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# Pyrylenes: A New Class of Tuneable, Redox-Switchable, Photo-Excitable Pyrylium-Carbene Hybrids with Three Stable Redox-States

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**ABSTRACT:** A new synthetic and modular access to a large family of redox-switchable molecules based upon the combination of pyrylium salts and carbenes is presented. The redox-properties of this new molecule class correlate very well with the  $\pi$ -accepting properties of the corresponding carbenes. While the pyrylium moiety acts as a chromophore, the carbene moiety can tune the redox-properties and stabilize the corresponding radicals. This leads to the isolation of the first monomeric pyranyl-radical in the solid-state. The three stable oxidation states could be cleanly accessed by chemical oxidation, characterized by NMR, EPR, UV-VIS, X-ray diffraction and supported by (TD)-DFT-calculations. The new hybrid class can be utilized as electrochemically triggered switch and as powerful photo-excited reductant. Importantly, the pyrylenes can be used as novel photo-catalysts for the reductive activation of aryl halides and sulfonamides by consecutive visible light induced electron transfer processes.

#### INTRODUCTION

Organic molecules featuring multiple stable redox-states offer various applications ranging from data<sup>1</sup> or energy<sup>2</sup> storage to logic operations suitable for quantum information science.<sup>3</sup> Furthermore, organic radicals generated by an external trigger such as light or electric fields, offer great potential for switchable electroconductive<sup>4</sup> and magnetic materials.<sup>5</sup> While heteroatom-centered radicals have been quite well studied, carbon centered radicals are much less well developed,<sup>6</sup> presumably a result of their usually high intrinsic reactivity. Nevertheless, they offer several applications ranging from photovoltaics, redox-flow batteries to spinmemory devices.<sup>7</sup> Electron-rich olefins are an interesting class of organic molecules as they feature a small HOMO-LUMO gap and can easily be oxidized to radical cations and dications, thereby acting as an organic reductant.<sup>8</sup> Tetraazafulvalenes (I) and tetrathiafulvalenes (II) are important representatives of this substance class, which have received tremendous attention as superelectron donors9 or advanced materials, respectively.10 While I and II can be considered as homodimers of 1,3-diaza and 1,3dithiol-2-ylidenes, we reasoned that the hybrid of stable carbenes with kinetically unstable pyran-4-ylidenes should lead to a new class of electron-rich alkenes (III; Scheme 1a). Importantly, one or two electron oxidation should give access to pyranyl radicals and pyrylium dications, respectively. While pyranyl radicals have been studied as transient, unstable intermediates by EPR spectroscopy,<sup>11</sup> their main reaction pathway is dimerization.<sup>12</sup> As carbenes have been shown to be suitable for stabilizing main-group radicals,<sup>13</sup> we were curious if a carbene substituent could lead to stable, isolable pyranyl radicals. Pyrylium salts have found various applications,<sup>14</sup> such as in laser dyes, Q-switches,<sup>15</sup> sensors,<sup>16</sup> nonlinear optical (NLO) materials,<sup>17</sup> or phototherapeutic agents;<sup>18</sup> most extensively they have been utilized as organic photosensitizers to undergo photo induced electron transfer (PET) processes (Figure 1b).<sup>19</sup> The singlet and triplet excited state of 2,4,6triphenylpyrylium tetrafluoroborate (TPT<sup>+</sup>) is a strong oxidant  $[E_{red}^* = ({}^{3}TPT^{*+}/TPT^{\cdot}) = ca. +1.9V], {}^{19b}$  easily generating the pyranyl radical by electron uptake from an electron donor such as a THF solvent molecule. One of the undesired reaction pathways of excited state pyrylium cations is the energy wasting back electron transfer (BET), which could be significantly disfavored by 4,2'-

or 4,4'pyrylogenes (**IV**).<sup>20,21</sup> As a result of the dicationic nature of **IV**, these sensitizers generate upon PET mutually repulsive radical-cation/radical-cation pairs leading to increased rate of diffusive separation and therefore disfavoring BET processes. Note, that the mono and/or bisreduced form of 4,2'- or 4,4'pyrylogenes (**IV**) could not be isolated,<sup>22</sup> and that **IV** is synthesized in several steps by an oxidative cyclization of a 1,5-dione as the key step. Furthermore, bispyrylium salts such as **V** have found various applications such as organic field-effect transistors (OFETs)<sup>23</sup> and in organic solar cells.<sup>24</sup> In the following we demonstrate that carbene/pyrylium hybrids can be straightforwardly accessed in one step, the oxidation state can easily be tuned, and that the properties combine the advantages in redox-chemistry from carbenes with the photo-physical advantages of pyrylium salts.

Scheme 1. (a) Electron-rich olefins and the partition into the corresponding carbenes. (b)  $TPT^+$  as photoredox-catalyst and derived pyrylium salts (bottom).



#### **RESULTS AND DISCUSSION**

We started our investigation by reacting two equivalents of free unsaturated N-heterocyclic carbene **a** (imidazol-2-ylidene) with 2,6-disubstituted pyrylium salt 1<sup>(Bu</sup>. The free carbene adds selectively to the 4-position of the pyrylium core,<sup>25</sup> while the second equivalent **a** deprotonates the addition intermediate **I** to give 4carbene-substituted pyran 2**a**<sup>(Bu)</sup>. Note, the isolation of the product is straightforward as the only byproduct (protonated carbene salt) is easily separated by extraction. This approach is broadly applicable and can not only be transferred from di-alkyl-pyrylium (2**a**<sup>(Bu)</sup>) to di-aryl-pyrylium (2**a**<sup>Ph</sup>), but most importantly can be performed with a series of different stable carbenes (Scheme 2).

Scheme 2. Synthesis of carbene-pyran hybrids.



 $\begin{array}{c|c} {\sf R} = {}^i {\sf Bu} \ ({\pmb{2a}}^{{\bf tBu}}; \, 78\%) & {\sf R} = {}^i {\sf Bu} \ ({\pmb{2b}}^{{\bf tBu}}; \, 72\%) & {\sf R} = {}^i {\sf Bu} \ ({\pmb{2c}}^{{\bf tBu}}; \, 82\%) & {\sf R} = {}^i {\sf Bu} \ ({\pmb{2d}}^{{\bf tBu}}; \, 68\%) \\ {\sf Ph} \ ({\pmb{2a}}^{{\bf Ph}}; \, 67\%) & {\sf Ph} \ ({\pmb{2b}}^{{\bf Ph}}; \, 52\%) & {\sf Ph} \ ({\pmb{2c}}^{{\bf Ph}}; \, 82\%) & {\sf Ph} \ ({\pmb{2d}}^{{\bf Ph}}; \, 70\%) \\ \end{array}$ 

