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Tuning the chemistry of organic-nitrogen compounds for promoting all-organic anionic rechargeable batteries

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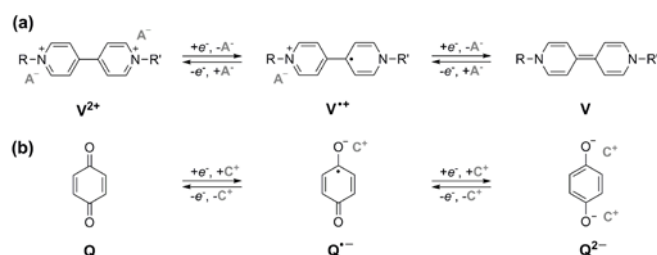
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Supporting information for this article is given via a link at the end of the document.

Abstract: The ever-increasing demand for rechargeable batteries induces significant pressure on the worldwide metal supply, depleting resources and arising cost and environmental issues. In that framework, developing the chemistry of anion-inserting electrode organic materials could promote the fabrication of molecular (metal-free) rechargeable batteries. However, few examples are reported because little effort has been made to develop such anionic-ion batteries. Here we show the design of two anionic host electrode materials based on *N*-substituted salts of azaaromatics (zwitterions). A combination of NMR, EDS, FTIR spectroscopies coupled with thermal analyses and single-crystal XRD allowed a thorough structural and chemical characterization of the compounds. Thanks to a reversible electrochemical anion-de-insertion process at ~ 2.2 V vs Li^+/Li , the coupling with dilithium 2,5-(dianilino)terephthalate (Li_2DAnT) as the positive electrode enabled the fabrication of the first all-organic anionic rechargeable batteries based on crystallized **host electrode** materials capable of delivering a specific capacity of ~ 27 $\text{mAh/g}_{\text{electrodes}}$ with a stable cycling **over dozen of cycles (~ 24 $\text{Wh/kg}_{\text{electrodes}}$)**.

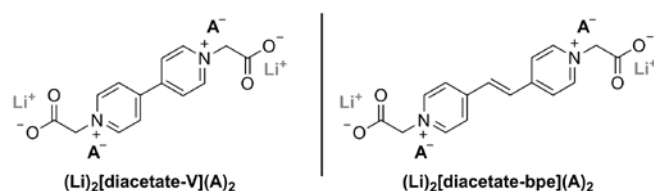
Since their discovery in the 30s by Michaelis and Hill,^[1] viologen derivatives (1,1'-disubstituted 4,4'-bipyridinium salts) have represented an important class of functional compounds beyond their interest as synthons in cyclization reaction in organic chemistry.^[2] Exhibiting strong electron-accepting properties (favoring host-guest interactions), viologens find applications in supramolecular chemistry for developing molecular machines (rotaxanes and pseudorotaxanes).^[3] Due to their three reversible redox states, the electroactivity of viologens has been intensively studied for a long time^[4]. Basically, viologens (V^{2+}) belong to p-type redox-active system^[5] (also named "System A" according to Hünig's classification^[6]), which involves after charge transfer an anion release forming successively the intermediate radical cation ($V^{\bullet+}$) and lastly the neutral form (V^0) as underlined in Scheme 1a. For comparison, a n-type redox-active species ("System B") works between its neutral state and the anionic one with cation uptake (Scheme 1b). Interestingly, the particular 4,4'-bipyridinium backbone stands out against other p-type systems by a low redox potential making it almost unique for a negative electrode application in electrochemical devices. In practice, electrochromic devices are the oldest applications using viologens as the negative electrode materials^[3a,7] (following pioneering research performed at the Philips Laboratories^[8]) because different absorption spectra characterize the three redox states. More recently, the use of viologen derivatives has also proved to be highly promising in the field of electrochemical storage notably as "negalyte" (soluble state) in aqueous redox flow batteries especially after the impressive results reported independently by Liu's group^[9] and Schubert's group.^[10] In addition, our group have just demonstrated that viologen-naphthalene diimide tandem materials^[11] give rise to impressive performances in aqueous organic batteries when paired with 2,2,6,6-tetramethylpiperidinyl-*N*-oxyl (TEMPO) derivatives as p-type positive electrode material^[12]. In non-aqueous media, it is worth noting that to our knowledge only two examples of full p-type organic battery are reported in the literature^[13] because viologens suffer from their solubility in commonly used carbonate-based liquid electrolytes. Yao and co-workers^[13a] from Japan reported the best results by assembling two redox-active polymers: poly(1,5-pentylene-4,4'-bipyridinium) dihexafluorophosphate as the negative electrode paired with poly(*N*-vinylcarbazole) as the positive electrode. This full organic cell achieved 1.8 V but its performances were hampered by a noticeable capacity loss upon cycling and an oversized negative electrode (i.e., the capacity of the negative electrode was adjusted to be more than twice that of the PVK electrode). However, this valuable study challenges us to investigate this unconventional cell configuration since the development of anionic "rocking-chair" organic batteries could pave the way for promoting molecular-ion rechargeable batteries.



