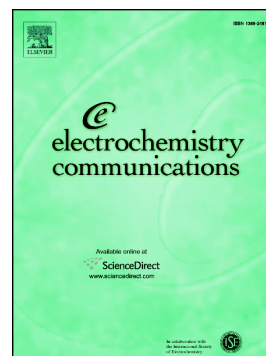


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# Stability of molecular radicals in organic non-aqueous redox flow batteries: A mini review

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## Keywords

- Redox flow batteries
- Redox active organics
- Non-aqueous electrolyte
- Molecular radicals

## Abstract

The application of novel organic redox materials is a plausible pathway towards techno-economic energy storage targets due to their low cost and sustainable design. Their operation in non-aqueous redox flow batteries affords researchers the opportunity to innovate, design and optimise these new chemistries towards practical energy densities. Despite this, the identification of high capacity organics which also display long-term stability is inherently challenging due to the high reactivity of molecular radicals.

## 1 Introduction

Energy management of intermittent renewable resources is a growing challenge for modern grid systems due to a current shortfall of high capacity energy storage implementation. Redox flow batteries (RFBs) are an already established technology which are ideally suited for renewable energy storage due to their decoupled power and capacity [1]. Aqueous designs such as the all-vanadium system [2] (V-RFB) encounter commercial difficulty because RFBs have intrinsically lower energy/power density and higher capital expenditure compared to other battery architectures which operate via electrode intercalation/deposition [3]. A pathway towards higher energy density RFBs is via solvent substitution as the low 1.23 V stability region of water limits the battery cell potential. By operating in a non-aqueous (NA) regime, researchers are afforded a larger design space to develop new materials and plausibly attain high electrolyte energy density via simultaneous enhancement of the cell potential, material solubility and the number of electrons stored per redox species [4]. Energy storage in redox-active organic molecules (ROMs) is a promising new pathway towards low-cost energy storage; however, their application is hindered at present by chemical instability which causes irreversible battery capacity loss. This short review will examine the nascent topic of applying organic neutral and ionic radicals in RFBs and their decomposition reactions in non-aqueous electrolyte. A wealth of literature provides complementary results in which ROMs are evaluated in aqueous media [5–7] and polymer-based designs [8–13].

## 2 Energy storage in molecular radicals

### 2.1 Organic redox materials

Early NA RFB literature primarily featured metal coordination complexes (MCCs) such as 2,2'-bipyridine (bpy) [14] or acetylacetonate (acac) [15] compounds. Although materials such as  $V(acac)_3$  [16] have realised high theoretical energy densities with cell potentials in excess of 2 V [17], MCCs are relatively insoluble and have low intrinsic capacity – a measure of the number of electrons stored per unit molecular weight. In contrast, low mass ROMs have much higher intrinsic capacity [18] and can be far more soluble in organic solvents (>1 M) or highly miscible liquids at room temperature [19]. Furthermore, as ROMs may in principle be mass-produced from biomass, they are more likely to achieve economic targets if their energy density is high enough [18]. Despite this, practical application of ROMs is a challenging new field as battery cycling produces chemical species with unpaired valence electrons called radicals which are inherently reactive. As a result, decomposition can rapidly occur via a variety of pathways, often involving the battery solvent or salt [19]. Hence, the chemical conditions of the battery must be carefully considered as the radical shelf-life may be highly dependent on the electrolyte composition, trace oxygen/water, material concentration or temperature. Understanding the reactivity of molecular radicals is therefore key to increasing radical persistence; however, it must first be acknowledged that neutral and ionic radicals are distinctly different chemical species.

