Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary information

Polyaniline and CN-functionalized polyaniline as organic cathodes for lithium and sodium ion batteries: a combined molecular dynamics and Density Functional Tight Binding Study in solid state

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Calculation of Na^+/Na potential:

$$E_{abs}(Na^+/Na) = E^{aqueous}_{abs}(Na^+/Na) + (E(Na^+_{solvent}) - E(Na^+_{aqueous}))$$

where $E^{aqueous}_{abs}(Na^+/Na) = E^{\circ}_{abs}(SHE) + E^{\circ}(Na^+/Na) = 4.44 - 2.71 = 1.73\,V$ [1]; $E(Na^+_{solvent})$ and $E(Na^+_{aqueous})$ are the total energies of Na^+ calculated in the solvent and the aqueous solution, respectively. In this work, the difference between $E(Na^+_{solvent})$ and $E(Na^+_{aqueous})$ is ~0.01 V, which was computed similarly as in Ref. [2]. Therefore, $E_{abs}(Na^+/Na) = 1.74\,V$.

Table S1. MD annealing and equilibration processes for amorphous PANI solid. The time step is set at 1 fs for all MD simulations.

Stage	Ensemble	Temp (K)	Time (ps)	Pressure (GPa)	Stage	Ensemble	Temp (K)	Time (ps)	Pressure (GPa)
1	NVT	750	30		9	NPT	298	100	3
2	NVT	600	20		10	NVT	600	20	
3	NVT	450	20		11	NVT	450	20	
4	NVT	298	100		12	NVT	298	100	
5	NPT	298	100	0.1	13	NPT	298	100	0.5
6	NVT	600	20		14	NVT	600	20	
7	NVT	450	20		15	NVT	450	20	
8	NVT	298	100		16	NVT	298	100	
					17	NPT	298	1000	0.0001

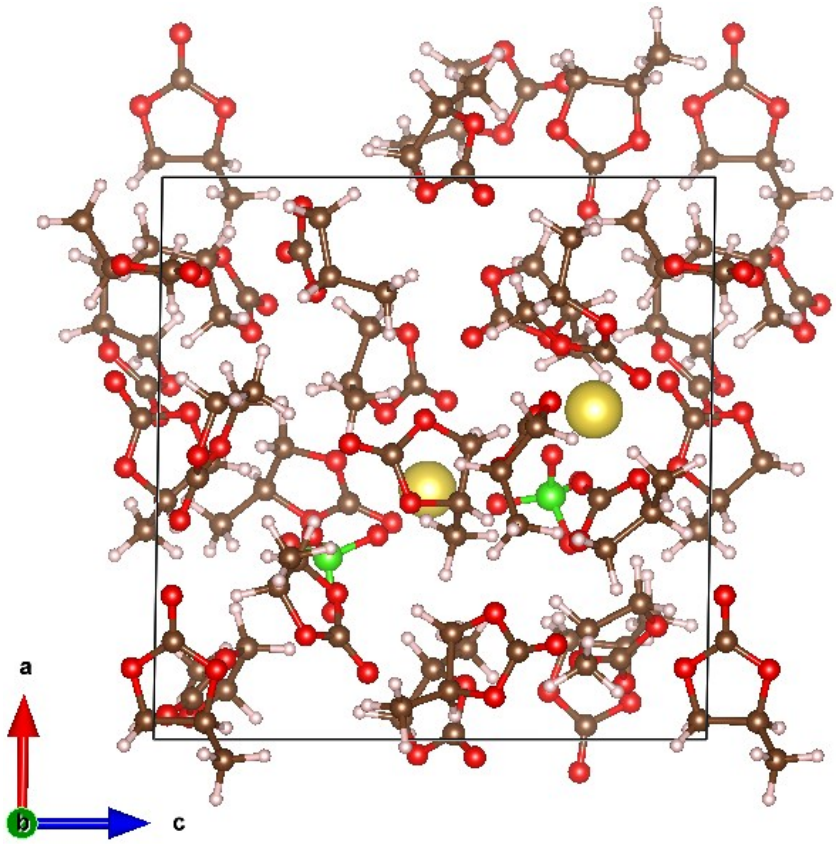

Figure S1. The periodic simulation cell of $NaClO_4$ in the solvent – propylene carbonate (PC), computed in DFTB+. Atom color code: C – brown, H – pink, Cl – green, O – red, Na - yellow.

