Electronic Supplementary Information

Opposite counter-ion effects on condensed bundles of highly charged supramolecular nanotubes in water

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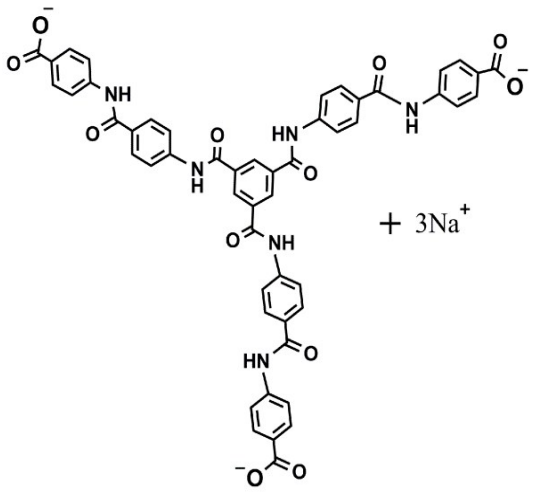
Part 1. Experimental Section

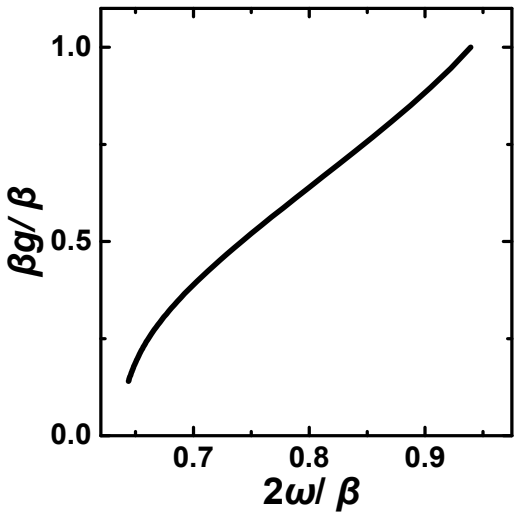


Scheme S1 Chemical structure of $P_7(COONa)_3$.

The peak broadening can be analyzed by the Voigt methods. The peak broadening due to micro-strain (β_g/β) can be estimated by form factor $2w/\beta$ of the principle peak where the integral breadth $\beta = A/I_0$ with A the peak area and I_0 the peak intensity of principle peak.

$$\frac{\beta_g}{\beta} = -\frac{\sqrt{\pi}}{2}k + \frac{1}{2}\sqrt{\pi k^2 + 4} - 0.23k\exp(-2.176k) \qquad (1)$$

$$\frac{2w}{\beta} = \sqrt{\frac{1+k^2}{\pi}}\left[-k\sqrt{\pi} + \sqrt{\pi k^2 + 4} - 0.1889\exp(-3.5k)\right] \qquad (2)$$



S-Figure 1. The peak broadening due to micro-strain (β_g/β) vs form factor $2w/\beta$.

Part 2. Result

S-Table 1. The Voigt function parameters of principle peak 01 of different mole ratio of Me_4NOH to 15mM-$P_7(COONa)_3$

Mole ratio	A	I_0	β	$2w$	$2w/\beta$	$\beta g/\beta$
0	1.4833	65.0342	0.02281	0.0152	0.66645	0.27376
0.1	1.5371	56.7792	0.02707	0.01837	0.67856	0.31993
0.3	1.0895	38.1346	0.02857	0.01972	0.69024	0.35939
0.4	1.2479	42.7313	0.02920	0.02052	0.70265	0.39583
0.5	2.4421	82.1961	0.02971	0.02095	0.70513	0.40422
0.75	1.0045	34.3474	0.02925	0.02131	0.72866	0.4674
1	1.0706	36.5192	0.02932	0.02155	0.73508	0.4823
2	1.2978	44.3938	0.02923	0.02150	0.73545	0.48409

S-Table 2. The Voigt function parameters of principle peak 01 of different mole ratio of Pr_4NOH to 15mM-$P_7(COONa)_3$

Mole ratio	A	I_0	β	$2w$	$2w/\beta$	$\beta g/\beta$
0	1.48326	65.0342	0.02281	0.0152	0.66645	0.27376
0.1	1.93321	71.3722	0.02709	0.01851	0.68337	0.33639
0.3	3.01448	105.3136	0.02862	0.01966	0.68684	0.34798
0.4	1.8132	61.6817	0.0294	0.0203	0.69057	0.36034
0.5	1.68966	56.3516	0.02998	0.02118	0.70637	0.40669
0.75	2.5268	81.2091	0.03111	0.02201	0.70738	0.41169
1	1.33379	33.364	0.03998	0.02943	0.73617	0.48574

