Recent advances in electrochemistry of pyridinium-based electrophores: A structronic approach

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REVIEW ARTICLE

Recent advances in electrochemistry of pyridinium-based electrophores. A structronic approach.

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Abstract

The context of molecular structronics (from "molecular structure" and "electronics") is that of molecular-level electrochemical storage of energy of sustainable origin (wind, solar). Due to its discontinuous availability, storage of this energy is a key issue. The targeted type of storage relies on implementing "electron reservoirs" within the structronic molecules by electrochemically forming dedicated chemical bonds according to non-catalytic processes. Reservoir bonds are therefore integral parts of the molecular backbone of structronic assemblies. When filled, electron reservoirs manifest themselves in the form of elongated covalent bonds that are to be cleaved for electron releasing (discharging) on demand. The scope of this short review is limited to pyridinium electrophores as particularly suited building blocks for the development of structronics.

Introduction

In the context of the structronic concept, it is worthwhile to compare functional structronic molecules with the catalysts, which regardless of their size integrate two functionalities of interest.

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Indeed, the *electron reservoir* and *bond formation* attributes are found directly in the definition of catalysts, which function as charge pools and contain reaction sites for the substrate(s) transformation. In the case of structronic molecules the two functionalities merge.

As stated by Nocera [1*] it is a matter of fact that "the smallest-volume element in which electrons may be stored is in the chemical bond". The smallest electron(energy) reservoir is a two-electron/two-center system of H_2 diatomic molecule. At first glance, one can regard H_2 as an energy vector that could serve as *electron reservoir* since its cleavage in a fuel cell (in the presence of an oxidizer such as dioxygen) produces electron flow (electricity) and water molecule as a by-product resulting from the bond formation. Although destroyed upon releasing its electrons, H_2 entity can be regenerated in a photoelectrochemical cell from water and solar energy (water splitting). However, H_2 is not functionally persistent as the electron reservoir. Moreover, the use of catalysts is mandatory for H_2 transformation. Thus, H_2 is not considered as structronic species that can be filled and emptied with electrons on demand.

Concerning the function of *bond formation*, one should distinguish between two types of chemical bonds that is bonds whose formation is either catalyzed or non-catalyzed. The structronic approach to electron storage via bond formation relies on a non-catalytic process of the bond formation allowing electron injection into a dedicated Lowest Unoccupied Molecular Orbital (LUMO) representing an *emerging empty reservoir bond*. In fact, confining two electrons within a chemical bond allows taking advantage of the quantum mechanical properties of covalent bonding (in particular spin pairing in order to overcome the electrostatic repulsion). At the same time, the covalent bond has to be weakened enough to be easily cleaved on demand for electron release. Such a bond is therefore expected to be elongated, which may be achieved by surrounding steric constraints. The molecular backbone hosting a functional reservoir bond should ensure the integrity of the structronic assembly with respect to redox cycling (charging/discharging). Precisely this structronic feature is lacking in H_2 molecule.

The LUMO of electrophores largely determines their reduction behavior. Delocalized LUMO(s) host electrons that electrostatically feel each other, which impacts unfavorably on the multielectron reduction processes. Indeed, heterogeneous electron transfers are then stepwise single-electron processes where the subsequent electron transfer is more energy demanding. This is exemplified by the electrochemically reversible twofold reduction of archetypal methyl viologen **MV** (Figure 1) as well as a six-fold monoelectronic reduction of prototypical C_{60} [2].