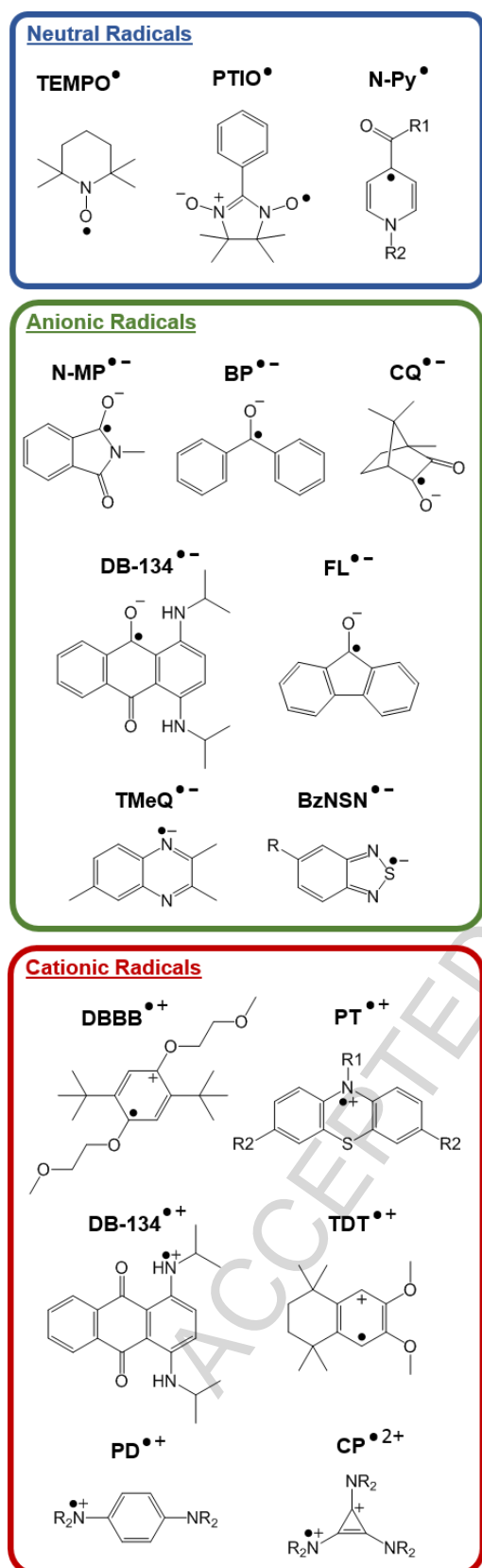


Figure 1. Chemical structures of redox-active organic molecule radical states described in the text. Readers should note that molecular spin and charge densities can be extensively delocalised and substantially decoupled when the neutral precursor molecule is polar.

## 2.2 Neutral radicals

Organic molecules are typically uncharged species without any net electron spin because all their valence electrons are paired into discrete molecular orbitals (MOs). Despite this, radicals can be easily generated through bond homolysis to produce species with a singly occupied molecular orbital (SOMO) [20]. Most radicals are reactive because spin-pairing is energetically favoured, hence radical coupling or dimerisation reactions are very facile. In addition, radical reactions with spin-paired molecules, via abstraction or addition mechanisms, are also possible causing the radical to propagate to other molecules and radical chain reactions to occur [21]. Therefore, most radicals are typically short lived as there are a plethora of possible decay pathways, although many stable radicals are known because the unpaired electron can be persistent. Radical stabilisation can be achieved by the presence of electron-withdrawing groups, -donating groups or conjugation near the radical locus; however, steric hindrance can significantly increase shelf-life by physically blocking bond formation [20]. For example, the perchlorotriptyl radical is possibly the most stable organic radical known as it has an estimated half-life of 100 years and is thermally stable to 300 °C in air [21].

The most studied neutral radical for energy storage is the relatively stable 2,2,6,6-tetramethyl-1-piperidinyloxy (**TEMPO**<sup>•</sup>) radical [20,21]. **TEMPO**<sup>•</sup> possesses a nitroxyl radical group which is stable due to steric protection by its methyl substituents preventing dimerisation, and a three-electron bond – a resonance effect involving the nonbonded electron pair on the nitrogen. Originally utilised as a lithium-ion overcharge protection redox-shuttle [22] **TEMPO**<sup>•</sup> derivatives have been applied in hybrid lithium-RFBs [23] and organic NA RFBs [12,24–27], due to their reversible one-electron oxidations to oxoammonium cations [24]. Pairing a **TEMPO**<sup>•</sup> catholyte with lithium results in a ~3.5 V cell potential and high >180 W h L<sup>-1</sup> theoretical energy density [23,27] because **TEMPO**<sup>•</sup> is soluble over 2 M in carbonate electrolyte [23] or capable of forming a solvated ionic liquid [27]. Such batteries have achieved very high ~99% coulombic ( $\eta_C$ ) and 86% energy efficiency ( $\eta_E$ ) with nominal capacity fade because of high radical stability. Asymmetric NA RFBs with anolytes *N*-methylphthalimide (**N-MP**) [24], benzophenone (**BP**) [28] and (1S)-(+)-camphorquinone (**CQ**) [25] have been explored; however, the system stabilities were not assessed as very limited battery cycling data was reported. A more rigorous stability assessment was achieved for 4-acetamido **TEMPO**<sup>•</sup> in a symmetric single-electrolyte cell which displayed near-constant and -theoretical capacity for 20 cycles [26].

