



Superbases Hot Paper

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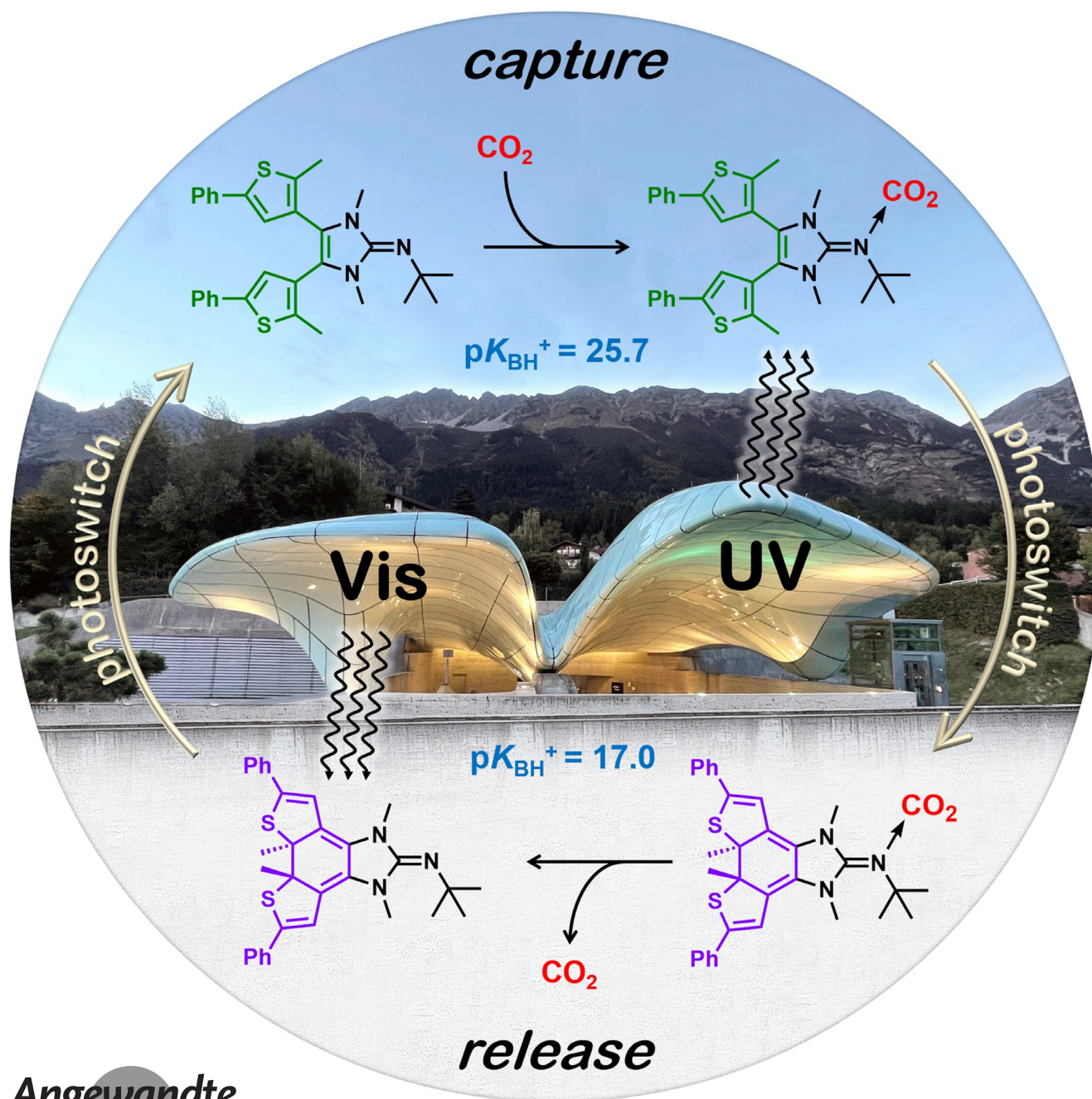
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Photoswitchable Nitrogen Superbases: Using Light for Reversible Carbon Dioxide Capture

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Dedicated to Professor Gerhard Erker on the occasion of his 75th birthday

