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Organic Redox-Systems Based on Pyridinium-Carbene Hybrids

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ABSTRACT: New redox systems with three oxidation states are highly sought-after, e.g. for redox-flow battery applications, selective reducing agents or organic electronics. Herein, we describe a straightforward and modular synthesis of a new class of such a three-state redox system based on the intermolecular reaction of a large variety of pyridinium salts with carbenes. Those hybrids represent organic (super) electron donors with tailored electro-chemical properties and feature three stable oxidation states, which could be fully characterized including X-ray diffraction. We elaborate which electronic factors govern to obtain either stable radicals through one electron transfer or instead favor 2e⁻ processes. Indeed, based on X-ray data a verification for a potential compression mechanism is given which originates through a large structural distortion in the first oxidation event. By geometrically locking this hybridization change a potential expansion can be realized. The new class of stable organic radicals are highly persistent and even moderately stable towards air. Additionally, we demonstrate that our modular synthesis approach is also applicable to remarkably strong multi-electron (4e⁻) donors by utilizing bridged pyridinium salts. Based on the stability and reversibility of the new redox system, we could demonstrate by charge-discharge experiments the use of the hybrid molecules as novel anolyte materials for nonaqueous redox-flow batteries.

INTRODUCTION

Organic redox systems provide a basis for the understanding of electron transfer processes and offer a variety of applications ranging from organic electronics, data storage, photovoltaics to batteries.¹ Tetrathiafulvalene $(\mathbf{A})^2$ and viologens such as paraquat (B)³ represent two well-studied examples of organic "Weitz type"⁴ redox systems existing in three stable oxidation states (Figure 1). Tetraaza-substituted olefins also belong to this class but predominantly received attention as organic reductants as a result of their electron rich ground state.5 Tetrakis(dimethylamino)ethylene (TDAE, C), cyclic tethered variants (D) or bispyridinylidenes $(\mathbf{E})^6$ have been utilized in organic synthesis as one electron or super-electron donors respectively.7 While previous work on super-electron donors as pioneered by Murphy et al. focused on the strength of the reducing power, little is known about the structural changes involved in the oxidation process or the stability of the radicals involved. Indeed, in most cases the electron rich compounds are prepared and reacted in situ and no data of either the neutral or radical oxidation state is given. Importantly, in two electron oxidation/reduction processes the question arises if the two electron transfer occurs stepwise (normally ordered) or "concerted" as a result of potential compression/inversion.8 Importantly, Lainé et al. proposed based on DFT modeling a potential compression mechanism for the single step two electron reduction process of pyridinium salts such as **F**.⁹ A key point of his theory for the potential compression in such branch expanded pyridinium systems is a large structural rearrangement process involving different electromers.9 Furthermore, stable organic radicals are particularly interesting as a result of their applications such as organic magnetic materials, spin-memory devices,¹⁰ or components in redox-flow batteries.¹¹ During the last years organic redox-flow batteries have emerged as a highly attractive option for energy storage, however a key challenge remains in identifying novel highly stable anolytes.^{11b} In this context the groups of Minteer, Sigman and Sanford could

design, based on the structure of the stable pyridinyl radical G,¹² pyridinium salt H as an efficient electrolyte in the one electron cycling (H/H') for redox-flow batteries.¹³ Besides, pyridinyl radicals are also of recent interest as transient highly reactive intermediates in photo catalysis.¹⁴ Currently, a major trend developed in the stabilization of transition metal or main group open shell species by carbene entities.¹⁵ Here, we will establish a simple synthetic route to a new class of organic redox system which will combine the concepts of pyridinyl radicals and carbene stabilization, analyze the electron transfer mechanism, generate multi-electron donors and finally apply the redox system in charge-discharge cycling experiments for redox-flow batteries.



Figure 1. Selection of electron rich olefins (A-E) with their corresponding redox potentials (vs. SCE), pyridinium salt F as well as stable radicals G and H'.

RESULTS AND DISCUSSION

Utilizing our recently discovered intermolecular carbene addition/elimination mechanism,¹⁶ we reacted two equivalents of 4,5-dimethyl substituted imidazolin-2-ylidene **a** with 2,6-disubstituted pyridinium salt 1^{II} (Scheme 1). Addition in 4-position of the pyridinium core affords intermediate **2** which leads upon deprotonation with a second equivalent of carbene to the neutral "carbene-pyridinium" hybrid $3a^{II}$ as an orange solid in

55% yield. This synthetic approach is not limited to classical *N*-heterocyclic carbenes such as IMes (**b**) or saturated IMes (**c**) but can also be performed with a series of stable carbenes such as cyclic (alkyl) amino carbene (CAAC)¹⁷ (**d**) and diamido carbene (DAC)¹⁸ (**e**) to afford hybrid molecules **3d** and **3e** respectively. In order to vary the electronics on the pyridinium core, a small library of electron donating (**1**^I) to withdrawing (**1**^{IV}) substituted pyridinium salts were reacted with IMes carbene (**b**) to give **3b**^I – **3b**^{IV}.

Scheme 1. Synthetic approach towards 2,6-diphenyl-*N*-aryl-pyridinium-carbene hybrids.



In contrast to donor-acceptor substituted 1,4-dihydropyridines, which have been exploited as fluorescent materials or biological relevant scaffolds,¹⁹ compounds **3** feature an unusual donor-donor substitution. This is reflected in the stability of $3a^{II}$ - $3d^{II}$, which are prone towards oxidation and must be handled under inert atmosphere, whereas $3e^{II}$ is stable towards air. Strikingly, in the solid-state structure of $3b^{II}$ and $3d^{II}$ (see SI) the *N*-aryl moiety is strongly pyramidalized out of the 1,4-dihydropyridine plane (distance *N*-plane: 0.27 Å), avoiding overlap of the *N*-lone pair with the electron rich plane (Figure 3 left).



