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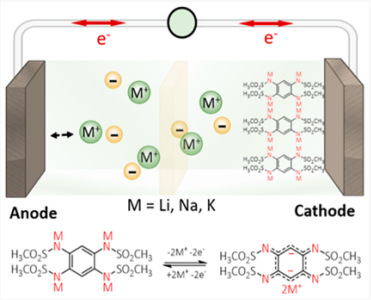

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A High Voltage Organic Framework for High Performance Na- and K-ion Batteries

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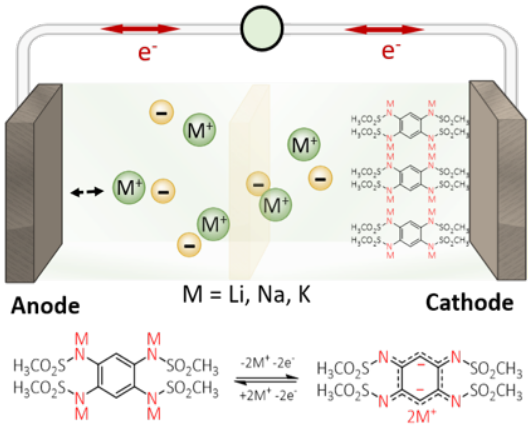
TOC GRAPHICS



An essential feature that can make the difference in the solid-phase (electro)chemistry of organic *vs*. inorganic phases is the nature and flexibility of the crystalline phases involved. Organic materials have a higher propensity for molecular crystal formation, are structurally more robust

and versatile so that phase changes proceed at lower energetic costs, with also presumably higher cation mobility in an open organic crystal framework [1-3]. It is thus not surprising to see the easiness with which organic redox materials are being used, and typically display enhanced stability, when changing the working cation from Li^+ to Na^+ or K^+, with recently emerging developments on divalent and trivalent cations[3-5]. On the contrary, considerable efforts are being required for inorganic crystalline phases, with contrasting properties observed for similar composition and phase structures when applied for different cation storage[6].

Despite this flexibility and many advances to date, the richness of organic chemistry still fails to provide positive electrode chemistries (cathode) that can be synthesized and handled in their alkali-cation reduced phase[7-10]. Despite a relatively rich library of electrochemically active Na- and K-ion ceramic (inorganic) phases[11-12], Na-ion organic positive electrode material developments are nearly absent to date; whereas no K-ion organic phase has been synthesized and tested to date (Table S1 and S2). Other than being a cation-reservoir material upon cell assembly (and thus suitable for Metal-ion cells), the intrinsic advantage of cation-reservoir chemistries is their higher redox potential, implying thus increased energy density. The highest redox potential for a *n*-type organic Na-ion chemistry is close to 2.7 V vs. Na^+/Na[13], while lower values are being attained for organic K-ion cathodes[14-16]. Investigating new metal-containing cathodes that can support reversible sodium/potassium ion storage at high voltage has become thus an urgent necessity in the community[17]. Furthermore, it is of utmost importance to note that whereas an impact of the cation nature (Li^+ *vs*. Na^+ *vs*. K^+) on the charge storage performance and physico-chemical properties is to be expected, a critical comparison, while relying on a same type of battery cathode material and configuration has been rarely investigated.

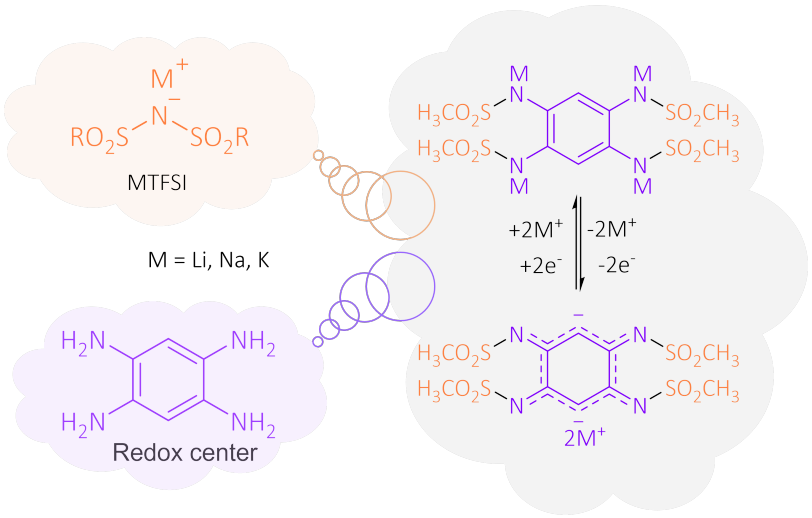


Figure 1. Compositional, structure and redox mechanism rationale for design and synthesis of M_4-PTtSA alkali cation reservoir phases.