Scheme 1. a) The three reversible redox states of viologens (p-type system). Note the intermediate radical cation ($V^{\bullet+}$) is considered among one of the most stable organic radicals. b) Example of benzoquinone (Q) / semiquinone ($Q^{\bullet-}$) / hydroquinone (Q^{2-}) as typical representative n-type system.

Having recently developed novel anion-inserting (p-type) positive electrode materials^[14] notably dilithium 2,5-(dianilino)terephthalate (namely Li_2DAnT) while being motivated to elaborate an efficient and non-polymeric p-type negative electrode material to be opposed to Li_2DAnT in an all-organic anionic "rocking-chair" cell, we present herein the synthesis and the electrochemical performance of two new *N*-substituted salts as azaaromatics able to reversibly store 1 e⁻/1 anions per ring in the solid state. The followed chemical strategy was aligned with our former achievements for promoting organic Li/Na-ion batteries based on the design of n-type organic salts as electrode materials. More particularly, we were the first to demonstrate that the incorporation of carboxylate functional groups^[5a,15] is extremely efficient to prevent solubilization of efficient n-type redox-active moieties in aprotic polar electrolytes; this property having recently successfully extended to p-type host materials with Li_2DAnT as representative example^[14a,b]. Therefore, we have attempted to apply a similar approach to the conventional 4,4'-bipyridinium (V^{2+}) redox center as well as to a homologous ethylenic derivative

(to proof the concept giving rise to original double zwitterionic organic skeletons bearing two carboxylate functional groups namely $(\text{Li})_2[\text{diacetate-V}](\text{ClO}_4)_2$ and $(\text{Li})_2[\text{diacetate-bpe}](\text{ClO}_4)_2$ (Scheme 2). Interestingly, we should underline that the bipyridinium-carboxylate units have been emerging for a decade as an interesting class of ligands in the field of Coordination Polymers (CPs) or Porous CPs (PCPs) exhibiting sometimes photochromic or thermochromic properties, for instance.^[16]



Scheme 2. Chemical structure of the two selected zwitterionic derivatives for the negative (p-type) electrode application. The presence of the two carboxylate functional groups enables to prevent solubility in aprotic polar electrolytes.

To prepare the two target compounds, our approach consisted in a two-step reaction starting with *N,N*-quaternization of either (E)-1,2-bis(4-pyridyl)ethylene or 4,4'-bipyridine in the presence of lithium iodoacetate followed by an anionic metathesis to exchange iodide for perchlorate anions (Scheme S1); all experimental details are reported in the Supplementary Information starting with the bpe derivative since the chemistry of this compound has never been reported before. Note that for the present study, perchlorate anions were deliberately preferred owing to the good anion-inserting electrochemical properties previously observed with Li_2DAnT .^[14a,b] The successive steps of the syntheses have been monitored by ^1H and ^{13}C liquid NMR, FTIR, ^{13}C CP MAS-NMR as well as thermal analyses. This series of characterizations are also provided in Supplementary Information (Figures S1-S21). In short, the compilation of all data confirmed the successful synthesis of the two targeted double zwitterions but as hydrated phases: $(\text{Li})_2[\text{diacetate-V}](\text{ClO}_4)_2 \cdot 1.2\text{H}_2\text{O}$ and $(\text{Li})_2[\text{diacetate-bpe}](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$. Temperature-resolved X-ray powder diffraction (TRXRPD) patterns coupled with thermal analyses data demonstrated however the possible preparation of the corresponding anhydrous phases by gentle thermal annealing at 110°C (6 (Figures S11-S12; S19-S20). Note that the efficiency of the metathesis reaction was readily checked by Energy Dispersive Spectroscopy analyses (EDS) (i.e., no trace of both I and Ag elements but the presence of Cl, Figures S10, S18) and corroborated by FTIR measurements (Figures S8, S12). Finally, Figure 1 shows the ^{13}C cross-polarization MAS-NMR spectra for both anhydrous $(\text{Li})_2[\text{diacetate-V}](\text{ClO}_4)_2$ (**1**) and $(\text{Li})_2[\text{diacetate-bpe}](\text{ClO}_4)_2$ (**2**) compounds. The presence of a unique carboxylate resonance at 170.4 or 170.6 ppm together with the single signal at 61.5 or 61.3 ppm of the adjacent methylene group unambiguously indicate the equivalency of the corresponding acetate functional groups and therefore the symmetric skeleton of the two zwitterions in the solid state.

