Electronic supplementary information (ESI)

Two-dimensional covalent organic frameworks made of triquinoxalinylene derivatives are promising anodes for high-performance lithium and sodium ion batteries

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List of Figures and Tables

1. Computational details

## S1.1 The effect of temperature and zero point energy

Note that the effect of the temperature is difficult to be considered for all the static energy calculations performed in VASP. Thus, we did not consider the effect of temperature, consistent with many previous studies.[1,2] To take the correction terms such as zero-energy and entropy contributions into account, we have performed the frequency analysis and found that the contribution of absolute zero-point energy value is no more than 0.02 eV. Therefore, the impact of zero-point energy is neglected during the discussion.

## S1.2 The choice of K-points sampling

Generally, the k-points can be sufficient if the value of the k points multiplied by the lattice constant is in range of 30 to 40. We have calculated the energy of 2D 3Q-COF monolayer with $5\times5\times1$ k-points sampling in comparison with that with $3\times3\times1$ k-points and found that the adsorption energy difference is within 0.01 eV, indicating that $3\times3\times1$ k-points sampling is enough in this study.

S1.3 The cohesive energy of bulk Li and Na

According to the equation $E_C = E_{bulk} - E_M$, the cohesive energy of bulk Li and Na can be obtained by subtracting the the total energy of free Li/Na metal atom with that of the stable bulk phase, which is -1.79 and -1.25 eV for Li and Na, respectively. Actually, the adsorption energy of Li/Na was obtained by considering the cohesive energy.
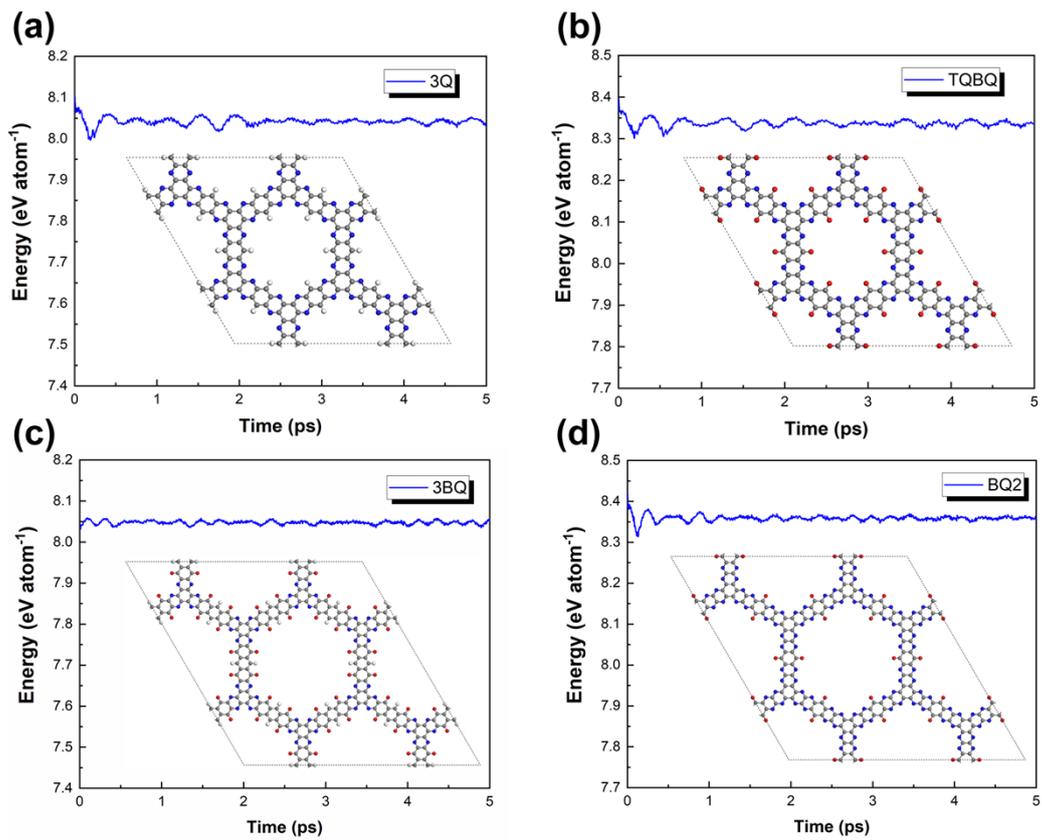
Figure S1. Total potential energy fluctuation of 2D COFs at the end of a 5 ps ab initio molecular dynamic (AIMD) simulation at the temperature of 500 K.
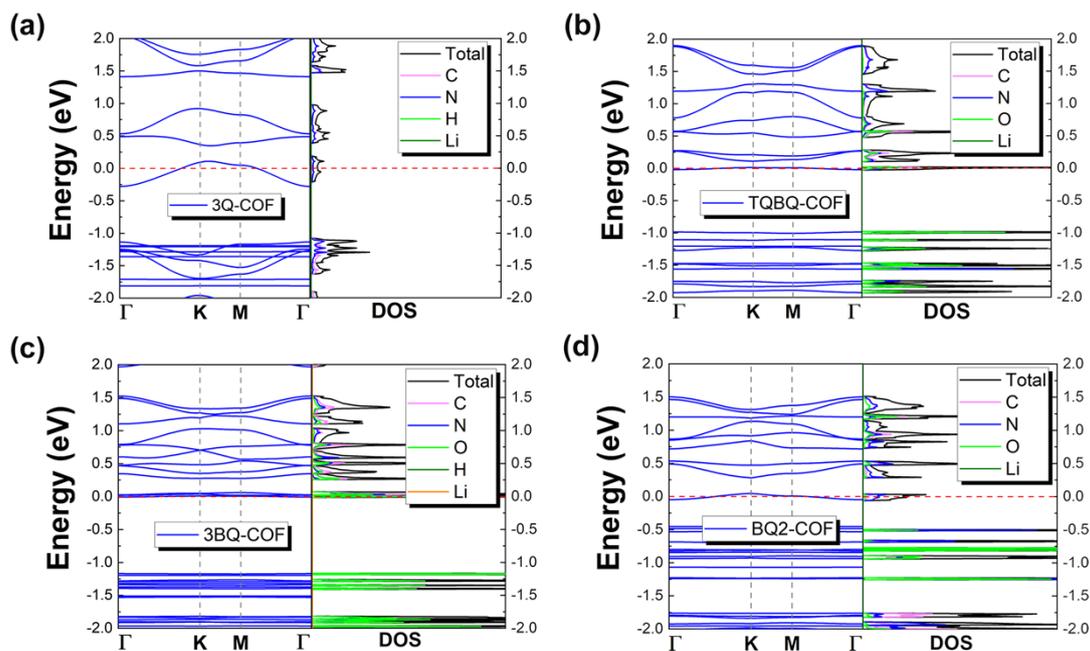
Figure S2. Band structure and DOS plots of 2D COFs of 3Q (a), TQBQ (b), 3BQ (c) and BQ2 (d) with Li adsorption at the S_{Py} site, respectively. The white, purple, pink, gray, blue and red balls represent H, Li, C, N and O atoms, respectively. The isosurface is set to 0.0013 e Å^{-3}. The Fermi level is depicted by the red dashed line.
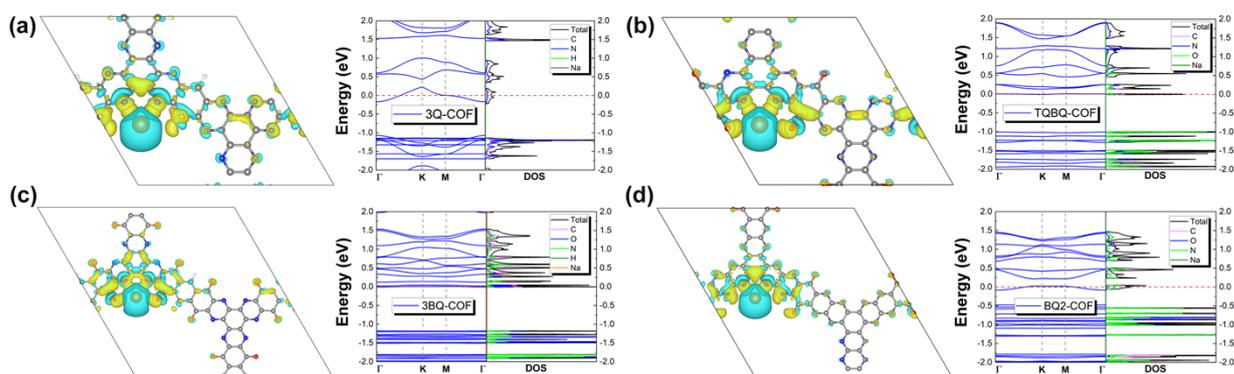

Figure S3. The differential charge distributions and band structure and DOS plots of 2D COFs of 3Q (a), TQBQ (b), 3BQ (c) and BQ2 (d) with Na adsorption at the S_{Py} site, respectively. The white, purple, gray, blue and red balls represent H, Na, C, N and