Herein, we extend the library of the recently developed new class of Li-ion sulfonamide cathodes[18] to Na- and K-containing organic phases (Fig. 1). Benzene-1,2,4,5-tetrayltetrakis methylsulfonyl-amide tetra-anion ($PTtSA^{4-}$) is selected as the working organic framework, and for the first time, alkali cation contained organic electrode phases (Li_4-PTtSA, Na_4-PTtSA and K_4-PTtSA) are presented and systematically studied. We find that the nature of the alkali cations (Li^+, Na^+, K^+) significantly impacts the charge conduction, crystallinity as well as physico-chemical and electrochemical properties at both, molecular and solid phase level. These systematic findings provide valuable information for the rationale development of suitable organic positive electrode materials with ever increasing performances for alkali-ion storage.

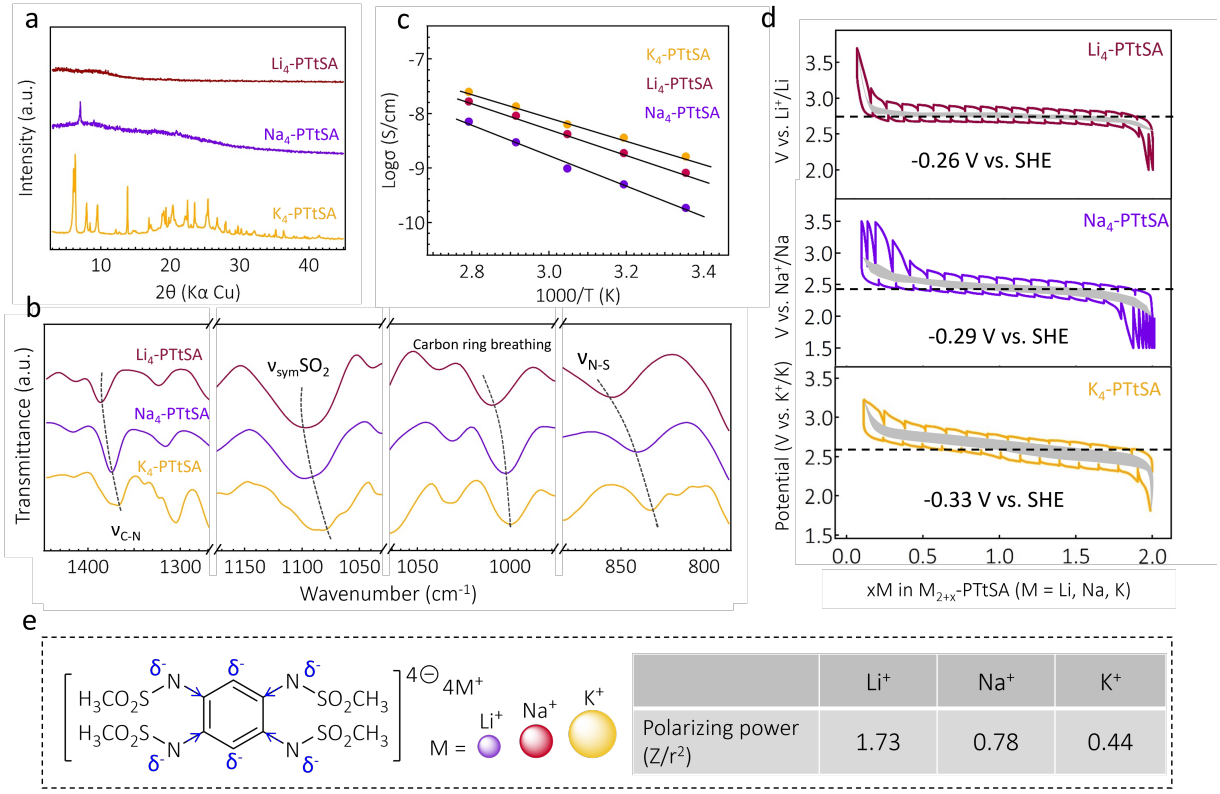
The structure and redox mechanism of M_4-PTtSA prepared with different alkali cations (M = Li^+, Na^+, and K^+, denoted as Li_4-PTtSA, Na_4-PTtSA and K_4-PTtSA) are depicted in Figure 1. The

design of organic tetra-anion framework draws inspiration from the widely used battery salts MTFSI (M = Li, Na, K). The Na_4/K_4-PTtSA derivatives were synthesized using modified methods of previously reported Li_4-PTtSA[18]. In short, a simple two-step process was applied: grafting the methanesulfonyl groups followed by sodiation/potassiation using stoichiometric amounts of sodium/potassium methoxide in anhydrous methanol under an inert atmosphere (refer to SI for detailed synthesis process, Fig. S1). The Li_4-PTtSA was also prepared and analyzed for comparative purposes.