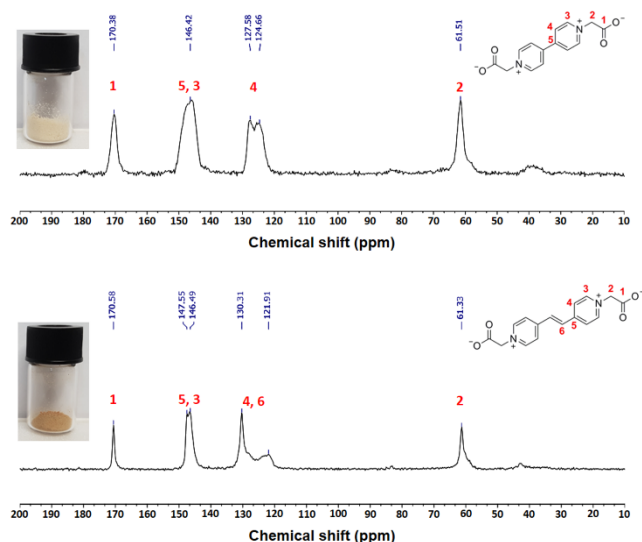


Figure 1. ^{13}C CP MAS-NMR spectra and corresponding resonance assignments of carbons atoms for (**1**) and (**2**), respectively.

The solubility of (**1**) and (**2**) in water urged us to grow single crystals but our different attempts failed. Nevertheless, for the bpe derivative, a slow recrystallization of either the iodide intermediate or the final perchlorate compound (**2**), led to unprecedented crystalline structures exhibiting asymmetrical molecules (Table S1) different from phases obtained as powder. In short, the [diacetate-bpe] skeleton can be described for one half of the zwitterionic unit by an inner self-charge