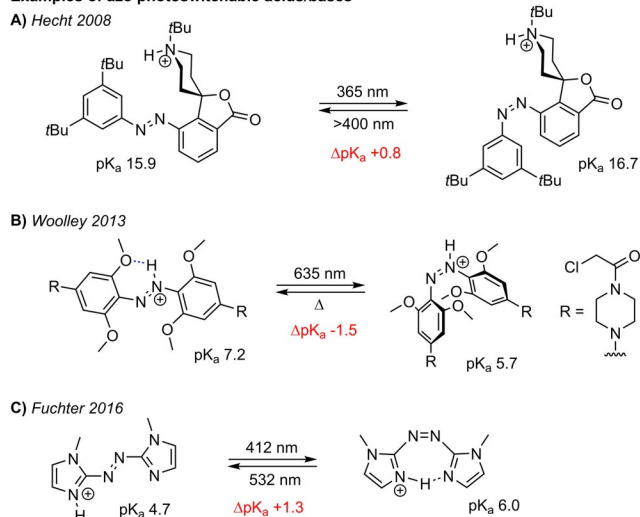


Abstract: Using light as an external stimulus to alter the reactivity of Lewis bases is an intriguing tool for controlling chemical reactions. Reversible photoreactions associated with pronounced reactivity changes are particularly valuable in this regard. We herein report the first photoswitchable nitrogen superbases based on guanidines equipped with a photochromic dithienylethene unit. The resulting *N*-heterocyclic imines (NHIs) undergo reversible, near quantitative electrocyclic isomerization upon successive exposure to UV and visible irradiation, as demonstrated over multiple cycles. Switching between the ring-opened and ring-closed states is accompanied by substantial pK_a shifts of the NHIs by up to 8.7 units. Since only the ring-closed isomers are sufficiently basic to activate CO_2 via the formation of zwitterionic Lewis base adducts, cycling between the two isomeric states enables the light-controlled capture and release of CO_2 .

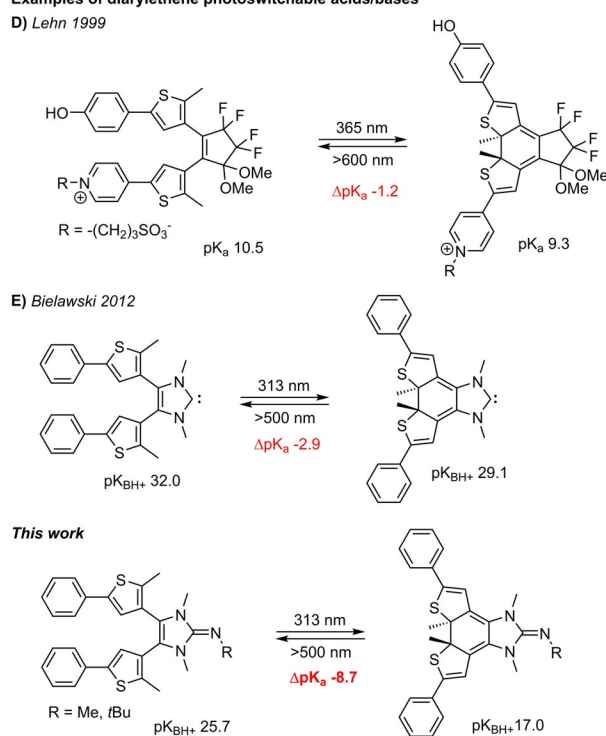
Introduction

The effectiveness of light in initiating and regulating complex molecular and biochemical processes is evident, for example, in photoresponsive reactions such as photosynthesis^[1] or vision.^[2] Light is non-invasive, provides excellent temporal and spatial control and can be precisely regulated with an appropriate light source. The remote-control of chemical reactions using light is therefore particularly attractive.^[3] In this context, the development of photoswitchable acids and bases has attracted considerable attention,^[4–10] as they enable external control of pH-dependent chemical/biochemical processes or can act as photoswitchable catalysts.^[4,11] Apart from photoresponsive molecules, whose acidity/basicity is irreversible altered by the release of a caged proton upon irradiation with light,^[11,12] a common approach for photoswitchable bases and acids is based on the reversible *cis-trans* photoisomerization of compounds containing azo^[4,5,7–9,13] or ethene groups^[6,10,14] (Scheme 1). Between the two configurational isomers, pK_a shifts of up to 1.5 units were

Examples of azo photoswitchable acids/bases



Examples of diarylethene photoswitchable acids/bases



Scheme 1. Examples for photoswitchable organic bases and their corresponding basicities [pK_a values determined in water (**B**, **C**), 5:2 methanol/water (**D**) and acetonitrile (**A**); pK_{BH^+} values (**E**, this work {depicted for $R = tBu$ }) calculated using PW6B95-D3//TPSS-D3/def2-TZVP + COSMO-RS(acetonitrile)].

