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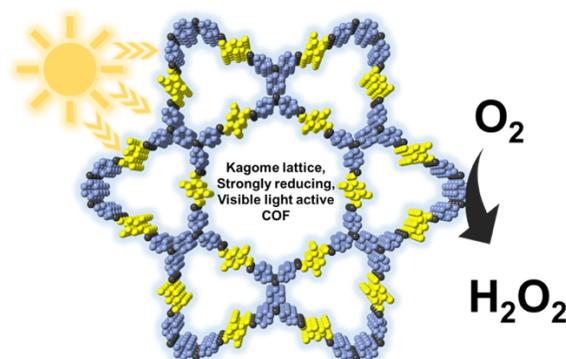
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Strongly Reducing (Diarylamino)benzene-Baesd Covalent Organic Framework for Metal-Free Visible Light Photocatalytic H₂O₂ Generation

Chidharth Krishnaraj, Himanshu Kekhar Jena, Laurens Bourda, Andreas Laemont, Pradip Pachfule, Jérôme Roeser, C. Vinod Chandran, Sander. Borgmans, Sven M. J. Rogge, Karen Leus, Christian V. Stevens, Johan A. Martens, Veronique Van Speybroeck, Eric Breynaert, Arne Thomas,* and Pascal Van Der Voort* (arne.thomas@tu-berlin.be or pascal.vandervoort@ugent.be)

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Abstract: Photocatalytic reduction of molecular oxygen is a promising route towards sustainable production of hydrogen peroxide (H₂O₂). This process requires photoactive semiconductors enabling solar energy driven generation and separation of electrons and holes with high charge transfer kinetics. Covalent organic frameworks (COFs) are an emerging class of photoactive semiconductors, tuneable at a molecular level for high charge carrier generation and transfer. Herein, we report two newly designed 2D COFs based on (diarylamino)benzene linkers which forms a kagome (kgm) lattice and shows strong visible light absorption, charge generation, and charge transfer properties. Their high crystallinity and large surface areas (up to 1165 m²·g⁻¹) allow efficient charge transfer and diffusion. The diarylamine (donor) unit promotes strong reduction properties, enabling these COFs to efficiently reduce oxygen to form H₂O₂. Overall, the use of a metal-free, recyclable photocatalytic system allows efficient photocatalytic solar transformations.

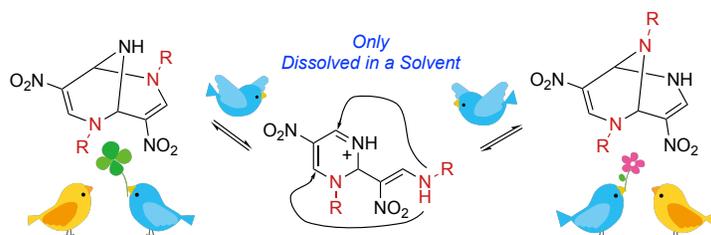
Synthesis and Intramolecular Ring Transformation of *N,N'*-Dialkylated 2,6,9-Triazabicyclo[3.3.1] Nonadienes

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Org. Biomol. Chem. **2020**, *18*, 9109–9116.

DOI: 10.1039/D0OB01950J



Abstract: The first and facile synthesis of *N,N'*-dialkylated 2,6,9-triazabicyclo[3.3.1]nonadienes was achieved by the [4 + 4] self-condensation of β -formyl- β -nitroenamine in the presence of ammonium acetate. The 2,6- and 2,9-dialkylated products were found to be interconvertible when dissolved in a solvent. This isomerization proceeds through intramolecular ring transformation via a common intermediate under equilibrium.