O atoms, respectively. The isosurface is set to 0.0013 e / Å^{-3}. The yellow and blue regions denote the accumulation and depletion of charge, respectively. The Fermi level is depicted by the red dashed line.
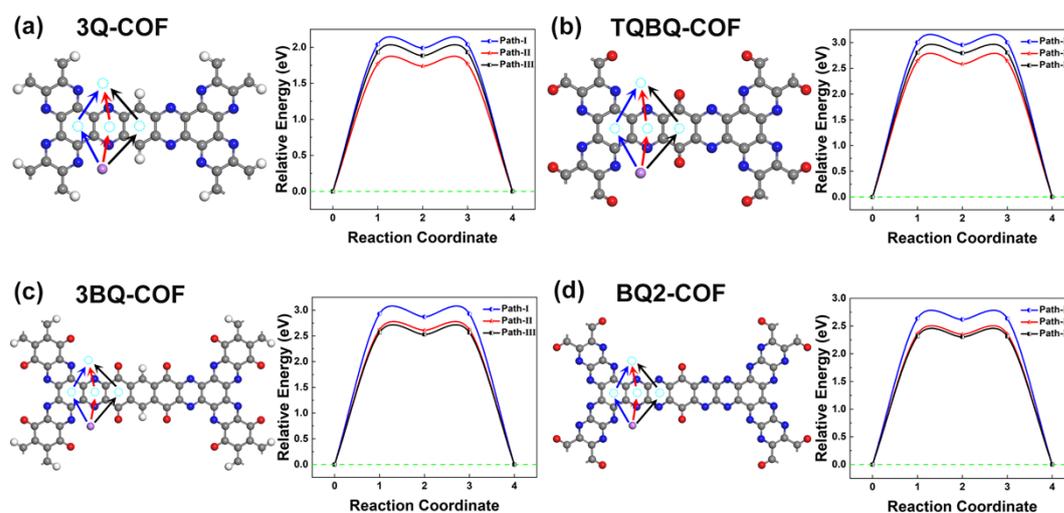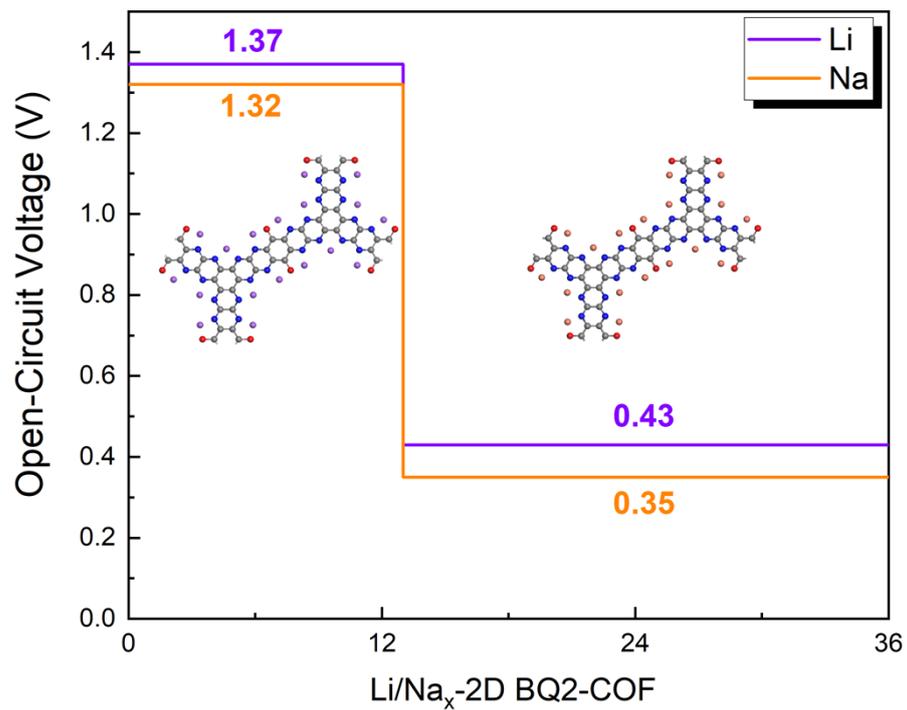