Following the outlined procedure, the saturated N-heterocyclic carbene **b** leads to **2b**<sup>tBu</sup>, while cyclic (alkyl)amino carbene  $(CAAC)^{26}$  c gives access to  $2c^{tBu}$  in 72 and 82% yield, respectively. In case of diamido carbene  $(DAC)^{27}$  d, the carbene can be generated in situ in THF at -40°C,<sup>28</sup> and reacts cleanly with the corresponding pyrylium salt to give 2dtBu/2dPh. Strikingly, the stability of the pyranes increases with the electron deficiency of the carbene; while DAC derived 2dtBu/2dPh can be purified by column chromatography in air, 2atBu/2aPh is only stable under inert atmosphere. Interestingly, the electron rich systems (2a<sup>tBu</sup>/2a<sup>Ph</sup>/2b<sup>Ph</sup>) show very broad <sup>1</sup>H NMR resonances which sharpen upon cooling (see Figure S1-S2). This dynamic behavior might be explained by a partial diradical character allowing the rotation of the central C-C bond (vide infra)<sup>29</sup> or by pyramidalization of the nitrogen atoms and fluctuation of the N-aryl-groups. Indeed, single X-ray crystallography shows a strong twisting of the N-aryl groups out of plane [2a<sup>tBu</sup>: ∢ C<sup>Ar</sup>–N1–C1–C2 31.3°; **2b**<sup>tBu</sup>:  $\triangleleft$  C<sup>Ar</sup>-N1-C1-C2 42.1°, **2b**<sup>Ph</sup>:  $\triangleleft$  N1-C1-C2-C3 31.4°]. while the central C-C bond is only slightly bend out of the carbene/pyrylium planes (up to 28°) and the C-C distances [1.359-1.373Å] are nearly independent of the carbene moiety (Figure 1; for the X-ray structures of 2b<sup>Ph</sup> and 2c<sup>Ph</sup> see SI). Computational data at the B3LYP-D3BJ/def2-TZVP level of theory are in very good agreement with the experimental data (see Table S13-S16).

Interestingly, while the neutral carbene-pyranes **2a-2d** can be described as electron rich alkenes, there is also the possibility to formulate diradical (**I**) and zwitter-ionic (**II**) mesomeric structures (Scheme 3 top). Preliminary multi-reference CAS-SCF/NEVPT2 calculations with a (10,10) active space of **2a<sup>IBu</sup>** indicate a low population of the antibonding lowest unoccupied molecular orbital (LUMO) by 0.11 electrons indicating a diradical (**I**) character of 11% (see SI). The charge-separated zwitter-ionic description **II**, typical for example for N-heterocyclic olefins,<sup>30</sup> seems

unlikely due to the anti-aromaticity of the resulting  $8\pi$ -electron pyrylium core. However, natural resonance theory (NRT) calculations on structurally simplified **2a** predict a 36% contribution of the zwitter-ionic structure (see SI). Importantly, as a result of the electron donating properties of carbenes, the polarized alkenes are strongly electron rich, therefore susceptible to one or two electron oxidation to give radical cations (**3**) or dications **4**, respectively (Scheme 3). In the reverse sense, upon reduction of the dication **4** to the radical cation **3**, the pyrylium core can act as a chromophore enabling PET processes, while the carbene moiety can stabilize the resulting radicals, a property which might be interesting for applications in photo-redox catalysis (vide infra).



**Figure 1.** X-ray solid-state structures of alkenes **2a**<sup>IBu</sup>-**2d**<sup>IBu</sup>. Hydrogen atoms and solvent molecules omitted for clarity. Ellipsoids shown with 50% probability. Selected bond parameters in [Å] and [°]: **2a**<sup>IBu</sup> (top left): N1–C1 1.411(8), C1–C2 1.371(8), C2–C3 1.456(4), C3–C4 1.338(8), N1–C1–C2–C3 5.2 (as mean over 6 independent molecules in the unit cell) **2b**<sup>IBu</sup> (top right): N1–C1 1.403(1), C1–C2 1.359(1), C2–C3 1.458(1), C3–C4 1.331(1), N1–C1–C2–C3 167.4; **2c**<sup>IBu</sup> (bottom left): N1–C1 1.4035(8), C1–C2 1.3729(9), C2–C3 1.4651(9), C3–C4 1.3400(9), N1–C1–C2–C3 179.9; **2d**<sup>IBu</sup> (bottom right): N1–C1 1.439(2), C1–C2 1.370(2), C2–C3 1.463(2), C3–C4 1.338(2), N1–C1–C2–C3 167.5.

Scheme 3. Redox-states of pyrylenes.



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In order to evaluate the oxidation potentials we measured cyclic voltammograms for all pyranes (Figure 2). Indeed, all compounds feature two distinctively separated quasi-reversible redox-waves with the first oxidation spanning a range of 1.19 V  $[E_1^0 (2a^{tBu}) = -$ 1.22 V to  $E_{1^0}$  (2d<sup>tBu</sup>) = -0.03 V] and the second of 0.55 V [ $E_{2^0}$  $(2a^{tBu}) = -0.34$  V to  $E_2^0$   $(2d^{tBu}) = +0.21$ V; all potentials against Fc/Fc<sup>+</sup>]. Pyran 2a<sup>tBu</sup> shows a strongly reducing character with both redox-events separated by 0.88 V ( $E_2^0 = -0.34$  V). Note, the electron donation ability of carbene a in combination with the gain of aromaticity upon oxidation, leads to a reduction potential of 2atBu in the same range with zinc or the strong organic reductant tetrakis(dimethylamine)ethylene [TDAE; E = -0.78/-0.61 vs. SCE or E = -1.18/-1.01 V vs. Fc/Fc<sup>+</sup> in CH<sub>3</sub>CN].<sup>8,9,31</sup> When moving from dialkyl-substituted pyranes  $(2a^{tBu}-2d^{tBu})$  to diarylsubstituted (2a<sup>Ph</sup>-2d<sup>Ph</sup>) the redox-potential systematically shifts by ca. 100-200 mV to more positive redox potentials, while a more  $\pi$ -accepting carbene significantly shifts the oxidation waves to more positive potentials. Note, the reduction potential of 2b is in a similar range to 2,4,6-triarylpyrylium tetrafluoroborate  $[E_0 = -$ 0.83V in CH<sub>2</sub>Cl<sub>2</sub> vs. Fc/Fc<sup>+</sup> (see SI)].



Figure 2. Cyclic voltammograms of  $2a^{iBu}-2d^{iBu}$  [*n*Bu<sub>4</sub>NPF<sub>6</sub> (0.1 M), Pt/C-graphite 100 mV s<sup>-1</sup>, versus Fc/Fc<sup>+</sup>, in THF]. Redox-potentials  $E_1^{0}/E_2^{0}$  in [V]  $2a^{iBu}$ : -1.22/-0.34;  $2a^{Ph}$ : -1.03/-0.17;  $2b^{iBu}$ : -0.89/-0.14;  $2b^{Ph}$ : -0.76/-0.07;  $2c^{iBu}$ : -0.55/0.08;  $2c^{Ph}$ : -0.42/0.04;  $2d^{iBu}$ : -0.03/0.19;  $2d^{Ph}$  0.10.