Figure 1
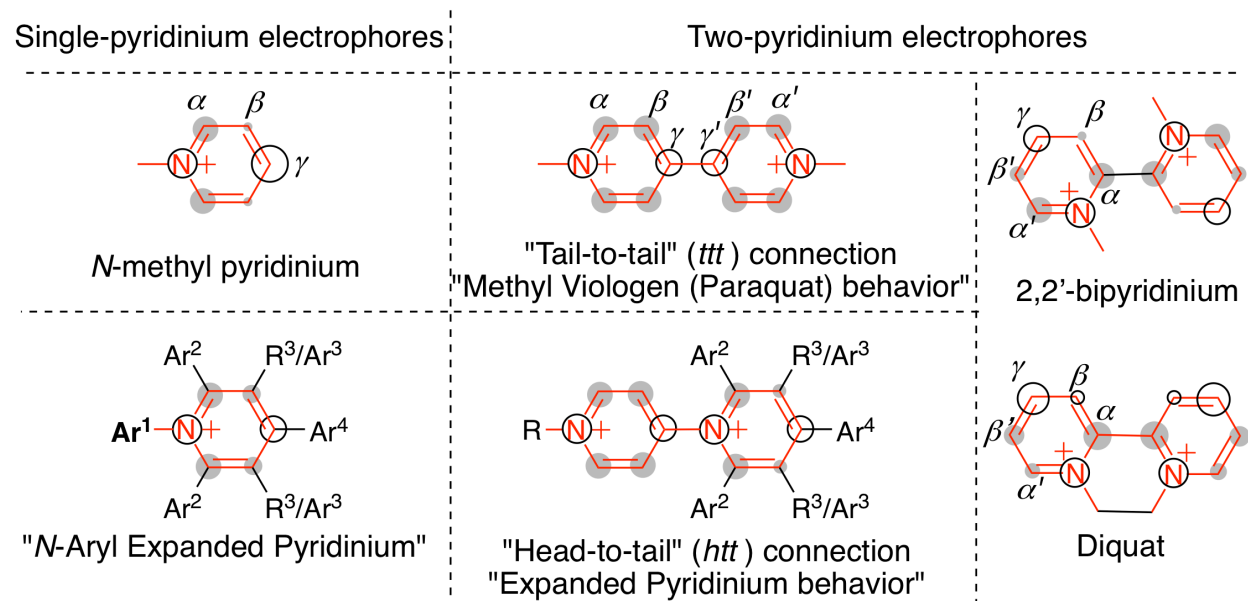
Schematic representation of weighted atomic contributions (open white and solid gray circles) to the LUMO of pyridinium rings in various chemical contexts (R = H or alkyl; Ar = aryl).

In addition to the great asset of promoting spin pairing, using the covalent (sigma) bond as electron reservoir precisely allows to locate the electron density in a dedicated part of the structronic assembly. From the standpoint of molecular design, one needs *to master features of the LUMO* meant to play the role of empty reservoir. The prerequisite for the LUMO engineering is therefore to manipulate the 3D structure of the assembly such that this dedicated (functional) LUMO results from an axial (sigma-type) overlap of preexisting directional atomic orbitals of proper energy and symmetry. These latter criteria naturally point to the use of pyridinium rings as structronic building blocks owing to appealing intrinsic features of their LUMO.

Rationale for the choice of pyridinium as pivotal building block.

Pyridinium kernel, as a redox-active dissymmetric platform, is a choice component – not to say: a tailor-made building block – for structronic purposes. Of utmost functional importance are the large atomic contributions of sites C(γ), firstly, and C(α), secondly, to pyridinium's LUMO (Figure 1). Pyridinium's multifaceted electrochemistry, beyond its chemical versatility, is illustrated by N-aryl Expanded Pyridiniums (Figure 1) whose separation of two single-electron

reduction potentials can either be *expanded, compressed, inverted* or of *Weitz type*.[3**] This tremendous versatility, which stems from sensitivity of pyridinium heterocycle to the steric hindrance of its substituents, shows that electrochemical regime (expansion/compression/ inversion of potentials) is best tuned by controlling the structure parameters rather than adjusting usual electronic effects.

Pyridinium is an archetypal redox-active platform, present at one and the same time in natural functional assemblies such as in $NADP^+$/NADPH cofactor and in abiotic species as in the famous methyl viologen (1,l'-dimethyl-4,4'-bipyridinium, see Figure 1) not only as a poison (herbicide Diquat, Figure 1) but also as an electrophore of reference, an electrochemical mediator or an electrochromic component. Besides, among its diverse uses, pyridinium is now a widely used radical precursor in synthetic chemistry for processes based on single-electron transfers [4,5].

As regards pyridinium species, the most popular strategy for enhancing their electrochemical properties relies on setting up oligomers and more especially dimers [6]. In such close-coupled covalent assemblies (see Figure 1), mutual electronic and electrostatic influences are at work. Thus, it is worth bearing in mind that pyridinium is, towards itself, the best auxo-electrochemical substituent. This is illustrated by comparing the value of the potential of the first one-electron reduction of *N*-methylpyridinium to that of its "tail-to-tail" (4,4')-dimer, namely *N*-methyl viologen (Figure 1), which shifts from −1.30 V [7,8] to approximately −0.44 V [9,10] vs. SCE in acetonitrile. The fine-tuning of electrochemical properties of the dimers [9,11] can be set up by adjusting the following parameters: i) the inter-annular torsional angle (*i.e.* the degree of π delocalization) [12−15], ii) the connection scheme of the pyridinium rings [9], iii) the nature of the $N_{pyridinio}$ substituent (alkyl or aryl) [6] and iv) the nature of the intervening spacer (if any) [10,16−19], which can be switchable [20,21].