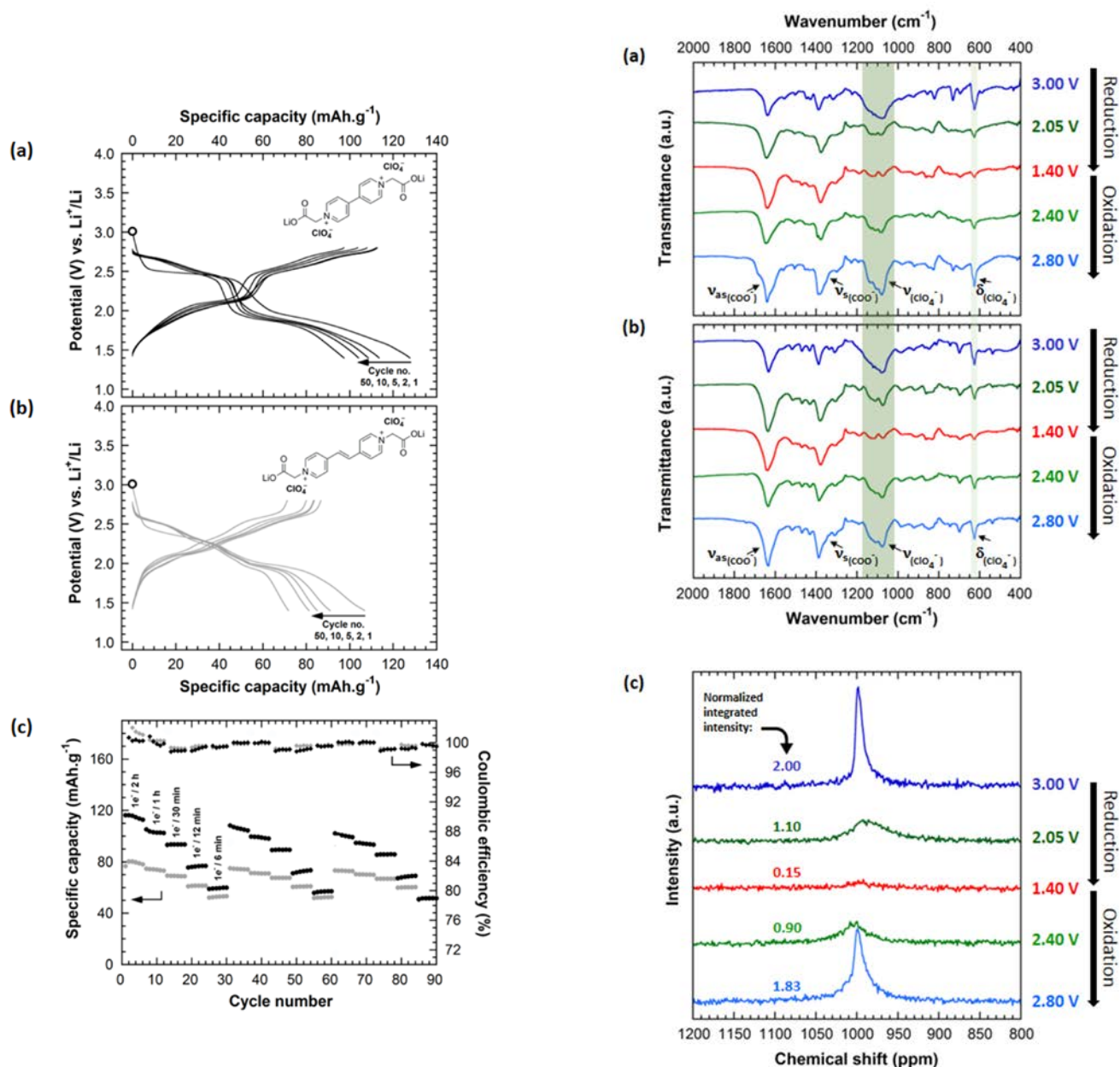
compensation between one N^+ center and its related acetate functional group. A similar arrangement was also observed by changing ClO_4^- for BF_4^- (Figs. S22-S26). As expected, the corresponding ^{13}C cross-polarization MAS-NMR spectrum of such phases confirms an asymmetric [diacetate-bpe] skeleton (Figs. S27-S28).

The electrochemical anionic deinsertion/insertion reactions of **(1)** and **(2)** were first evaluated in Li half-cells (dual-ion cell configuration^[5b]) within the 1.4–2.8 V potential range using $LiClO_4$ 1 M in PC as the electrolyte and a cycling rate of 1 electron exchanged per ring in 5 h (i.e., 1 e⁻/5 h or C/10). For this preliminary investigation, the composite electrodes were prepared without binder by simply adding 33 wt.% of carbon additive to the active materials without optimization. Remarkably, the as-obtained galvanostatic cycling curves (Figure 2a,b) displayed an efficient reversible electrochemical response and similar voltage profile. More precisely, during the first reduction 2 visible pseudo-plateaus are observed at ~2.4 and ~1.9 V vs Li^+/Li corresponding to capacities of 130 and 110 mAh/g for **(1)** and **(2)**, respectively, quite close to the expected two-electron reaction depicted in Scheme 1a for the viologen redox center. Subsequent cycles seem more complex with the appearance of several successive phenomena suggesting a possible rearrangement in the stacking since the two tested materials are crystallized host structures and not polymers. A progressive decrease in the reversible capacity is noticed during the cycling due to a slight dissolution of the active materials in the electrolyte as also observed by Yao with poly(1,5-pentylene-4,4'-bipyridinium) dihexafluorophosphate.^[13a] Nevertheless, we used large amounts of electrolyte for such preliminary cycling tests making room to improvements (see later). Additional power capability tests achieved through galvanostatic cycling at different regimes ranging from 1 e⁻/2 h (C/4) to 1 e⁻/6 min (5C) repeated three times were also performed (Figure 2c). Although the coulombic efficiency was not good enough when cycling at low rate due to the slight dissolution of the active materials, these tests unambiguously highlight the capability of non-polymeric *N*-

substituted salts of azaaromatic materials to support high cycling rates by providing about 50% of the initial reversible capacity at 1 e⁻/6 min (5C) although no optimized cell configuration was performed even if a progressive decrease in the reversible capacity is observed during the first ten cycles related to a slight dissolution of the active material.