S-Table 3. The Voigt function parameters of principle peak 01 of different mole ratio of KOH to 15mM -$P_7(COONa)_3$

Mole ratio	A	I_0	β	$2w$	$2w/\beta$	$\beta g/\beta$
0	0.10984	3.82344	0.02873	0.01993	0.69375	0.37012

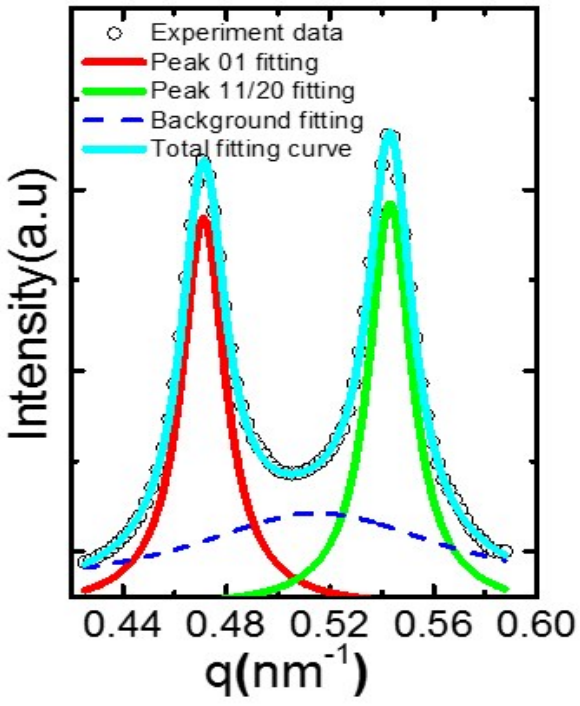
0.1	0.11274	3.78069	0.02982	0.02099	0.70394	0.40028
0.2	0.10251	3.56205	0.02878	0.02216	0.77012	0.56951
0.3	0.12879	4.41653	0.02916	0.0201	0.68941	0.35645
0.5	0.14254	4.78803	0.02977	0.01987	0.66731	0.27733
0.75	0.1399	4.9133	0.02847	0.01878	0.65945	0.24227
1	0.16756	5.808	0.02885	0.01871	0.64863	0.17946

S-Table 4. The Voigt function parameters of principle peak 01 of different mole ratio of NaOH to 15mM -$P_7(COONa)_3$

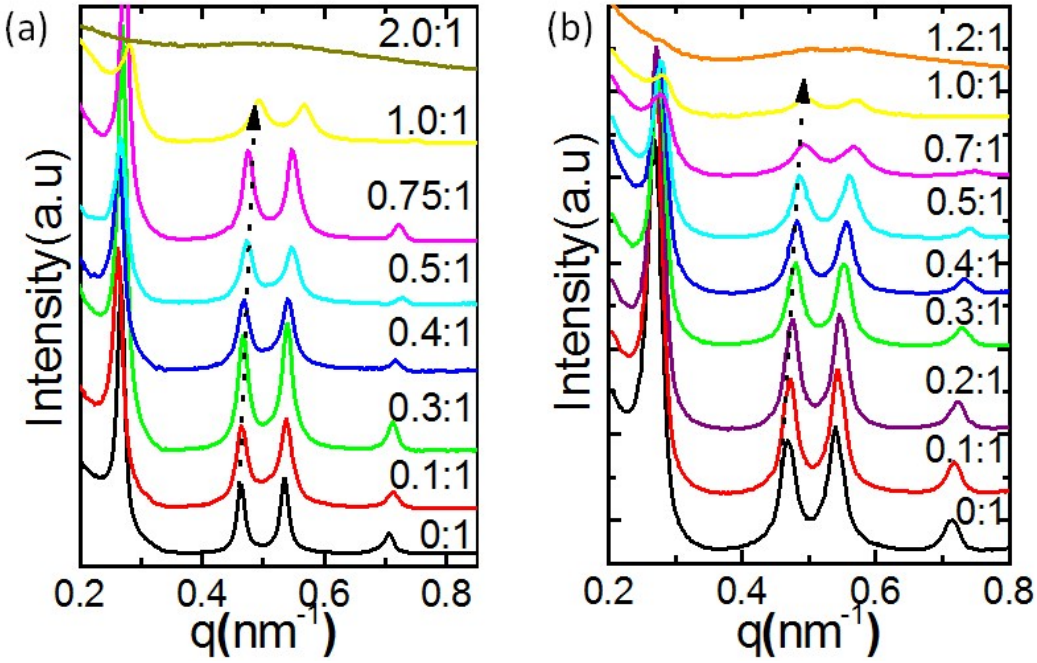
Mole ratio	A	I_0	β	$2w$	$2w/\beta$	$\beta g/\beta$
0	0.1704	6.7673	0.02518	0.0174	0.69103	0.36133
0.1	0.22383	7.8872	0.02838	0.0197	0.69418	0.37146
0.2	0.27025	9.8327	0.02748	0.0199	0.72403	0.49631
0.5	0.4017	14.408	0.02788	0.0188	0.67431	0.30492
0.75	0.39103	14.855	0.02632	0.0177	0.67239	0.25609