One-electron electrochemistry of simple pyridinium salts is essentially that of dimer formation referred to as sigma dimerization (whether at α or γ positions) [22**,23**,24,25*]. When α/γ sites of N-aryl-functionalized pyridiniums are sterically blocked, as is the case of branched Expanded Pyridiniums (**EP**s) [26*], (Figure 1 and Figure 2), relatively stable radical species can be generated (as far as *expansion of potentials* and, to a lesser extent, *compression of potentials* are operative). When *potential inversion* is at work, *i.e.* when second one-electron reduction(oxidation) is energetically less demanding than the first one [27**], one no longer deals with one-electron but with two-electron processes, that are accompanied by the anion formation in the case of **EP**s or

sigma-bond formation in the case of Structronic Assemblies, **SA**s (see Figure 2 and representative cyclic voltammograms in Figure 3).

Engineering pyridinium-based electrophoric assemblies arguably provides the most prolific and multifaceted outcomes within the context of molecular design activity dedicated to electrochemistry. Beyond abundant literature devoted to viologens [6] and varied Weitz-type systems [11] there are various ways to combine pyridinium as electrophoric synthon and aryl components, which yield sharply different electrochemical behavior as discriminated based on topology-related mechanistic criteria.

The most popular approach is to place phenylene connectors as π-conjugation extensions between two pyridinium units transforming methyl viologen (Paraquat, Figure 1) to extended viologens **EV**s [16−18] (Figure 2), and *ortho*-isomer of Paraquat (colloquially referred to as Diquat, Figure 1) to helquats **HQ**s [19] (Figure 2). In the latter instance, *ortho-ortho* connection scheme combined with inner steric hindrance gives chirality (helical chromophore) as emerging property [28*]. For both **EV**s and **HQ**s, the electrochemical behavior is characteristically of the Weitz type [11] with charge/electronic *delocalization* (embodied in bond alternation pattern) and overall propensity to structure planarization.

Another approach consists of decorating a centrally-positioned pyridinium core with aryls that essentially play a steric role whether for blocking α (2,6) and γ (4) reactive sites upon reduction (2,4,6-triaryl decoration pattern) or for assisting hybridization change of $N_{pyridinio}$ atom upon reduction (1,2,6-triaryl decoration pattern) [29*], overall affording the characteristic 1,2,4,6-tetraaryl decoration of prototypical **EP**s. Redox-induced structural distortion (pyramidalization) is accompanied by *charge localization, i.e.* the anion formation at γ site upon two-electron reduction. Tuning the redox-triggered distortion via steric hindrance of peripheral aryls allows setting up the manner by which reduction occurs: from stepwise regimes (expansion or compression of the separation of standard redox potentials) to single-step two-electron reduction regime (inversion of standard redox potentials) as is demonstrated in Figure 3. [3**] The latter regime is in particular observed in the case of a pendant pyridylium serving as the $N_{pyridinio}$ substituent, thereby forming a "head-to-tail" bipyridinium, *i.e.* a positional isomer of methyl viologen (which is a "tail-to-tail" bipyridinium, see Figure 1). There, the pronounced distortion (pyramidalization) no longer results from a hybridization change of the $N_{pyridinio}$ atom but from a structural relaxation following a steric clash between bulky aryls at either side (2,6) and planarized quinoidal form of the reduced pendant