Figure 2. Selected X-ray solid-state structures of **3b^{II}** (A) and **3e^{II}** (B) with their corresponding views from the side (C/D). Hydrogen atoms and solvent molecules omitted for clarity. Ellipsoids shown with 50% probability. Selected bond parameters in [Å] and [°]: **3b^{II}**: N1–C1 1.383(2); N2–C1 1.377(3); C1–C2 1.408(3); C2–C3 1.441(3); C3–C4 1.352(3); C4–N3 1.447(3); N3–C5 1.418(3); N1–C1–C2–C3 –151.5; **3e^{II}**: N1–C1 1.432(1); N2–C1 1.433(1); C1–C2 1.375(1); C2–C3 1.456(1); C3–C4 1.353(1); C4–N3 1.411(1); N3–C5 1.454(1); N1–C1–C2–C3 162.5.



Figure 3. Degree of structural distortion of the neutral hybrids based on the substitution.

In case of the more π -accepting DAC moiety (**3e**^{II}) the *N*-aryl moiety is nearly in plane (0.08 Å) indicating π -delocalization, while the aryl moiety is rotated perpendicular (Figure 2 and 3; for a summary of structural parameters see Figure S1). Note, an imidazole⁺-CH₂⁻ bond polarization such as seen in *N*-heterocyclic olefins,²⁰ also favors a *N*-distortion/pyramidalization process in order to avoid an anti-aromatic 8 π -electron system (**3**^{*}; Scheme 2). The *N*-pyramidalization is also detected in solution by ¹⁵N-NMR of the *N*-dihydropyridine core, following the trend δ [ppm] = -291 (**3b**^{II}), -287 (**3c**^{II}), -280 (**3d**^{II}) to -258 (**3e**^{II}).

Cyclic voltammetry measurements of **3** show two quasireversible redox events for the stepwise oxidation to radical cation **4** as well as dication **5** (Scheme 2) ranging from E = -1.18 V to – 0.14 V vs. Fc/Fc⁺ (Figure 4). The position of the redox couple can be tailored by changing the π -accepting properties of the carbene moiety, while the variation in the *N*-aryl pyridinium-moiety relates to the separation of the two redox potentials. Upon reducing the electron density in the *N*-aryl moiety [R = *p*-NMe₂ (**3b**^I), *p*-'Bu (**3b**^{II}), *p*-CF₃ (**3b**^{III}) to *m*,*m*-CF₃ (**3b**^{IV})] the two redox-events merge towards a one-step two electron reduction as observed for electron deficient **F** (Figure 1).

Scheme 2. Redox-states of pyridinium-carbene hybrids.



Figure 4. Cyclic voltammograms of $3a^{II}-3e^{II}$. [*n*Bu₄NPF₆ (0.1 M), Pt/glassy carbon 200 mV s⁻¹, versus Fc/Fc⁺, in thf]. Redox potentials E_1^{0}/E_2^{0} in [V]: $3a^{II}$: -1.13/-0.88; $3b^{II}$: -1.18/-0.85; $3b^{II}$: -1.10/-0.83; $3b^{III}$: -0.93/-0.79; $3b^{IV}$: -0.85/-0.74; $3c^{II}$: -0.94/-0.66; $3d^{II}$: -0.77/- 0.38; $3e^{II}$: -0.41/-0.14.

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Stoichiometric chemical oxidation of 3a-3e with one equivalent of AgSbF₆ affords the corresponding stable radical cations 4a-4e, which could be fully characterized including X-ray diffraction (Figure 5; for 4b^{III} see SI). Note, the new radicals are remarkably persistent even in air. Time dependent UV-vis spectroscopy for **4b^{II}** shows a decomposition half-life of $t_{1/2} \sim 5-$ 6 h in air at 35°C (Figure S93), while under inert atmosphere the radical remains highly persistent. Interestingly, in the solid-state structure of the monomeric radical cation the N-aryl fragment is positioned in the heterocyclic plane, while the former carbene moiety is slightly twisted (22°) (Figure 5). Note, based on the structural data obtained a significant redox-induced structural distortion with a large inner reorganization energy in the first oxidation step can be detected, while this is not the case for the second oxidation (vide infra). Electron withdrawing substituents on the N-aryl pyridinium moiety stabilize the strongly distorted "spring-loaded" geometry (Figure 3 left) thereby increasing the inner reorganization energy for the first electron transfer step. This finding is in line with a transient shift from normal ordered redox potentials towards potential compression (3b^{III}/3b^{IV}). For the first time experimental X-ray structural data for this so far only theoretically proposed9 potential compression mechanism for pyridinium systems is given.



Figure 5. X-ray solid-state structure for radical cation $4c^{II}$. Hydrogen atoms omitted for clarity. Ellipsoids shown with 50% probability. Selected bond parameters in [Å] and [°]: N1–C1 1.354(3); N2–C1 1.345(3); C1–C2 1.431(3); C2–C3 1.416(3); C3–C4 1.363(3); C4–N3 1.403(3); N3–C5 1.440(2); N1–C1–C2–C3 158.2.

According to its mesomeric structures, the radical could either be localized on the carbene or pyridinyl moiety (4/4'; Scheme 2). X-band EPR studies (Figure 6) indicate delocalization of the spindensity with large *N*-hyperfine coupling constants to all *N*-atoms [4b^{II}: 2xN (carbene): 6.7 MHz; 1xN (pyridinyl): 14.7 MHz; for all EPR spectra see SI], in line with theoretical calculated values (Figure 7 and Figures S99-S102).



Figure 6. Selected X-band EPR spectra with their simulated EPR parameters [in MHz] for A: **4a^{II}**: 2xN: 6.8, 1xN 15.1, 6xH: 3.3, 2xH: 1.3; B: **4b^{II}**: 2xN: 6.7, 1xN: 14.7, 2xH: 2.5, 2xH: 0.6; C: **4c^{II}**: 2xN: 5.5, 1xN: 15.5, 4xH: 7.2, 2xH: 3.2 and D: **4d^{II}** 1xN: 14.1, 1xN: 13.3, 1xH: 5.1, 1xH: 5.2.