A symmetric all-organic NA RFB was proposed featuring 2-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide (**PTIO**<sup>•</sup>) as both catholyte and anolyte [29]. **PTIO**<sup>•</sup> is another stable neutral nitroxyl radical; however, in addition to reversible oxidation to an oxoammonium cation, **PTIO**<sup>•</sup> also undergoes reversible reduction to an aminoxyl anion giving a 1.73 V cell potential. Validation of the symmetric principle was achieved for **PTIO**<sup>•</sup>, via electron spin resonance (ESR), by proving that the **PTIO**<sup>+</sup> and **PTIO**<sup>-</sup> species do indeed regenerate **PTIO**<sup>•</sup> when mixed, hence allowing a non-selective porous separator to be employed and high 20 mA cm<sup>-2</sup> current density achieved. Despite the high ~2.6 M acetonitrile (MeCN) solubility limit of **PTIO**<sup>•</sup>, only a maximal 0.5 M concentration was

demonstrated in a flow cell due to increased electrolyte viscosity and separator crossover. Relatively low 90%  $\eta_C$  and 60%  $\eta_E$  was observed due to self-discharge via electrolyte crossover; however, the cell did not cycle at constant capacity as expected suggesting chemical instability.

The electrochemical reduction of low molecular weight pyridinium (**N-Py**) cation derivatives yield enduring neutral radical species [30–32]. Based on the observation that 2,2'-bipyridine derivatives exhibit reversible redox couples, several alkyl pyridinecarbonates were examined, the *para-N* of which giving reversible one electron voltammetry to radical anion states. Evolution of the structure led to *N*-alkyl pyridinium cations which undergo two electron transfer to anions via stable neutral radical intermediates. Despite this, the anionic *N*-methyl pyridinium ester enolates were unstable due to their high basicity causing rapid decay via protonation. In contrast the less basic ketone enolate anions were significantly more stable, with both the neutral radical and anion forms persisting for several days [30]. Further attempts to extend the radical half-life yielded 4-benzoyl-*N*-(2,6-dimethylphenyl)pyridinium, the neutral radical of which has a predicted half-life of over a month (0.5 M, 70 °C) due to high electron delocalisation and steric protection [31]. Results showed an inverse correlation between radical persistence and intrinsic capacity, hence a more balanced material was proposed; 4-benzoyl-*N*-ethyl-2,6-dimethylpyridinium. Constant capacity over 200 cycles in a symmetric electrochemical cell was observed for this redox material [31].

### 2.3 Radical anions

Electrochemical reduction of a neutral spin-paired molecule injects an electron into the lowest unoccupied molecular orbital (LUMO) to produce a species which has a formal negative charge and an unpaired electron. The SOMO therefore determines the molecular charge and spin distribution as well as the ease of formation due to the difference in energy between the SOMO and next occupied orbitals [21]. In addition, as the SOMO is typically antibonding or nonbonding in character, occupation of the LUMO may cause significant structural changes, such as loss/gain of planarity, which inevitably results in slow electron transfer kinetics [33]. Once formed, radical anions can be relatively short-lived states due to their tendency to disproportionate into a dianion and the parent neutral molecule. Furthermore, due to their basicity, radical anions are susceptible to hydrogen abstraction or protonation and in addition, fragmentation to an anion and a radical via mesolytic cleavage is also possible [21].