Interestingly, the oxidation potentials of the carbene/pyrylium hybrids do not correlate with the overall donor ability of the corresponding carbenes. For example CAAC c is a much stronger overall donor ligand with a Tolman electronic parameter (TEP) of ~2042 cm<sup>-1</sup> compared to NHC **a** with ~ 2051 cm<sup>-1</sup>, however **2a** is more readily oxidized than 2c. The <sup>77</sup>Se-NMR shifts of carbeneselenium adducts is a well-established scale for  $\pi$ -accepting properties of carbenes.<sup>32</sup> Very interestingly, the redox potentials of the first oxidation to give **3a-d** show a linear correlation with the  $\pi$ accepting properties of the corresponding carbenes based on <sup>77</sup>Se NMR shifts (Figure 3).<sup>33</sup> This correlation is reasonable since the oxidation step reduces electron density in the  $\pi$  and not  $\sigma$ -system of the pyrylium/carbene hybrids and paves the way for an electro-chemical derived  $\pi$ -accepting scale.<sup>34</sup> Furthermore, it allows to predict the right choice of carbene for a specific application with the pyrylium/carbene hybrids. Additionally, there is also a good linear correlation between  $\Delta E(E_1^0/E_2^0)$  with the <sup>77</sup>Se-NMR shifts (see Figure S22). Considering IV (Scheme 1) as a formal twice oxidized adduct of two unknown pyran-4-ylidene and 4pyridylidenes,<sup>35</sup> it is possible to predict, based on the reported redox-potential difference of IV ( $\Delta E(E_1^0/E_2^0) = 0.52V$ ),<sup>20</sup> together with the here developed electrochemical correlation, similar  $\pi$ -accepting properties of 4-pyridylidenes compared to stable CAACs.<sup>36</sup>



**Figure 3**. Correlation of the redox-potentials  $E_1^0$  with the <sup>77</sup>Se NMR of the corresponding carbene-Se adducts.

We performed spectroelectrochemistry experiments on all carbene/pyrylium hybrids to study the photochemical properties (Figure 4; for 2b<sup>tBu</sup>-2d<sup>tBu</sup> see SI). Each compound and oxidation state features characteristic UV-vis transitions (for a summary of all transitions of each oxidation state with isobestic points and exctinction coeficients see Table S11/12). While in general the alkyl substituted series 2a-4a<sup>tBu</sup> shows transitions at the edge to the UV-spectrum  $\lambda \sim 300-400$  nm ( $\epsilon \sim 5000-15000 \text{ cm}^{-1}\text{M}^{-1}$ ), the aryl-subsituted compounds (2a-4a<sup>Ph</sup>) show additional strong transitions for all oxidation states in the VIS-area ( $\lambda \sim 400-600$ nm;  $\varepsilon \sim 20000-60000 \text{ cm}^{-1}\text{M}^{-1}$ ; Figure 4 A, B). A general trend of  $\lambda_{max}$  (neutral) <  $\lambda_{max}$  (dication) <  $\lambda_{max}$  (radical) was detectable. Time dependent (TD)-DFT B3LYP/def2-TZVPP//B3LYP/def2-TZVP calculations of the neutral, alkyl series  $(2a^{tBu}-2d^{tBu})$  predict strong  $\pi$ - $\pi$ \* transitions for the central carbene/pyran moiety in good agreement with the experimental data (see SI). In case of aryl substitution (2a<sup>Ph</sup>-2d<sup>Ph</sup>) an additional strong UV-VIS band arises from the charge transfer from the central carbene/pyran moiety onto the arvl groups (see Figures S87-S91). Interestingly, in case of pyrylium salts, Balaban et al. introduced an X,Y-band notation based on two perpendicular chromophores polarized in the X and Y directions.<sup>14,37,38</sup> Note, 2,4,6-triphenylpyrylium tetrafluoroborate (TPT<sup>+</sup>) shows two transitions at 355 nm and 401nm, which have been assigned as Y and X-band, respectively.<sup>20</sup> This assignment is also valid for the dications (4a<sup>Ph</sup>-4d<sup>Ph</sup>) and is supported by TD-DFT B3LYP/def2-TZVPP calculations (see SI). In the dications the X-band arises from the charge transfer from the aryl-groups to the pyrylium core, which is as expected, nearly independent of the carbene (480-494 nm) (Figure 4, bottom right). Interestingly, the radicals (3a<sup>Ph</sup>-3d<sup>Ph</sup>) also feature the characteristics of the X and Y-bands, both however shifted to significantly higher wavelengths.

While the carbene moiety can significantly alter the electrochemical properties, we were also interested in tuning the photochemical properties. Furthermore, in order to validate the modularity of our outlined synthesis, we reacted CAAC (c) and 2,6bis(4-methoxyphenyl)pyrylium tetrafluoroborate to give cleanly hybrid  $2c^{Ph-OMe}$  (see SI). While the UV-vis spectra of  $2c^{Ph}$  and  $2c^{Ph-OMe}$  on the neutral oxidation state are fairly similar, the donation of electron density from the p-OMe groups in the monocationic and dicationic oxidation states leads to pronounced bathochromically shifted UV-Vis transitions (Figure 5). Note, the introduction of p-OMe groups results in a relative small oxidation



**Figure 4**. Spectroelectrochemistry of  $2a^{tBu}$  (A)  $2a^{Ph}$  (B),  $2a^{Ph}$  (C),  $2c^{Ph}$  (D),  $2d^{Ph}$  (E) [in  $nBu_4NPF_6$  (0.1 M) in DCM; 2.5 mV/s, against Ag/AgNO<sub>3</sub> (0.01M)] and visualization (TD-DFT B3LYP/def2-TZVPP) of representative X,Y-transitions for the dications  $4a^{tBu}$  and  $4d^{Ph}$ .

potential shift by ca. 100 mV to more negative values [ $E_1^0$  -0.53V and  $E_2^0$  -0.11 V (**2**c<sup>Ph-OMe</sup>)] (Figure S15/16).

The large electrochemical separation of first and second oxidation, together with the spectroelectrochemical data indicated the potential of isolating stable radicals. Indeed, chemical oxidation of all pyranes **2a-2d** with one equivalent AgSbF<sub>6</sub> gives the pyranyl radicals **3a-3d**, which could be characterized by their UV-VIS and EPR spectra (Figure 6; EPR spectra of **3b**<sup>Ph</sup>-**3d**<sup>Ph</sup>, see SI). Note, the very electron rich alkenes **2a/b** are prone to be oxidized by air to give the radicals; for example the UV-VIS spectrum of neutral **2a**<sup>Ph</sup> changes in seconds upon exposure to air to the UV-VIS spectrum of radical **3a**<sup>Ph</sup>.

Interestingly, all radicals can be fully characterized, are indefinitively stable under inert conditions, even stable for minutes to hours in air, and the UV-VIS spectra of the isolated species match the corresponding spectra obtained by spectroelectrochemistry (see SI). The EPR spectra feature in each case <sup>14</sup>N hyperfine couplings (hfcs) of the carbene moiety [ $3a^{tBu}$ :  $a_N = 2.63$  G;  $3b^{tBu}$ :  $a_N = 1.66$  G;  $3c^{tBu}$ :  $a_N = 5.42$  G;  $3d^{tBu}$ :  $a_N = 2.63$  G], but also hfcs to the meta-pyrylium H-atoms. Comparison of EPR spectra of  $3a^{tBu}$  and  $3a^{Ph}$  (Figure 6a/b) clearly indicates hfcs also into the aromatic groups in 2,6-position demonstrating spin delocalization across the  $\pi$ -system (see also SOMOs Figure 7 A/B). All EPR parameters were rationalized at the B3LYP-D3BJ/def2-TZVPP//B3LYP-D3BJ/def2-TZVP level of theory and show very good agreement with the experimental data (see Figures S82-S86).







**Figure 6**. Experimental (top) and simulated (bottom) room temperature X-band EPR spectra of  $3a^{IBu}-3d^{IBu}$  and  $3a^{Ph}$  in THF; fitting parameters (a)  $3a^{IBu} 2xN$ : 2.63 G, 2xH: 1.06 G, 2xH: 0.50 G; (b)  $3a^{Ph} 2xN$ : 2.31 G, 2xH: 1.83G, 2xH: 0.92 G, 2xH: 1.1 G, 4xH: 0.32 G; (c)  $3b^{IBu} 2xN$ : 1.66 G, 4xH: 2.56 G; 2xH: 0.13G; (d)  $3c^{IBu} 1xN$ : 5.42 G, 2xH: 0.61 G; (e)  $3d^{IBu} 2xN$ : 1.00 G, 2xH: 1.11 G.