Figure 2
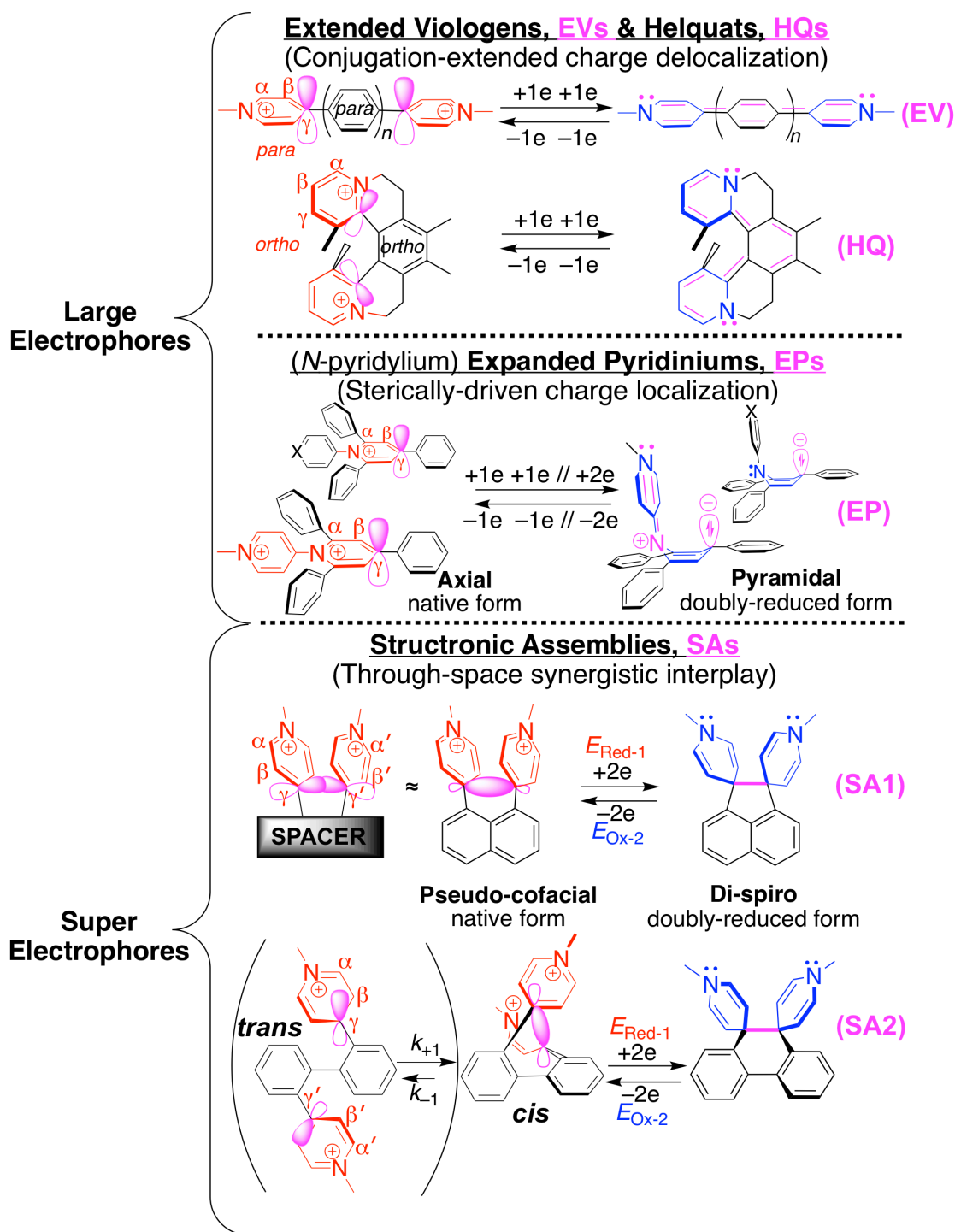
Electrochemical reactivity of various prototypes of electrophoric assemblies based on bis-pyridiniums: from large electrophores (**EV**s, **HQ**s, **EP**s) with through-bond-mediated interelectrophoric interplay to supramolecular multicomponent architectures with through-space-mediated interelectrophoric interplay (**SA**s).

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Figure 3

Sterically-driven electrochemical behavior

Structronic system: through-space synergy
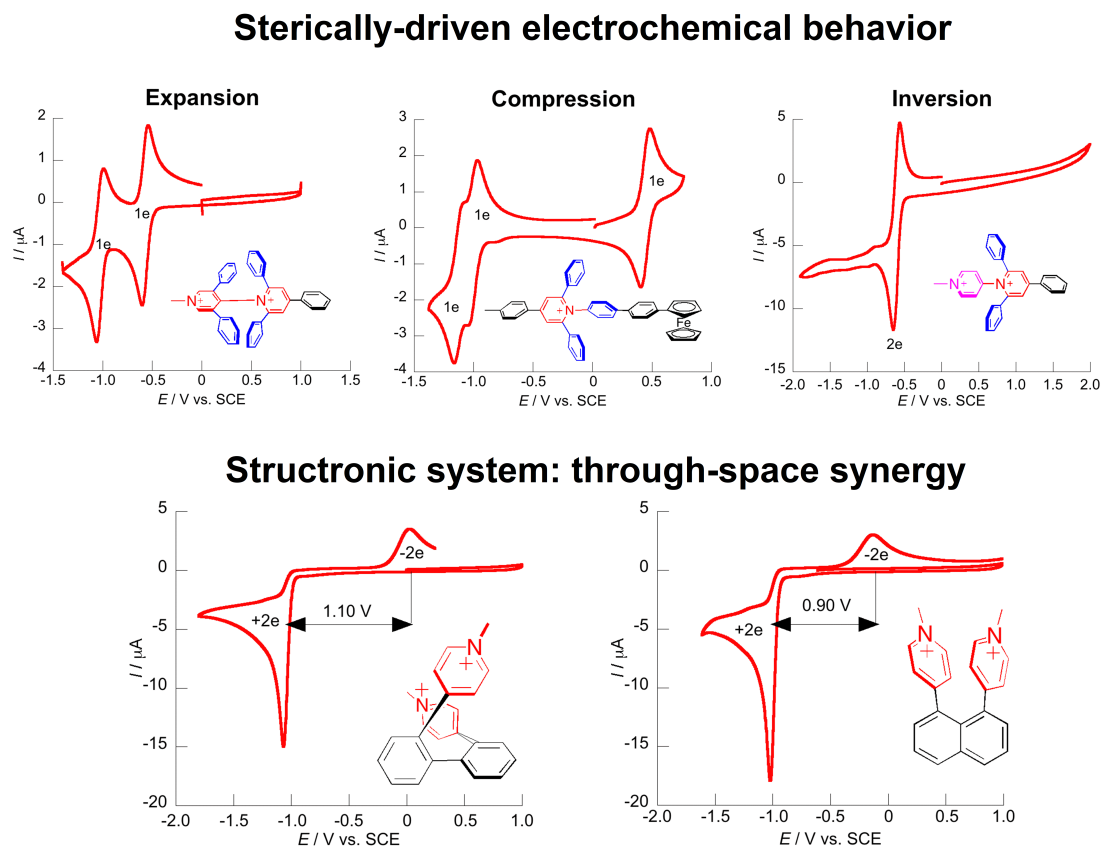
Representative cyclic voltammograms for various prototypes of large electrophores (**EP**s) showing potential expansion, compression and inversion (upper panel) and electrophoric assemblies with structronic properties (lower panel). Data were obtained on Pt electrode, supporting electrolyte was 0.1M tetrabutylammonium hexafluorophosphate in acetonitrile.

