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## Carbene-derived $\alpha$ -acyl formamidineium cations: organic molecules with readily tunable multiple redox processes†

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**A series of  $\alpha$ -acyl formamidineium ions and their corresponding 1-electron reduced neutral radicals were synthesized, and their electrochemical properties were evaluated. These cations exhibit multi-electron redox processes that are highly electrochemically reversible at rapid scan rates (100 mV/s), and the redox potentials were readily tailored by up to  $\sim 1.0$  V, making them ideal candidates for organic radical-based charge storage materials.**

The design of simple organic and main group molecules that are stable in multiple redox states and can be easily synthesized has become an increasingly active area of research.<sup>1</sup> Such compounds are valued for their potential application in both data<sup>2,3</sup> and energy<sup>4</sup> storage at the molecular level.<sup>5-7</sup> Organic compounds are particularly promising candidates for energy storage due to their high energy densities, metal free-compositions, use of low cost, renewable precursors, and energy-efficient processing.<sup>8, 9</sup> While organic radicals based on open-shell graphene fragments are promising,<sup>8, 10, 11</sup> they suffer from multi-step syntheses precluding simple synthetic modification. Prior work on organic radical-based energy storage includes the use of nitroxide and phenoxy radicals,<sup>12-14</sup> whereas main group radicals of the general formula  $(t\text{Bu}_2\text{MeSi})_3\text{E}\cdot$  (E = Si, Ge, or Sn) have been prepared. Sekiguchi and Nakano have shown that these radicals are excellent anode materials within a supercapacitor cell configuration.<sup>15</sup> These compounds have been shown to be stable in three distinct redox states: the neutral radical, the fully reduced anion, and the fully oxidized cation, enabling their use in energy storage devices.

The use of organic radicals and ions for storing charge opens up new classes of compounds that feature high charge storage capacities with the ability to control structure at the molecular level. The storage and release of charge using multi-electron redox processes offers significantly higher storage capacities compared to typical single electron processes used

for energy storage devices.<sup>16</sup> The electrochemical potential of a material affects cell voltage, specific energy and power, as well as stability, and the ability to control the potential of redox processes allows for the design of improved materials and cells.<sup>17-19</sup> To further advance this field, materials that (i) store and release multiple electrons using stable radical and ionic forms, (ii) exhibit readily tunable redox potentials, and (iii) can be synthesized using simple synthetic approaches would be highly desirable from both a cost and applications standpoint.

Singlet carbenes offer a promising avenue to explore in this area as they are capable of stabilizing both main group element-centred as well as carbon-centred radicals.<sup>20-22</sup> Recently, the group of Bertrand demonstrated that  $\alpha$ -acyl iminium cations derived from cyclic(alkyl)(amino) carbenes exhibited multistage redox behaviour.<sup>25</sup> Moreover, the 1-electron reduced neutral radicals of these ions were found to be quite stable. By simple modification of the acyl substituent the stability of the radicals toward air could be easily tailored.<sup>26</sup>

The introduction of carbonyl groups into the backbone of an N-heterocyclic carbene (NHC) was first explored by the groups of Bielawski, Lavigne, and Ganter.<sup>27-30</sup> As carbonyls are incorporated to afford monoamido(amino) carbenes (MAACs) and diamidocarbenes and (DACs) a gradual lowering of the LUMO energy concomitant with an increase in  $\pi$  accepting properties is observed (Figure 1).<sup>31-36</sup> We now demonstrate that the electrochemical properties of  $\alpha$ -acyl formamidineium cations can be easily tailored by judicious choice of a carbene.