Localized Mulliken spin densities and the plots of the singly occupied molecular orbitals (SOMOs) indicate that the spindensity being located on the carbene moiety is moderate but increases in the order unsaturated NHC ~ saturated NHC (ca. 26-27%) < CAAC (35%) < DAC (42%) [This distribution is nearly independent on the pyrylium substitution (<sup>I</sup>Bu *vs.* Ar), see SI]. Note, in case of NHCs there is nearly no spin-density located on the carbene carbon atom (1-8%) in contrast to other main-group NHC-radicals,<sup>13</sup> but instead smeared over the NHC moiety. In the case of CAAC the carbene spin-density is partially localized onto the N (23%) and C(12%) atoms, while in case of DAC the carbene C-atom spin-density increases to 22% with 10% spin-density localized onto the oxygen-atoms of the backbone (Figure 7).



Figure 7. SOMOs, Mulliken spin-densities (in %) and EPR-hfcs [G] calculated at the B3LYP-D3BJ/def2-TZVPP//B3LYP-D3BJ/def2-TZVP level of theory for  $3a^{tBu}$  (A),  $3a^{Ph}$  (B),  $3b^{tBu}$  (C),  $3c^{tBu}$  (D),  $3d^{tBu}$  (E).

Importantly, while pyranyl radicals, such as derived from 2,4,6triarylpyrylium, are known to dimerize,<sup>11,12</sup> which represents a serious deactivation pathway in photo-redox catalysis,<sup>39</sup> we were able to obtain single crystals of the monomeric pyranyl radical **3c**<sup>tBu</sup> (Figure 8). As far as we know this is the first structurally characterized pyranyl radical. In the solid-state structure the N1–C1 bond [1.339(2)] and C1–C2 [1.433(2)] distances are positioned between the neutral [1.4035(8); 1.3729(9); **2c**<sup>tBu</sup>] and dicationic [1.291(2); 1.485(2); **4c**<sup>tBu</sup> vide infra] bond lengths, in very good agreement with the calculated data (see Table S15).



**Figure 8**. X-ray solid-state structure of radical cation **3c<sup>tBu</sup>**. Hydrogen atoms omitted for clarity. Ellipsoids shown with 50% probability. Selected bond parameters in [Å] and [°]: C1–N1 1.339(2), C1–C2 1.433(2), C2–C3 1.432(2), C3–C4 1.356(3), N1–C1–C2–C3 172.0.

Interestingly, two electron oxidation of 2 with either two equivalents of AgSbF<sub>6</sub> in CH<sub>2</sub>Cl<sub>2</sub> or two equivalents of NOSbF<sub>6</sub> in a CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN solvent mixture gives clean access to all dications 4. <sup>1</sup>H NMR spectroscopy indicates a clear shift of the pyran alkene protons from  $\delta(^{1}H) = 4.21$  ppm (2a<sup>tBu</sup>) to the aromatic pyrylium shift  $\delta({}^{1}\text{H}) = 8.26 \text{ ppm } (4a^{tBu})$ . In case of  $4c^{tBu}$  and  $4d^{Ph}$ we were able to obtain single crystals suitable for X-ray diffraction (Figure 9). Most strikingly, in the solid-state the pyrylium moiety is twisted perpendicular to the carbene plane (4c<sup>tBu</sup>: N1-C1-C2-C3 96.1°; 4d<sup>Ph</sup>: N1-C1-C2-C3 69.3°) while the C-C bond is significantly elongated to 1.485(2) ( $4c^{tBu}$ ) and 1.510(7) Å  $(4d^{tBu})$ . This rotation motion might be interesting in respect to an application as electrochemical switch (vide infra). Importantly, the neutral compounds 2 and dications 4 not only feature strong UV-vis absorptions, but also show fluorescence properties, rendering them suitable for PET processes (see SI). The emission wavelengths for the dications are in a range of 458 nm (4dPh) to 565 nm (4b<sup>Ph</sup>) (see SI). Note, 2,4,6-triphenylpyrylium tetrafluoroborate shows an emission band at 472 nm.

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**Figure 9.** X-ray solid-state structures of the dications  $4c^{tBu}$  (left) and  $4d^{Ph}$  (right). Counter anions (SbF<sub>6</sub><sup>-</sup>) as well as hydrogen atoms omitted for clarity. Ellipsoids shown with 50% probability. Selected bond parameters in [Å] and [°]:  $4c^{tBu}$ : N1–C1 1.291(2), C1–C2 1.485(2), C2–C3 1.392(2), C3–C4 1.380(2), N1–C1–C2–C3 96.1;  $4d^{Ph}$ : N1–C1 1.337(6), C1–C2 1.510(7), C2–C3 1.380(7), C3–C4 1.375(7), N1–C1–C2–C3 69.3.

Additionally, we generated enantiomerically pure pyrylium/carbene hybrids. For this purpose we chose the combination of chiral menthyl substituted cyclic (alkyl)aminocarbene  $M^{\text{enth}}CAAC$ ,<sup>26</sup> with 2,6-diphenylpyrylium  $1^{Ph}$  (Scheme 4).

Scheme 4. Synthesis of chiral  $2e^{Ph}$  and its oxidation-states. (inset top right: X-ray solid-state structure of  $2e^{Ph}$ ; inset bottom left: X-band EPR spectrum of  $3e^{Ph}$  (simulated parameters: a(N): 4.81 G; a(H): 1.22 G).



Following the above established synthesis,  $2e^{Ph}$  can be isolated as intense red solid in 52% yield in a single-step. Interestingly, in the X-ray solid-state structure the menthyl moiety, which is usually used as sterically confined bulky group,<sup>40</sup> is widened away from the pyran moiety, as a result of the repulsion between the Hatom in the 3-position with the menthyl moiety. CV measurements ( $E_1^0 = -0.41 \text{ V}$ ;  $E_2^0 = 0.03 \text{ V}$  against Fc/Fc<sup>+</sup> see Figure S20) give similar data compared to diethyl-CAAC ( $2c^{Ph}$ ).  $2e^{Ph}$  can be conveniently oxidized with one equivalent of AgSbF<sub>6</sub> to afford the stable, enantiomerically pure, red colored radical cation  $3e^{Ph}$ or oxidized with two equivalents of AgSbF<sub>6</sub> to obtain the chiral yellow colored dication  $4e^{Ph}$ .

In a next step, we investigated preliminary applications for this new hybrid class. First we demonstrated the use as electrochemical switch with color being an output function. By applying a time dependent current [cycles of 300s at each +0.2 V/-0.8V and +0.2 V/+0.9V, see SI for more details] to solutions of  $2c^{Ph}$  we could selectively and reversibly switch between three different colors correlating to the neutral, radical and dicationic species (Figure 10).<sup>41</sup> Importantly, while photo switches typically can only vary between two different colors (on or off), we can selectively address three different colors depending on the potential applied. Moreover, switching between neutral and dicationic form also goes in hand with a fixed and flexible rotation of the central C-C bond, which translates into a non-directed motion. Obviously, in case of chiral  $4e^{Ph}$  it would be interesting to transfer this motion into a directed pathway.