observed due to the stabilization of one isomer by hydrogen bonding interactions (Scheme 1 B,C) or on/off steric shielding of the basic site (Scheme 1 A). Another concept to modify basicity/acidity of chemical species takes advantage of the electronic changes that occur upon photocyclization of dithienylethene (DTE) derivatives. For example, Lehn and co-workers showed that the acidity of phenol can be

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modulated by 1.2 pK_a units by photochemically establishing or disrupting the electronic communication with an electron-withdrawing pyridinium group across a DTE backbone (Scheme 1D). Branda and co-workers showed that more significant reactivity changes were observed for DTE-based switchable acids/bases when the central ethene unit is directly involved.^[15] An effective system was obtained by incorporating the photochromic DTE unit into the backbone of imidazolium salts.^[16–20] The corresponding N-heterocyclic carbenes (NHCs)^[21,22] function as photoswitchable ligands,^[23] organocatalysts^[24,25] or for reversible activation of ammonia.^[21]

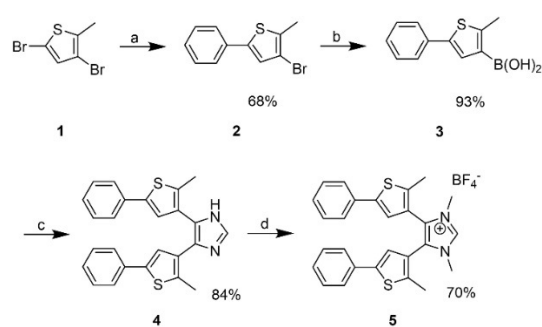
Recently, we have become interested in developing superbases capable of reversible CO₂ capture via zwitterionic adducts.^[26,27] This kind of low-energy bond formation is a promising way to activate and capture the relative inert CO₂ molecule.^[28] Since nitrogen bases have the advantage of being less sensitive towards oxidation with molecular oxygen and hydrolysis than carbon or phosphorus bases, we recently explored the fixation of CO₂ using N-heterocyclic Imines (NHIs) and showed that both the basicity of NHIs and the CO₂ binding energies are largely governed by the nature of the N-heterocycle. Accordingly, Lewis base adducts between CO₂ and NHIs with imidazoline backbone are sufficiently stable to be isolable, whereas the complexation of CO₂ with benzimidazoline-2-imines is endergonic.^[27] We therefore envisaged to synthesize photoswitchable NHIs based on the NHC-scaffold developed by Yam and Bielawski,^[16,18–20,25] which will allow switching between these two states and thus enable light-triggered reversible CO₂ capture (Scheme 1).

Using (sun)light to drive the capture and release of CO₂ is particularly attractive due to its abundance and facile usage. Photoresponsive systems capable of reversible CO₂ uptake have been reported based on reversible structural changes of metal-organic frameworks (MOFs),^[29] yet covalent CO₂ binding with photoswitchable bases is unknown.

Results and Discussion

The synthesis of photoswitchable imidazolium salts has been reported by Bielawski and co-workers.^[19,21] However, since Bielawski's original synthesis of the hexafluorophosphate derivative of **5** gives only a combined yield of 3.3% in 7 steps from expensive 2-methyl-5-phenylthiophene, we developed a new synthetic route by which the imidazolium salt **5** was synthesized in 5 steps and an overall yield of 32% starting from more readily available 2-methylthiophene (Scheme 2), which provided facile access to multiple grams of the imidazolium salt.

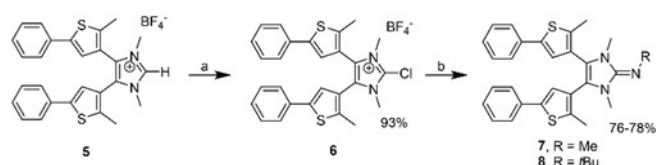
Following a literature procedure by Barbour and his co-workers,^[30] 3,5-dibromo-2-methylthiophene (**1**) was synthesized by bromination of 2-methylthiophene. The Suzuki coupling reaction between **1** and iodobenzene as coupling partner is selective and gave the desired 3-bromo-2-methyl-5-phenylthiophene **2** in good yield.^[31] The boronic acid **3** was prepared in a one-pot procedure with very good yield by subjecting **2** to lithium-halogen exchange, followed by boronylation and hydrolysis of the in situ formed boronic esters.



Scheme 2. Synthesis of the imidazolium salt **5**. a: *n*BuLi, B(O^{*t*}Bu)₃, THF, −78 °C to RT, then Pd(PPh₃)₄, PhI, ethylene glycol, aq. Na₂CO₃, 80 °C, 16 h; b: *n*BuLi, B(O*n*Bu)₃, THF, −78 °C to RT, then aq. HCl; c: Pd(PPh₃)₄, 4,5-diiodo-2,5-dihydro-1*H*-imidazole, K₂HPO₄, *n*Bu₄NBr, MeOH-H₂O, 120°, 16 h; d: MeI, K₂CO₃, MeCN, 80 °C, 16 h, then NaBF₄ in EtOH-H₂O.