pyridylium extending with an exo-cyclic double-bond involving the $N_{pyridinio}$ atom (Figure 2) [3**]. In this special case of **EP** with a "head-to-tail" bipyridinium motif, there is a tradeoff between charge delocalization (appended pyridinium) and charge localization (core pyridinium) upon two-electron reduction.

A third strategy (referred to as *structronic approach*) stems from pre-organization of electrophoric pyridiniums so as to set up a close contact of two vicinal pyridinium rings at site $C(\gamma)$ such that the distance between $C(\gamma)$, $d(C\gamma–C\gamma)$, must be at most equal to the sum of van der Waals radii of C atoms, *i.e.* 3.40 Å. This can be achieved by using a relatively rigid spacer as is

the case of cross-conjugated 1,8-disubstituted naphthalene (**SA1** in Figure 2) [30**] or a semi-rigid one as is the case of biphenyl (**SA2** in Figure 2) [31*]. For characteristic voltammograms of **SA1** and **SA2** see Figure 3. From through-space overlap of $C(\gamma)$ $2p_z$ atomic orbitals that significantly contribute to respective LUMO of individual pyridiniums (Figure 1) a "supramolecular LUMO" (SupLUMO) emerges being the signature of the synergistic interplay of two pyridinium subunits. On injecting electrons into this bonding virtual MO, an elongated covalent bond forms (reservoir bond) along with a 5- or 6-membered ring comprised of two adjacent spiro $C(\gamma)$ atoms.

In the case of **EP**s, anion at $C(\gamma)$ site that results from two-electron reduction, is pointing towards the reaction medium, being barely stabilized by vicinal aryl group via slight electron delocalization over it. Under these "electronic protection" conditions, the couple of paired electrons is likely to react with an electrophile. In the case of structronic assemblies (**SA**s), this couple of paired electrons is buried into a sigma bond sterically protected by its direct surrounding and electronically protected by energy stabilization intrinsic to sigma-bond nature.

Actually, *what could appear as an "intramolecular dimerization" definitively originates in a basically different mechanism* insofar as the sigma bond formation does not proceed from usual onset, via the fortuitous formation of an encounter pair of pyridinyl radicals (singly-reduced pyridinium electrophores), as is the case for classical (intermolecular/bimolecular) dimerization. Indeed, an empty virtual bonding MO pre-exists on site and results from the programmed formation of a pseudo encounter pair made up of native, cationic electrophores. By design, this leads to the LUMO propagating through space between two $C(\gamma)$ intended to host electrons. This LUMO, referred to as SupLUMO, is exemplified in **SA**s of Figure 2. Thus, the electrons in such SupLUMO correlate during the actual bond formation by their spin pairing. Experimentally, this close interaction translates into an inversion of the standard redox potentials of respective one-electron reduction(oxidation) processes. In doing so, we are shifting from the situation where multi-electrophoric reductions are independent to the situation where one-electron reduction processes of multi-electrophoric components are interdependent owing to their synergistic interaction. This synergy results in the *potential inversion* and a one two-electron process, that is, it results in a sharply different situation from that resulting from LUMO delocalization over a large electrophore (like in methyl viologen or C_{60}). In the latter case, two or more one-electron processes with well separated standard redox potentials are observed.