Figure 10. Electrochemical switching of  $2c^{Ph}$  between neutral (black) – radical (red) and radical (red) – dication (blue).

Finally, we focused on the application of the hybrid molecules as photo-excited oxidants or reductants, as both the neutral ( $2^{Ph}$ ) and dicationic redox-states ( $4^{Ph}$ ) feature strong UV-vis absorptions and fluorescence. Importantly, as the ground-state reduction potentials of the dications [ $E_2 = +0.33$  ( $4a^{Ph}$ ) to +0.6 ( $2d^{Ph}$ ) vs. SCE] are significantly more positive compared to the well-known 2,4,6-triphenylpyrylium salt [-0.32 V vs. SCE],<sup>19</sup> the excited state reduction potentials of the dicationic pyrylium salts (4c) are remarkably high and clearly succeed the already very high oxidizing power of standard pyrylium salts. In a first approximation the excited state reduction potential ( $E_{red}^*$ ) of the dications 4 can be calculated according to Eq. I:

$$E_{red}^*[4^*/3] = E_{red}[4/3] + \Delta E_{excit}[3/4^*]$$
 (I)

While the first reduction potential  $E_{red}$  can be obtained by cyclic voltammetry measurements (E<sub>2</sub> in eV), the excitation energy  $\Delta E_{excit}$  can be obtained from the fluorescence spectra (more precisely from the crossing point of normalized absorption and fluo-

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rescence). This leads to all dications 4 exhibiting an excited state reduction potential of  $E_{red}^* > 2.5 \text{ V}$  [~ 2.8 eV (4a<sup>Ph</sup>), ~ 2.9 eV  $(4b^{Ph})$ , ~ 3.09  $(4c^{Ph})$ , ~ 2.5 eV  $(4d^{Ph})$ . In order to test the strong photo-excited oxidants we selected a known pyrylium photocatalyzed Diels-Alder (D.-A.) reaction, in which the excited state photo-catalyst oxidizes an alkene to its radical cation triggering an electron-transfer mediated hetero-D.-A. reaction (Scheme 5).<sup>[42]</sup> Upon irradiation of N-benzylideneaniline (5) and trans-anethole (6) in the presence of catalytic amounts (10 mol%)  $2d^{Ph}$  with a blue light-emitting diode (LED,  $\lambda_{exc.}$  390 nm), we could isolate the desired product 7 in 60% yield as a 5:1 mixture of two diastereomers (7/7'). However, importantly, the control experiment without light at 60°C gave nearly identical results, indicating that in the presence of 2d<sup>Ph</sup> the reaction is not photo-chemical induced, but instead 2d<sup>Ph</sup> acts as a strong Lewis-acid triggering the reaction. Note, the thermal control experiment utilizing 2,4,6triphenylpyrylium BF4 did not lead to the desired D.A. product, highlighting the difference of mono vs. dicationic pyrylium salts. This result clearly demonstrates the high Lewis acidity of the dicationic ground-state of 4, which has to be considered developing photo-catalytic reactions with such systems.

Scheme 5. Lewis-acid catalyzed hetero-D.A. reaction.



Importantly, classical pyrylium salts are exclusively excited state oxidants, however, the existence of three stable oxidation states in the pyrylium/carbene adducts, also allows to develop excited state reductants. Moreover, as neutral **2a-2d** can be widely tuned in their ground state reducing properties (Figure 2), we selected **2c** as a moderate ground state reductant [E<sub>1</sub> = + 0.12 V vs. SCE]. In contrast to **2a** and **2b**, which both feature more negative redox potentials, **2c** is stable in air and therefore more convenient to use. **2c** shows two strong UV-vis absorptions centered at  $\lambda_{abs} = 388$  nm ( $\varepsilon = 49422$  M<sup>-1</sup>cm<sup>-1</sup>) and 406 nm ( $\varepsilon = 53176$  M<sup>-1</sup>cm<sup>-1</sup>) (with fluorescence at  $\lambda_{emis} = 561$  nm). In analogy to Eq. 1, the excited state oxidation potential of **2** can be calculated according to Eq. II:

$$E_{ox}^{*}[2^{*}/3] = E_{ox}[2/3] - \Delta E_{excit}[3/2^{*}]$$
 (II)

Applying Eq. II in case of  $2c^{Ph}$  leads to  $E_{ox}^* \sim -2.4$  eV, indicating  $2c^{Ph}$  to be a very powerful excited state reductant. In order to investigate the strong photo-induced oxidation potential we studied the stoichiometric dehalogenation of arvl halides, which is a classic transformation for super-electron donors.9,43 Typically, aryl iodides are utilized in photo-redox catalysis, as aryl bromides, due to their more negative reduction potentials, remain very challenging substrates. Importantly, upon 12 h irradiation of ethyl 4-bromobenzoate (8) in the presence of one equivalent of  $2c^{Ph}$  with a blue LED ( $\lambda_{exc.}$  390 nm) in DMF, we observed the formation of the reductive dehalogenation product ethyl benzoate (9) in 78% yield (Scheme 6). Control experiments either under exclusive thermal conditions (no light at 60°C), or without  $2c^{Ph}$ , showed no conversion and clearly demonstrates the high reducing power of photo-excited 2c<sup>Ph</sup>. As proof of concept, also the more challenging 4-bromo-1,1'-biphenyl (10), bearing no electronwithdrawing group, could be reduced with photo-excited  $2c^{Ph}$  in 54% yield.

**Scheme 6**. Reductive photo-excited dehalogenation. Yields determined by GC/MS analysis with calibration against an internal standard.



Recently, König et al. demonstrated a new concept in photocatalysis using the energy of two photons in one catalytic cycle.<sup>[44]</sup> In this case, utilizing a compound featuring two intensely colored oxidation states, an excited radical anion was generated acting as strong electron donor. Inspired by this approach, we reasoned that in our system radical cation 3 might also be photoexcitable and in its excited state oxidize a sacrificial electron donor such as Et<sub>3</sub>N to regenerate electron rich neutral 2 (Scheme 7).<sup>[45]</sup> In this case a full catalytic! cycle could be constructed which involves two single photon absorption processes on two different oxidation states (Scheme 7). In contrast to König's system, which proceeds through an excited radical anion, the strong reducing power in our system would be harnessed from a neutral excited state as a result of the electron rich ground state of 2. Radical cation  $3c^{Ph}$  shows an intense absorption at a similar energy  $[\lambda_{abs} = 394 \ (\epsilon = 18601 \ \text{M}^{-1} \text{cm}^{-1})]$  compared to the neutral species 2c<sup>Ph</sup> and therefore is likely to be excitable under identical experimental conditions at the same wavelength as neutral 2cPh (see SI).