The physico-chemical and electrochemical analyses of Li_4-, Na_4-, and K_4- phases have revealed a series of predictable analogies along with also unexpected differences (Fig. 2). Fig. 2a shows that with increasing the ionic radius of the host cations (from Li^+ to Na^+ and K^+) the crystallinity is improved. Shannon ionic radius, polarizing power and coordination number can be put forward to explain the difference although further studies may be required to understand in depth the correlation. Similar trend was also observed with inorganic cathode phases, like Li_2MoS_4, Na_2MoS_4[19] and K_2MoS_4[20] (the former being amorphous whereas the latter is crystalline).

The polarizing power, a value proportional to the ratio of the electrical charge by the ionic radius, decreases from Li^+ to Na^+ and K^+ due to the increasing ionic radius for the same electrical charge. It has been recently shown that the polarizing power of spectator cation tunes the electron density and thus the redox potential[7, 21]. Analysis of Li_4-, Na_4-, and K_4-PTtSA series corroborates Poizot's and our seminal hypothesis proving the universal applicability of tunning the redox potential through spectator cations. First, the ^{1}H NMR analysis reveals the aromatic proton shift in the Li_4-, Na_4-, and K_4-PTtSA series shielded from 6.89, 6.73 to 6.71, respectively (Fig. S3). This is a clear indication of lower electron density for Li_4-PTtSA and highest for K_4-PTtSA, according to lower polarizing power of K^+. Similar correlation is further noticed in vibration frequencies of bands of

interest. Fig. 2b displays the blueshift of $\nu_{C\text{-}N}$, $\nu_{sym}SO_2$, carbon ring breathing and $\nu_{N\text{-}S}$ bands, all rationalized by the decrease of the electron density on the redox center, via the electrostatic effect of the alkali cation used.



	Li⁺	Na⁺	K⁺
Polarizing power (Z/r^2)	1.73	0.78	0.44

Figure 2. Comparative analysis and correlations in the Li_4-PTtSA, Na_4-PTtSA and K_4-PTtSA series. (a) PXRD crystallinity survey; (b) FTIR close-up on the specific bands that correlate with charge density and redox potential; (c) Arrhenius plots of electrical conductivity; and (d) GITT

data for M_4-PTtSA (M = Li, Na, K) cells as measured in half cell configuration with the specific metals used as pseudo-reference and counter-electrodes; shaded region indicates the close to equilibrium redox potential. (e) The tetranionic PTtSA frameworks with different cations together with partial charges (in blue), and the blue arrows indicate the donor inductive effect (+I); right panel indicate the polarizing power difference of alkali cations.

The electrical conductivity of these phases was next evaluated (Fig. 2c). Despite being a critical factor for efficient material utilization in an electrochemical cell, electrical conductivity remains scarcely studied for organic electrode materials, with only few examples such as $Li_2C_6O_6$ (2.5×10^{-5} S cm^{-1})[22] and Li_4-DHT (1.1×10^{-7} S cm^{-1})[23] reporting practically relevant high conductivities. The Li_4-, Na_4-, and K_4-PTtSA phases display also intrinsic electrical conductivities, all reaching 10^{-8} S/cm at room temperature. The temperature dependence of the conductivity reveals a semiconducting type of thermally activated transport, as expected from the molecular structure of these materials. Redox mediated charge transport can be excluded in these alkali metal organics, and hopping type is probably the most plausible charge conduction mechanism. Interesting to note, there is no obvious trend in conductivity in the Li-Na-K series, which could be a complex interplay between the improved crystallinity and molecular stacking compensating the charge de/localization as discussed earlier (Figs. 2a and S3).

Lastly, according to the above analysis, galvanostatic intermittent titration technique (GITT) was used to determine the redox potential values for the Li_4-, Na_4- and K_4-PTtSA series and assess the effect of electron density change via spectator cation on the redox potential. The measured data vs. Li^+/Li^0, Na^+/Na^0 and K^+/K^0 are shown in Fig. 2d. For better comparison, the average estimated

redox potentials are referred versus Standard Hydrogen Electrode (SHE) according to the electrode potentials of respective couples, namely, -0.26, -0.29 and -0.33 V vs. SHE for Li_4-PTtSA, Na_4-PTtSA and K_4-PTtSA, respectively.