A modified and optimized reaction procedure^[32] was adopted for making the imidazole scaffold **4**. Two-fold Suzuki coupling reaction between 4,5-diiodoimidazole and the boronic acid **3** was performed to form the desired dithienyl imidazole derivative **4**. The final imidazolium salt **5** was obtained in good yield by methylation of **4** with iodomethane in MeCN,^[19] followed by a crystallization through anion exchange by addition of a sodium tetrafluoroborate solution (for detailed procedure see ESI).

Following a protocol by Kunetskiy et al. for the synthesis of NHIs,^[33] we prepared the photoswitchable NHIs **7** and **8** starting from imidazolium salt **5** (Scheme 3). Deprotonation



Scheme 3. Synthesis of N-heterocyclic imines **7** and **8**. a: NaHMDS, C₂Cl₆, THF, −78 °C; b: MeNH₃Cl or *t*BuNH₂, KF, MeCN, RT, 3 d, then KO*t*Bu, THF.

of **5** gave the corresponding free carbene which was treated with hexachloroethane to afford the 2-chloroazolium salt **6** in very good yields. The KF-mediated coupling of **6** with methylammonium chloride or *tert*-butylamine in acetonitrile and subsequent deprotonation of the iminium salts (**7**HBF₄ and **8**HBF₄) gave the NHIs **7** and **8** as colorless solids in good yields. The NHIs **7** and **8** are soluble in common organic solvents including nonpolar media like *n*-hexane or Et₂O. The IR spectra show strong, characteristic absorption bands for the asymmetric ν_{as}(C=N) (**7**: 1656 cm^{−1}, **8**: 1685 cm^{−1}) and ν_{as}(C-S) (**7,8**: 689 and 755 cm^{−1}) stretching vibrations.

Both NHIs **7** and **8** undergo electrocyclic isomerization upon exposure to UV irradiation (λ_{irr} = 313 nm), while exposure to visible light (λ_{irr} = 520 nm) reversed the reaction. The NHIs can thus be switched reversibly between the open (**7o, 8o**) and closed (**7c, 8c**) form.

The UV/Vis spectra recorded for **7o** and **8o** dissolved in MeCN (Figure 1) are very similar to those of Bielawski's

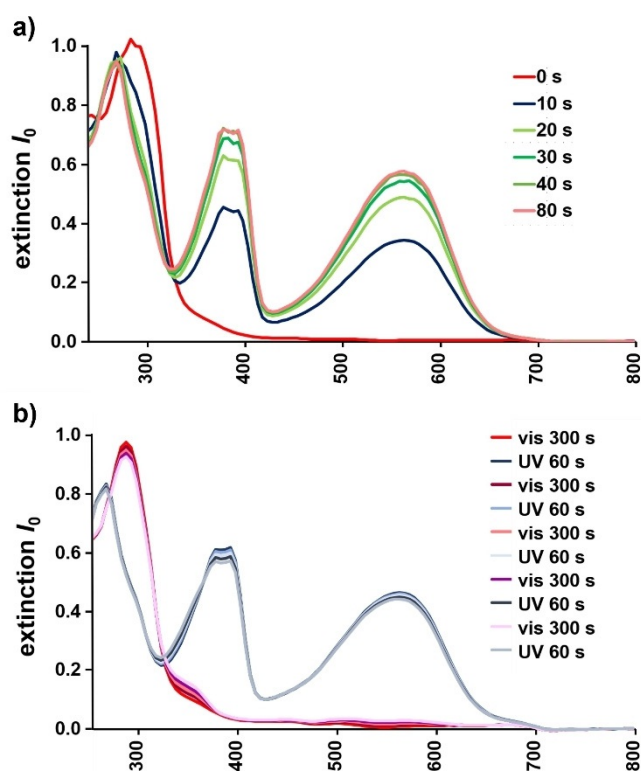


Figure 1. a) UV/Vis spectral changes of **7o** upon UV irradiation ($\lambda_{\text{irr}} = 313 \text{ nm}$). b) UV/Vis spectral changes of **7o** upon successive UV ($\lambda_{\text{irr}} = 313 \text{ nm}$, $t = 60 \text{ s}$) and visible-light irradiation ($\lambda_{\text{irr}} = 520 \text{ nm}$, $t = 300 \text{ s}$). Measured in MeCN ($[\text{7o}] = 7.1 \times 10^{-4} \text{ M}$).