Indeed, calculated spin-densities indicate a significant carbene dependency (Figure 7): While $4b^{II}$ is best represented by mesomeric structure 4 featuring mostly pyridinyl radical character

(69% spin density), **4e^{II}** containing the significant more π accepting DAC is best described as **4'** exhibiting 55% spindensity on the carbene moiety. Oxidation of **3** with two equivalents of AgSbF₆ affords the corresponding colorless dications **5a** – **5e** in good yields (54-75%), which can be fully characterized as stable compounds. The formation is detectable by ¹H NMR in which the former 1,4-dihydro-pyridine moiety [δ (¹H) \sim 5 – 6.5 ppm] is shifted into the pyridinium range [δ (¹H) \sim 8 ppm]. The step wise oxidation process starting from the neutral compounds can also be monitored by UV-vis spectroelectro chemistry (UV-vis SEC; Figure 8) and matches with the UV-vis spectra of the isolated compounds (see SI).



Figure 7. SOMOs (B3LYP/def2-TZVP), Mulliken spin-densities and EPR-hfcs [MHz] calculated at the M06-2X/cc-pVDZ//B3LYP-D3/def2-SVP level of theory for $4b^{II}$ (A), $4c^{II}$ (C), $4d^{II}$ (C) and $4e^{II}$ (E).



Figure 8. Spectroelectrochemistry of 3b^{II} and 3e^{II} in CH₂Cl₂.

Typically the neutral species **3** absorb at $\lambda \sim 400 - 500$ nm, while the radical cations **4** are bathochromically shifted and split into two absorptions, whereas the dications **5** exclusively absorb in the UV region. Interestingly, radical cation **4e**^{II} is intensively blue colored showing a strong broad absorption at $\lambda = 623$ nm (Figure 8) presumably due to charge transfer from the pyridinyl to DAC moiety.

After analysis of the triarylpyridinium hybrid series we investigated the pyridinium scope of our synthetic approach. Interestingly, N-methyl lutidinium $\mathbf{1}^{V}$ reacts cleanly with two equivalents IMes carbene b to afford 3bV in 56% yield (Scheme 3). Importantly, no deprotonation of the alkyl moieties occurs. Intermediate $2b^{V}$ could be isolated upon using only one equivalent of carbene and transformed stepwise into $3b^{V}$ by addition of one equivalent of KHMDS. The connectivity could be clearly established by X-ray diffraction (Figure 9A), which revealed a bending of the alkyl moiety out of plane (sum of angles at N: 347°). CV measurements indicate two quasi-reversible oxidations at a negative potential ($E_1 = -1.63$ V and $E_2 = -1.10$ V vs. Fc/Fc⁺; Figures S35-S36) in a typical range for super electron donors and significantly more negatively shifted compared to the triaryl-series $3a^{II} - 3e^{II}$. Chemical oxidation with one or two equivalents $AgSbF_6$ leads to the stable radical cation $4b^V$ (EPR see Figure 9B) and dication $5b^{V}$, the latter also verified by X-ray diffraction (see SI).

Scheme 3. Synthesis of trialkyl-hybrid $3b^{V}$ with its corresponding redox-states.



Figure 9. X-ray solid-state structure of $3b^{V}$ (A) and X-band EPR spectrum of radical-cation $4b^{V}$ with its simulation (B). Hydrogen atoms omitted for clarity. Selected bond parameters for $3b^{V}$ in [Å] and [°]: N1–C1 1.401(4); N2–C1 1.409(4); C1–C2 1.375(4); C2–C3 1.463(4); C3–C4 1.347(4); C4–N3 1.426(4); N3–C5 1.470(4). Simulated EPR parameter [in MHz]: 2xN: 9.3, 1xN: 14.3, 2xH: 3.1, 6xH: 7.5, 3xH: 13.4, 2xH: 1.2.

Remarkably, while classical nucleophiles show low regioselectivity for nucleophilic attack in 2- or 4-position of the pyridinium core,²¹ two equivalents carbene **b** react cleanly with structurally simple *N*-alkyl pyridinium salts such as *N*-methyl pyridinium (**1**^{VI}) to afford exclusively the 4-addition product **3b**^{VI} in 66% yield (Scheme 4; X-ray see Figure 10A). Intrigued by the relationship between redox potential and structural distortion we investigated if strong reductants can be obtained by geometrically constraining the *N*-aryl fragment. Therefore 2,4,6-triisopropylaryl (Trip) substituted pyridinium salt **1**^{VII} was selected and reacted with carbene **a** to afford **3a**^{VII} (Scheme 4). Besides the desired product we could also detect the dimerization product **6** of the

reduced pyridinium starting material (for an X-ray structure of **6** see Figure S14), presumably arising through reduction by formed **3a^{VII}**. This is quite remarkable as the reduction potential of **1^{VII}** is high $[E \sim -1.56 \text{ V} (vs. \text{ Fc/Fc}^+, \text{see SI})]$ outside of the triaryl hybrid series **3b^I** – **3b^{IV}** (see above). Indeed, X-ray crystallography supports the geometrical fixation of the *N*–aryl plane being orthogonal to the *N*–1,4-dihydropyridine plane thereby inhibiting a hybridization change at nitrogen (Figure 10 C and D; for the X-ray of **3b^{VII}** see SI). In agreement, the first redox potential: $E_1 = -1.58 \text{ V} (E_2 = -0.86 \text{ V}; vs. \text{ Fc/Fc}^+)$ is significantly more negatively shifted compared to the triaryl series **3b^I** – **3b^{IV}** (Figure 11). The large separation of the redox events of $\Delta E = 720 \text{ mV}$ agrees with a normally ordered step wise electron transfer and can be classified, as introduced by Lainé *et al.*,^{9b} as potential expansion through a geometrically locked distortion.

Scheme 4. Reaction pathways of *N*-alkyl/*N*-aryl pyridinium-salts with carbenes.



