Chimia 72 (2018) 725 © Swiss Chemical Society

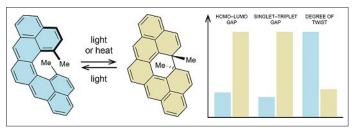


Swiss Science Concentrates

CHIMIA Column

Dimethylcethrene: A Chiroptical Diradicaloid **Photoswitch**

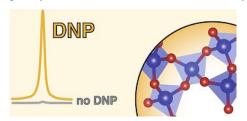
P. Ravat, T. Šolomek, D. Häussinger, O. Blacque, and M. Juríček*, J. Am. Chem. Soc. 2018, 140, 10839. University of Zurich Chemical reactivity of diradicaloid π -conjugated molecules is typically an undesired feature that impedes their preparation and usability. The Juríček group has found a way to translate the reactivity of helical diradicaloids into a useful function by using 13,14-dimethylcethrene as a model system, which allows them to switch on and off by light the two most common characteristics of diradicaloids, small HOMO-LUMO and singlet-triplet energy gaps, in addition to alteration of the degree of helical twist. Their system acts as a prototype of a chiral diradicaloid photoswitch, the working principle of which can be employed in the design of non-metal-based magnetic switches operated by light.



Bulk Nuclear Hyperpolarization of Inorganic Solids by Relay from the Surface

S. Björgvinsdóttir, B. J. Walder, A. C. Pinon, and L. Emsley*, J. Am. Chem. Soc. 2018, 140, 7946. EPFL Lausanne.

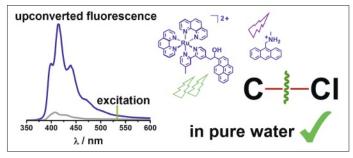
Inorganic solids constitute a key focal area of materials science research, where solid-state NMR is often used to characterize noncrystalline materials. Impregnation dynamic nuclear polarization has recently been applied to boost solid-state NMR sensitivity. In a typical experiment, spin hyperpolarization of protons is generated and transported to the surface. For organic solids, this hyperpolarization is spontaneously transported into the bulk of the solid by proton spin diffusion and can then be transferred to boost the signals of other nuclei. However, many important inorganic materials contain no protons. Emsley and co-workers have shown that spin diffusion between low-γ, spin-½ nuclei can be used for transferring surface-based hyperpolarization into the bulk material for ²⁹Si, ³¹P, ¹¹³Cd and ¹¹⁹Sn nuclei. This approach greatly increases solid-state NMR sensitivity.



Sensitized Triplet-Triplet Annihilation Upconversion in Water and its Application to Photochemical **Transformations**

C. Kerzig* and O. S. Wenger* Chem. Sci. 2018, 9, 6670. University of Basel

Kerzig and Wenger introduced a new method for sensitized triplet-triplet annihilation (TTA) that exhibits high efficiency in water. By combining water-soluble ruthenium-pyrene dyads as sensitizers, and anthracenes as acceptors/annihilators, they achieved photonupconversion with unprecedented quantum yields. They went on to demonstrate potential applications of their system, including photochemical carbon-chlorine bond activation driven by green photons in oxygenated water. This method is therefore a promising approach for sustainable photochemistry in the 21st century.



Direct Nanospectroscopic Verification of the Amyloid Aggregation Pathway

E. Lipiec, D. Perez-Guaita, J. Kaderli, B. R. Wood, and R. Zenobi*, Angew. Chem. Int. Ed. 2018, 57, 8519. ETH Zurich As populations age, the frequency of neurodegenerative diseases such as Alzheimer's continue to increase. Neurodegeneration is often associated with the poorly understood process of protein aggregation. For the first time, Zenobi and co-workers were able to directly characterize protein aggregation using a combined technique of tip-enhanced Raman spectroscopy (TERS), atomic force microscopy (AFM), and attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR). Their nanoscale mapping of single amyloid fibrils at various stages of aggregation can be conducted on biologically relevant, heterogeneous samples to reveal new information about the relative content of turns, structured coils and β-sheet secondary structures.

