Supplementary Information

PNTCDA: A Promising Versatile Organic Electrode Material for Alkali-metal Ion Batteries

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Bond ID	11	12	13	14	15	16	17	18	19	110
Length (Å)	1.540	1.470	1.410	1.230	1.485	1.416	1.390	1.425	1.406	1.090
Angle ID	θ1	θ2	θ3	θ4	θ5	θ6	θ7	θ8	θ9	θ10
Angle (°)	111.3	107.2	107.4	117.5	125.2	116.6	120.8	122.6	120.2	119.7
Angle ID	θ11	θ12	θ13	θ14	θ15	θ16				
Angle (°)	120.0	120.5	118.5	121.0	119.5	121.1				

Table S1. Structural parameters of bond length and angle of PNTCDA. The positions of the specific bond and angle are labeled in Fig. 1a in the main manuscript.

Table S2. Relative formation energy of AM ion after fully optimization at differentbinding sites. The value corresponding to site 1 is taken as zero.

	Site 1	Site 2	Site 3	Site 4	Site 5'	Site 6	Site 7
Relative formation energy with respect to site 1 (eV)	0	2.143	transfer to 1	transfer to 1	1.422 (transferred from 5)	transfer to 2	1.851



Figure S1. The initial adsorption sites of AM ion on pristine PNTCDA chain.



Figure S2. (a) Top (left) and side (right) views for AA-stacking type. (b) Top (left) and side (right) views for AB-stacking type.



Figure S3. Structure and energy characterizations of bulk PNTCDA from molecular dynamics (MD) simulations. (a) The side view of the bulk PNTCDA model. Black lines indicate the simulation box. The carbon, oxygen, nitrogen and hydrogen atoms are represented as grey, red, blue, and white spheres, respectively. (b) The potential energy of the bulk PNTCDA with respect to simulation time. (c) The root-mean-square deviation (RMSD) of structure with respect to the first principle optimized structure with respect to simulation time. (d) The inter-layer distance of PNTCDA chains with respect to simulation time.

The MD simulations were performed with GROMACS 4.6.7¹. As depicted in Fig. S3a, the bulk model contains 6 PNTCDA layers; each layer is composed of 3 chains. Each chain comprises 3 PNTCDA units. The initial stacking pattern was adopted from the VASP optimized structure. The interactions between atoms are described by GAFF² force field. Partial charges of the molecule were fitted using the Restrained Electrostatic Potential (RESP) method by Gaussian 09 at the level of HF/6-31G*. A leap-frog algorithm was used to integrate Newton's equation of motion, and the time step was 2 fs. The cutoff for both van der Walls (VDW) interaction and electrostatic interaction were 1.0 nm. After energy minimization, 10 ns data production simulation was conducted in the NPT ensemble. The temperature and pressure were 300 K and 1

bar, respectively. A V-rescale³ method and an isotropic Berendsen⁴ method were used for the temperature coupling and pressure coupling, respectively.

As summarized in Fig. S3b, the potential energy is almost constant with fluctuations around -2.0×10^4 kJ/mol. At 300 K, the PNTCDA maintains very stable stacking pattern with RMSD (Fig. S3c) of only 0.3 Å with respect to the first principle results. From Fig. S3d, the interlayer distance is 3.4 Å which is also consistent to the first principle results.



Figure S4. The maximal capacity and the voltage profile for (a) Li, (b) Na (c) K intercalation in bulk PNTCDA. Stars indicate the calculated maximum theoretical capacity for each metal.

References

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