Figure 10. X-ray solid-state structures of **3b^{VI}** (A), monomeric radical cation **4b^{VI}** (B) and neutral **3a^{VII}** viewed from the top (C) and from the side (D). Hydrogen atoms and solvent molecules omitted for clarity. Ellipsoids shown with 50 % probability. Selected bond parameters in [Å] and [°]: **3b^{VI}**: N1–C1 1.412(1), N2–C1 1.409(1), C1–C2 1.372(1), C2–C3 1.463(1), C3–C4 1.343(1), C4–N3 1.396(1), N3–C5 1.449(1), N1–C1–C2–C3 171.4; **4b^{VI}**: N1–C1 1.372(2), N2–C1 1.374(2), C1–C2 1.424(2), C2–C3 1.435(2), C3–C4 1.358(2), C4–N3 1.371(2), N3–C5 1.461(2), N1–C1–C2–C3 157.2; **3a^{VII}**: N1–C1 1.418(4); N2–C1 1.413(4); C1–C2 1.371(4); C2–C3 1.476(4); C3–C4 1.340(4); C4–N3 1.391(4); N3–C5 1.432(3); N1–C1–C2–C3 176.8; C3–C4–N3–C5 177.8.



Figure 11. Potential expansion through geometrical fixation.

Interestingly, we noticed a different reaction outcome when a simple sterically less demanding *N*-aryl pyridinium salt such as **1**^{VIII} was reacted with carbene **b**. Performing the reaction at – 78 °C gave rise to the so far not detected, highly distorted 2-addition product **7b**^{VIII}, which could be structurally verified by X-ray diffraction (Scheme 5*i*). In contrast performing the reaction at room temperature leads to a 1:1.3 mixture of 4- and 2-addition products **3b**^{VIII} and **7b**^{VIII}, which can both be separated by crystallization. Calculations at the B3LYP/cc-pVDZ level of theory indicate **3b**^{VIII} to be the thermodynamic and **7b**^{VIII} the kinetic product ($\Delta G = -11.0$ kcal/mol; see SI). In case the 4-position is substituted such as in **1**^{IX} the exclusive formation of the 2-adduct (**7b**^{IX}) can be forced (Scheme 5*i*).²²

Scheme 5. Formation of 2-addition products with *N*-aryl pyridinium-salts and the corresponding X-ray solid-state structure.



All hybrid molecules, except 2-addition product 7bVIII, feature two reversible single electron oxidation steps (for a summary see Figure S17). The radical cation of 7bVIII presumably dimerizes in 4-position, which can be efficiently inhibited by blocking this position. Indeed, the CV of 7bIX featuring a 4-tert-butyl group shows two reversible redox waves at $E_1 = -1.46$ V and $E_2 =$ -1.09 V (see SI). Importantly, even the sterically least hindered *N*-methyl pyridinium hybrid $3b^{VI}$ forms upon oxidation a monomeric pyridinyl radical (4b^{VI}) clearly shown by its X-ray solid-state structure (Figure 10B). Note, we do not observe the formation of radical-cation π -complexes as typically observed for bipyridines,²³ or proposed for pyridinyl radicals,¹² presumably due to the steric shielding given by the carbene moiety. Even though the radicals derived from 2,6-non (H) substituted pyridinium salts are significantly more reactive towards air [for example: 4b^{XII} (vide infra): $t_{1/2} \sim 20$ min at 25 °C, see Figure S95] they are stable under inert atmosphere ($t_{1/2} > 15$ h at 50 °C for **4b**^{XII}, Figure S94). Note, while recently developed photocatalytic cycles rely on the N-C bond cleavage in pyridinyl radicals,¹⁴ we could not detect such a potential decomposition pathway presumably due to the stabilization given by the imidazolium ("carbene") moiety.

In order to demonstrate the power of the here described synthetic approach we investigated the synthesis of multi-electron donors by utilizing alkyl bridged bispyridinium salts (Scheme 6). Indeed the reactions of carbene **b** with bispyridinium salts 1^{x} or $1^{x_{I}}$, featuring a *n*-propyl spacer element, cleanly afford the neutral hybrids $3b^{x}$ and $3b^{x_{I}}$ in 56% and 61% yield respectively (for an X-ray structure of $3b^{x}$ see Figure 12A). CV measurements indicate two quasi-reversible two electron oxidations at $E_{1} = 1.56 \text{ V} (3b^{x})/-1.53 \text{ V} (3b^{x_{I}})$ and $E_{2} = -1.01 \text{ V} (3b^{x})/-0.91 \text{ V}$ $(3b^{x_{I}})$. In agreement, chemical oxidation with two equivalents AgSbF₆ affords the stable dicationic diradicals $4b^{x}$ and $4b^{x_{I}}$ in ACS Paragon

58% and 72% yield, respectively. Note, organic diradicals stabilized by carbene entities have recently attracted large interest as a result of their attractive magnetic and photochemical properties.²⁴ Interestingly, while there has been a debate about the dimerization of bridged pyridinyl radicals,²⁵ the X-ray solid-state structure of 4b^{XI} clearly demonstrates the two pyridinyl radical moieties pointing away from each other with a N(3)-N(4) through space distance of d ~ 5.0 Å (Figure 12B). In order to investigate the degree of radical-radical interaction X-band EPR as well as UV-vis studies were performed. EPR studies with solid 4bXI did not show a half-field signal down to 240 K, while in solution the EPR signal displayed only a broad single wave which could not be further resolved to a triplet spectrum (Figure S75). We also prepared the monomeric reference system 3bXII, which displayed a well resolved EPR spectrum (Scheme 6, see also Figure S73). UV-vis SEC of 3bXII and 3bXI indicate nearly identical absorption properties (Figures S91 and S92) in agreement with the UV-vis spectrum of isolated radical cation 4bXII and diradical 4bXI (Figure S98). Also T-dependent UV-vis spectroscopy down to -90 °C showed little change in absorption in agreement with a monomeric species as observed with X-ray diffraction (Figures S96 and S97). Those results indicate only a weak coupling between the two pyridinyl radical sites and clearly no dimerization. It should be highlighted that currently strong multielectron donors have found significant interest. For example, Himmel et al. reported the strongest neutral organic four electron donor featuring redox events at $E_{1/2} = -0.96$ V and $E_{1/2} = -0.43$ V (vs. Fc/Fc⁺).²⁶ Even though our system is clearly not as strongly coupled as the reported hexakis(guanidine) redox system and could be viewed in the extreme case as two individual hybrid molecules, both 3b^X and 3b^{XI} demonstrate significantly stronger 4e⁻ donor properties as the current record value.

