at 9.064, 9.042, 9.036 and 9.016, which is a characteristic of monomers, (b) CS at 50 mM conc shows broadening of peaks, showing the interaction of protons with other Coronene molecule and (c) PS also has a two pairs of peak, but no broadening even at 100 mM conc.

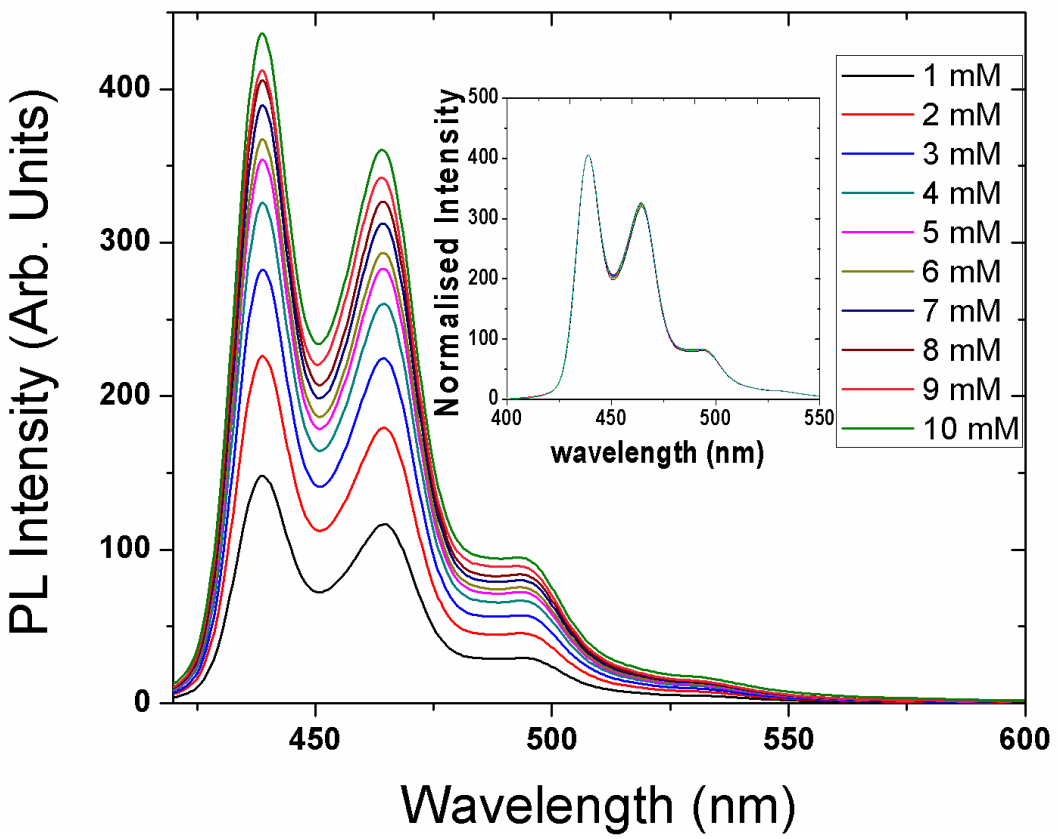

Figure S9. The photoluminescence spectra of coronene tetracarboxylate at different concentration in experimental buffer show characteristic peaks at 439 nm and 464.5 nm. Inset normalized spectra shows no shift in peaks for the range of concentration used in the experiment.