photoswitchable NHCs.^[21] Intense absorption bands appear at 285 nm, which can be assigned to the $n \rightarrow \pi^*$ - and $\pi \rightarrow \pi^*$ transitions of the N-heterocycle and the thiophene system, respectively. Irradiation of a colorless solution of **7o** or **8o** with UV light (313 nm) resulted the development of an intensive purple color, as expected for an extended conjugated π system. Concomitantly, the intensity of the absorption bands at 285 nm decreased and two new bands appear in the UV/Vis spectra at 398 nm and 564 nm.^[34] Isosbestic points were detected at 337 nm, indicating that the photoisomerization proceeds without the formation of significant by-products and is therefore stoichiometric.^[35] After 40 s of UV irradiation, the spectral changes subsided. Subsequent irradiation of the solutions containing **7c** and **8c** with visible light (520 nm) for 300 s resulted in colorless solutions, and the initial UV/Vis spectra were restored. For fatigue resistance testing, the solution of **7** and **8** were irradiated cyclically with UV and visible radiation. The UV/Vis spectra show only minimal changes when switching between the open (**7o**) and closed state (**7c**) over several cycles (Figure 1B). Similar rapid switching and reversibility of photoisomerization was observed for imine **8** (Figure S39).

The photoisomerizations were further confirmed by ^1H NMR spectroscopy. In the ^1H NMR spectrum of **7o** in C_6D_6 the resonance for the thiophene CH protons is detected at 6.98 ppm and the resonance for the methyl groups at the endocyclic N atoms appears at 3.07 ppm (Figure 2). After irradiation of the NMR tube containing the solution at

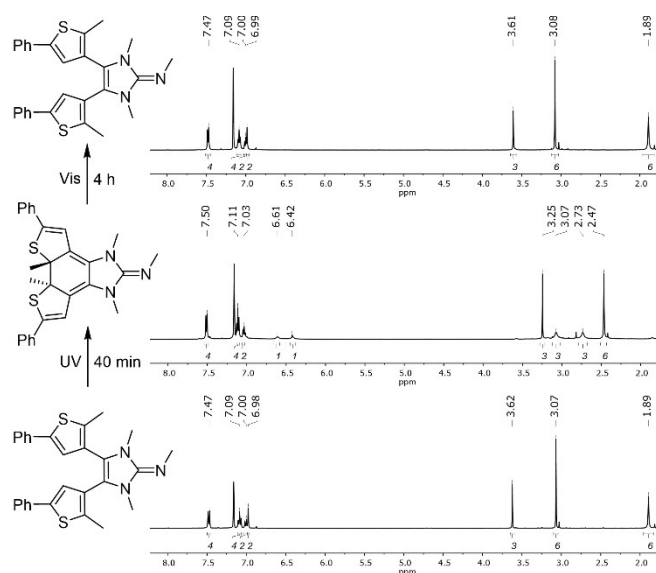


Figure 2. ^1H NMR spectra of **7o** in C_6D_6 (bottom), of **7c** after irradiation of the solution with UV light (313 nm) for 40 min (middle) and of **7o** after further irradiation of the solution with visible light (500 nm) for 4 h (top).

313 nm for 40 min, the solution turns deep purple and the ^1H NMR spectrum shows a new set of signals revealing the full conversion to **7c**. The resonances assigned to the thiophene CH protons (6.61/6.42 ppm) and the methyl groups at the endocyclic N atoms (3.07/2.73 ppm) are no longer magnetically equivalent. In addition, a significant shift was observed for the proton signals of the exocyclic methyl group and the thiophene-methyl groups from 3.62 ppm to 3.25 ppm and 1.89 ppm to 2.47 ppm, respectively. After exposure of the solution of **7c** for 4 h with light at 500 nm, the ^1H NMR spectrum of **7o** was recovered. Similarly, the photoinduced cyclization of **8** was observed upon irradiation with UV and visible light, and in the ^1H and ^{13}C NMR spectra in $\text{MeCN-}d_3$ different signals for **8o** and **8c** were detected (Figure S38). As shown by the NMR experiments, photoswitching between the two states is almost quantitative. Moreover, the closed form is stable for months in the absence of light at room temperature.