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Since electrochemically non-innocent pyridiniums are held together by redox-neutral spacers and their synergistic interaction takes place through space, one may regard these multi-electrophoric assemblies as "supramolecular architectures" endowed with electrophoric activity, *i.e.* super-electrophores (Figure 2). An emerging property of such super-electrophores is the single-step two-electron reduction(oxidation) relying on the inversion of standard redox potentials concomitant to formation(cleavage) of an elongated covalent bond due to steric restraints. From a mechanistic standpoint, chemical processes (bond formation/cleavage) and electrochemical processes (heterogeneous electron transfers) are therefore closely coupled. We demonstrated that two distinct EEC pathways describe the redox mechanism of the formation and cleavage of the electron reservoir bond, which translates into an electrochemical behavior characterized by a hysteresis (see Figure 3). [30**] In other words, structronic assemblies (*i.e.* super-electrophores) are bistable systems.

Electron *accumulation* versus electron *storage* in pyridinium-based molecular organic systems: comments on selected representative case studies.

In this section, case studies of discrete pyridinium assemblies that are electronically loosely coupled such as dendrimeric electrophores, [32] electrophoric foldamers [33] and π-dimers based on oligoviologens [34,35] are not considered.

Introducing Super Electron Donors (SED): organic molecules using bonds as electron reservoirs.

Super Electron Donors (SED) are electron-rich, neutral organic molecules that can be used in synthetic organic chemistry as multi-electron reducing agents replacing usual metallic reagents, hence their colloquial name "organic sodium". [36,37] SED species are synthesized following purely chemical routes (*i.e.* no intervening electrochemical step) and are made up of two pro-aromatic fragments that are linked by a double bond. An example showing chemical transformation of molecule **1A** to SED is shown in Figure 4. When engaged in a redox reaction, the interannular reservoir bond of SED is partly cleaved upon releasing a couple of electrons. This irreversible two-electron donation is accompanied by intramolecular electron redistribution giving a doubly oxidized (dicationic) species (SED^{2+}) made up of two aromatic subunits linked by a single bond. It is noteworthy that the pyridinylidene moiety, as the pro-aromatic form of pyridinium moiety, was among the first to be used as components of these SED, along with sulfur-containing

1,3-dithiole and imidazole derivatives (giving aromatic dithiolium and imidazolium fragments upon oxidation). In the context of structronics, once two electrons are released, there is no way (including electrochemistry) to refill the SED^{2+} molecule to restore the SED form, hence the lack of cycling (charging/discharging) possibility. This limitation can be withdrawn by engineering the pyridinium-carbene hybrids (Figure 4) from pyridinium-based molecules **1B** as recently demonstrated by Hansmann *et al.* [38]. So-obtained three-state redox systems can indeed be reversibly charged and discharged (one-electron processes) on demand via the formation of a relatively stable radical state, thereby opening the way to novel anolyte materials for nonaqueous redox-flow batteries and to reusable SED reagents.

Figure 4
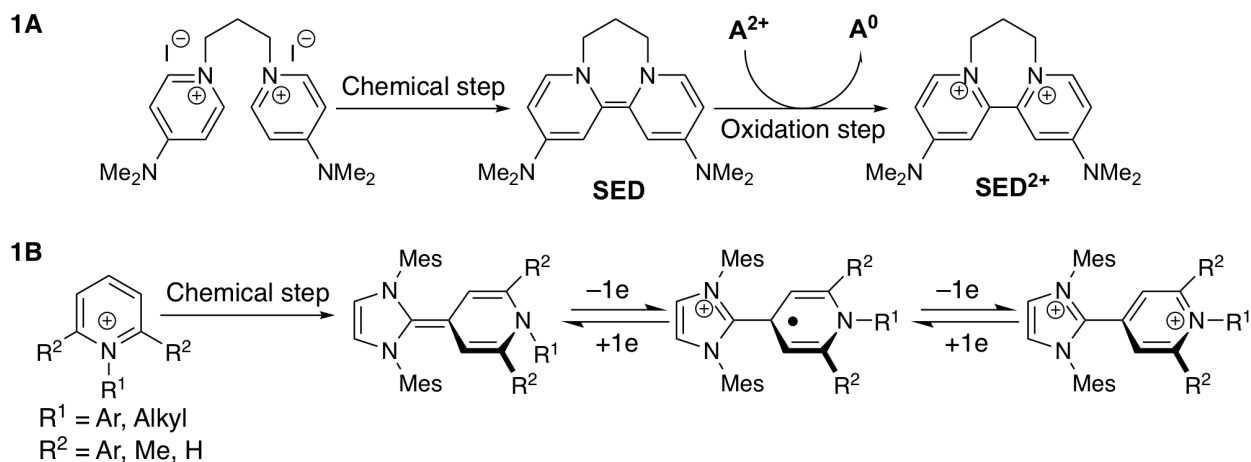
Super Electron Donors (SED) chemically prepared from **1A** and advanced pyridinium-carbene hybrids chemically prepared from **1B**.