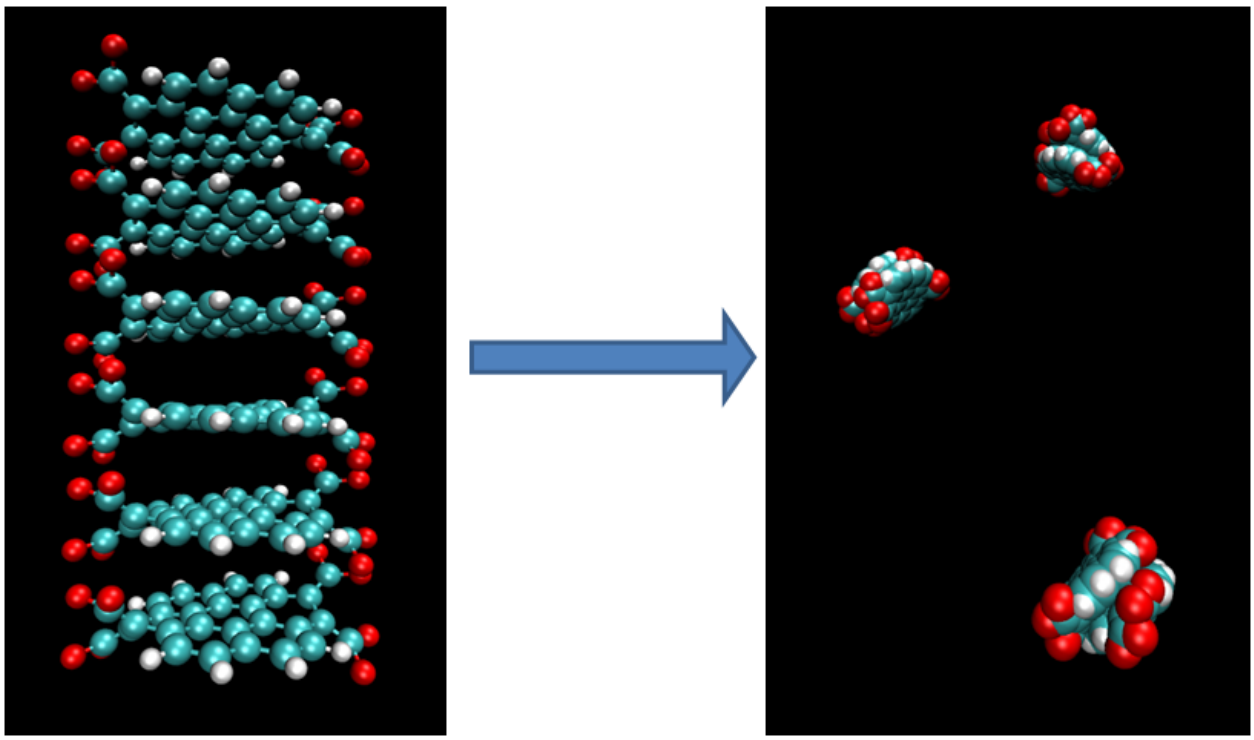

Figure S10: Energy minimization and equilibration of hexamer of coronene salt in water shows the tendency of molecules to be in dimer form. Computational setup: CHARMM force field, Total Atoms: 23127, Total Residues: 7639.

Name of the molecules	Numbers of Molecules	Charges
Coronenes (44 atoms in each molecule)	6	- 18.0 (-3.0 * 6)
Ions (K+)	18	+18.0 (1.0* 18)
Water	7615	0

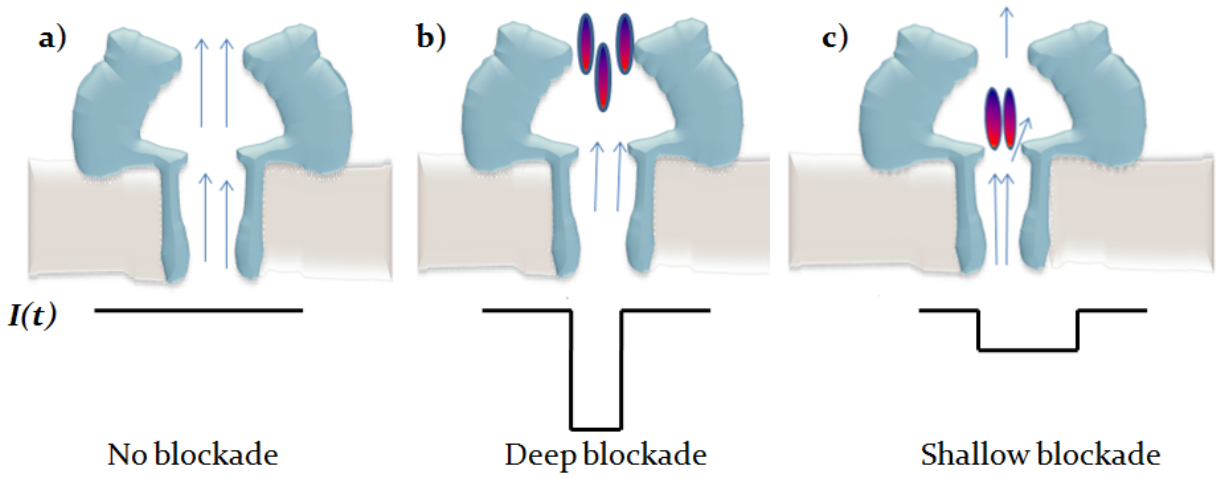

Figure S11: Schematic of blocking events. (a) no blockade, (b) deep blockade and (c) shallow blockade