As shown by data in Fig. 2d (the referenced values vs. SHE), there is clear redox potential descending trend when increasing the electron density of the PTtSA redox center, induced by decreasing the polarizing power of the contained alkali cation. Whereas the precise crystal structure is not available (and subject of further research), it is reasonable to assume that two of the alkali cations remained after full two electron oxidation have a permanent electrostatic effect on the organic redox unit, and the two mobile cations have a variable, content dependent effect.

Besides solid-phase electrochemistry, the redox potentials in liquid state for M_4-PTtSA (M = Li, Na, K) were also analysed (Fig. S2), revealing the same downward trend as the solid-state electrochemistry data. These results are in perfect agreement with ^{1}H NMR data (Fig. S3): ascending trend in the electron density of the redox center with the increased monovalent cation radius (thus lower polarizing power), noting that higher electron density causes lower redox potential. FTIR analysis (Fig. 2b) also corroborates the hypothesis that the redox potentials can be directly related to the electron density of specific bonds, no matter directly or indirectly participating in the redox process.

In order to have better understanding of the effect of different alkali cations on the redox potentials, DFT calculation was also conducted (refer to SI file: DFT calculation section). The results show that the different redox potential in M_4-PTtSA (M = Li, Na, K) is related to properties of the π-ring, as well as the differences in electronegativity of the Li^+, Na^+ and K^+. The coordination of alkali cations to PtTSA molecule induces different degrees of destabilization and modification of

aromaticity of central ring. The role of central π-ring was emphasized also in our previous paper[18]. An schematic illustration is given in Fig. 2e, where different polarizing effect of the alkali cation provides different donor inductive effect (+I).

Furthermore, all the three phases display high material utilization (>90%) and low polarization (< 200 mV), indicative of fast kinetics, which could be in part attributed to their intrinsic electrical conductivity as well as easier cation diffusion within an organic framework (Fig. 2c). Overall, the comparative results not only reveal the universal applicability of M_4-PTtSA as positive electrode materials for alkali-ion batteries, but also offer valuable information on tuning the redox potential of organic electrode materials by spectator cation exchange.