Figure 2. a, b) Galvanostatic cycling curves of (Li)₂[diacetate-V](ClO₄)₂ (**1**) and (Li)₂[diacetate-bpe](ClO₄)₂ (**2**) measured in Li half-cell (rate: 1 e⁻/5 h; carbon content: 33 wt.%; electrolyte: 1 M LiClO₄ in PC). c) Specific capacity retention curves (in oxidation) together with the coulombic efficiency obtained for different cycling rates ranging from 1 e⁻/2 h to 1 e⁻/6 min per ring.

The reversibility of the anion-inserting electrochemical process at the electrode level was readily checked by *ex situ* FTIR



analyses for (**1**) and (**2**). Experimentally, five representative points were selected describing the first cycle (Figure 3). Comparison of the series of recorded spectra unambiguously confirms the reversibility of the insertion mechanism thanks to the obvious evolutions of ClO₄⁻ vibrations bands.^[17] The progressive disappearance of ClO₄⁻ anions vibrations bands at 1070 cm⁻¹ and 613 cm⁻¹ during the reduction (discharge) clearly demonstrates the extraction of perchlorate anions from the host structure. These two characteristic bands reappear progressively during the subsequent oxidation (charge) anions content.

Figure 3. a) *Ex situ* FTIR spectra recorded at different reduction and oxidation stages during the first cycle for Li half-cell containing $(\text{Li})_2[\text{diacetate-V}](\text{ClO}_4)_2$ (**1**) as active electrode material. b) Same experiment using $(\text{Li})_2[\text{diacetate-bpe}](\text{ClO}_4)_2$ (**2**). Rate: $1 e^-/5 h$; carbon content: 33 wt.%; electrolyte: 1 M LiClO_4 in PC. c) corresponding *ex situ* ^{35}Cl MAS NMR spectra $(\text{Li})_2[\text{diacetate-bpe}](\text{ClO}_4)_2$

The ^{35}Cl MAS NMR spectra fully support the FTIR results (see supporting information for detailed analysis) as they allow probing the ClO_4^- both from the quantitative and the electronic environment point of view. The spectrum of the pristine electrode displays one sharp resonance at 997 ppm, assigned to the identical environments of the two perchlorate anion in the $(\text{Li})_2[\text{diacetate-bpe}](\text{ClO}_4)_2$ unit. After the reduction to 2.05V corresponding to the extraction of one perchlorate and the formation of the intermediate radical cation form, one broad resonance is detected at 990 ppm, in agreement with the formation of the radical species and the change in the electronic state of the molecule. After the reduction to 1.4V, no ^{35}Cl signal is observed, showing clearly the complete extraction of all perchlorate anions from the electrode. The reduction process appears reversible since the subsequent oxidation goes through similar stages : one broad resonance after the insertion of one perchlorate anion per formula unit, sign of the presence of the radical cation form and finally a sharp resonance similar to that of the pristine electrode. The evolution of the normalized integrated intensity is also in agreement with the good reversibility of the electrochemical reaction as well as with the two successive steps, involving one electron/perchlorate each.