**Scheme 7**. Mechanistic hypothesis for a catalytic cycle involving two photon induced SET reactions.



In order to investigate such a catalytic process as outlined in Scheme 7, we performed the reaction of bromo ester 8 and a catalytic amount  $2c^{Ph}$  (10 mol%) in the presence of excess Et<sub>3</sub>N (20 eq.) as sacrificial electron donor (Scheme 8). After 12 h irradiation with a LED ( $\lambda_{exc}$ . 390 nm) we could observe full conversion to give dehalogenation product 9 in 87% yield. In a next step we tried more challenging catalytic reduction reactions. The reaction of 4-bromo-1,1'-biphenyl 10 under identical reaction conditions, gave the desired dehalogenation product in 62% yield. Remarkably, we were not only able to cleave the Ar-X bonds, but also to reductively cleave a sulfonamide. Under the non-

optimized reaction conditions we could observe full conversion of indolesulfonamide to give indole in 85% yield. Note, sulfonamides have very negative reduction potentials, typically around -2 V vs. SCE and are traditionally cleaved by alkali metals.<sup>[46]</sup> It should be highlighted that we can deprotect catalytically in the presence of a sacrificial electron donor under mild reaction conditions, while for the same deprotection reaction, even neutral organic super-electron donors require super-stoichiometric (6 equivalents) reducing agents at forcing conditions (110°C).<sup>[46]</sup> Furthermore, we could also trap the proposed transient arylradical by addition of N-methyl pyrrole (20 eq.) to form the C-C coupled 2-aryl pyrrole 14 in 71% yield. Interestingly, the reductive dehalogenation product 9 was formed in only minor quantities (6%) indicating a sufficient trapping by the pyrrole. Control experiments showed no reaction of bromo ester 8 under identical thermal conditions (60°C) but exclusion of light. Importantly, irradiation without photo catalyst 2cPh under otherwise identical conditions, also did not lead to any conversion, clearly proving the necessity of photo catalyst  $2c^{Ph}$ . We are currently investigating the mechanism and scope of these new photo catalyzed reactions, not ruling out the option of even three oxidation states being mechanistically involved.

**Scheme 8**. Catalytic dehalogenation (*i-ii*), reductive cleavage of a N-tosyl group (*iii*) and a C-C bond forming reaction (*iv*). Yields determined by HPLC analysis (**9**, **11**) and isolated yields (**13**, **14**).



#### CONCLUSIONS

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In summary we report an easy, fast and modular approach towards a library of carbene/pyrylium hybrids which feature three stable redox-states, rendering them suitable as novel class of redox-switch. The choice of carbene can modulate the electrochemical properties by over 1 V, while the choice of pyrylium can control the photo-physical properties proven by strong UV-VIS transitions coupled with fluorescence. There is an excellent correlation of the redox-properties with the  $\pi$ -accepting properties of the carbene, which can be fitted by linear regression with the <sup>77</sup>Se-NMR  $\pi$ -accepting scale. The one electron oxidation gives access to stable radical cations from which we could structurally characterize the first stable monomeric pyranyl radical. While typically new main-group radicals are stabilized with only one type of carbene, we present a comprehensive study on the influence of radical stabilization as a function of carbene. Furthermore, we could show that these hybrid molecules can be excited by light and represent either very strong oxidants in their dicationic oxidation state, but also extraordinary strong reductants in their neutral

redox state. The later could be clearly demonstrated by stoichiometric photo-induced dehalogenation reactions. More importantly, the stability of the radical cation oxidation state allows subsequent excitation processes, leading to catalytic cycles involving strong neutral photo-excited organic reductants. The simple synthetic access and ability to tune the redox and photo-physical properties of the carbene/pyrylium hybrids, should allow to specifically design novel photo-catalysts based on the here presented approach. Furthermore, as pyrylium cations are also an important synthetic precursor and easily transformed into pyridines, phosphinines etc., the dications offer a broad range of functionalization strategies to new exciting molecules, which is under current investigation.

#### **EXPERIMENTAL SECTION**

General procedure for the synthesis of 2: To a suspension of pyrylium tetrafluoroborate salt (1.0 eq.) in THF was added under inert conditions at room temperature a solution of free carbene (2.05 eq.). The solution was stirred for 16h, the solvent evaporated under reduced pressure and the product extracted twice with Et<sub>2</sub>O. Evaporation of the solvent gives the desired pyrylium/carbene hybrid 2. Single crystals can be obtained from a saturated pentane or Et<sub>2</sub>O solution upon cooling to -30°C. Note, the remaining solid (protonated carbene can be recycled with base to give the free carbene). General procedure for the synthesis of **3**: To a solution of neutral 2 (1.0 eq) in CH<sub>2</sub>Cl<sub>2</sub> or THF was added at room temperature AgSbF<sub>6</sub> (1 eq). The solution was stirred for 1h, then filtered and the solvent removed to give the corresponding radicals 3. General procedure for the synthesis of 4: To neutral 2 (1.0 eq.) in CH<sub>2</sub>Cl<sub>2</sub> was added at 0°C dropwise a solution of  $NOSbF_6$  (2.0 eq.) dissolved in CH<sub>3</sub>CN. [Alternatively, AgSbF<sub>6</sub> (2eq.) was added directly as solid]. The solution was warmed up to room temperature, stirred for 1h and the solvent removed under reduced pressure. The remaining solid was washed with Et<sub>2</sub>O and dried under reduced pressure to give the desired product 4.

Synthesis and characterization data for selected compounds: 2a<sup>tBu</sup>: To a suspension of 2,6-di-tert-butylpyrylium tetrafluoroborate 1<sup>tBu</sup> (200 mg, 0.71 mmol, 1.0 eq.) in THF (15 mL) was added free carbene a (434 mg, 1.43 mmol, 2.0 eq.). The yellow/orange solution was stirred for 14h and the solvent evaporated under reduced pressure. The obtained solid was extracted with pentane (15 mL + 5 mL) and filtered. The solvent of the orange solution was removed under reduced pressure to give 2atBu as orange solid (275 mg, 0.55 mmol, 78%). Single crystals suitable for X-ray diffraction can be obtained by slow evaporation from a saturated pentane solution. m.p. 155°C; <sup>1</sup>H-NMR (d<sup>8</sup>-THF, 400MHz, 208K): 6.97 (s, 4H), 6.15 (s, 2H), 4.21 (s, 2H), 2.27 (s, 6H), 2.24 (s, 12H), 0.63 (s, 18H); <sup>13</sup>C-NMR (d<sub>8</sub>-THF, 100MHz, 298K): 159.4, 151.2, 138.0, 137.9, 131.3, 129.5, 116.6, 96.9, 93.9, 77.5, 35.1, 28.0, 21.3, 19.0; IR [cm<sup>-1</sup>]:  $\tilde{v} = 2961$ , 2913, 2864, 1614, 1578, 1480, 1457, 1392, 1280, 1223, 1156, 1086, 1033, 961, 919, 851, 755; HR-MS-ESI(+) calc. C<sub>34</sub>H<sub>45</sub>N<sub>2</sub>O<sup>+</sup> [M+H]<sup>+</sup> 497.3526; found 497.3527.