Several carbonyl-containing compounds, which produce ketyl radicals, have been explored for NA RFB energy storage [19,24,25,28,34–36]. Quinones are of particular interest as they are reduced to dianions, via radical anion semiquinone intermediates, allowing two electrons to be stored per molecule [34,37,38]. Stability of the radical intermediate arises from high delocalisation, a property further demonstrated by diaminoanthraquinones (**DB-134**) which are capable of a reversible five-membered redox series; dianion to dication, allowing a symmetric RFB to be constructed whereby two electrons are stored per **DB-134** molecule in both the catholyte and anolyte [37]. In contrast, compounds such as 9-fluorenone (**FL**) [19] or **BP** [28] possessing only one carbonyl can only readily access a radical

anionic state. Battery cycling of **FL** and catholyte 2,5-di-*tert*-butyl-1-methoxy-4-[2'-methoxyethoxy]benzene (**DBMMB**) gave unstable battery cycling with rapid capacity fade due to radical decay of both species as shown in Figure 2 [19]. ESR showed that **FL**<sup>•-</sup> and **DBMMB**<sup>•+</sup> shelf-life is dependent on the electrolyte composition such that TEA BF<sub>4</sub> (tetraethylammonium tetrafluoroborate) / MeCN gave worst radical retention whereas TEA TFSI (tetraethylammonium bis(trifluoromethylsulfonyl)imide) / DME (1,2-dimethoxyethane) significantly prolonged it [19]. Instability of **FL**<sup>•-</sup> was attributed to reaction with MeCN (addition, hydrogen abstraction or protonation) or a pinacol dimerisation coupling reaction. Such coupling is expected in all ketyl radical anions unless the dimer is significantly sterically destabilised [20,21].

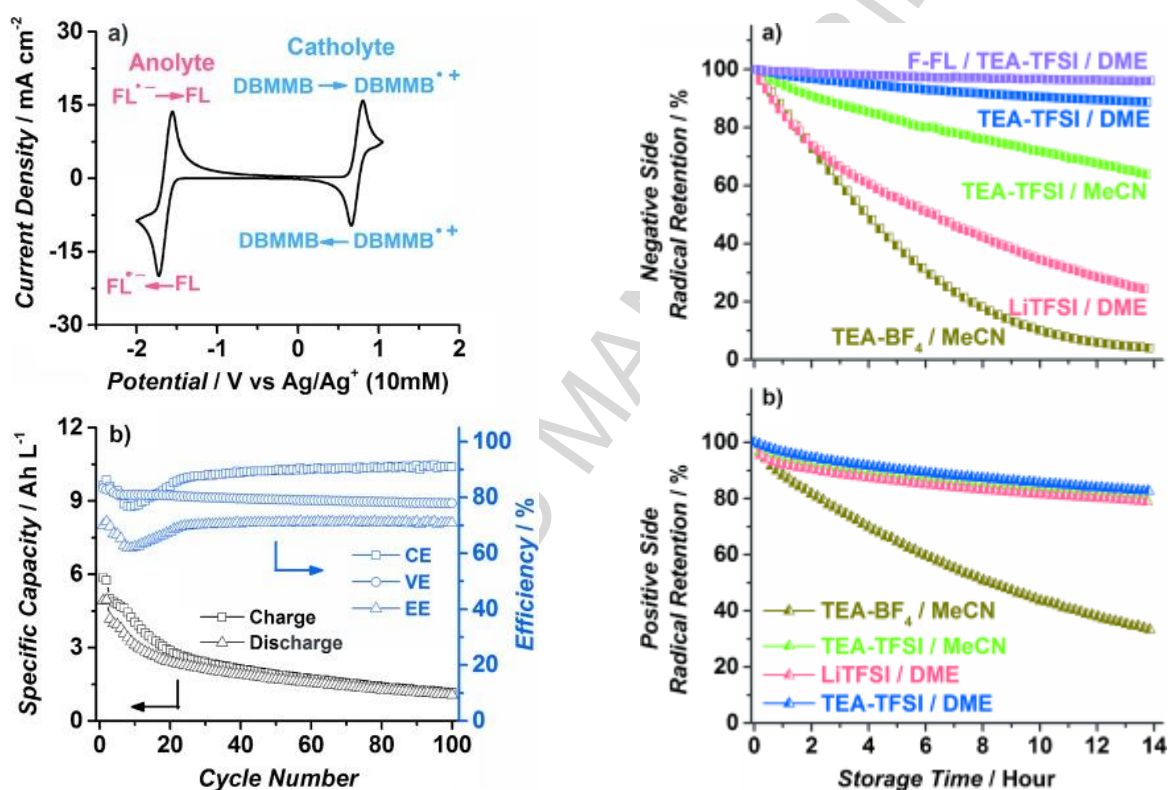


Figure 2. Left) a) cyclic voltammetry of **FL** and **DBMMB** and b) cycling efficiency of the **FL/DBMMB** system. Right) ESR radical decay as a function of time for a) **FL** and b) **DBMMB**. Reprinted from [19] with permission of Angewandte Chemie International Edition, © 2015 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