Introducing so-called "Dynamic Redox" (Dyrex) Behavior (when electrochromism and fluorescence switching are coupled to reductive formation of elongated C-C bonds).

   Dynamic redox "Dyrex" electrochemical behavior, first quoted by Suzuki *et al.* [39], refers to the reversible electrochemical bond formation. An early example reported by his group concerns the formation of an elongated carbon-carbon (C-C) bond between two triarylmethylenium carbocationic chromophores incorporating a biphenyl motif as a linker, see **2A** in Figure 5. The formation of this bond (X = NMe2) occurs at a potential of −0.45 V (E_{Red1}) and undergoes a homolytic cleavage at +0.77 V (E_{Ox2}) vs SCE. The biphenyl scaffold used in this system gives rise

to a huge conformational change during the bond formation. Another example described by the same Japanese group concerns the reductive formation of an elongated C-C bond (length equal to 1.696(3) Å) between two acridiniums (*i.e.* dibenzoannulated pyridiniums) borne by a rigid scaffold, namely a naphthyl (see **2B** in Figure 4). In this case, an analogous hysteretic behavior was observed in which $E_{Red1} = -0.07$ V and $E_{Ox2} = +0.14$ V vs SCE. [40]

Figure 5
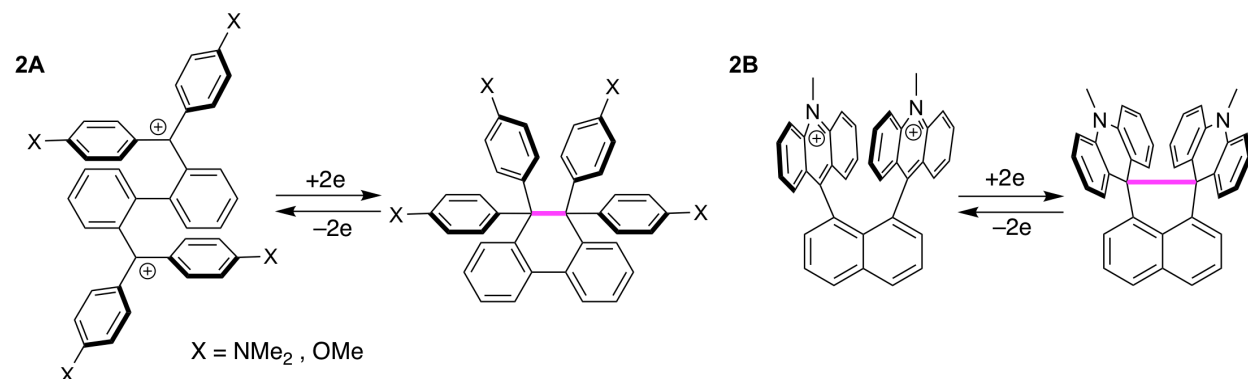
Reversible electrochemical bond formation in Dynamic Redox systems **2A** and **2B**.

Interestingly, these systems conceived for electrochromic purposes and for redox-triggered fluorescence switching [41] show an electrochemical hysteresis behavior that reveals their bistable nature. They are therefore potential candidates for structronic purposes provided certain improvements regarding electrophoric moieties (compare **SA1** and **SA2** in Figure 2), which are here essentially selected on the basis of chromophoric criteria (Dyrex context). The bond formation mechanism proposed by Suzuki relies on an intramolecular dimerization and may be reconsidered within the conceptual framework of structronics. To do so, the existence of SupLUMO must be established, which remains contingent on the compliance to certain energy, symmetry and structural criteria, including that the sum of van der Waals radii of cationic C atoms involved in the bond formation (3.40 Å) is not exceeded. If this is not the case for trityl derivative (**2A**) for which this sum amounts to 3.66(2) Å [39], the naphthyl derivative (**2B**) does fulfil this criterion since the distance between relevant C atoms amounts to 3.020(2) Å [40]. Whether the SupLUMO can extend beyond 3.40 Å is still under the investigation.

Multi-electron reduction within pyridinium-based closely-coupled multi-electrophoric assemblies: case studies.