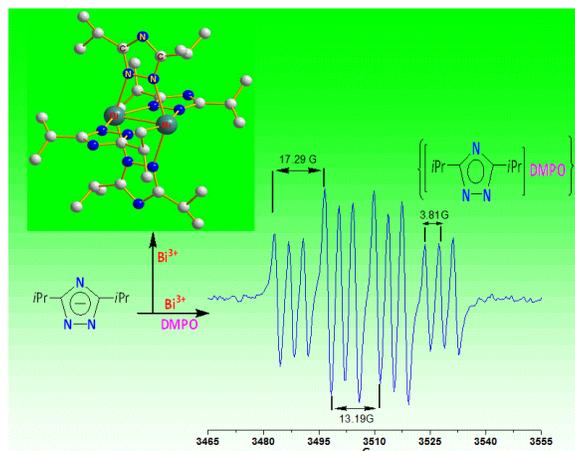
1,2,4-Triazolato Paddlewheel Dibismuth Complexes with Very Short (Bi(II)–Bi(II) Bonds: Bismuth(III) Oxidation of 1,2,4-Triazolato Anions into Neutral *N*-1,2,4-Triazolyl Radicals

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Dalton Trans. **2020**, *49*, 15190–15194.

DOI: 10.1039/d0dt03225e



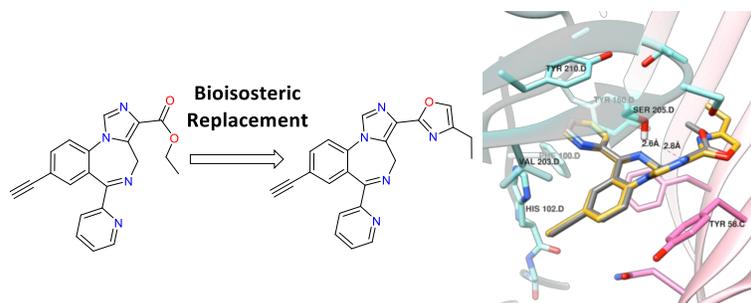
Abstract: Bismuth(III) oxidation of 3,5-di-substituted-1,2,4-triazolato anions afforded paddlewheel 1,2,4-triazolato dibismuth complex $[L_2(Bi-Bi)L_2]$ ($L = \eta^1, \eta^1\text{-}3,5\text{-R}_2\text{tz}$, $R = \text{Ph}$ (**3**), $i\text{Pr}$ (**4**)) with very short Bi(II)–Bi(II) bonds (2.8650(**4**)–2.8721(**3**) Å). The reaction involved the intermediates of organobismuth radical $[Bi(R_2\text{tz})_2]^*$ and neutral *N*-1,2,4-triazolyl radical $[3,5\text{-R}_2\text{tz}]^*$. The dimerization of the former produced the corresponding dibismuth complex while the latter was trapped by spin trap 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) to give the radical adduct of $\{(3,5\text{-R}_2\text{tz})(\text{DMPO})\}^*$ which was unambiguously evidenced by EPR analysis.

Design, Synthesis and Characterization of Novel Gamma-Aminobutyric Acid Type A Receptor Ligands

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DOI: 10.24820/ark.5550190.p011.398



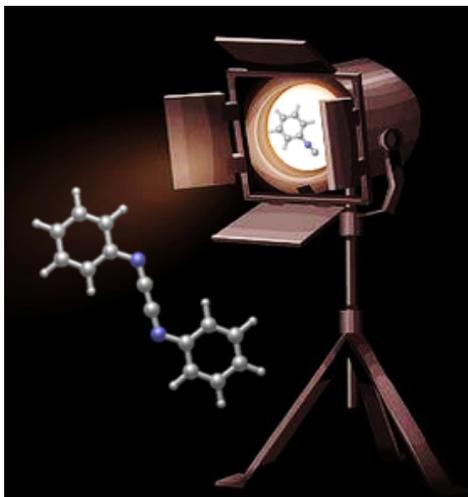
Abstract: Antinociceptive ligand HZ-166 is a GABA_A $\alpha 2/\alpha 3$ receptor subtype-selective potentiator. It has been shown to exhibit anxiolytic-like effects in rodent and rhesus monkeys, as well as reduced sedative/ataxic liabilities. In order to improve the metabolic stability of HZ-166, the ethyl ester moiety was bioisosterically replaced with 2,4-disubstituted oxazoles and oxazolines. The new analogs of HZ-166 were synthesized, characterized, and evaluated for their biological activity and docked in the human full-length heteromeric $\alpha 1\beta 3\gamma 2L$ GABA_A receptor subtype CryoEM structure (6HUO). Importantly no sedation nor ataxia was observed on the rotorod for LKG-I-70 (**6**) or KPP-III-51 (**6c**) at 100 and 120 mg/kg, respectively. There was also no loss of righting response for either ligand.