Non-ketyl type radical anions such as the heteroatomic 2,3,6-trimethylquinoxaline (**TMeQ**<sup>•-</sup>) [39] and 2,1,3-benzothiadiazole (**BzNSN**<sup>•-</sup>) [40] have also been targeted for energy storage. Although quinoxaline has a low molecular weight and is soluble to ~7 M in propylene carbonate (PC) its electrochemical response is poor, therefore **TMeQ** was proposed as its electron-donating methyl substituents result in two quasi-reversible reductions [39]. When paired with catholytes 2,5-di-*tert*-butyl-1,4-bis(2-methoxy-ethoxy)benzene (**DBBB**) [39] or 3,7-bis(trifluoromethyl)-*N*-ethyl-phenothiazine (**BCF3EPT**) [41], unstable battery cycling and low  $\eta_E$  was observed; however, the degradation mechanisms were not identified. Given that

a similar system featuring highly soluble (5.7 M in MeCN) **BzNSN** with **DBMMB** catholyte gave very little capacity loss over 160 cycles [40], it is likely that **TMeQ<sup>•+</sup>** instability was a significant contribution to the poor cycling above. High stability of the **BzNSN<sup>•-</sup>** radical anion was attributed to superior charge delocalisation compared to other radical anions suggesting that **BzNSN<sup>•-</sup>** is less vulnerable to protonation or electrophilic attack [40]. Further stability of **BzNSN<sup>•-</sup>** has also been achieved through functionalisation with electron-withdrawing groups, the fluoro-derivative of which significantly increased the radical half-life [42].

#### 2.4 Radical cations

Electrochemical oxidation of a neutral spin-paired molecule removes an electron from the highest occupied molecular orbital (HOMO) to produce a species which has a formal positive charge and an unpaired electron. Whereas destabilisation of bonding in radical anions typically occurs via gaining antibonding character, bonding in radical cations is significantly weakened by loss of a bonding MO electron [21]. As such, radical cations are considered  $\pi$ - or  $\sigma$ -type; however, their geometry can be significantly distorted compared to the neutral precursor, leading to twisted  $\pi$ -bonds or elongated  $\sigma$ -bonds and relatively slow heterogeneous rate constants. Unsurprisingly, radical cations are significantly acidic and electrophilic, hence rapid decomposition can occur by mesolytic cleavage, dimerisation, nucleophilic attack or deprotonation. In addition, radical cations can also undergo electron-hole transfer with other molecules, causing the unstable state to migrate to other species [21].

Substituted dialkoxybenzenes such as **DBBB** [39,41], **DBMMB** [19,36,40] or other derivatives [43–45] have been employed as lithium-ion redox shuttles and NA RFB catholytes because their radical cations are stable due to delocalisation, electron-donating substituents and steric protection [18]. While **DBBB** displays poor solubility ( $\sim 0.4$  M in PC) [46,47], **DBMMB** is a highly miscible liquid at room temperature [19,43]. Despite this, as their high molecular weight is undesirable for energy storage, low-weight derivatives with ‘pruned’ substituents have been explored but decreased stability was generally found due to loss to steric protection [18,48]. Structural isomers were found to have different radical shelf-lives and battery capacity retention due to irreversible degradation via radical addition or disproportionation forming dimers or quinones respectively [18]. In addition, a mechanism for self-discharge was observed whereby deprotonation and hydrogen abstraction with the solvent would occur in sequence, causing solvent decomposition instead of a loss of redox material [18].

Phenothiazine (**PT**) derivatives are another example of a lithium-ion redox shuttle being considered for NA RFB energy storage [41,49–53]. Formation of the radical cation results in a significant change in geometry as neutral **PTs** are substantially bent symmetrically through the nitrogen and sulfur atoms, whereas oxidation results in a more planar molecule [49]. Hence addition of different *N*-alkyl substituents can have varying effects on **PT<sup>•+</sup>** stability; while *N*-ethyl and *N*-alkoxy **PT<sup>•+</sup>** [50] display long term stability ( $> \text{DBBB}$ ) [41], *N*-*tert*-butyl **PT<sup>•+</sup>** is counter-intuitively far less stable because of strained geometry, allowing fragmentation to oligomerisation-prone **PT<sup>•+</sup>** [49]. 3,7-disubstituted (*para*-*N*) **PT** derivatives



with electron-donating or withdrawing groups have also been examined with **BCF3EPT** giving an increase in redox potential and stability with 2 M solubility [32,38,41,50,52,54]. The intrinsic capacity of phenothiazine has been further increased by stabilising the irreversible second oxidation of phenothiazine to a dication, via addition of *para-N* methyl [38] or methoxy groups [54], allowing two electrons to be stored per **PT** molecule.