The molecular structures of **7HBF₄**, **8HBF₄**, **8o** and **8c** were established using single-crystal X-ray crystallography (Figure 3, Table 1).^[36] The thiophene rings of the open structures adopt antiparallel orientations and are almost orthogonal to the plane of the imidazole ring in the case of the iminium ions **7HBF₄** ($67.8^\circ/75.5^\circ$) and **8HBF₄** ($87.3^\circ/88.3^\circ$), while being more tilted towards the plane of the imidazole ring for the neutral NHI **8o** ($36.6^\circ/56.7^\circ$). The guanidine unit of the iminium ions exhibit very similar C–N bond lengths (**7HBF₄**: 1.339–1.356 Å; **8HBF₄**: 1.344–1.375 Å) rendering the delocalization of the positive charge in the imidazole ring. In contrast, the exocyclic N1–C2 bond in the neutral NHI **8o** (1.278 Å) is significantly shorter than the C2–N2 (1.384 Å) and C2–N3 (1.411 Å) bonds. This pronounced double bond character leads to steric strain between the methyl and the *tert*-butyl substituents as indicated by the unusual pyramidalization of the N3 atom (sum of angles: 335.6°). Comparison of the molecular structures of **8HBF₄** and **8o** corroborate the

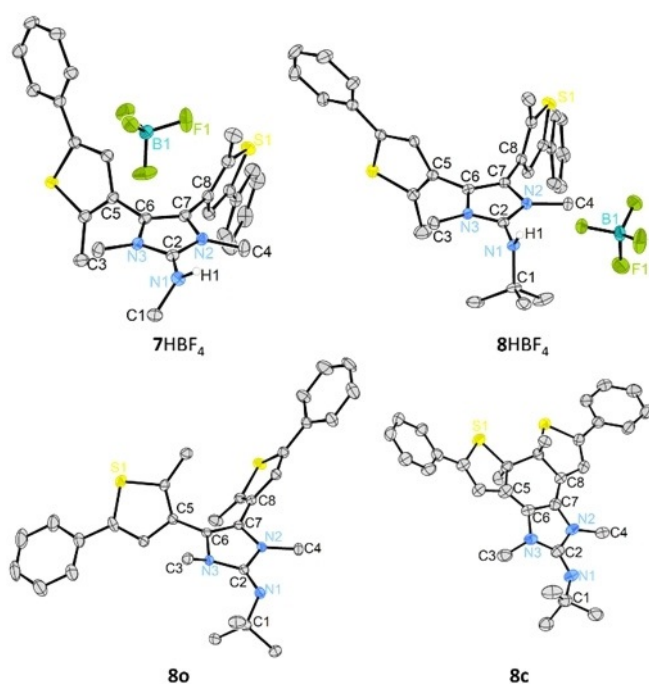


Figure 3. Molecular structure of **7HBF₄**, **8HBF₄**, **8o** and **8c** with ellipsoids set at 50% probability. Hydrogen atoms except the NH-atoms of **7HBF₄** and **8HBF₄** are omitted for clarity.

Table 1: Selected bond lengths [Å] and angles [°] of **7HBF₄**, **8HBF₄**, **8o** and **8c**.

Entry	7HBF₄	8HBF₄	8o	8c
N1-C2	1.356(2)	1.375(3)	1.278(3)	1.282(7)
C2-N2	1.342(2)	1.350(4)	1.384(3)	1.406(9)
C2-N3	1.339(2)	1.344(3)	1.411(3)	1.379(8)
C1-N1-C2	122.17(14)	120.1(2)	127.5(2)	132.6(6)
N1-C2-N2	125.11(14)	127.4(3)	121.0(2)	118.1(6)
N1-C2-N3	126.6(2)	125.0(2)	134.0(2)	136.0(6)
N1-C2-N2-C4	9.3(2)	1.7(5)	2.7(4)	5.6(9)
N1-C2-N3-C3	6.1(3)	7.5(5)	43.5(5)	25.3(10)
C1-N1-C2-N3	45.8(2)	83.8(4)	21.6(5)	9.9(10)
C5-C6-C7-C8	167.6(3)	178.8(5)	0.7(6)	4.2(10)

effect described by Kunetskiy that protonation of the imine N atom of NHIs leads to steric relaxation in the molecule and thus increased basicity of the NHIs.^[33]

Single crystals of **8c** were obtained by storing a saturated acetonitrile solution in the absence of light. The molecular structure confirms that the two thiophene rings in **8c** are connected via a C–C single bond of 1.533 Å. Changes in bond length and angles from **8o** to **8c** are consistent with the aforementioned photoisomerization reaction and formation of a delocalized π system. Most notably, the elongation and reduced double bond character of the C6–C7 bond (**8c**: 1.444 Å, **8o**: 1.352 Å) hampers the stabilization of a positive charge in the imidazole ring via formation of a 6π system, which should translate into a significantly lower basicity of the closed form compared to the open structure.