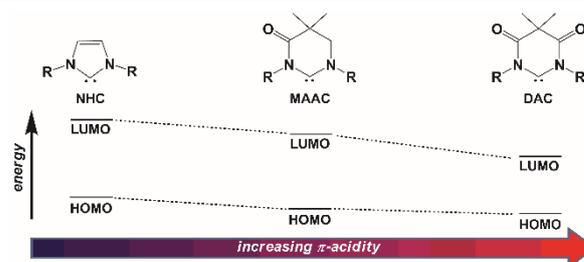
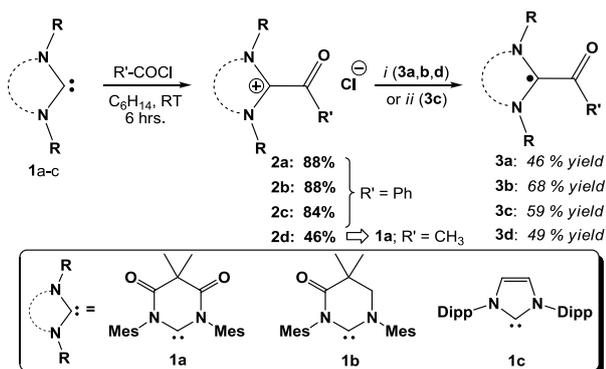


Fig 1. Frontier orbital energies (arbitrary units) of NHCs, MAACs, and DACs.

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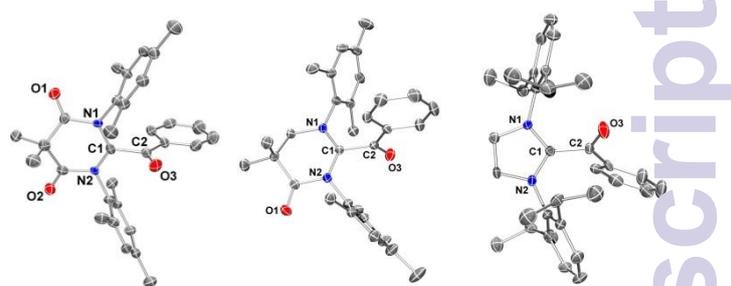
† Electronic Supplementary Information (ESI) available: full experimental and computational details are provided. See DOI: 10.1039/x0xx00000x



**Scheme 1** Synthesis of cations **2** and radicals **3** isolated yields indicated. *Conditions:*  $C_6H_5-COCl$  (**2a-c**),  $CH_3-COCl$  (**2d**); (i) TDAE (0.5 eq.),  $C_6H_6$ , RT, 2 hrs; (ii)  $KC_8$  (1 eq.),  $C_6H_6$ , RT, 2 hrs. (Mes = 2,4,6- $(CH_3)_3-C_6H_2$ ; Dipp = 2,6- $(iPr)_2-C_6H_3$ ).

Amidinium ions **2a-c** were prepared in good yields using a simple one step procedure by treating the desired carbene (**1a-c**) with benzoyl chloride in hexanes (Scheme 1).<sup>7e</sup> To determine if the acyl substituent influences the redox properties, **2d** was prepared by treating **1a** with acetylchloride. Cations **2** were fully characterized by NMR spectroscopy and **2a-c** were further characterized by single crystal XRD (Figure 2). Compounds **2a-c** all exhibited characteristic signals in the <sup>13</sup>C NMR ( $CDCl_3$ ) at  $\delta = 179$  ppm, corresponding to the carbonyl moiety, whereas the analogous carbon in **2d** was observed downfield at 186 ppm. In the solid state, the structures of **2a** and **2b** are similar to what Bertrand observed, with the carbene ligand adopting an orthogonal orientation to the planar benzoyl group (N1–C1–C2–O3 torsion angle avg. = 93.3°). In addition, the C1–C2 distance is elongated (avg. = 1.55 Å) and the C2–O3 distance is shortened (1.21 Å) owing to their cationic nature. For the NHC-derived **2c**, there appears to be a stronger overlap between the carbene and acyl  $\pi$  systems as evidenced by the obtuse torsion angle (125.15°). The C1–C2 and C2–O3 distances observed in **2c** (1.515(7) and 1.206(5) Å, respectively) are similar to those in cations **2a** and **2b**.