The Elusive 1,4-Diazabutatrienes: Lurking in the Shadows

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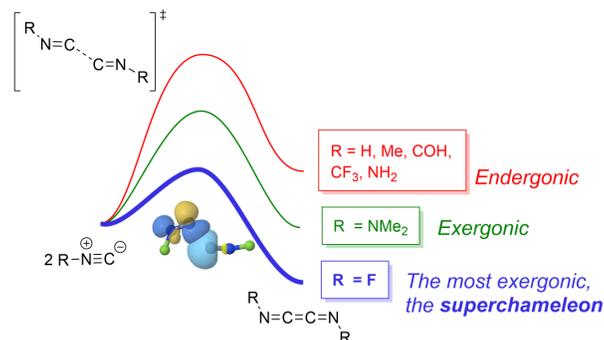
Abstract: Isocyanides are isomers of cyanides in which the terminal carbon atom can exist in a divalent state. Their ambivalent electronic nature as nucleophile or electrophile and wide reactivity make the isocyanide scaffold a valuable synthon for the synthesis of structurally complex molecules, in particular azacycles. Although they are known to polymerize easily, the dimerization of isocyanides affording head-to-head dimers, namely 1,4-diazabutatrienes $R^1-N=C=C=N-R^1$, has been scarcely explored. Nowadays the experimental isolation of this kind of heterocumulenes is still a challenge. In this minireview, covering a period of sixty years, we highlight the role of 1,4-diazabutatrienes as putative reaction intermediates in the homo- and heterodimerization of different types of isocyanides. Furthermore, we revise a set of reported reactions in which the formation of a transient 1,4-diazabutatriene intermediate has not been proposed but could be considered as a plausible alternative.

In Search of 1,4-Diazabutatrienes, the Elusive Isocyanide Homodimers: The Superchameleonic F–NC

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DOI: 10.1021/acs.joc.0c01685



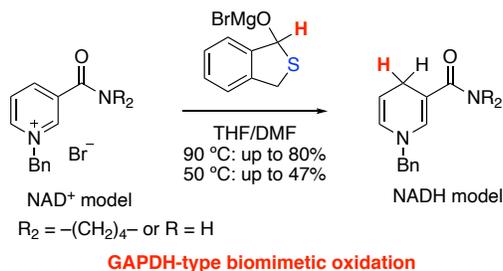
Abstract: Isocyanides might dimerize forming 1,4-diazabutatrienes, never isolated but eventually proposed as reaction intermediates. We herein disclose a computational study on the homo- and heterodimerization of isocyanides, in particular on the influence of the substituents onto the structural and energetics parameters of these processes. As a result, we have identified some reaction partners that are predicted to give stable 1,4-diazabutatrienes by surpassing low energy barriers. Of special significance is the homodimerization of F–NC, in which this species is revealed as an excellent acceptor and, quite surprisingly, also as a suitable donor.

Biomimetic Systems Involving Sequential Redox Reactions in Glycolysis – The Sulfur Effect

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Chem. Commun. **2020**, 56, 12917–12920.

DOI: 10.1039/d0cc05185c



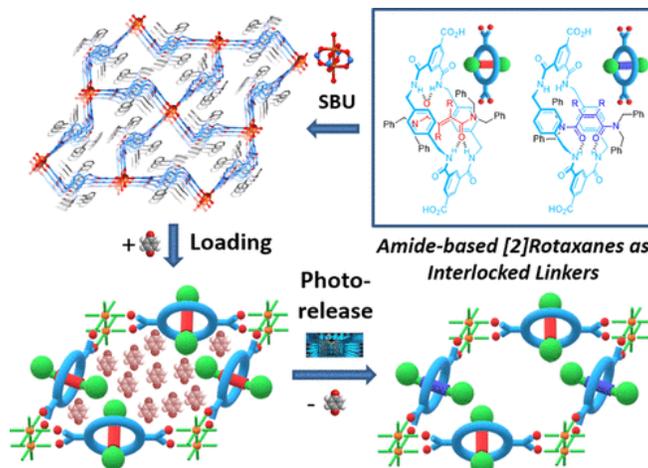
Abstract: Magnesium hemithioacetates were used as model cysteine compounds to mimic natural hemithioacetals, and their biomimetic oxidation reactions using a model NAD⁺ compound were investigated. Cyclic hemithioacetate was found to be the best substrate for the reaction with the model NAD⁺ compound, which gave the corresponding NADH analog in excellent yield.