S-Table 5. The Voigt function parameters of principle peak 01 of different mole ratio of GdL to 15mM-$P_7(COONa)_3$

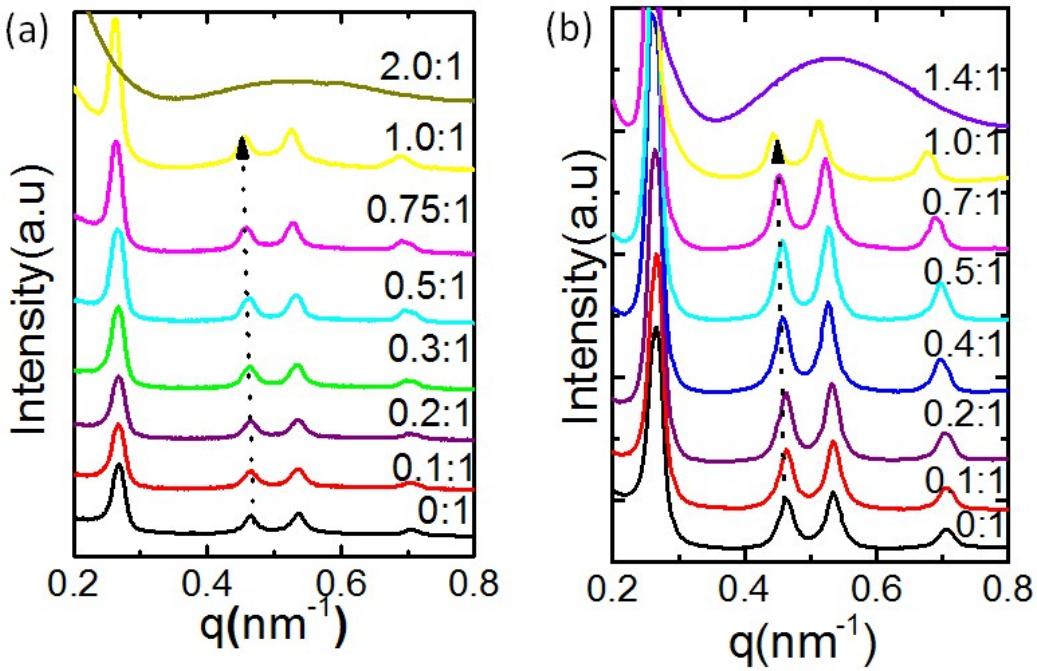
Mole ratio	A	I_0	β	$2w$	$2w/\beta$	$\beta g/\beta$
0	0.1704	6.7673	0.02518	0.0174	0.69103	0.36133
0.1	0.1694	5.8767	0.02833	0.02017	0.69972	0.38776
0.2	0.18757	5.0314	0.03728	0.02727	0.73149	0.47392
0.3	0.11324	3.2107	0.3527	0.02442	0.69238	0.36532
0.4	0.05145	1.7826	0.02886	0.01918	0.66453	0.26576