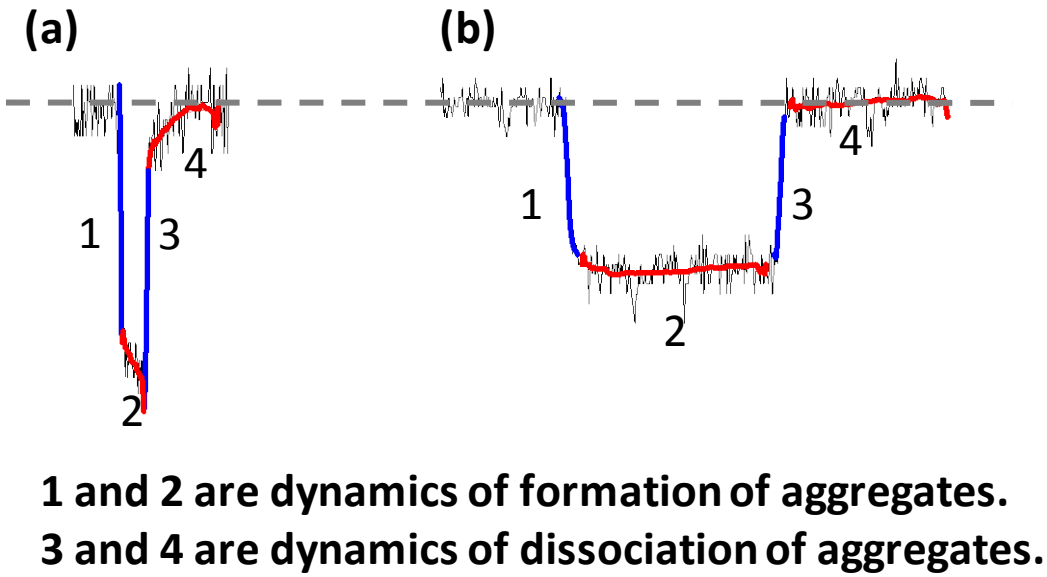

Figure S12: Rise and fall kinetics of blockade events. (a) For deeper blockade, the dissociation of aggregate follows a fast-instantaneous initial step, altering the magnitude by 80 %, and then exhibits an exponential type increase with time constant of ≈ 1.4 ms to reach the base-line value. (b) Shallow blockade shows a faster transient for both formation and dissociation of aggregates without having any tailing decays. These blockades are observed for the CS salt at 2 mM bulk concentration in the cis chamber with 100 mV voltage bias.

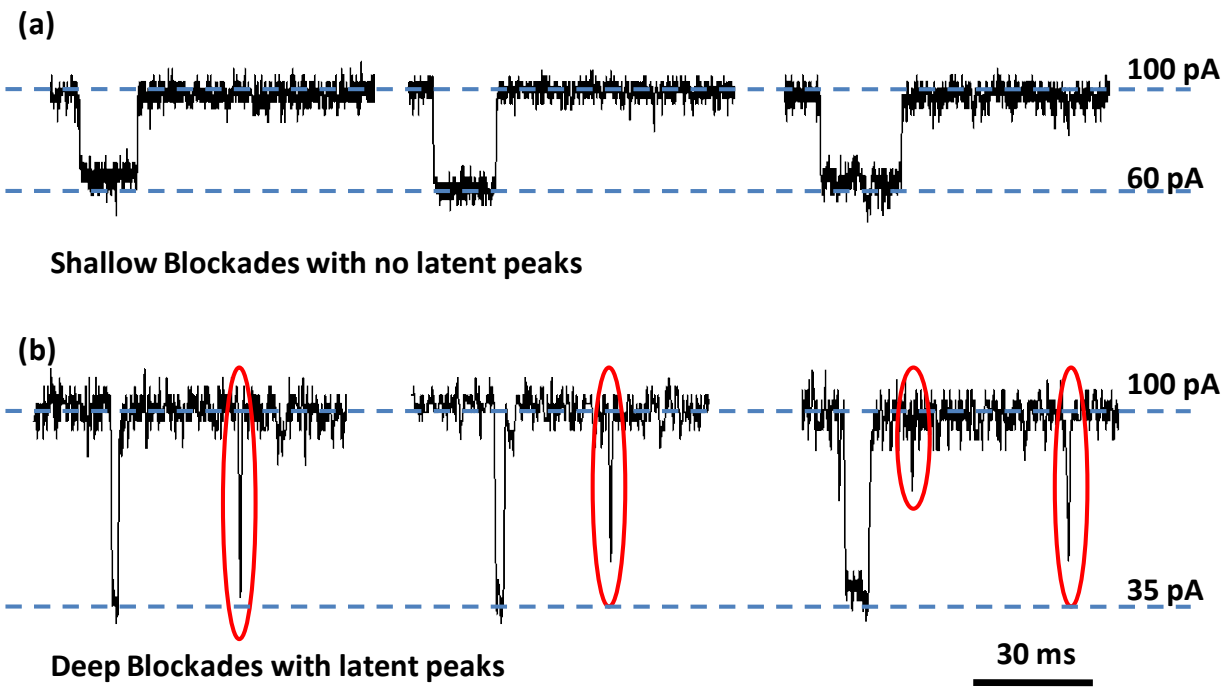

Figure S13: Translocation events of CS salt at 2 mM bulk concentration in the cis chamber with 100 mV applied bias. (a) No latent peaks following >50 ms after shallow blockades. (b) One or more latent peaks following deep blockades, these latent peaks are due to dissociated monomer or dimer once again checked at the ≈1.4 nm constriction. However, these latent peaks are not having the same property of shallow blockades.