Scheme 6. Synthesis of multi-electron hybrid donors.



Figure 12. X-ray solid-state structures of $3b^x$ (A) and diradical $4b^{x1}$ (B). Hydrogen atoms and solvent molecules omitted for clarity. Ellipsoids shown with 50% probability. Selected bond parameters in [Å] and [°]: $4b^{x1}$: N1–C1 1.365(4); N2–C1 1.367(4); C1–C2 1.423(4); C2–C3 1.433(4); C3–C4 1.358(4); C4–N3 1.370(4); N4–C5 1.374(4); C5–C6 1.358(4); C6–C7 1.428(4); C7–C8 1.426(4); C8–N6 1.369(4); N1–C2–C2–C3 155.4; C6–C7–C8–N6 152 1



Finally, in order to explore applications of our new redox systems we investigated the use of these hybrids as analyte for redox-flow batteries. Organic redox-flow batteries have recently emerged as highly attractive options for energy storage and thus there is a large interest in identifying novel high density anolytes operating at relatively low potentials.^{11b,27} As a proof of principle we subjected 3b^{VI}, featuring the lowest molecular weight below the molecules investigated, to 1e- charge-discharge cycling. A symmetric static H-cell with 5 mM solutions of isolated neutral 4b^{VI} 3b^{VI} and cationic was loaded [DMF; 0.5 M tetrabutylammonium hexafluorophosphate $(TBAPF_6)$] and galvanostatic charging (5 mA) with reticulated vitreous carbon electrodes was performed (see SI). This setup adapted from Sanford et al. allows to evaluate the anolyte's electrochemical cycling stability without applying the full redox flow cell.13 Remarkably, the redox system 3b^{VI}/4b^{VI} is stable over 100 charge-discharge cycles (cut off potentials at E = -1.2 V and -1.9V vs. Ag/AgNO₃) with perfect Coulombic efficiency and only ca. 5% capacity loss (Figure 13, see also Figure S61). Note, literature known reference 8/8' (Scheme 7) featuring the identical 1,4dihydro-pyridine core was reported to show $\sim 20\%$ capacity fade after 75 charge-discharge cycles,13b indicating a significantly higher stability given by the carbene entity.

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Scheme 7. Comparison of redox cycling of **3b^{VI}/4b^{VI}** with literature known **8/8**'.

Radical-cation

Neutral



Figure 13. One electron cycling of $3b^{VI}/4b^{VI}$ (top) with the corresponding capacity curve (middle) and two electron cycling (bottom).

Importantly, it has been reported that the anionic redox state (8"; Scheme 7) is reactive and not stable.^{13d} Thus this molecule is not suitable for charge-discharge experiments, limiting the ACS Paragon

cyclization to the neutral/cationic (8'/8) oxidation states, thereby restraining the redox potential to $E \sim -1$ V. While computational evolution resulted in H (Figure 1) with remarkably high cycling stability and a record potential of $E \sim -1.2$ V (vs. Fc/Fc⁺), ^{13b} the here presented hybrid class allows to cycle at a much lower redox potential $E \sim -1.6$ V as a result of the stable electron rich neutral redox state. In preliminary work we also investigated the 2ecycling^{13c} $(3b^{VI} \leftrightarrow 4b^{VI} \leftrightarrow 5b^{VI})$ by placing equal amounts of radical cation 4b^{VI} as isolated BF₄ salt into both sides of the symmetrical H-cell and applying cut-off potentials at 0 and -1.9 V with 5 mA galvanostatic charging. Interestingly, several chargedischarge cycles can be performed, showing two plateaus at $E \sim -$ 1.6 V and -1.0 V in cell voltage curves (Figure 13, bottom) in agreement with the CV data. However, a relatively strong capacity decay was detectable ($\sim 40\%$ over 25 cycles; see Figures S63 and S64) indicating the instability of the dicationic oxidation state under the specific cycling conditions. While multi-electron cycling remains rare for nonaqueous anolytes,^{13c} it seems very likely that an evolutionary design strategy should lead to robust 2e⁻ cycling. Based on the outlined hybrid approach we are currently investigating smaller carbene entities to access higher energy densities for practical applications.

In summary, we report a rapid, simple and modular synthetic approach to a new class of hybrid molecules which feature a fully reversible redox system with three stable oxidation states. While the approach is compatible with a variety of stable carbenes it is also applicable to a broad range of alkyl and aryl pyridinium salts. Importantly, we isolate and structurally compare the neutral and mono-oxidized radical compounds and relate the reducing power and single electron transfer mechanism with the structural information given by X-ray crystallography. Furthermore, the structurally new class of stable pyridinyl radicals can be tailored electronically and shows remarkable persistency even towards air. Considering the simplicity of this approach and that both pyridinium salts and carbenes are largely available, the methodology can be expected to lead to a variety of new redox architectures. As a proof of concept we could show that alkyl bridged pyridinium systems lead to exceptional strong multielectron (4e⁻) donors. In general, any pyridinium salt can be converted in one step into a new redox system and therefore broaden the interest in applications such as strong (multi e-) reducing agents or redox-flow batteries. As a proof of principle, we could show that low potential ($E \sim -1.6$ V) charge-discharge experiments with the new hybrids demonstrate a high cycling stability with no significant capacity decrease over 100 cycles, thereby clearly highlighting the large potential of this hybrid class as new structural motive in redox-flow chemistry. Future work is focused on the evolution of the here described redox systems.