The electrochemical properties of all four cations were then interrogated by CV (Figure 3). By modifying the structure of the cation through varying the carbene, we demonstrated the ability to tune the redox potential as well as reversibility of the redox events. The CV data supports that these ions undergo two sequential 1-electron reduction processes from the fully oxidized cation, to the neutral radical, and then to the fully reduced enolate anion (see ESI).<sup>†</sup> CV data also shows that both redox processes are highly reversible for all cations with the exception of **2c**: the anion can be fully oxidized back to the neutral radical and then the cationic form. Reversibility was demonstrated by the similar peak currents for the 2<sup>nd</sup> and 5<sup>th</sup> cycle for each redox process and by the analysis of the relative reduction and oxidation peak currents for each redox process, as shown in Table 1.<sup>†</sup> The relative reduction/oxidation peak current ratios for each process ranged from 0.76–1.04, for all compounds other than **2c**. In the case of **2c**, the irreversibility of the second reduction event is not surprising given that a 2-electron reduction would formally disrupt the 6  $\pi$  electron aromatic ring in **2c** and result in an 8  $\pi$  electron antiaromatic



**Fig. 2** ORTEP diagrams of **2a-c** the thermal ellipsoids are drawn at 50% probability and H-atoms have been omitted for clarity. Pertinent metrical parameters are provided in the text

enolate.

The redox reversibility depends on several factors including electron transfer rates, diffusion coefficients, and solvent interactions,<sup>37</sup> and further examination of the reversibility in solution and in solid-state is currently under investigation. However, solution-phase redox compounds are currently not utilized for redox flow batteries,<sup>38-40</sup> and a number of groups have demonstrated that organic compounds could be effectively utilized within a solid-state electrochemical configuration.<sup>15,19</sup> The first three cycles of **2a** show higher than unity peak current ratios and subsequent cycles show ratios at or below unity;<sup>†</sup> however, this phenomenon is common in electrochemical charge storage materials and does not preclude their use in practical devices.<sup>41</sup>

We also note that a high scan rate of 100 mV/s (~11 sec charge/discharge time for the 2-electron redox process) was used which supports that these compounds can be rapidly charged and discharged. The theoretical specific capacity and specific capacitance of these molecules is between 51–110 mAh/g and 265–380 F/g, respectively, indicating that these organic compounds have capacities that make them promising candidates for batteries and supercapacitors.

The CV data clearly shows the significant degree to which the electrochemical potential can be tuned by changing the carbene ligand. Specifically, we found that the  $E_{1/2}$  values were anodically shifted by ~1.0V for the DAC-supported amidinium cations **2a** and **2d** relative to the NHC derivative **2c** ( $E_{1/2} = 0.43, -0.48, -0.98,$  and  $-1.32$ V for **2d**, **2a**, **2b**, and **2c**, respectively Table 1 and Figure 3). Importantly, the acyl substituent has little effect on the  $E_{1/2}$  of cations **2** ( $E_{1/2}$  for **2a** and **2d** were nearly identical). When comparing the DAC supported cations **2a** and **2d** to the MAAC-supported cation

**Table 1** Ratios of peak currents for oxidation/reduction peak R1/O1 and R2/O2 as shown in Fig 3. Voltage is versus  $Fc/Fc^+$ : +0.51 V vs Ag/AgCl;  $Li/Li^+$ : -3.237 V vs Ag/AgCl.

Cmpd.	Ratio of peak current (R1/O1) <sup>a</sup>	$E_{1/2}$ R1/O1 (V)	Ratio of peak current (R2/O2) <sup>a</sup>	$E_{1/2}$ R2/O2 (V)
<b>2a</b>	1.04	-0.48	0.94	-1.06
<b>2b</b>	0.76	-0.98	0.82	-1.56
<b>2c</b>	0.90	-1.32	---	---
<b>2d</b>	0.94	-0.43	0.86	-1.01