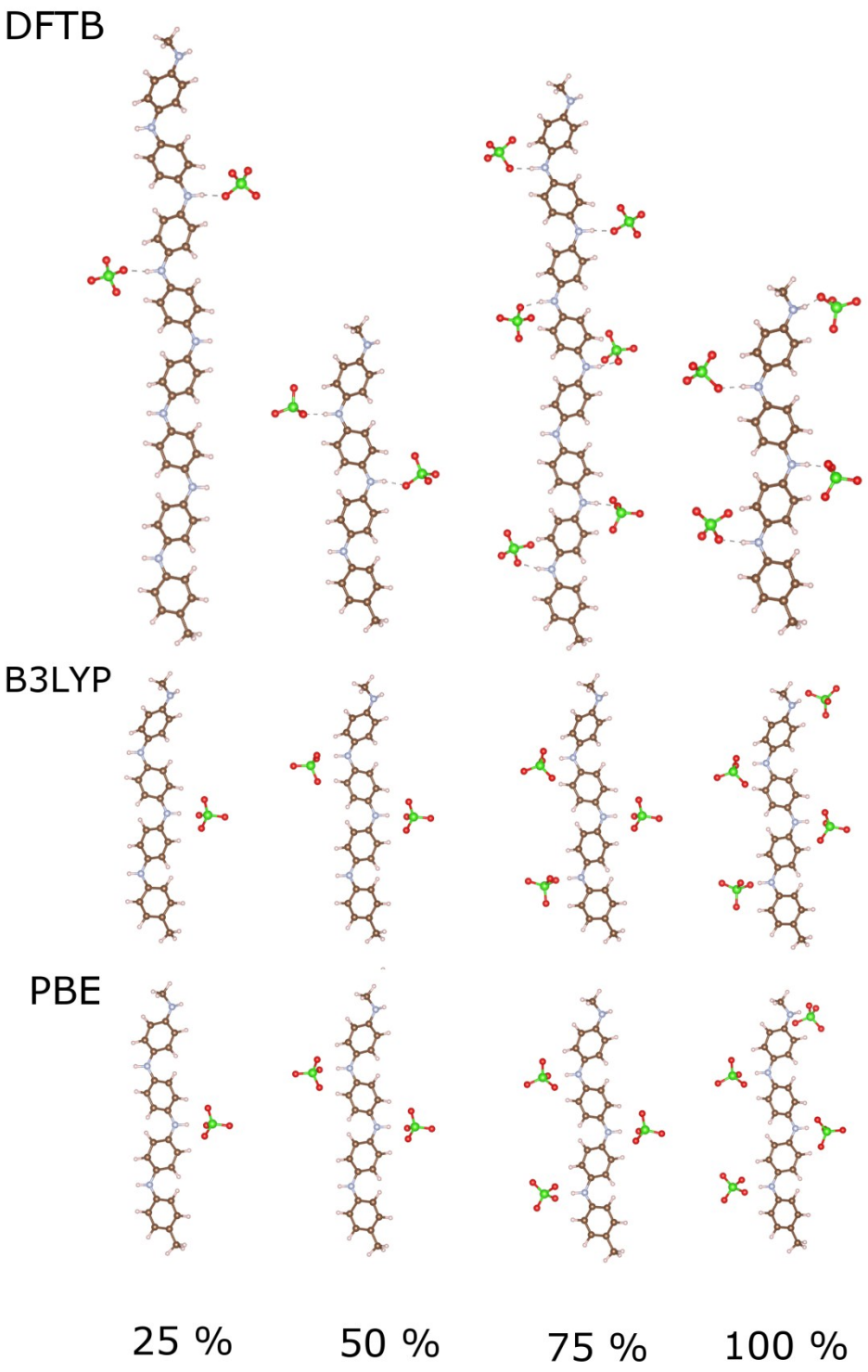

Figure S2. Lowest-energy structures of PANI oligomers coordinated to different numbers of ClO_4 anions, computed with different functionals (see the main text for ωB97XD structures).