EXPERIMENTAL SECTION

For full characterization data for all compounds, see SI. Representative procedures and selected characterization data for: Neutral **3b^{II}**: To a suspension of **1^{II}** (282 mg, 0.63 mmol, 1.00 eq.) in thf (10 mL) was added free IMes carbene (400 mg, 1.31 mmol, 2.10 eq.). The yellow/orange solution was stirred for 14 h and the solvent evaporated under reduced pressure. The obtained solid was extracted with Et₂O (20 mL + 20 mL) and filtered. The solvent of the orange solution was removed under reduced pressure to give **3b^{II}** as a bright orange solid (282 mg, 0.422 mmol, 67 %). Single crystals suitable for X-ray diffraction can be obtained by slow evaporation from a saturated Et₂O solution. **m.p.** 250 °C; **¹H-NMR** (C₆D₆, 400 MHz, 298 K): 7.49 (d, *J* = 7.0 Hz, 4H), 7.18 (d, *J* = 7.9 Hz, 4H), 7.04 – 6.93 (m, 6H),

6.84 (s, 4H), 6.35 (s, 2H), 5.56 (s, 2H), 2.25 (s, 6H), 1.96 (s, 12H), 1 1.19 (s, 9H); ¹³C-NMR (C₆D₆, 101 MHz, 298 K): 150.3, 141.7, 2 140.5, 140.3, 139.2, 136.7, 135.6, 129.7, 129.3, 128.8, 125.0, 3 124.5, 123.9, 120.1, 117.0, 116.6, 85.1, 33.9, 31.8, 21.1, 17.9; ¹H/¹⁵N HMBC (400/41 MHz, C₆D₆, 298K): -290.4, -247.1; IR 4 $[cm^{-1}]: \tilde{v} = 3048, 3026, 2961, 2915, 2862, 1609, 1594, 1570,$ 5 1516, 1508, 1472, 1444, 1412, 1378, 1361, 1349, 1330, 1301, 6 1288, 1255, 1216, 1202, 1184, 1163, 1153, 1135, 1117, 1102, 7 1083, 1072, 1053, 1031, 1014, 994, 966, 933, 922, 903, 893, 851, 8 820, 757, 731, 689, 674, 633, 623, 575, 547, 525, 506; UV-vis 9 [nm]: (in CH₂Cl₂): 284 (ϵ = 12498 M⁻¹cm⁻¹), 462 (ϵ = 23752 M⁻¹ 10 1 cm⁻¹); **HR-MS-ESI(+)** calc. C₄₈H₅₀N₃O₂⁺ [M+O₂+H]⁺ 700.3898; 11 found 700.3883. 12

Radical cation 4b^{II}: To a mixture of solids of 3b^{II} (50 mg, 13 0.07 mmol, 1.00 eq.) and AgSbF₆ (27 mg, 0.08 mmol, 1.05 eq.) 14 was added CH₂Cl₂ (10 mL) at room temperature and stirred for 15 90 min. The red solution was filtered, the solvent evaporated 16 under reduced pressure and the resulting solid washed with 17 Et₂O/CH₂Cl₂ (3/1; 10 mL). Drying under reduced pressure affords 18 $4b^{II}$ as dark red solid (72 mg, 0.04 mmol, 57 %). X-band EPR g = 19 2.0029 (2xN: 6.72 MHz; 1xN: 14.7 MHz; 2xH: 2.48 MHz; 2xH: 0.59 MHz); **IR** [cm⁻¹]: $\tilde{v} = 3174$, 3142, 2959, 2919, 2867, 1621, 20 1577, 1557, 1504, 1478, 1445, 1399, 1380, 1364, 1336, 1316, 21 1286, 1269, 1223, 1189, 1168, 1155, 1111, 999, 991, 925, 885, 22 860, 850, 821, 807, 784, 764, 744, 728, 699, 654, 612, 571, 559, 23 537; UV-vis [nm]: (in CH₂Cl₂): 389 (ε = 7660 M⁻¹cm⁻¹), 525 (ε = 24 3662 M⁻¹cm⁻¹); **HR-MS-ESI(+)** calc. $C_{49}H_{52}N_3^{+-}$ [M+OMe]⁺⁻ 25 698.4105; found 698.4090. 26