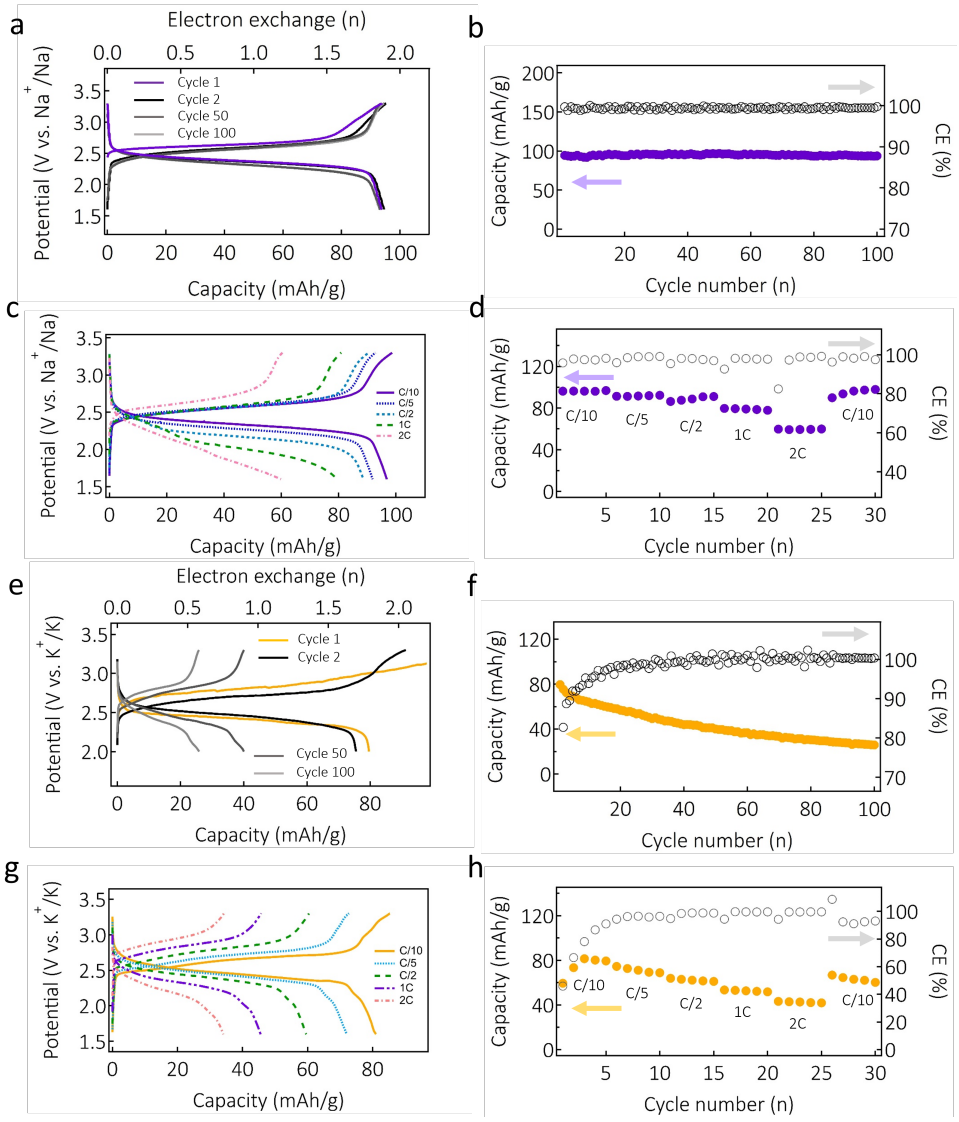


Figure 3. Electrochemical performance of the electrode materials in Na and K half-cells. (a) Na_4-PTtSA/Na cell galvanostatic charge-discharge curves of selected cycles at C/10. (b) long-term cycling performance of the corresponding cell. (c) Charge/discharge curves and (d) cycling data of rate performance of the Na_4-PTtSA/Na cell at various current densities ranging from C/10 to 2C, respectively. (e) K_4-PTtSA/K cell galvanostatic charge-discharge curves of selected cycles at C/10; (f) long-term cycling performance of the corresponding cell. (g)

Charge/discharge curves and (h) cycling data of rate performance of the K_4-PTtSA/K cell at various current densities ranging from C/10 to 2C, respectively.

The electrochemical performances of Na_4/K_4-PTtSA phases in solid-phase cells are evaluated and discussed next (for characteristic performances of Li_4-PTtSA, refer to[18]). The galvanostatic cycling of Na_4-PTtSA/Na cell was tested in potential window between 1.7 and 3.3 V vs. Na^+/Na with a current density of one Na^+ exchanged in 5 hours. As can be seen from Fig. 3a, the cell displays a flat charge/discharge plateau at around 2.5 V vs. Na^+/Na (refer to Fig. S5 for dQ/dV plots), with a reversible specific capacity of 95 mAh g^{-1}, corresponding to approximately 1.9 Na equivalents exchanged per formula unit. It is worth noting that 2.5 V vs. Na^+/Na is the among highest attained to date for a Na-ion organic positive electrode material that is directly synthesized in the Na-reservoir phase. Even among all the n-type organic compounds, only tetrachloro-1,4-benzoquinone is known to have a higher potential of 2.72 V vs. Na^+/Na, but this compound can barely support stable cycling due to the high solubility in electrolytes[13]. The high attained redox potential is attributed to the four strong electron withdrawing sulfonyl groups, inducing high electron delocalization. In the long-term cycling, Na_4-PTtSA/Na cell shows remarkable cycling stability with insignificant capacity decay: 99.7% capacity retention after 100 cycles and average coulombic efficiency ≥ 99.5%, which is, to the best of our knowledge, among the best cycling performance of an organic cathode for SIBs reported so far[24] (Fig. 3b). The Na_4-PTtSA shows excellent cycling stability because it maintains permanent charges during charge-discharge that help stabilizing the intermolecular network between the anions and Na^+ (Na_4-PTtSA ↔ Na_2-PTtSA, refer to Fig. S4 for ex-situ mechanistic analyses)[25]. Thus, at any stage during the redox

process the electrodes are insoluble, guaranteeing the excellent cycling stability of the electrode, given the solubility being known as the major degradation pathway in organic batteries[21, 26]. The Na_4-PTtSA/Na cell also displays very promising rate capability, as shown in Figure 3c and 3d. Despite of minor polarization, the cell maintains 80 mAh g^{-1} (80% of theoretical capacity) and 60 mAh g^{-1} (60% of theoretical capacity) at high charge-discharge rates of 1C and 2C, respectively.