Figure S4. The possible diffusion paths and energy barrier of single Li atom on 2D (a) 3Q (b) TQBQ (c) 3BQ and (d) BQ2 COF, respectively.
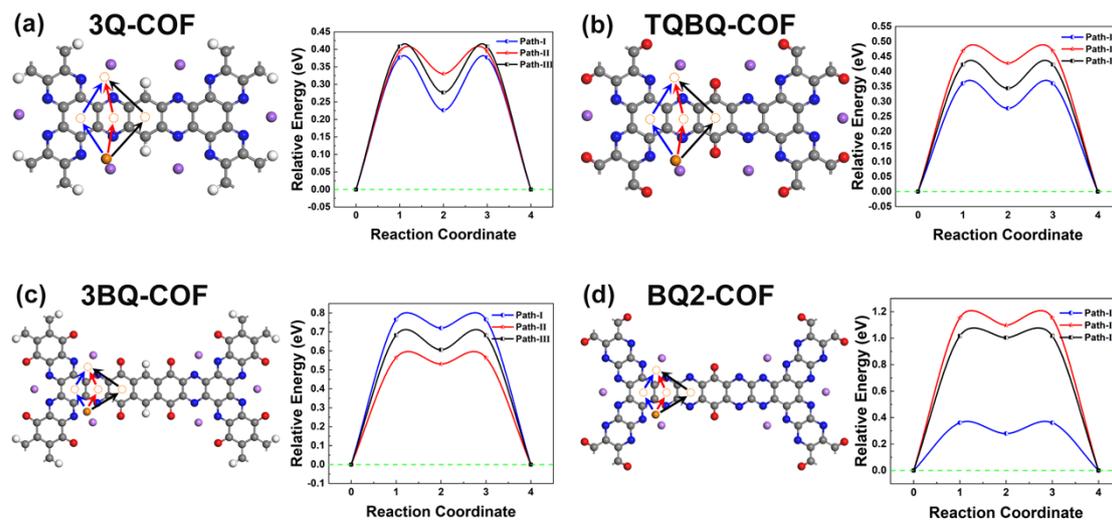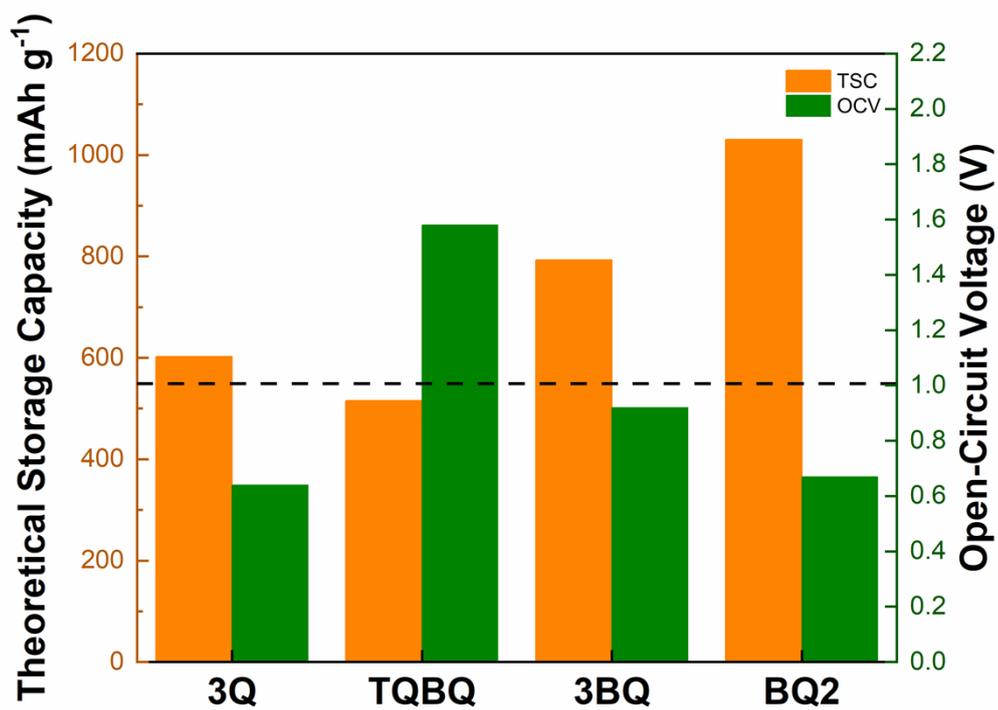
Figure S5. The possible diffusion paths and energy barrier of Na atom on 2D (a) 3Q (b) TQBQ (c) 3BQ and (d) BQ2 COF, respectively.
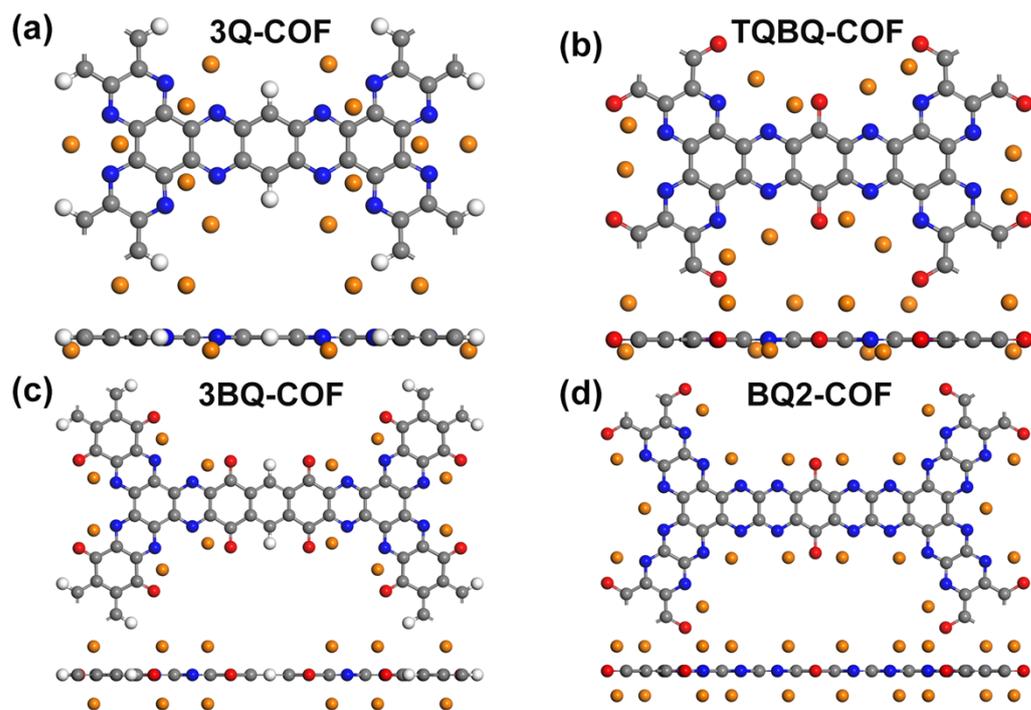
Figure S6. Top and side views of the optimized configuration of 2D (a) 3Q (b) TQBQ (c) 3BQ and (d) BQ2 COF with maximum adsorbed Na atoms.