Further radical cations have been recently employed for energy storage, including **DB-134<sup>•+</sup>** [37], *p*-phenylenediamine (**PD<sup>•+</sup>**) [55], 1,2,3,4-tetrahydro-6,7-dimethoxy-1,1,4,4-tetramethylnaphthalene (**TD<sup>•+</sup>**) [56] and radical dication cyclopropenium salts (**CP<sup>•2+</sup>**) [57]. Although the oxidations of **PD** (known as Wurster's salts [21]) to dications are quasi-reversible, stable battery cycling of over a month has been reported [55]. Stability of **TD<sup>•+</sup>** has been found to be dependent on the electrolyte composition such that **TD** coordination with Li<sup>+</sup> in solution leads to enhanced cyclability in lithiated electrolytes [56]. Oxidation of **CP<sup>•+</sup>** salts yield radical dications via reversible redox couples. Depending on the *N*-alkyl substituents, variable stability has been found with the isopropyl derivative giving near-constant capacity over 200 cycles [57].

### 3 Conclusions

Applying ROMs in NA RFBs is a promising pathway towards low-cost energy storage as organics are in principle highly soluble, tunable and capable of high redox potentials. Their application is intrinsically challenging as radical states are prone to various decomposition pathways and parasitic reactions with the battery electrolyte. Cyclic voltammetry has been incorrectly used to assess stability as it is not representative of the timescales or material concentrations encountered during battery operation. Instead, researchers should aspire to isolate ROM radical states (either synthetically or electrochemically) and measure their shelf-life via spectroscopy techniques such as ESR, nuclear magnetic resonance or UV-vis under controlled conditions [19,30,31,50]. Few studies have yet to directly examine decomposition reactions [18,30] and acknowledge the intricacies of different radical types; however, significant progress to improve stability has been made via modifying ROM structure [30,31,49,52,55] and electrolyte conditions [19,40]. Understanding degradation and self-discharge is key to improving stability as persistent radicals with long lifetimes are possible given adequate electron delocalisation and steric protection.

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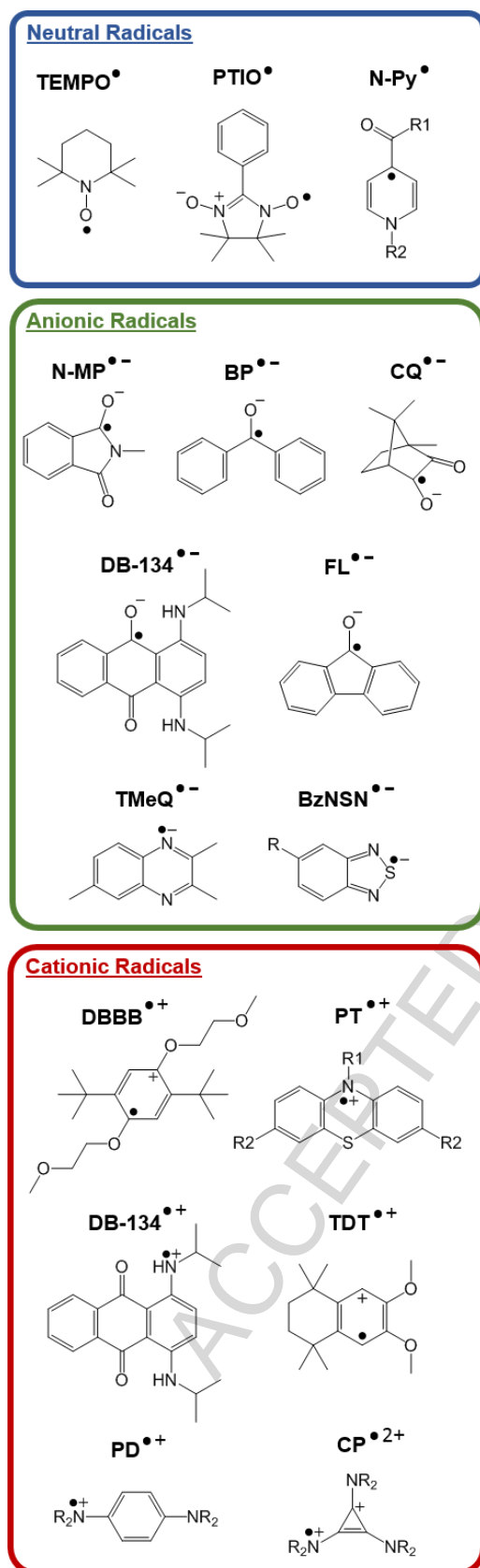