Dication **5b^{II}**: To a mixture of solids of **3b^{II}** (50 mg, 0.07 mmol, 27 1.00 eq.) and AgSbF₆ (51 mg, 0.15 mmol, 2.05 eq.) was added 28 CH₂Cl₂ (10 mL) at room temperature and stirred for 90 min. The 29 grey suspension was filtered, the solvent evaporated under 30 reduced pressure and the resulting solid washed with Et₂O/CH₂Cl₂ 31 (5/1; 10 mL) and Et₂O (5 mL). Drying under reduced pressure 32 affords 5b^{II} as a colorless solid (55 mg, 0.04 mmol, 65 %). ¹H-33 **NMR** (CD₂Cl₂, 500 MHz, 298 K): 7.91 (s, 2H), 7.35 (t, J = 7.6Hz, 2H), 7.28 (s, 4H), 7.25 (s, 2H), 7.20-7.17 (m, 4H), 7.14 (d, J= 34 8.8 Hz, 2H), 6.97 (d, J = 8.8 Hz, 2H), 6.80 – 6.73 (m, 4H), 2.45 35 (s, 6H), 2.18 (s, 12H), 1.13 (s, 9H); ¹³C-NMR (CD₂Cl₂, 126 MHz, 36 298K): 159.4, 155.4, 144.5, 136.9, 135.7, 135.3, 134.9, 131.9, 37 131.9, 131.8, 131.7, 131.0, 130.3, 128.8, 127.9, 126.8, 126.4, 38 35.3, 31.2, 21.5, 17.8; **IR** $[cm^{-1}]$: $\tilde{v} = 3166$, 3142, 2965, 2873, 39 1620, 1578, 1550, 1503, 1478, 1442, 1412, 1397, 1365, 1325, 40 1284, 1269, 1251, 1223, 1188, 1175, 1152, 1113, 1091, 1080, 41 1031, 1001, 984, 931, 905, 884, 872, 861, 846, 829, 807, 783, 42 767, 743, 726, 697, 655, 610, 595, 585, 575, 564, 552, 540, 522, 43 509; UV-vis [nm]: (in CH₂Cl₂): 297 (ϵ = 14186 M⁻¹cm⁻¹); HR-44 **MS-ESI(+)** calc. C₄₈H₄₉N₃²⁺ [M]²⁺ 333.6958; found 333.6963. 45 Neutral 3bV: To a suspension of 1V (169 mg, 0.63 mmol, 1.0 eq.) 46 in thf (10 mL) was added free IMes carbene (400 mg, 1.31 mmol, 47 2.10 eq.). The orange solution was stirred for 12 h and the solvent 48 evaporated under reduced pressure. The obtained solid was 49 extracted with pentane (15 mL + 5 mL) and filtered. The solvent of the orange solution was removed under reduced pressure to 50 give $3b^{V}$ as a bright orange solid (150 mg, 0.35 mmol, 56 %). 51 m.p. 158 °C; ¹H-NMR (C₆D₆, 400 MHz, 298 K): 6.80 (s, 4H), 52 5.59 (s, 2H), 4.57 (s, 2H), 2.42 (s, 12H), 2.24 (s, 3H), 2.15 (s, 6H), 53 1.28 (s, 6H); ¹³C-NMR (C₆D₆, 100 MHz, 298 K): 137.9, 137.2, 54 136.4, 131.4, 129.2, 116.6, 104.8, 85.0, 33.0, 21.1, 20.9, 18.7; IR 55 $[cm^{-1}]: \tilde{v} = 2908, 2872, 1599, 1568, 1483, 1447, 1391, 1373,$ 56 1347, 1327, 1236, 1179, 1145, 1112, 1090, 1077, 1031, 1010, 57 925, 913, 852, 810, 712, 671, 648, 606, 589, 577, 567, 509; UV-58 vis [nm]: (in thf): 333 ($\varepsilon = 29758 \text{ M}^{-1}\text{cm}^{-1}$); HR-MS-ESI(+) calc. 59 C₂₉H₃₄N₃⁺ [M-H]⁺ 424.2747; found 424.2733. ACS Paragon Plus Environment 60

Radical cation **4b**^V: To a mixture of solids of **3b**^V (40 mg, 0.093 mmol, 1.00 eq.) and AgSbF₆ (32 mg, 0.093 mmol, 1.00 eq.) was added thf (10 mL) at room temperature and stirred for 30 min. The red solution was filtered, the amount of solvent was reduced to 1 mL under reduced pressure and the crude product was precipitated by addition of Et₂O (20 mL). The solid was washed twice with Et₂O (5 mL) until the supernatant became colorless. Drying under reduced pressure affords **4b**^V as olive green solid (37 mg, 0.056 mmol, 60%). X-band **EPR** g = 2.0031 (2xN: 9.3 MHz; 1xN: 14.3 MHz; 2xH: 3.1 MHz; 6xH: 7.5 MHz; 3xH: 13.4 MHz; 2xH: 1.2 MHz); **IR** [cm⁻¹]: $\tilde{v} = 3103$, 2947, 1561, 1525, 1487, 1455, 1395, 1267, 1232, 1204, 1035, 862, 819, 735, 650, 594, 576; **HR-MS-ESI(+)** calc. C₂₉H₃₄N₃⁺ [M-H]⁺ 424.2747; found 424.2734.

Dication **5b**^V: To a mixture of solids of **3b**^V (20 mg, 0.047 mmol, 1.00 eq.) and $AgSbF_6$ (32 mg, 0.093 mmol, 2.00 eq.) was added thf (5 mL) at room temperature and stirred for 15 min. The gray suspension was filtered and the amount of solvent was reduced to 1 mL under reduced pressure. The product was precipitated by addition of Et₂O (15 mL) and washed twice with Et₂O (5 mL) to afford 5b^V as a colorless solid (32 mg, 0.036 mmol, 75 %). ¹H-NMR (CD₃CN, 400 MHz, 298 K): 8.04 (s, 2H), 7.15 (s, 4H), 7.04 (s, 2H), 3.85 (s, 3H), 2.51 (s, 6H), 2.35 (s, 6H), 2.07 (s, 12H); ¹³C-NMR (CD₃CN, 101 MHz, 298 K): 159.5, 143.5, 138.9, 135.3, 135.2, 131.2, 130.2, 128.4, 127.0, 42.2, 22.6, 21.2, 17.9; IR $[cm^{-1}]$: $\tilde{v} = 3179$, 3149, 3121, 3088, 3042, 3002, 2969, 2926, 2863, 1641, 1604, 1567, 1495, 1447, 1408, 1390, 1377, 1345, 1284, 1228, 1206, 1174, 1120, 1102, 1089, 1075, 1034, 1015, 993, 966, 931, 896, 885, 873, 860, 797, 780, 766, 743, 725, 716, 654, 642, 604, 590, 577, 552, 533, 508; UV-vis [nm]: (in thf): 285 $(\varepsilon = 9289 \text{ M}^{-1}\text{cm}^{-1});$ HR-MS-ESI(+) calc. $C_{29}H_{35}N_2^{2+}$ [M]²⁺ 212.6410; found 212.6414.