Figure S7. The plateau of OCV and capacity of 2D BQ2-COF with the change of Li/Na content.

Figure S8. Theoretical storage capacity (orange) and average open-circuit voltage (green), respectively.

Table S1. Adsorption energy (E_{ad}) of Li/Na atom at possible embedding sites between the atom and the substrate after structural optimization.

electrode material	site	E_{adLi} (eV)	E_{adNa} (eV)
3Q	H_B	-0.63	-0.65
	H_{Py}	-0.48	-0.57
	H_{Pyb}	-1.86	-0.43
	S_{Py}	-2.22	-1.87
TQBQ	H_B	-0.12	-0.39
	H_{Py}	-0.27	----
	H_{Pyb}	0.01	-0.26
	S_{Py}	-2.93	-3.03
3BQ	H_B	-0.56	-0.6
	H_{Py}	-0.16	-0.33
	H_{Pyb}	0.08	-0.16
	H_{CB}	-2.63	-0.42
	S_{Py}	-2.78	-2.84
BQ2	H_B	-0.38	-0.75
	H_{PyB}	-0.36	-0.65
	S_{PC}	-2.93	-2.79
	S_{Py1}	-2.97	-2.9
	S_{Py2}	-2.68	-2.76

The Na originally placed on the H_{Py} site of 2D TQBQ-COF spontaneously moves to the S_{Py} site after structural optimization.

Table S2. Lattice patameter, pore size, theoretical storage capacity (TSC), average open-circuit voltage (OCV) of 2D 3Q, TQBQ, 3BQ and BQ2 COF.

electrode material	lattice (Å)	pore (Å)	TSC (mAh·g⁻¹)	OCV$_{Li}$ (V)	OCV$_{Na}$ (V)
3Q	16.50	11.46	602.27	0.94	0.64
TQBQ	16.63	11.16	515.40	1.89	1.58
3BQ	25.18	20.20	792.93	1.13	0.92
BQ2	24.52	19.05	1030.08	0.74	0.67

References

1. Science, 2017, **355**, eaad4998.
2. Nat Catal **1**, 935–945 (2018).