Figure 1. Chemical structures of redox-active organic molecule radical states described in the text. Readers should note that molecular spin and charge densities can be extensively delocalised and substantially decoupled when the neutral precursor molecule is polar.

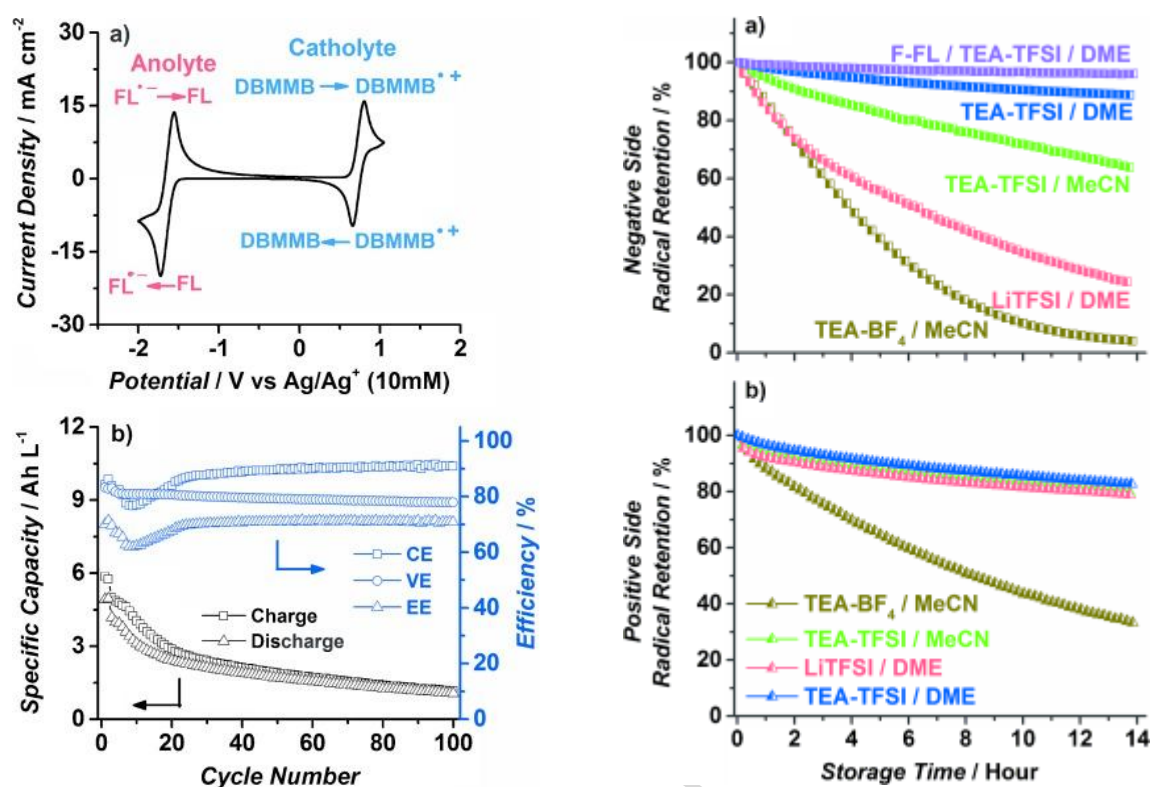


Figure 2. Left) a) cyclic voltammetry of **FL** and **DBMMB** and b) cycling efficiency of the **FL/DBMMB** system. Right) ESR radical decay as a function of time for a) **FL** and b) **DBMMB**. Reprinted from [19] with permission of Angewandte Chemie International Edition, © 2015 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