Copper-Linked Rotaxanes for the Building of Photoresponsive Metal Organic Frameworks with Controlled Cargo Delivery

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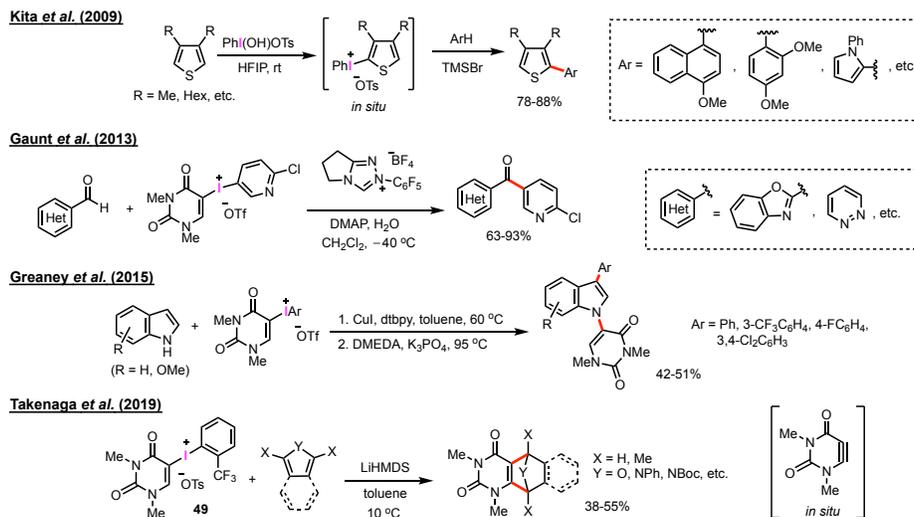
Abstract: We have prepared a photoresponsive metal–organic framework by using an amide-based [2]rotaxane as linker and copper(II) ions as metal nodes. The interlocked linker was obtained by the hydrogen bond-directed approach employing a fumaramide thread as template of the macrocyclic component, this latter incorporating two carboxyl groups. Single crystal X-ray diffraction analysis of the metal–organic framework, prepared under solvothermal conditions, showed the formation of stacked 2D rhombohedral grids forming channels decorated with the interlocked alkenyl threads. A series of metal–organic frameworks differing in the *E/Z* olefin ratio were prepared either by the previous isomerization of the linker or by postirradiation of the reticulated materials. By dynamic solid state ²H NMR measurements, using deuterium-labeled materials, we proved that the geometry of the olefinic axis of the interlocked struts determined the obtention of materials with different independent local dynamics as a result of the strength of the intercomponent noncovalent interactions. Moreover, the usefulness of these novel copper-rotaxane materials as molecular dosing containers has also been assayed by the diffusion and photorelease of *p*-benzoquinone, evaluated in different solvents and temperatures.

Heteroaryliodonium(III) Salts as Highly Reactive Electrophiles

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Abstract: In recent years, the chemistry of heteroaryliodonium(III) salts has undergone significant developments. Heteroaryliodonium(III) salts have been found to be useful synthetic tools for the transfer of heteroaryl groups under metal-catalyzed and metal-free conditions for the preparation of functionalized heteroarene-containing compounds. Synthetic transformations mediated by these heteroaryliodonium(III) salts are classified into two categories: (1) reactions utilizing the high reactivity of the hypervalent iodine(III) species; and (2) reactions based on unique and new reactivities not observed in other types of conventional diaryliodonium salts. The latter feature is of particular interest and so has been intensively investigated in recent decades. This mini-review therefore aims to summarize the recent synthetic applications of heteroaryliodonium(III) salts as highly reactive electrophiles.