<sup>a</sup>Ratios were averages of cycles 2-5.<sup>†</sup>

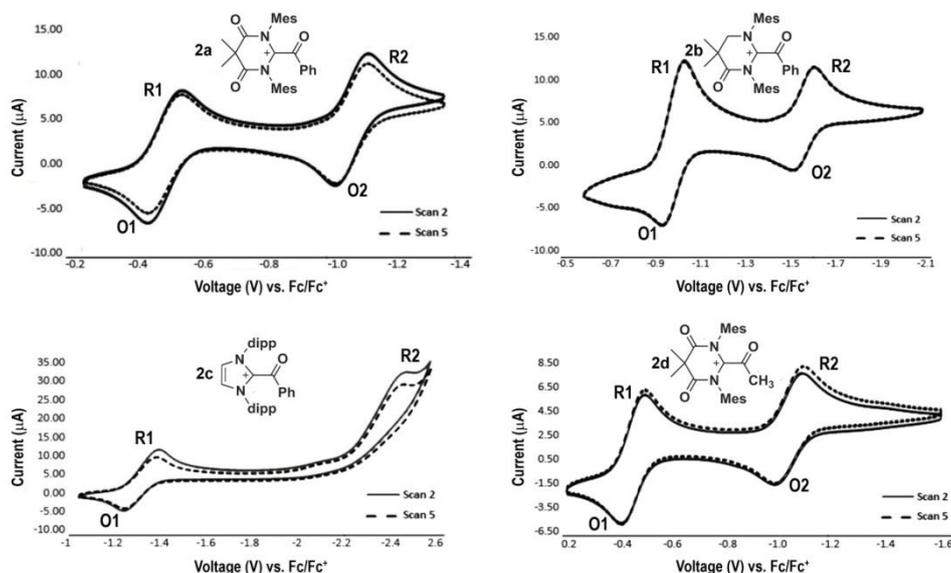


Fig. 3 Cyclic voltammograms of cations **2a–d** recorded in dichloromethane ( $n\text{Bu}_4\text{NPF}_6$  0.1M,  $100\text{mVs}^{-1}$  vs.  $\text{Fc/Fc}^+$ ).

**2b**, it can be noted that the removal of a carbonyl group accounts for a decrease in the  $E_{1/2}$  by 500 mV. Remarkably, this value is more than 300 mV greater than what Bielawski observed in the complexes  $\text{L}:\rightarrow[(\text{cod})\text{IrCl}]$  (where  $\text{L} = \mathbf{1a}$  and  $\mathbf{1b}$ ) which had a  $\Delta E_{1/2} = 165$  mV for the iridium I/II couple.<sup>30</sup>

While the ability to tune redox potentials has been shown in electroactive polymers and organic compounds,<sup>17–19</sup> the degree to which the  $E_{1/2}$  values in these carbene-derived amidinium cations is extremely unique and highly significant. The wide range of accessible redox potentials facilitates the molecular-level design of cathodic and anodic compounds derived from **2**, since as mentioned above, tailoring the electrode potential is a critical design parameter that affects cell voltage, specific energy, specific power, and stability. The redox potentials of cations **2** ( $-1.05$  –  $+0.08$  V vs  $\text{Ag/AgCl}$ ;  $+2.19$  –  $+3.32$  V vs Li) compare well to other reported redox organic compounds ( $\sim -1.7$  –  $+0.26$  V vs  $\text{Ag/AgCl}$ ;  $\sim 1.5$ – $3.5$  V vs Li), which allows for coupling to other redox compounds.<sup>8,13–15,18–19</sup>

Another important consideration in the design of energy storage compounds is the stability of the individual redox states of the electrode materials. The reversibility of the first reduction wave suggested that the corresponding 1-electron reduced neutral radicals may be stable. Indeed radicals of type **3** could all be readily synthesized and isolated using tetrakis(dimethylamino) ethylene (TDAE)<sup>42, 43</sup> (**3a**, **3b**, and **3d**) or  $\text{KC}_8$  (**3c**)