Having demonstrated the electrochemical stability of the two p-type zwitterionic structures in dual-ion cell configuration, a full anionic rocking-chair battery consisting of $\text{Li}_2\text{DAnT}^{[14a]}$ as the positive electrode faced to $(\text{Li})_2[\text{diacetate-V}](\text{ClO}_4)_2$ as negative electrode was assembled; the half-cell reactions are shown in Scheme S2. Note that the viologen derivative (**1**) was preferred due to its lower molar mass for an equivalent average working potential. In a first step, the two composite electrodes were prepared again without binder by simply adding 33 wt.% of carbon additive to the active materials without any optimization. The galvanostatic cycling test was then performed within the 0.05–1.5 V voltage range at a rate of $1 e^-$ exchanged per mol of Li_2DAnT in 5 h. Figure 4a,b show the resulting voltage profile together with electrochemical performance upon cycling. With an average output voltage of ~ 0.9 V, this prototype cell based on non-polymeric active materials exhibits a very stable capacity retention for more than 400 cycles (115 days of cycling) giving rise to a limited value of ~ 20 mAh per gram of both positive and negative electrodes notably due to the large content of carbon additive in electrodes. Having previously recognized that Li_2DAnT can be cycled at low carbon content,^[14a,b] we again tried to reduce the carbon amount mixed with (**1**). After a first optimization step and addition of Polytetrafluoroethylene (PTFE) as binder, the conductive carbon in the composite electrodes were decreased to 15 wt.% for Li_2DAnT and 5 wt.% for (**1**), which is also quite remarkable for organic electrodes. The corresponding capacity retention curves are reported in Figure 4c, which exhibit now a recovered capacity at ~ 27 mAh per gram of electrodes (i.e., 35% as gain).

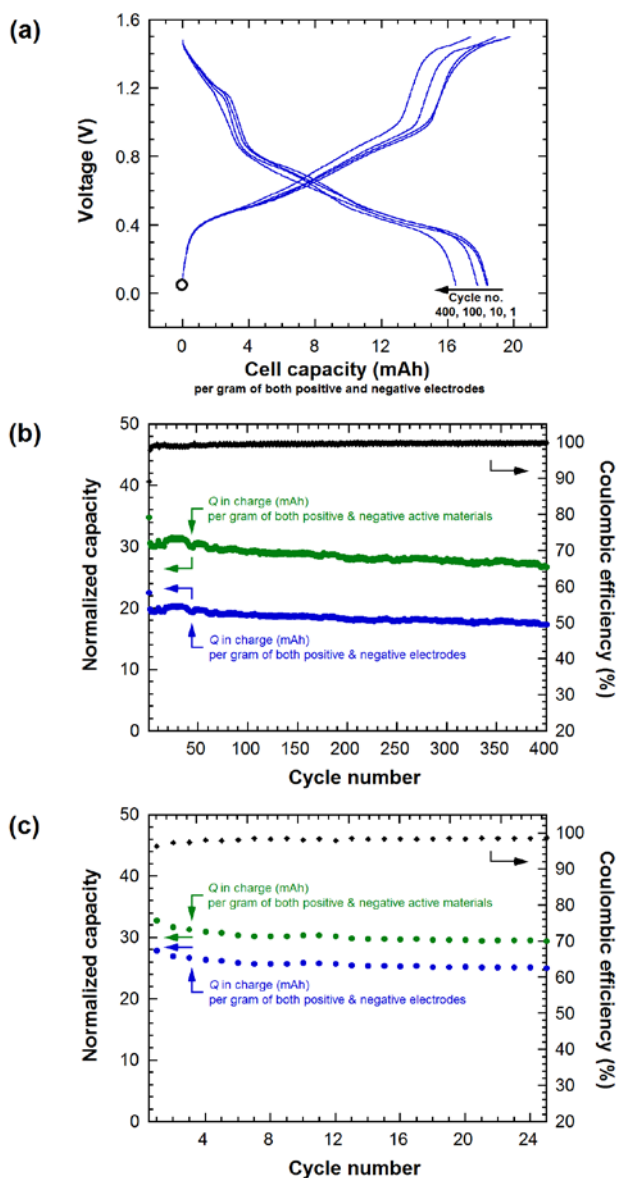


Figure 4. a) Galvanostatic cycling curves for a full cell assembly pairing Li_2DAnT as the positive electrode with $(\text{Li})_2[\text{diacetate-V}](\text{ClO}_4)_2$ as the negative electrode measured at a rate of $1 e^-$ exchanged per mole of Li_2DAnT in 5 h; carbon content: 33 wt.% for the two electrodes; electrolyte: 1 M LiClO_4 in PC. b) Corresponding normalized capacity retention curves (in charge) together with the coulombic efficiency. c) Normalized capacity retention curves (in charge) together with the coulombic efficiency for an optimized cell containing only 15 wt.% of carbon for the positive electrode and 5 wt.% for the negative electrode.