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The archetype of the organic "electron carriers" is methyl viologen **MV**, which can be looked upon as a pyridinium dimer. Benniston *et al.* [42] used **MV** functionalized with a disulfide bridge **3A** to accumulate up to four electrons, see Figure 6. In this case study, the first two electrons are added stepwise to the molecule on the viologen subunit and they are then internally transferred to the ancillary disulfide bond, leading to its cleavage. **MV** somehow plays the role of an "electron antenna" system. Thereby restored, the native **MV** subunit, bearing the cleaved disulfide bond, is then capable of accepting two more electrons (stepwise reduction). [43]

Figure 6
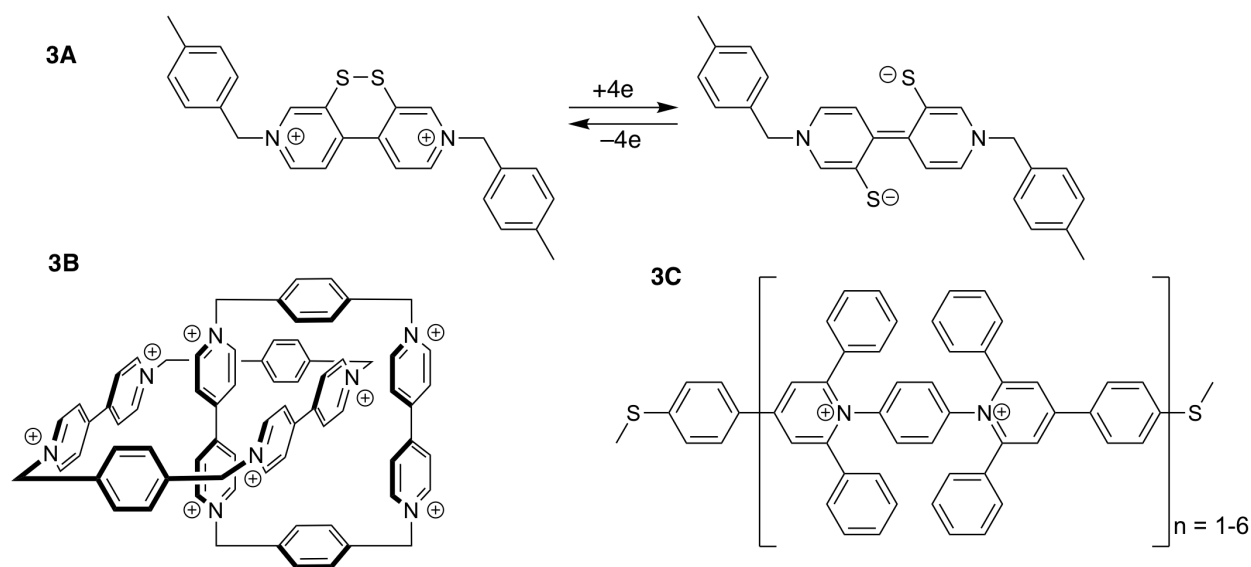
Examples of pyridinium-based closely-coupled assemblies accumulating multiple electrons.

Using **MV**, Stoddart and his group [44,45] were able to synthesize a homocatenane (**HC**) based on two interlocked cyclophanes, each incorporating two electrophoric subunits, see **3B** in Figure 6. This molecule can accept in principle up to eight electrons. However, it was demonstrated that **3B** can undergo five reversible redox processes and has six redox states (from 8^+ to 0 charge state) that are accessible electrochemically. **HC** was isolated under ambient conditions as a mixture of 6^+ diradical (the electrons are spin-paired and form a singlet state) and a 7^+ stable paramagnetic monoradical. The stability of the diradical is a consequence of the topology of the molecule. Overall, the molecule can load up to six electrons from its stable state.

Based on a strategy involving the repetition of pyridinium electrophoric units, Hromadová *et al.* [46] have investigated the capability of "extended viologen" oligomers to capture reversibly

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electrons, see **3C** in Figure 6. Several rod-like oligomers (n = 1 to 6) were studied where the smallest unit (containing two pyridiniums linked via their 1-positions) can accept in total four electrons (two per each pyridinium), whereas the biggest unit (including twelve pyridiniums) can carry up to 10 electrons. In the latter case, two electrons are accepted per each extended viologen subunit linked by the 4-positions according to a stepwise addition.

These three types of multi-electrophoric assemblies show reversible electrochemistry, *i.e.* no hysteretic behavior, implying that they are eligible for electron accumulation, serving as multielectron mediators/relays or doped wires (depending on the topology), but not suited for storage of electrons that, strictly speaking, relies on bistable systems.

Conclusions

At the core of the structronic approach is the desire to confine more than one electron in a predefined inner space of a molecule whilst circumventing the adverse effects of Coulombic repulsion with a view to manage the electron storage. The whole idea is to take advantage of quantum mechanical properties of covalent bonds to build an *electron reservoir*. This approach relies on the engineering of a dedicated LUMO, referred to as a SupLUMO, that can be electrochemically filled up (charging) to build a bond as a storage state. This covalent reservoir bond has to be properly weakened (elongated) by an on-site steric strain so as to be cleavable on demand for electron releasing (discharging). This review shows that dipyridylium assemblies preorganized with scaffolds of naphthyl and biphenyl type enable conceiving such bistable structronic devices.

Acknowledgements

Declaration of competing interest

The authors declare no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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