K_4-PTtSA as positive electrode material was also evaluated in K_4-PTtSA/K cells. It must be emphasized again that K_4-PTtSA is the first K-reservoir organic cathode material reported so far. Fig. 3e shows the selected voltage-potential traces of the K_4-PTtSA/K cell cycled at a rate of one K^+ exchanged in 5h. Compared to only one plateau for Li_4- and Na_4- electrodes, K_4-PTtSA displays two redox plateaus with high redox potential averaged at 2.6 V vs. K^+/K (Fig. 3e and S5). The cell reaches a capacity of 80 mAh g^{-1} corresponding to an overall of 1.8 K^+ reversible exchange per formula unit. After 100 cycles at C/10 (over two-months of cycling), nearly 50% of the initial capacity was obtained (Fig. 3f). It is worth noting that the coulombic efficiency was very low at the first few cycles and increases to 100% after 50 cycles. Generally, electrode dissolution is one of the main causes for capacity decay in organic electrode materials, yet this reason is excluded for K_4-PTtSA because the compound is not soluble at all during cycling (Fig. S6). The reason of degradation in turn is assigned to the poor potassium plating/stripping efficiency, given the low coulombic efficiency of the K_4-PTtSA/K cell, and the unstable interface between the K metal and the used electrolyte. To confirm this hypothesis, a potassium plating-stripping test was carried out using copper foil as counter and reference electrode (Fig. S7). The plating-stripping efficiency was also very low in the first cycle, and gradually increases to ~100% after ~50 cycles, which is in good agreement with the cycling efficiency of the K_4-PTtSA/K cell, indicating the problem of potassium in the electrolyte instead of the electrode material. The rate performance of K_4-PTtSA

electrode was also evaluated in K_4-PTtSA/K cells, shown in Figure 3g and 3h. The cell can maintain 45 and 35 mAh g^{-1} (~ 50% and 40% of the theoretical capacity) at high current density of 1C and 2C, respectively, which is slightly lower than of the Na-version because of the larger size and slower diffusion of K^+.

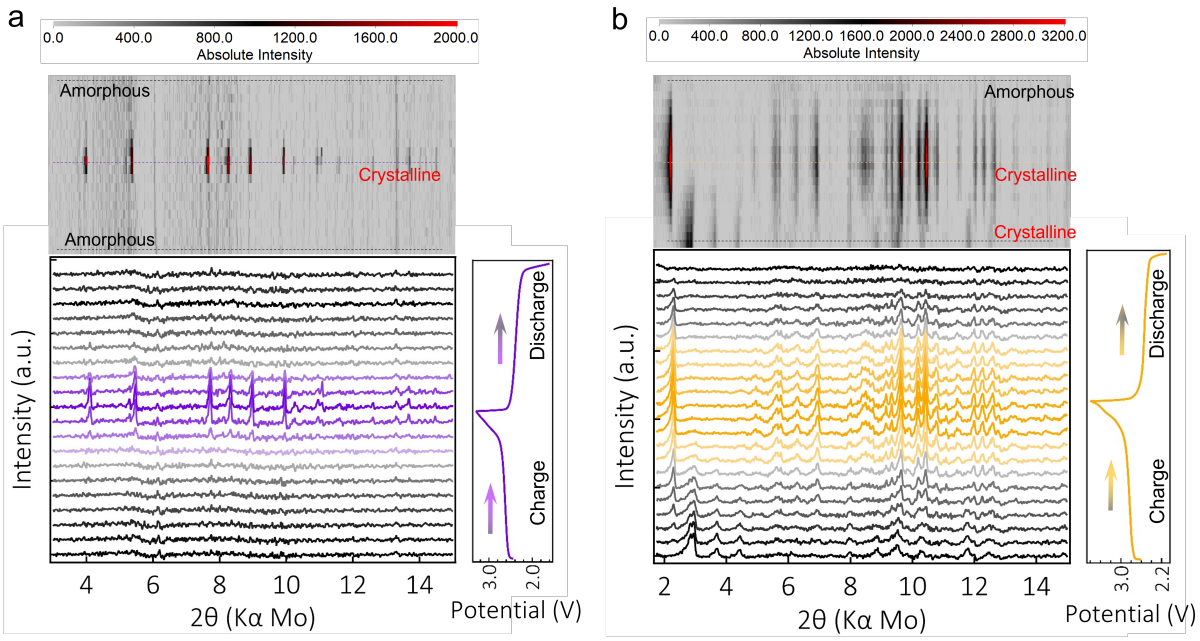


Figure 4. In situ XRD survey of the first charge/discharge cycle for (a) Na_4-PTtSA and (b) K_4-PTtSA electrode. The 2-D contour plots are shown on the top of the figure. The line plot of the in situ XRD patterns at different charge-discharge states are shown at the bottom, and the corresponding galvanostatic charge-discharge profiles are displayed to the right.