In summary, we have successfully designed and fabricated the third example in the literature of all-organic anionic “rocking-chair” battery while being the first example for which not polymers but discrete crystalline host electrode materials are used based on organic-nitrogen redox-active moieties. In addition, very good cycling stabilities were observed for these symmetric zwitterions even at low added carbon contents in the composite electrodes. This study was also the occasion to explore the chemistry of the [diacetate-bpe] skeleton, never explored to date, and to report unprecedented crystalline structures exhibiting asymmetrical units characterized by an inner self-charge compensation between one N^+ center and its related acetate functional group. This work opens up new opportunities to construct next-generations of rechargeable batteries potentially free of metals and points out interesting perspectives for the use of viologen derivatives with carboxylate functions to limit their solubility.

Experimental Section

The synthetic protocols of the series of compounds reported in this study as well as the common characterization techniques used are thoroughly detailed in the Supplementary information. ^{13}C Cross-polarization MAS-NMR spectra were acquired on a Bruker Avance 500 spectrometer ($B_0 = 11.8\text{ T}$) using R.F. pulses at Larmor frequency of 125.7 MHz. The samples were packed in 2.5 mm diameter zirconia rotors and spun at 11 kHz. For the FTIR *ex situ* analysis of composite electrodes containing either **(1)** or **(2)**, the corresponding Swagelok® cells (5 representative points) were disassembled in an argon-filled glovebox (MBRAUN, H_2O , $\text{O}_2 < 1\text{ ppm}$). The collected samples were gently washed with DMC, centrifuged to remove any trace of LiClO_4 then placed in a drying glass oven (Büchi B-585 glass-oven Kugelrohr) and heated during 6 h at a 70°C under vacuum. Finally, the FTIR analyses were performed on the resulting dried powders using KBr pellets in the range $4000\text{--}400\text{ cm}^{-1}$ on a FTIR Bruker Vertex 70. Air-free pellets were prepared in an argon glove box by mixing the sample with spectroscopic-grade potassium bromide at 1 wt.%. **Preparation of samples for ^{35}Cl MAS NMR *ex situ* analyses was performed similarly.**

The preliminary electrochemical investigations of the two zwitterions **(1)** and **(2)** as electrode materials were performed in dual-ion cell configuration using Swagelok-type cells, a Li metal disc as the negative electrode and a Whatman® separator soaked with LiClO_4 1 M in PC as the electrolyte ($V \approx 600\ \mu\text{L}$). The composite positive electrode was prepared without binder in an argon-filled glovebox by grinding powders of the two active materials with 33 wt.% carbon additive (Ketjenblack EC-600JD, Akzo Nobel) with mortar and pestle; $m_{\text{electrode}}$: 6-7 mg. A cycling rate of 1 electron exchanged per ring in 5 h (i.e., $1\text{ e}^-/5\text{ h}$) was applied corresponding to C/10 because of the bi-electronic electrode reaction. For the first full cell assembly, the two organic electrode materials were also prepared the same way with 33 wt.% carbon additive and no binder. The capacity of the negative electrode was oversized by 20% relative to the capacity of the positive electrode ($Q_{(+), \text{theo.}} = 75\text{ mAh/g}_{\text{Li}_2\text{DAnT}}$). After optimizations to reduce the carbon content, the positive electrode composition was 81 wt.% active material (Li_2DAnT), 14 wt.% carbon additive, 5 wt.% PTFE ($m_{(+)\text{total}} = 7.5\text{ mg}$) whereas the negative electrode composition was 90 wt.% active material ($(\text{Li})_2[\text{diacetate-V}](\text{ClO}_4)_2$), 5 wt.% carbon additive, 5 wt.% PTFE ($m_{(-)\text{total}} = 6.5\text{ mg}$); each electrode having been pressed at 2 tons on a stainless steel mesh (AISI 316L). The electrochemical cell was then cycled in galvanostatic mode at a rate of one electron exchanged in 5 hours per mole of Li_2DAnT . All cells were assembled in an argon-filled glove box and cycled in galvanostatic mode using a MPG-2 multi-channel system (Bio-Logic SAS, Seyssinet-Pariset, France).

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Keywords: zwitterions • redox chemistry • p-type organic electrode • all-organic anionic batteries • organic battery

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