To elucidate the influence of the photocyclization reaction on the basicity, the gas phase basicity (GB), proton affinity

Table 2: Calculated gas phase basicity (GB), proton affinity (PA) and predicted pK_a values of the corresponding protonated bases BH^+ in CH_3CN ($pK_{BH^+}(MeCN)$), using PW6B95-D3//TPSS-D3/def2-TZVP + COSMO-RS.

Compound	GB [kcal mol ⁻¹]	PA [kcal mol ⁻¹]	$pK_{BH^+}(MeCN)$
7o	251.1	258.8	23.4
7c	241.1	248.4	17.3
8o	256.6	264.7	25.7
8c	245.6	253.3	17.0
NHC-o	263.8	271.4	32.0
NHC-c	258.9	266.3	29.1

(PA) and $pK_{BH^+}(MeCN)$ values of **7o**, **7c**, **8o**, **8c** and of Bielawski's carbene (Figure 1E) **NHC-o** and **NHC-c** were computed (Table 2). The predicted pK_{BH^+} values were referenced to the experimental value of an NHI (see the SI for details).^[33] In line with our previous study, the substituent at the exocyclic nitrogen atom has a significant influence on the basicity of the NHI as shown by the increased dissociation constant of **8o** compared to **7o** by a factor of 200. Upon photocyclization to the closed form, both NHIs **7** and **8** exhibit a substantially lower basicity with pK_a shifts of 6.1 and 8.7 units, respectively. In comparison, the pK_a value of the corresponding photoswitchable NHC is reduced by only 2.9 units upon cyclization of the dithienylethene backbone.

We previously showed that the minimum basicity of nitrogen bases required for the formation of isolable CO_2 adducts is in the range of that of DBN (1,5-Diazabicyclo-[4.3.0]non-5-en, GB = 249.5 kcal mol⁻¹). The DBN- CO_2 adduct is stable in the solid state at 21 °C under an CO_2 atmosphere but shows a fluxional behavior in solution.^[27] The two distinct electronic states of NHIs **7** and **8** could therefore be suitable for the photo-triggered capture and release of CO_2 .

To investigate the formation of NHI- CO_2 adducts, MeCN- d_3 solutions of **7o** and **8o** were pressurized with 2 bar ^{13}C -enriched $^{13}CO_2$ under strictly anhydrous condition and analyzed by 1H and ^{13}C NMR spectroscopy. Upon addition of $^{13}CO_2$ to the acetonitrile solution of **7o** the 1H NMR spectrum at 298 K shows slightly shifted signals for the nitrogen-bound methyl groups from 3.13 and 3.28 to 3.21 and 3.49 ppm (Figure S36). However, the characteristic signal for the N- CO_2 unit in the range of 156 ppm^[27] was not detected in the $^{13}C\{^1H\}$ NMR spectrum. Instead, the ^{13}C resonance of $^{13}CO_2$ appeared as broad signal at 126.6 ppm slightly downfield to the chemical shift of free CO_2 (125.9 ppm)^[37] indicating fluxional behavior involving short-lived **7o** CO_2 complexes (Figure 4). A variable-temperature NMR study revealed that the $^{13}CO_2$ carbon resonance is sensitive to temperature and splits into two sharp signals at 154.4 ppm and 125.3 ppm that are unambiguously assigned to **7o** CO_2 and free CO_2 , respectively (Figure S37). An attempt to precipitate the CO_2 adduct from a nonpolar solvent by exposing a solution of **7o** in *n*-hexane solution with 2 bar CO_2 was unsuccessful. By contrast, exposing a solution of **8o** in MeCN- d_3 with 2 bar $^{13}CO_2$ leads to the quantitative formation of **8o** CO_2 as evident by a new set of signals in the 1H and

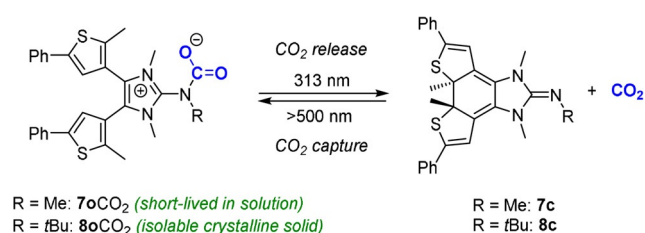


Figure 4. Light-controlled CO₂ activation.

¹³C NMR spectrum including the indicative ¹³CO₂ carbon resonance of the adduct **8o**CO₂ at 154.6 ppm (Figure S35).