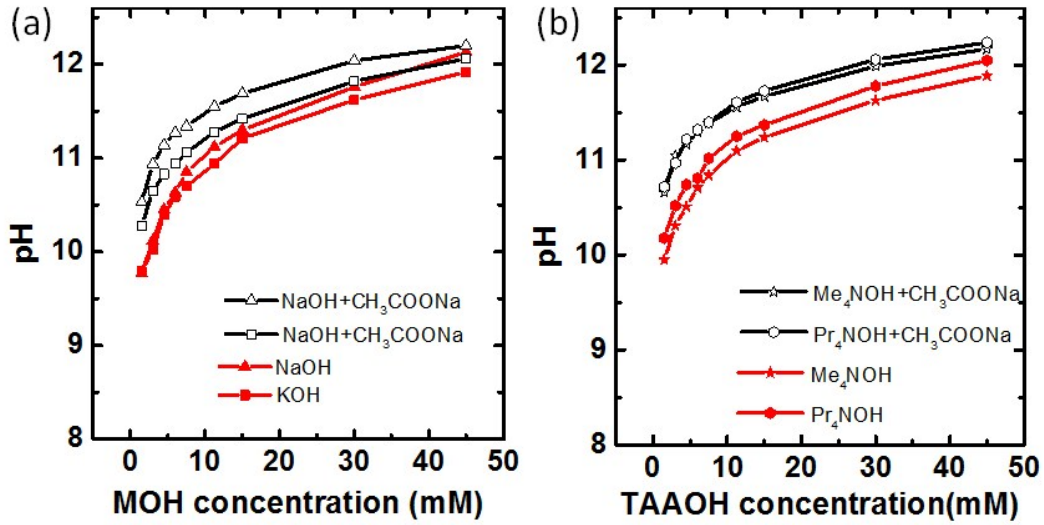
S-Figure 2. Lorentz two peaks fitting of 01 and 11/20 peaks after subtracting a broad peak (the blue dotted line) as background.



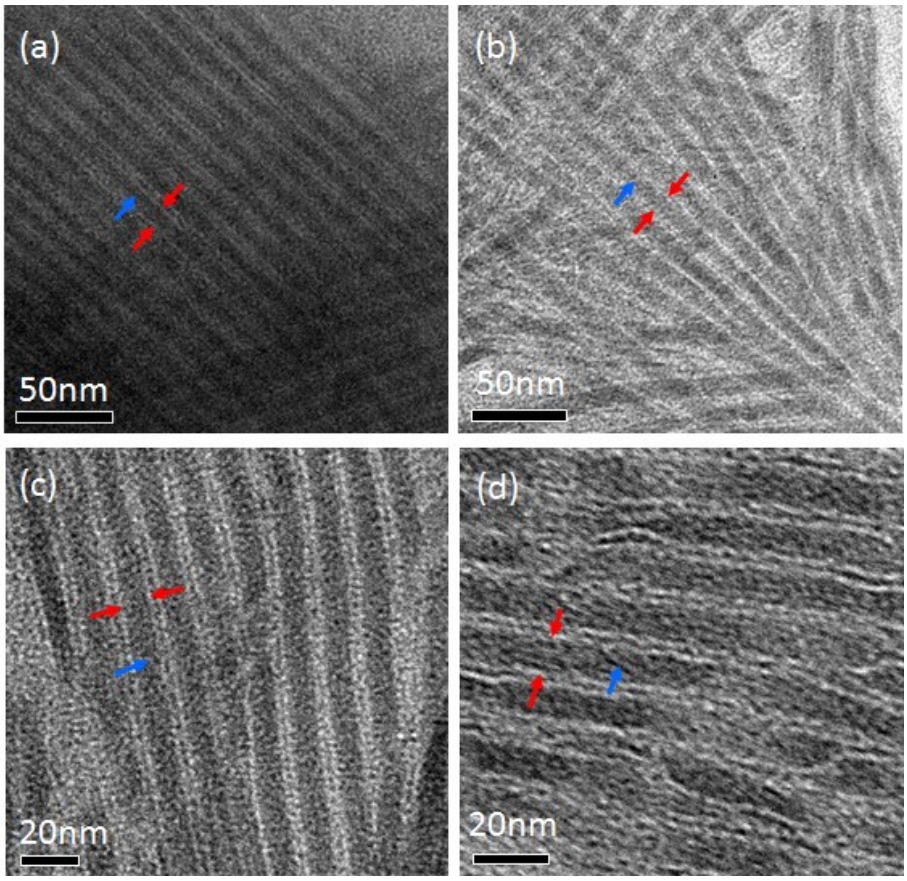
S-Figure 3. 1D SAXS curves of different mole ratio of (a)Pr_4NOH, (b)Pr_4NCl to $P_7(COONa)_3$ in aqueous solution



S-Figure 4. 1D SAXS curves of different mole ratio of (a)KOH,(b)KCl to $P_7(COONa)_3$ in aqueous solution



S-Figure 5. pH of aqueous solution of pure (a) NaOH/ KOH;(c) Me_4NOH / Pr_4NOH in solid symbols and the pH of aqueous solution of 45mM CH_3COONa mixed with the bases in hollow symbols vs the concentration of the latter.