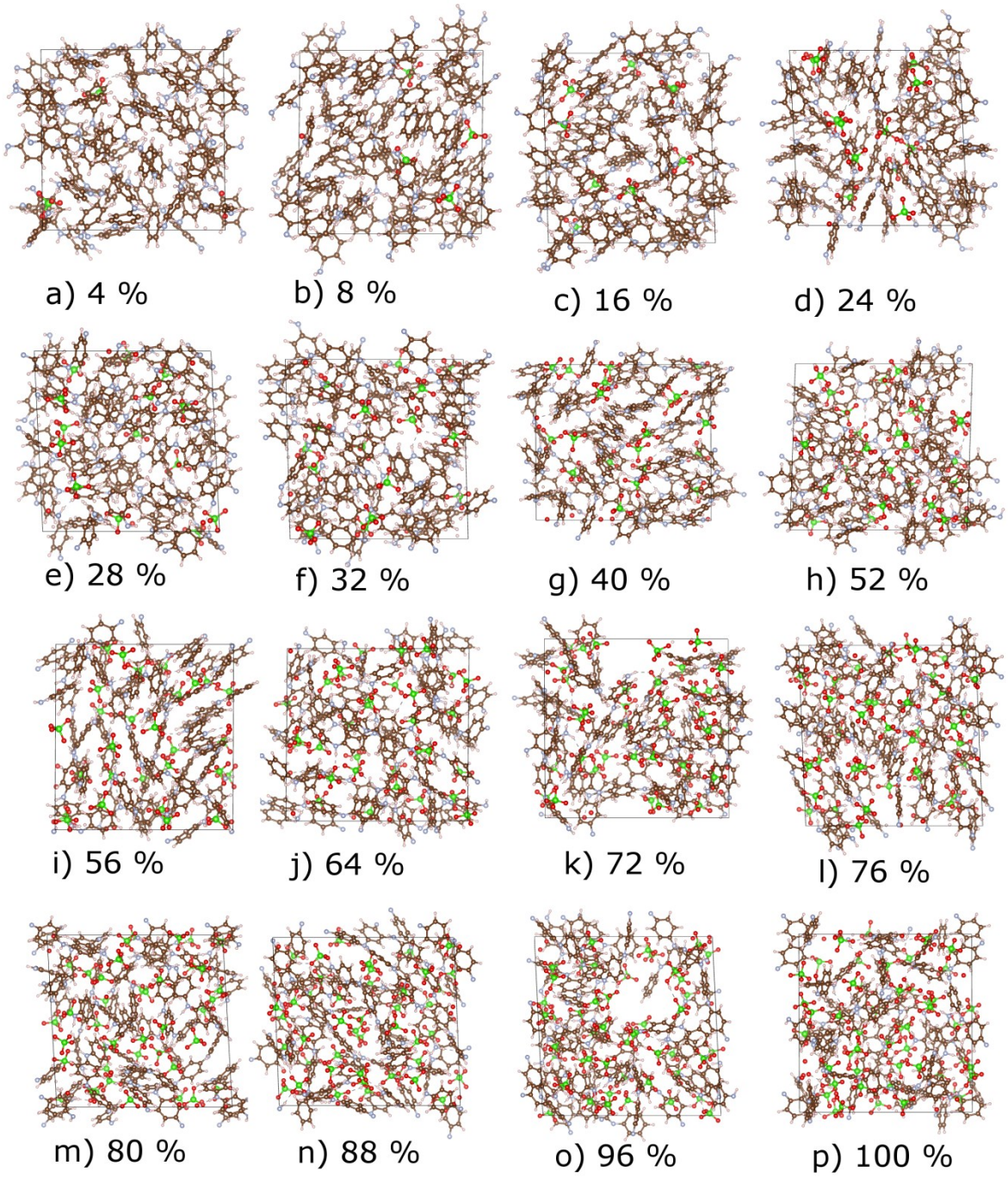

Figure S3. Optimized structures of PANI at different degrees of oxidation from 4 % in (a) to 100% in (p).

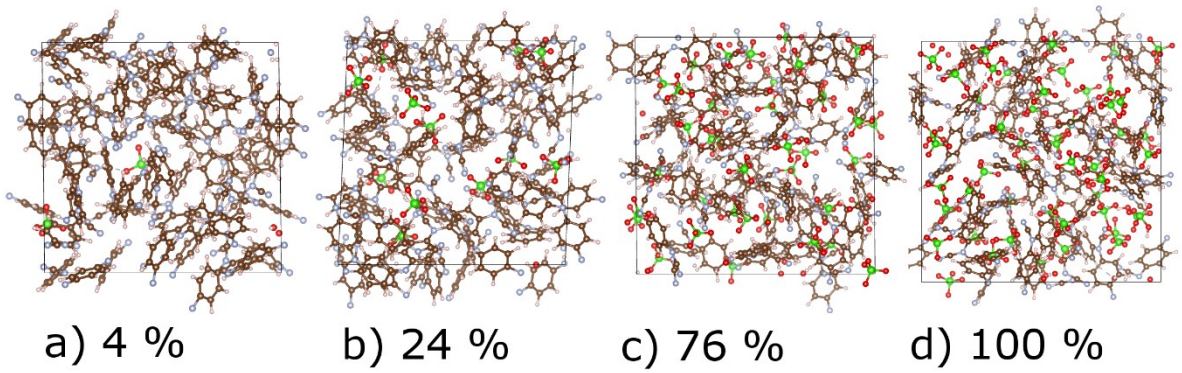

Figure S4. Optimized structures of PANI functionalized with cyano groups at different degrees of oxidation from 4 % in (a) to 100% in (d).