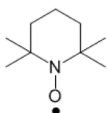


### Highlights

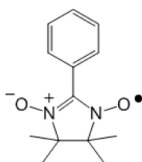
- Redox-active organic molecules are promising new energy storage materials
- The stability of molecular free radicals is concisely reviewed
- Decomposition of radical states results in irreversible battery capacity loss
- Radical half-life depends on chemical structure and electrolyte conditions
- Neutral, anionic and cationic radicals are distinct chemical species

## Neutral Radicals

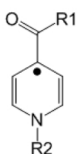
TEMPO<sup>•</sup>



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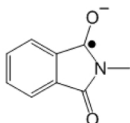


N-Py<sup>•</sup>

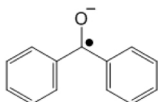


## Anionic Radicals

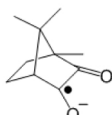
N-MP<sup>•-</sup>



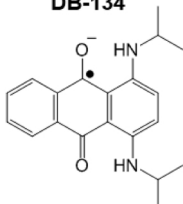
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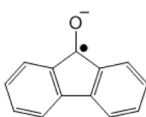
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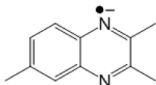
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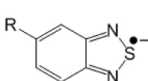
FL<sup>•-</sup>



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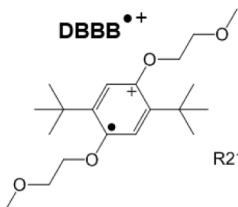


BzNSN<sup>•-</sup>

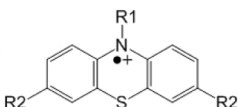


## Cationic Radicals

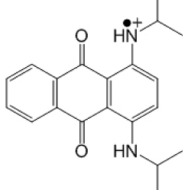
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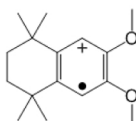
PT<sup>•+</sup>



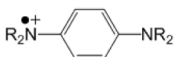
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TDT<sup>•+</sup>



PD<sup>•+</sup>



CP<sup>•2+</sup>

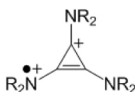


Figure 1

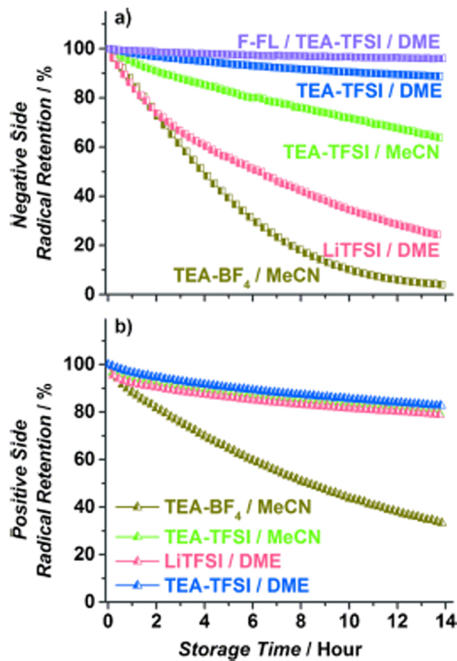
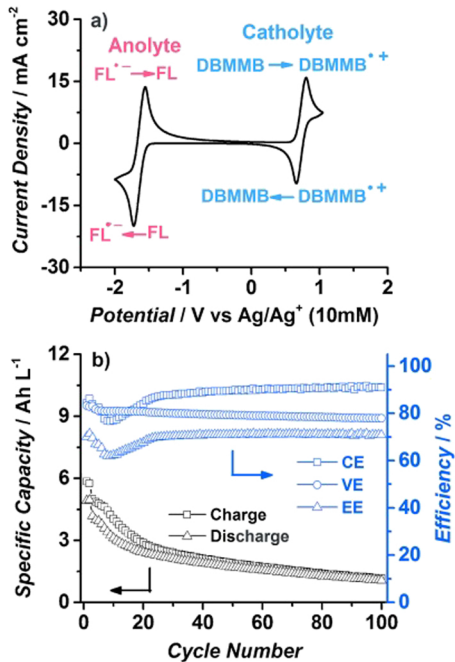


Figure 2