S-Figure 6. (a) TEM images of 15mM $P_7(COONa)_3$ solution sample and TEM images of samples mixed of 3mM (b)GdL, (c)NaOH, (d)KOH with 15mM $P_7(COONa)_3$.

The samples were stained by 2% neutral phosphotungstic acid for 5 min. The blue arrows highlight the tubular structure of the supra-molecular nanostructures and the

red arrows reveal the shell of hollow nanotubes. The distances between the two red arrows highlight in the images exhibit the diameter of the nanotubes. The diameter is obtained by collecting the distances of eight cases with different location then take average. It is found that the diameters of the nanotubes retain about 12.8nm even added acid or alkali to the aqueous solution of $P_7(COONa)_3$.

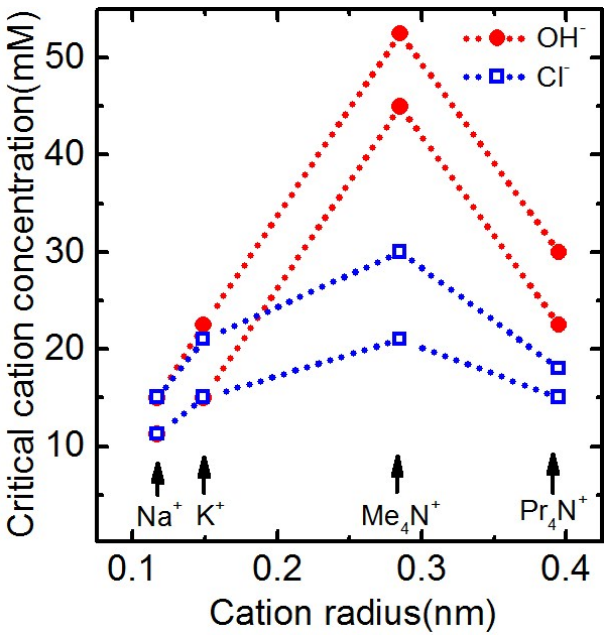
S-Table 6. Statistics of diameter of nanotubes in the mixture of 15mM $P_7(COONa)_3$ and 3mM GdL, NaOH, KOH respectively from TEM images

	$P_7(COONa)_3$-15mM	$P_7(COONa)_3$-15mM+3mM GdL	$P_7(COONa)_3$-15mM +3mM NaOH	$P_7(COONa)_3$-15mM+3mM KOH
1	12.73nm	13.07nm	12.49nm	12.86nm
2	13.08nm	12.56nm	13.06nm	13.10nm
3	12.67nm	13.08nm	12.89nm	12.49nm
4	12.98nm	12.63nm	12.83nm	12.79nm
5	12.32nm	12.79nm	12.67nm	13.08nm
6	13.14nm	13.02nm	12.55nm	12.93nm
7	12.81nm	12.65nm	13.12nm	12.62nm
8	12.68nm	12.86nm	12.63nm	12.81nm
Average	**12.80nm**	**12.83nm**	**12.76nm**	**12.84nm**

The Debye screening length is calculated by the below formula.

$$\lambda_D = \sqrt{\frac{\varepsilon_r \varepsilon_0 k_B T}{2 N_A e^2 I}}$$

where I is the ionic strength in the bulk solution, ε_0 is the permittivity of free space, ε_r is the relative dielectric constant, k_B is the Boltzmann constant, T is the absolute temperature in kelvins, N_A is the Avogadro number, e is the elementary charge.



S-Figure 7. The cations' radius vs the upper and lower bound of the critical concentration at which the orthorhombic arrangement of nanotubes vanished for the cases of different co-ions to demonstrate their stabilization ability. Note that the accurate values should be located among the upper and lower bound.