To have a better understanding of the redox mechanism as well as the structure evolution of the studied electrode materials during cycling, *in situ* XRD surveys of the Na_4-PTtSA and K_4-PTtSA were conducted over one complete charge-discharge cycle, respectively (Figure 4). As discussed

previously in Figure 2a, Na_4-PTtSA adopts a poorly crystalline or amorphous phase, which is also observed in the *in situ* XRD measurement (Figure 4a). At the beginning of the first charge, Na_4-PTtSA maintains amorphous, while the appearance of a crystalline phase is observed close to end of first charge (corresponding to Na_2-PTtSA), with several peaks appearing (at 4.1°, 5.5°, 7.7°, 8.3°, 9.0° and 10.0°, Mo-Kα). Then to further cycle, the crystallinity is progressively lost at the early stages of the discharge, and the amorphous phase is preserved upon complete sodiation. It is interesting that despite of the amorphous nature of Na_4-PTtSA, the structure of the compound is electrochemically reversible. For K_4-PTtSA electrode, the pristine compound is an crystalline phase, with main peaks at 2.8°, 2.9°, 3.7° and 4.4° et al., which is observed in the first PXRD pattern of the *in situ* measurement (Figure 4b). During charging, the pristine phase gradually vanishes, and is replaced by the appearance of a better crystalline new phase of K_2-PTtSA thorugh a biphasic solid reaction. However, with further discharge, the structure does not return to the pristine crystalline but an amorphous K_4-PTtSA phase. The crystalline K_2-PTtSA and amorphous K_4-PTtSA phases are proved to be reversible in the following cycles (Fig. S8). In this particular series of compound M_4-PTtSA (M = Li, Na and K), the fully 2-electron oxidized states M_2-PTtSA (M = Li, Na and K) are crystalline, while the fully reduced phases generally adopt amorphous feature during electrochemical charge-discharge, probably due to the structure distortion from the dislocation of the additional alkali cations.

To consolidate the applicability of M_4-PTtSA as alkali-ion cathodes, we conclude this study by detailing a new prototype concept of Na-ion full-cell: a nitrogen redox based all-organic Na-ion battery (NAOSIB). Figure 5a schematizes the construct and operation of the NAOSIB prototype cell, where Na_4-PTtSA was used as cathode material and azobenzene-4,4'-dicarboxylic acid lithium salt (ADALS)[27] as anode material (Fig. 5b). The reversible redox of the *azo* group allows

for two Na^+ storage at an average potential of 1.3 V vs. Na^+/Na[28]. Therefore, both electrode materials can reversibly shuttle two electrons concomitantly with two Na^+, based exclusively on an organic nitrogen redox center. As shown in Fig. 5c, the NAOSIB has an average output voltage of ~1.15 V with a slightly sloped voltage profile. The NAOSIB can deliver a capacity equivalent to 1.9 electrons exchange (around 95 mAh g^{-1}, based on the mass of positive electrode material) at a cycling rate of C/10 (Fig. 5c). Finally, the NAOSIB displays excellent power performance as proven by the stable cycling and good capacity retention at different cycling C-rates ranging from C/10 to 5C (corresponding to 1 Na^+ in 5 h to 6 min, Fig. 5d), with above 60 mAh g^{-1} capacity retention even at high current density of 1C. Besides Na-ion full cell, a K-ion full cell can be also envisioned to have similar performance by combining K_4-PTtSA cathode material with different types of organic anodes, such as ADALS[29] or dipotassium terephthalate[30] et al.