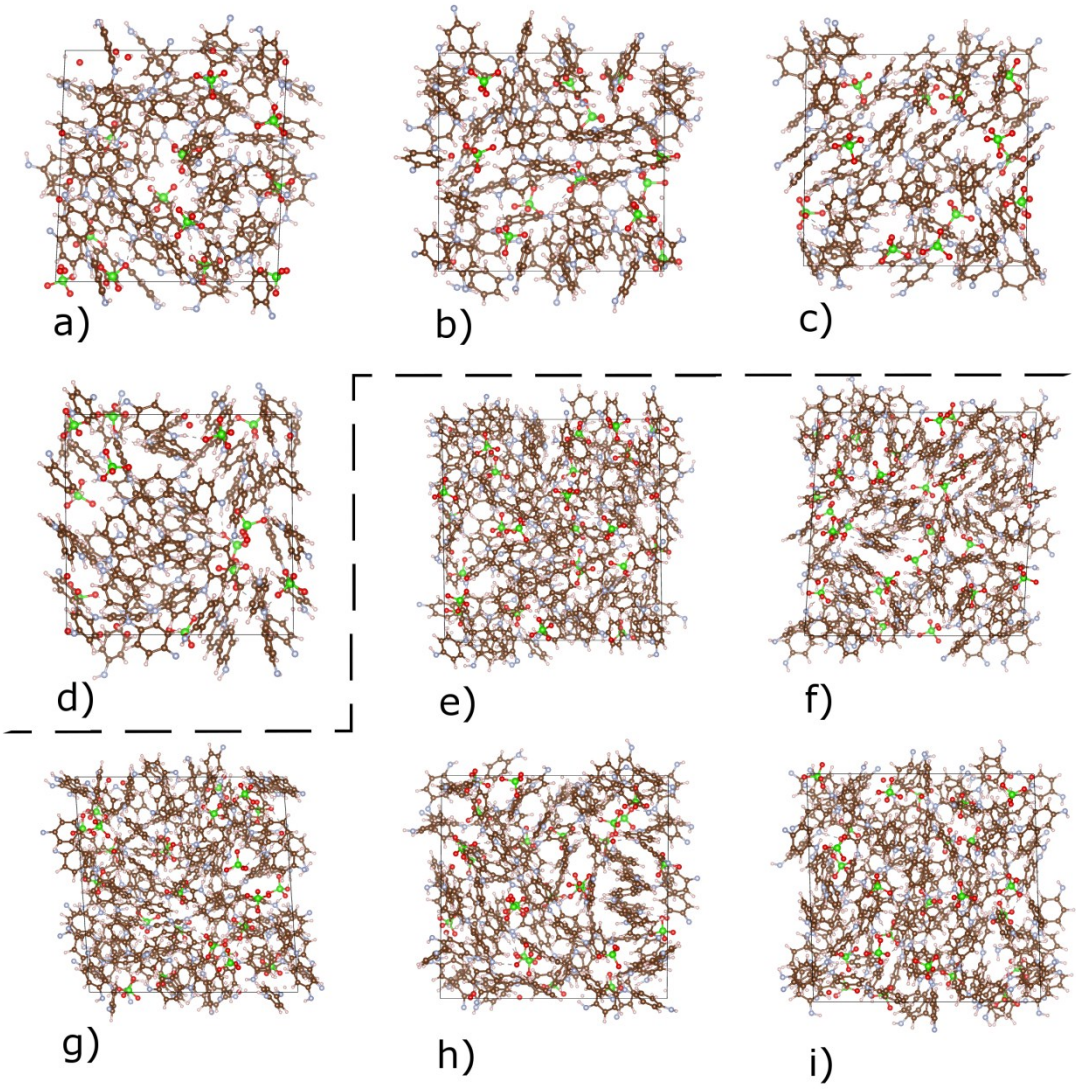

Figure S5. Computed structures for different distributions of counter ions in 24 % oxidized PANI. (a) to (d) show the structures containing 5 oligomer chains and (e) to (i) those containing 10 oligomer chains.

References

[1] D.D. Ebbing, General Chemistry, 3rd ed., Houghton Mifflin, Boston, 1990.
[2] Y. Chen, S. Manzhos, Voltage and Capacity Control of Polyaniline Based Organic Cathodes: An Ab Initio Study, *Journal of Power Sources*, **336** (2016) 126-131.