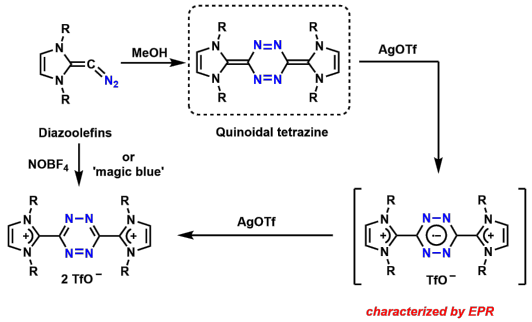
Head-to-Tail dimerization of N-heterocyclic Diazoolefins

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Room temperature stable N-heterocyclic diazoolefins were isolated by our group[1] and by Hansmann's group[2] in 2021. N-heterocyclic diazoolefins can undergo [2+3] cycloaddition reactions. The ylidic carbon can also coordinate with metal complexes and Lewis acids. Our group recently discovered an unprecedented type of cycloaddition reaction for N-heterocyclic diazoolefins: the head-to-tail dimerization.[3] This formal [3+3] cycloaddition gives strongly reducing quinoidal tetrazines. The oxidation of quinoidal tetrazines proceeds in a stepwise manner, with an isolable and room temperature-stable radical cation as an intermediate. The radical could be characterized by EPR spectrometry, and a singlet with hyperfine splitting due to the coupling to four ^{14}N nuclei was observed. The final oxidation product contains a tetrazine core with two imidazolium substituents. The dication can also be prepared from diazoolefins directly by reactions with oxidants like nitrosonium tetrafluoroborate or 'magic blue'.



[1] P. Varava, Z. Dong, R. Scopelliti, F. Fadaei-Tirani, K. Severin, *Nat. Chem.* **2021**, *13*, 1055–1060.

[2] P. W. Antoni, C. Golz, J. J. Holstein, D. A. Pantazis, M. M. Hansmann, *Nat. Chem.* **2021**, *13*, 587–593

[3] P. Varava, T. H. Wong, Z. Dong, A. Yu. Gitlina, A. Sienkiewicz, W. Feuerstein, R. Scopelliti, F. Fadaei-Tirani, K. Severin, *Angew. Chem. Int. Ed.* **2023**, e202303375.