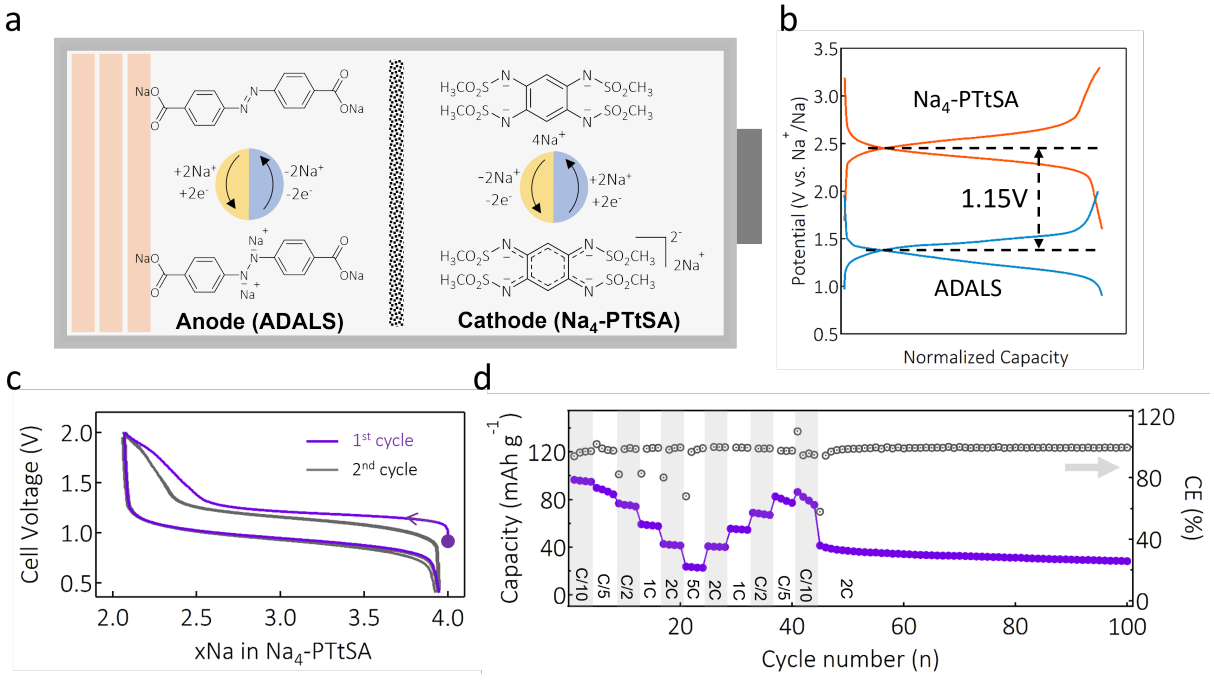


Figure 5. The prototype of the nitrogen redox based all-organic Na-ion battery (NAOSIB). (a) Schematic diagram of the full cell construction and the redox mechanism at play in the anode and the cathode. (b) Galvanostatic charge–discharge profiles for Na_4-PTtSA and ADALS as measured in half cells vs Na metal pseudo-reference and counter electrode. (c) The first two cycle voltage profiles of the NAOSIB cycled at a rate of 0.1C. (d) Specific capacity vs. cycle number at different cycling rate for the NAOSIB prototype cell.

In conclusion, the tetra-anionic PTtSA framework is shown to perform as a universal redox centre yielding organic cathodes for high performance alkali-ion batteries (Li, Na and K so far). This chemistry is not only reported as novel in the context of SIBs and PIBs, but also the first one to disclose Na-ion and K-ion reservoir organic cathode materials. The Na_4- and K_4- phases show reversible exchange of two Na^+/K^+ at a high redox potential of 2.5 V vs. Na^+/Na and 2.6 V vs. K^+/K, respectively, with excellent cycling stability and power performances. In the systematic study of the Li_4- vs. Na_4- vs. K_4-PTtSA derivatives we identify trends in structural order and charge localization with direct impact on redox performances. The high intrinsic electrical conductivity, scarcely studied for organic battery materials, enables fast kinetics, full material utilization and low electrode polarization, aspects highly sought for practical battery material utilization. Based on these unique features, the first nitrogen-redox based all-organic Na-ion battery prototype was assembled, with an output voltage of 1.15 V, good rate capability up to 5C, and excellent cycling stability. The reported positive electrode materials may be still not competitive with their inorganic counterparts, such as layered metal oxides and Prussian blue cathodes. However, compared with the inorganic cathodes benefiting from decades of extensive research, development and optimization, the first generation of PTtSA cathodes already show promising electrochemistry,

and there is still large room to explore and improve. Overall, this study not only enriches the emerging library of high voltage SIB and PIB organic cathode materials but also the knowledge of alkali-ion chemistries, cells, and devices for next generation energy storage. With this work, we pave new avenues in the field of alkali-ion organic cathodes, and we believe it will arouse extensive interests in organic materials for alkali-ion batteries with functional molecular design and unearth new possibilities of using organic cathode materials for future practical applications.

ASSOCIATED CONTENT

Supporting Information. Details of materials synthesis and characterizations, cyclic voltammetry data, as well as the DFT calculations.

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Notes

The authors declare no competing financial interest.

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