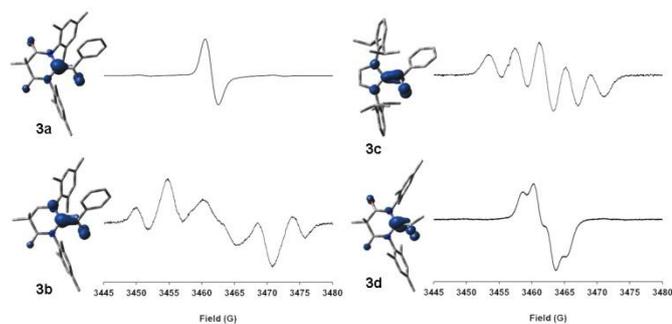
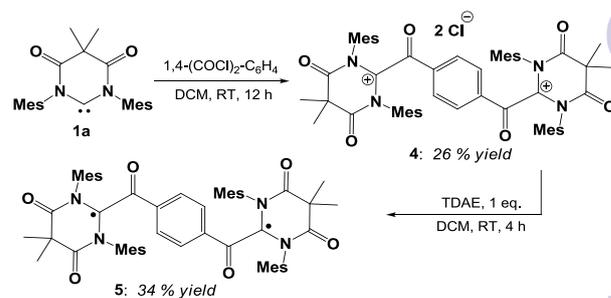


Fig. 4. Computed spin densities (isovalue = 0.02, density = 0.008) and EPR spectra (benzene solution, room temperature) of **3a–d**.

(Scheme 1). Radicals **3** were isolated as dark red (**3a,b**) purple (**3c**) or orange (**3d**) solids and the structure of **3a** was further confirmed by single crystal XRD (ESI). The paramagnetic nature of radicals **3** was first observed by silent  $^1\text{H}$  NMR spectra ( $\text{C}_6\text{D}_6$ ), and then confirmed by EPR spectroscopy. Interestingly, the degree of hyperfine coupling of the unpaired electron to the  $^{14}\text{N}$  nuclei of the carbene ligand is dependent on the number of carbonyl groups present. To further understand this phenomenon, the electronic structures of radicals **3** were investigated through DFT computations, and the localized spin densities (UB3LYP/6-311g\*\*) were determined (Figure 4; see ESI for full discussion).

We further questioned if we could tailor the redox potentials of these cations by increasing the overall positive charge of the molecule. Therefore, dication **4** was prepared in low yield by treating terephthaloyl chloride with two equivalents of **1a** (Scheme 2). The dication was fully characterized by NMR, XRD, and CV (see ESI for full discussion). The cyclic voltammogram of **4** featured four reversible redox events. By increasing the charge from +1 to +2, the first reduction wave for dication **4** was anodically shifted by  $\sim 15$  mV relative to **2a**. While this shift is small, it demonstrates that **4** is more electron-deficient than **2a** and thus easier to reduce.



Scheme 2 Synthesis of dication **4** and diradical **5** isolated yields indicated.

Dication **4** could also be converted into diradical **5** using 1 equivalent of TDAE. **5** was isolated as a dark red solid in 34% yield and exhibited an EPR spectrum that was nearly identical to that obtained for **3a** (see ESI).

This series of  $\alpha$ -acyl formamidinium cations was prepared via a one-step synthetic methodology which greatly reduced the number of steps typically needed to prepare organic molecules that are often used in energy storage applications.<sup>8, 10, 11</sup>

These cations exhibit highly reversible redox processes with potentials that can be tailored to span nearly 1V by judicious selection of a carbene. Reversibility of the redox events was demonstrated over multiple cycles indicating that in solution cations **2** could be effectively charged and discharged at high rates. Finally, the 1-electron reduced neutral radicals **3** were found to be stable, isolable species. The tunable and highly reversible multi-electron charge storage abilities of cations **2** provide significant opportunities to utilize these cations as a new class of organic molecules for high rate batteries and supercapacitors as well as uses in other applications.

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