**2c<sup>Ph</sup>**: To a suspension of 2,6-di-phenylpyrylium tetrafluoroborate (200 mg, 0.62 mmol, 1.0 eq.) in THF (10 mL) was added the free carbene EtCAAC (392 mg, 1.25 mmol, 2.0 eq.) and the intensely orange/red solution stirred for 14h. The solvent was removed under reduced pressure and the remaining solid extracted with Et<sub>2</sub>O (20 mL + 5 mL). The solvent was removed under reduced pressure to give 2cPh as an intense red solid (278 mg, 0.51 mmol, 82%). m.p. 200°C; <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>, 400MHz, 298K): 7.80 (d, J = 7.4 Hz, 2H), 7.36-7.26 (m, 3H), 7.22-7.14 (m, 6H), 7.08-7.01 (m, 2H), 6.63 (d, J = 2.0 Hz, 1H), 5.46 (d, J = 2.0 Hz, 1H), 3.40 (sept., J = 6.8 Hz, 2H), 2.08-1.97 (m, 2H), 1.84-1.74 (m, 2H), 1.80 (s, 2H), 1.27 (d, J = 6.7 Hz, 6H), 1.23 (d, J = 6.7 Hz, 6H), 1.07 (s, 6H), 1.03 (t, J = 7.4 Hz, 6H); <sup>13</sup>C-NMR (d<sub>8</sub>-THF, 100 MHz, 298K): 149.7, 145.1, 144.5, 141.6, 138.4, 136.0, 135.4, 128.7, 128.5, 127.3, 127.0, 125.2, 123.7, 123.7, 96.4, 63.9, 50.6,

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47.4, 32.8, 30.1, 29.1, 25.1, 24.4, 9.2; IR  $[cm^{-1}]$ :  $\tilde{v} = 2962$ , 2868, 1590, 1550, 1491, 1457, 1329, 1279, 1188, 1074, 1019, 930, 756; UV-VIS [nm]: in THF: 261 ( $\varepsilon = 46372 \text{ M}^{-1} \text{ cm}^{-1}$ ), 388 ( $\varepsilon = 49422 \text{ M}^{-1} \text{ cm}^{-1}$ ), 406 ( $\varepsilon = 53176 \text{ M}^{-1} \text{ cm}^{-1}$ ), 461 ( $\varepsilon = 9085 \text{ M}^{-1} \text{ cm}^{-1}$ ); Emission [nm]: 562; HR-MS-ESI(+) calc. C<sub>39</sub>H<sub>47</sub>NO<sup>+</sup> [M]<sup>+</sup> 545.3652; found 545.3653.

5 3a<sup>tBu</sup>: To a mixture of solids of 2a<sup>tBu</sup> (16 mg, 0.03 mmol) and 6 AgSbF<sub>6</sub> (11 mg, 0.03 mmol, 1.0 eq.) was added CH<sub>2</sub>Cl<sub>2</sub> (5 mL) at 7 room temperature and stirred for 30min. The solution was filtered 8 and the solvent evaporated under reduced pressure to give  $3a^{Ph}$  as red solid (17 mg, 0.02 mmol, 72%). m.p. > 150°C; X-band EPR g 9 = 3359 G (2xN: 2.63G; 2xH: 1.06G; 2xH: 0.50G); IR  $[cm^{-1}]$ :  $\tilde{v}$  = 10 2961, 2924, 2868, 1677, 1616, 1559, 1484, 1461, 1365, 1259, 11 1230, 1083, 1015, 797; HR-MS-ESI(+) calc. C<sub>34</sub>H<sub>45</sub>N<sub>2</sub>O<sup>+</sup> [M+H]<sup>+</sup> 12 497.3526; found 497.3521.

13 3cPh: To a solution of 2cPh (100 mg, 0.18 mmol, 1.0 eq.) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was added AgSbF<sub>6</sub> (63 mg, 0.18 mmol, 1 eq.) and 14 the intense dark red solution stirred for 30 min. The solution was 15 filtered and the solvent evaporated to give 3cPh as dark red solid 16 (98 mg, 0.13 mmol, 70%). m.p. > 150°C; X-band EPR g = 3362 17 G (1xN: 5.10 G; 2xH 0.68G), IR [cm<sup>-1</sup>]:  $\tilde{v} = 2974$ , 2934, 2874, 18 1632, 1463, 1446, 1388, 1348, 1249, 1153, 1130, 946, 904, 766, 19 654; UV-VIS [nm]: in CH<sub>2</sub>Cl<sub>2</sub>: 269 ( $\varepsilon = 19137 \text{ M}^{-1}\text{cm}^{-1}$ ), 394 ( $\varepsilon =$ 20 18601 M<sup>-1</sup>cm<sup>-1</sup>), 503 (17496); HR-MS-ESI(+) calc. C<sub>39</sub>H<sub>47</sub>NO<sup>+</sup> [M]<sup>+</sup> 545.3652; found 545.3650. 21

4a<sup>tBu</sup>: To a solution of 2a<sup>tBu</sup> (47 mg, 0.09 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 22 mL) was added AgSbF<sub>6</sub> (65 mg, 0.19 mmol, 2.0 eq.) and the dark 23 suspension stirred for 30 min under exclusion of light. The solu-24 tion was filtered and the solid washed with CH2Cl2. The remain-25 ing solid was extracted with CH<sub>3</sub>CN (10 mL) to give a yellow 26 solution. The solvent was removed under reduced pressure to give 4a<sup>tBu</sup> as yellow solid (57 mg, 0.06 mmol, 65%). m.p. > 250°C; 27 <sup>1</sup>H-NMR (CD<sub>3</sub>CN, 400MHz, 298K): 8.26 (s, 2H), 7.27 (s, 4H), 28 7.03 (s, 2H), 2.40 (s, 6H), 2.10 (s, 12H), 1.22 (s, 18H); <sup>13</sup>C-NMR 29 (CD<sub>3</sub>CN, 100MHz, 298K): 192.2, 145.0, 144.5, 135.9, 135.5, 30 131.7, 130.8, 130.5, 118.3, 40.8, 28.2, 21.1, 17.9; IR  $[cm^{-1}]$ :  $\tilde{v} =$ 31 3164, 3148, 2975, 1627, 1615, 1562, 1547, 1485, 1438, 1384, 32 1366, 1228, 1197, 1147, 1036, 869, 839; HR-MS-ESI(+) calc. C<sub>35</sub>H<sub>47</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> [M+CH<sub>3</sub>O<sup>-</sup>]<sup>-</sup> 527.3632; found 527.3634. 33

4cPh: To a solution of 2cPh (42 mg, 0.077 mmol) in CH2Cl2 (5 34 mL) was added at 0°C a solution of NOSbF<sub>6</sub> (41 mg, 0.15 mmol, 35 2 eq.) (the solution turns from bright red to dark red to yellow 36 upon dropwise addition of the NOSbF<sub>6</sub> solution). The solution 37 was stirred for 10 min at 0°C, then 10 min at room temperature 38 and the solvent removed under reduced pressure. The resulting 39 solid was washed with Et2O (10 mL) followed by CH2Cl2/Et2O (5 mL/ 5mL). The remaining solid was dried under reduced pressure 40 to give 4c<sup>Ph</sup> (67 mg, 0.066 mmol, 86%). m.p. > 200°C; <sup>1</sup>H-NMR 41 (CD<sub>3</sub>CN, 400MHz, 298K): 8.37 (d, *J* = 7.8 Hz, 4H), 8.06 (s, 2H), 42 8.00-7.93 (m, 2H), 7.84-7.77 (m, 4H), 7.56-7.50 (m, 1H), 7.41 (d, 43 J = 7.8 Hz, 2H), 2.78 (sept., J = 6.4 Hz, 2H), 2.74 (s, 2H), 2.29-44 2.11 (m, 4H), 1.64 (s, 6H), 1.45 (d, J = 6.3 Hz, 6H), 1.17 (t, J = 7.3 Hz, 6H), 1.07 (d, J = 6.4 Hz, 6H); <sup>13</sup>C-NMR (CD<sub>3</sub>CN, 45 100MHz, 298K): 174.1, 152.5, 145.0, 138.9, 133.5, 131.6, 130.8, 46 128.3, 127.9, 116.6, 88.8, 61.6, 43.8, 30.9, 30.5, 29.5, 27.1, 24.6, 47 10.0; UV-VIS [nm]: in CH<sub>2</sub>Cl<sub>2</sub>: 471 ( $\epsilon = 25051 \text{ M}^{-1}\text{cm}^{-1}$ ), 297 ( $\epsilon$ 48 = 20933 M<sup>-1</sup>cm<sup>-1</sup>), 268 ( $\epsilon$  = 24322 M<sup>-1</sup>cm<sup>-1</sup>); Emission [nm]: in 49 CH<sub>2</sub>Cl<sub>2</sub>: 506, 524; IR [cm<sup>-1</sup>]:  $\tilde{v} = 3116$ , 2979, 2944, 2883, 1639, 50 1612, 1489, 1456, 1425, 1370, 1267, 1183, 1103, 998, 898, 870, 51 781; HR-MS-ESI(+) calc. C<sub>40</sub>H<sub>50</sub>NO<sub>2</sub><sup>+</sup> [M+CH<sub>3</sub>O<sup>-</sup>]<sup>+</sup> 576.3836; 52 found 576.3827.