Electrochemical measurements: The setup of the Siewert group (Göttingen University) was used for CV/UV/vis-SEC, see for example ref. 28. CVs were measured with a Gamry Instruments Reference 600 and iR compensation using the positive feedback method which is implemented in the PH200 software of Gamry. Samples were measured under inert atmosphere in a nitrogen glove box at room temperature in dry thf solution containing tetrabutylammonium hexafluorophosphate (0.1 M). The setup consist of a three-neck flask with a three electrode setup containing a glassy carbon working electrode (GC: CH Instruments, ALS Japan; $A = 7.1 \text{ mm}^2$), a platinum wire as a counter electrode, and an Ag/AgNO₃ reference electrode (0.01 M AgNO₃ in 0.1 M nBu₄NPF₆ in CH₃CN). The reference electrode was freshly prepared by using a fritted sample holder (Vycor glass), which was activated by storing in a CH₃CN solution for one night, followed by diluted HCl (1M) for one night, dried and stored in thf for at least one additional night. To the fritted sample holder was added a freshly prepared 0.01 M AgNO₃/0.1 M *n*Bu₄NPF₆ solution in CH₃CN and a silver wire. The working electrode was cleaned before measuring a new compound by standard methods: washed with water, polished with an alox-slurry (0.05 µm), washed with millipore water, sonicated in millipore water for 3 minutes, rinsed with millipore water, and dried. Initially a blank sample only containing electrolyte in thf (0.1M) was measured and the potential cycled for 3-5 scans until a stable and clean potential was reached. Then the 3-neck cell was emptied and a specific amount of compound dissolved in 3 mL thf added and the CV measured. The system was furthermore referenced internally by addition of diacetyl ferrocene or ferrocene. The values obtained were corrected against ferrocene (diacetyl ferrocene to ferrocene $\Delta E = 430$ mV in thf).¹⁶

Spectro-electrochemical measurements were measured with the setup of the Siewert group (Göttingen University) and is Environment

recorded with a Gamry Instruments Reference 600. The samples were measured in CH₂Cl₂ starting from the neutral compounds, containing a three electrode setup (platinum wire, platinum net and Ag/AgNO₃ reference electrode) in a UV-vis cell (1mm diameter from ALS Co., Ltd; SEC-C spectroelectrochemical cell) under nitrogen. For a picture of the setup see Figure S76. In order to guarantee a clean oxygen free setup the measurement was performed in a nitrogen glove box. The reference electrode was freshly prepared by using a fritted sample holder, which was activated by storing in a CH₃CN solution for one night, followed by diluted HCl (1M) for one night, dried and stored in thf for at least one additional night. To the fritted sample holder was added a freshly prepared 0.01 M AgNO₃/0.1 M nBu₄NPF₆ solution in CH₃CN and a silver wire. The light source was a deuterium/tungsten light source and detected with a BWTEK ExemplarLS. A blank spectrum and a reference spectrum with just solvent was taken in advance and was subtracted from the measured data. In general, a UV-vis spectrum was taken every 10 seconds, while the electric current was scanned from negative potentials to positive potentials (usually around 1 V) by a step size of 2-2.5 mV/s.

Electrochemical charge-discharge experiments: Chargedischarge experiments were performed in analogy to reports by Sanford et al.13 in a custom made H-cell in a nitrogen filled glovebox. Both cell chambers were separated by a P5-frit (15 mm diameter, porosity 5 from Robu®). Reticulated vitreous carbon (RVC) electrodes (100 ppi Duocel®) were cut into rods of the dimensions 0.5 cm x 0.5 cm x 4 cm and positioned ca. 2 cm deep in solution (see Figure S60). To rule out contamination processes the electrodes were single used. As reference an Ag/AgNO₃ reference electrode (0.01 M AgNO₃ in 0.1 M *n*Bu₄NPF₆ in CH₃CN) was used. The reference electrode was freshly prepared by using a fritted sample holder, which was activated by storing in a CH₃CN solution for one night, followed by diluted HCl (1M) for one night, dried and stored in DMF for at least one additional night. To the fritted sample holder was added a freshly prepared 0.01 M AgNO₃/0.1 M *n*Bu₄NPF₆ solution in CH₃CN and a silver wire. Tetrabutylammonium hexafluorophosphate (electrochemical grade from Sigma Aldrich) was molten under high vacuum prior to use. A 0.5 M tetrabutylammonium hexafluorophosphate solution in DMF (anhydrous grade dried additionally over 4Å molecular sieves) was freshly prepared. For 1e cycling the following procedure was used: Solutions (0.5 M TBAP) of neutral (5 mM) and radical cation (5 mM) were separately prepared and filled into the chambers of the cell (each 6 mL). Then a 5 mA current was applied with cut-off potentials at -1.9 V and -1.2 V (against the internal Ag/AgNO₃ reference). For 2e⁻ electron cycling: A 5 mM solution (0.5 M TBAP) of radical cation was equally filled into the left and right side of the chambers. Then a 5 mA current was applied with cut-off potentials at -1.9 V and 0 V (against the internal Ag/AgNO3 reference). During chargedischarge experiments both cells were stirred constantly at 500 rpm.

ASSOCIATED CONTENT

Supporting Information. Experimental procedures, characterization data, spectra, crystallographic data as well as computational details included in the supporting information. This material is available free of charge via the Internet at <u>http://pubs.acs.org</u>.

- 56 Crystallographic data for **3d^{II}**
- 57 Crystallographic data for **3b**^{II}
- Crystallographic data for $3a^{VII}$
- 58 Crystallographic data for **6**
- 59 Crystallographic data for $3e^{II}$
- 60

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Crystallographic data for **3b**^X Crystallographic data for **3b**^{VII} Crystallographic data for **5b**^V Crystallographic data for **4b**^{III} Crystallographic data for **3b**^{VI} Crystallographic data for **4b**^{VI} Crystallographic data for **7b**^{VIII} Crystallographic data for **4b**^{XI} Crystallographic data for **4c**^{II} Crystallographic data for **3b**^V

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Notes

The author declare no competing financial interests.

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ABBREVIATIONS

NHC, N-heterocyclic carbene; CAAC, cyclic (alkyl)amino carbene; DAC, diamido carbene; SEC, spectro electrochemistry; TBAP tetrabutylammonium hexafluorophosphate; hfc, hyperfine couplings

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