Owing to the low solubility of **8o**CO₂ in nonpolar solvents, the adduct readily precipitates as white solid from Et₂O solutions under an atmosphere of CO₂. The decarboxylation temperature of **8o**CO₂ was estimated by heating the suspension in a closed system showing gas evolution at 70 °C concomitant with the formation of a clear solution. **8o**CO₂ can be stored in the absence of light under an argon atmosphere for months without noticeable decomposition. In the FT-IR spectrum of **8o**CO₂, the CO₂ stretching band $\nu_{\text{as}}(\text{CO})$ is detected at 1650 cm⁻¹ consistent with that of other NHI-CO₂ adducts (1650–1673 cm⁻¹).^[27]

We next investigated the possibility of photo-triggered capture and subsequent release of CO₂ by utilizing the two distinct electronic states of **8** over the course of a single experiment (Figure 5). Using ¹³C-enriched ¹³CO₂, a solution of **8o**CO₂ in MeCN-*d*₃ was prepared in an NMR tube and sealed with a Teflon screw cap. The ¹³C{¹H} NMR spectrum showed the characteristic ¹³CO₂ signal of the adduct **8o**CO₂ at 154.6 ppm. Subsequently, the same solution was subjected to UV irradiation (313 nm) for 30 min, which resulted in a color change from colorless to dark purple. The ¹³C{¹H} NMR spectrum of the purple solution showed the signal of free CO₂

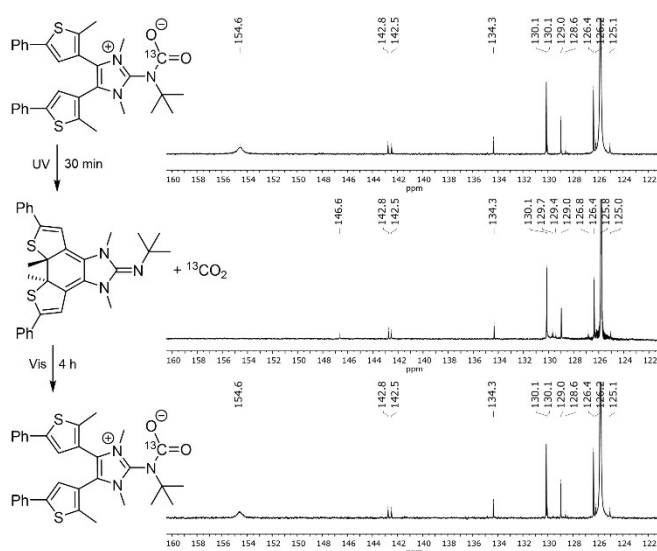


Figure 5. ¹³C{¹H} NMR spectra of **8o**CO₂ in MeCN-*d*₃ (top), after irradiation of the NMR tube with UV light (313 nm) for 30 min showing the signals of **8c** (middle), and after further irradiation with visible light (500 nm) for 4 h (bottom).

at 125.8 ppm, but no signal for the carboxylate carbon atom at 154.6 ppm was detected. Further visible-light irradiation (500 nm) of the solution for 4 h resulted in decoloration of the solution and the ¹³C{¹H} NMR spectrum matched that previously observed, confirming the reversibility of the photo-driven CO₂ capture and release process.

Conclusion

We report the synthesis and properties of the first photoswitchable nitrogen superbases, namely N-heterocyclic imines (NHI), outfitted with a photochromic dithienylethene unit. The NHIs **7o** and **8o** were found to undergo reversible photoinduced electrocyclization to their ring-closed isomer **7c** and **8c** as evidenced by UV/Vis and NMR spectroscopy as well as XRD studies. The closed form is stable for months in the absence of light at room temperature. Successive exposure of the NHIs to UV ($\lambda_{\text{irr}} = 313$ nm) and visible ($\lambda_{\text{irr}} = 520$ nm) irradiation led to near quantitative switching between their ring-opened and ring-closed states over multiple cycles. Computational studies reveal that the changes in basicity between the two electronic states are significantly higher for NHIs (**7**: $\Delta pK_{\text{a}} = 6.1$, **8**: $\Delta pK_{\text{a}} = 8.7$) than for the corresponding NHC ($\Delta pK_{\text{a}} = 2.9$). This substantial pK_{a} difference provides new opportunities for light-controlled chemical reactions as demonstrated by the reversible capture and release of CO₂ using **8** over the course of a single experiment. Given the ubiquity of the guanidine function in many fields of research, access to photoswitchable NHIs that exhibit profound light-triggered basicity alterations is expected to drive the development of new photoswitchable transformations.

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: CO₂ activation · N-heterocyclic imines · nitrogen superbases · photochromism · photoswitches

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