53 Irradiation reactions were performed at 390 nm using a LED
54 photo-redox light Kessil PR 160 (390nm) with maximum 40W.
55 The light was placed typically 5-8cm in front of a vial.
55 Statistic light promoted dehalemention reactions: A

Stoichiometric light-promoted dehalogenation reactions: A
3 mL screw cap vial was charged with solid 2c<sup>Ph</sup> (21.8 mg, 0.04
mmol, 1.0 eq.) and a solution of the substrate (0.04 mmol, 1.0 eq.)
in 1 mL degassed DMF. The reaction mixture was irradiated at
390 nm for 12 h and a sample was taken for GC/MS analysis. The

solvent was carefully evaporated under reduced pressure and the sample redissolved in 1 mL EtOAc. The yield was determined by integration of the resulting spectra in comparison to a previously measured standard calibration curve.

**Photocatalytic deprotection reaction:** In a 3mL screw cap vial, to a solution of  $2c^{Ph}$  (6.5 mg, 0.012 mmol, 10 mol%) in 1 mL degassed DMF was added a solution of N-tosylindole (0.12 mmol, 1.0 eq.) in 2 mL degassed DMF. The reaction mixture was irradiated at 390 nm. After 12 h the solvent was evaporated under reduced pressure and the residue purified by flash column chromatography (SiO<sub>2</sub>; hexanes:EtOAc = 20:1) to give the desired product **13** as a colorless solid (11.2 mg, 0.095 mmol, 85%). Spectroscopic data are in good agreement with previous literature reports.

Radical trapping experiment: To a solution of 4'bromoethylbenzoate (27.5 mg, 120  $\mu$ mol, 1.0 eq) and  $2c^{Ph}$ (6.6 mg, 0.012 mmol, 10 mol%) in 2.5 mL DMF was added triethylamine (334 µL, 2.4 mmol, 20 eq.) and N-methylpyrrole (213 µL, 2.40 mmol, 20 eq.). After irradiating the reaction mixture at 390 nm for 12 h a 200 µL sample was subjected to GC/MS. The solvent was removed under reduced pressure and the residue purified by flash column chromatography (SiO2; hexanes: EtOAc = 20:1) to give the desired product 14 as slightly yellow solid (18.3 mg, 0.079 mmol, 71%). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400MHz, 298K): 8.06 (d, J = 8.7 Hz, 2H), 7.47 (d, J = 8.7 Hz, 2H), 6.77-6.75 (m, 1H), 6.33 (dd, J = 3.7 Hz, 1.8 Hz, 1H), 6.22 (dd, J = 3.7 Hz, 2.7 Hz, 1H), 4.39 (q, J = 7.1 Hz, 2H), 1.41 (t, J = 7.1 Hz, 3H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100MHz, 298K): 166.6, 137.8, 133.7, 129.9, 128.5, 128.0, 125.2, 110.1, 108.4, 61.1, 35.5, 14.5. The spectral data is in good agreement with the reported literature.

Electrochemical measurements: 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 a Ag/AgNO3 reference electrode (0.01 M AgNO3 in 0.1 M nBu4NPF6 in CH3CN) (for the setup see also Figure S3). The reference electrode was freshly prepared by using a fritted sample holder, which was activated by storing in a CH<sub>3</sub>CN 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 AgNO<sub>3</sub>/ 0.1 M nBu<sub>4</sub>NPF<sub>6</sub> solution in CH<sub>3</sub>CN and a silver wire. The working electrodes were prepared according to the following procedure before each scan: 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 3neck cell was emptied and a specific amount of compound dissolved in 3mL THF added and the CV measured. The system was furthermore referenced internally by addition of diacetyl ferrocene. The values obtained were corrected against ferrocene (diacetyl ferrocene to ferrocene  $\Delta E = 430$  mV in THF), which was determined under identical measurement conditions by measuring ferrocene against diacetylferrocene (see Figure S4).

**Spectro-electrochemical measurements** were recorded with a Gamry Instruments Reference 600. The samples were measured in CH<sub>2</sub>Cl<sub>2</sub> starting from the neutral compounds, containing a three electrode setup (platinum wire, platinum net and Ag/AgNO<sub>3</sub> 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 S43. 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 CH<sub>3</sub>CN 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 AgNO<sub>3</sub>/ 0.1 M nBu<sub>4</sub>NPF<sub>6</sub> solution in CH<sub>3</sub>CN and a silver wire. The light source was a deuterium/tungsten light source. 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 1V) by a step size of 2.5 mV/s. Electrochemical switch: For the application as an electrochemical switch the same setup was used as for the spectroelectrochemistry. An initial CV (40 mV/s) of a 55 µM solution in 0.7 mL CH<sub>2</sub>Cl<sub>2</sub> of **2c<sup>Ph</sup>** was recorded to determine the oxidation potentials in the spectroelectrochemistry cell. The solution was replaced with a fresh solution of 2c<sup>Ph</sup> under identical conditions and a UV-VIS spectrum taken every 20 s, while the potential was adjusted to +0.2V for 300 s (radical cation 3cPh) then to -0.8V for 300 s (neutral 2c<sup>Ph</sup>); followed by +0.2V for 300 s (all potentials against the Ag/AgNO<sub>3</sub> reference). This procedure was repeated again and then the potential changed (3 times) between +0.2V for 300 s and +0.9V (dication 4c<sup>Ph</sup>). In a first approximation the diffusion of solution in the UV-VIS cell is fairly slow (> 10min). However, there is very small diffusion between the volume of the light beam/platinum net space to the solvent volume of the space in which counter-electrode and reference electrode are positioned. This leads to a slight decrease of the radical cation concentration over time as neutral compound diffuses into the cell. In order to minimize this effect the solution amount above the net was also minimized, the only limitation that the platinum counter electrode and the reference cell were still in contact with the solution. For the analysis of the switch data, the absorption at three different wavelengths was detected: 406 nm for neutral 2c<sup>Ph</sup>, 503 nm for radical cation  $3c^{Ph},$  and 471 nm for dication  $4c^{Ph}$  (see UV-VIS data). The raw data for the absorption is plotted in Figure S44. The absorption was normalized from 0 to 1.

## 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 http://pubs.acs.org.

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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; PET photo-induced electron transfer; BET back electron transfer; hfc, hyperfine couplings.

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