

Transport Phenomena through Porphyrin Nano-Architectures

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Porphyrins are key components in nature machinery to store sunlight as chemical energy. In spite of their prominent role in cascades separating charges and their potential as sensitizers, reports concerning their transport characteristics are inconsistent. Therefore, we investigated the electronic transport through seven structurally related porphyrin derivatives in an automatized mechanically controlled break-junction identifying and distinguishing three electronic paths.^[1] Recently, we communicated our efforts towards the synthesis of a mechano-sensitive porphyrin-cyclophane.^[2] Based on this experience, we designed a new cyclophane comprising two co-facial porphyrins for mechanosensitive molecular junctions. The molecule is decorated with one gold-anchoring group per porphyrin sub-unit, pointing into the opposite directions of the macrocycle. Planar xanthene units bridge the macrocycle in the lateral positions of the porphyrins with respect to the anchoring groups. This design ensures rigidity of the macrocyclic structure, acetylenes between the bridge and the porphyrins allow for rotation over the C-C triple bond and thus, mechanical manipulation into the direction of the electrodes. Over a 15 step synthesis with a fourfold *Sonogashira* macrocyclization as key step, we isolated and characterized this unique porphyrin-cyclophane with a face-to-face distance of 0.37 nm in the solid-state structure - almost the van-der-Waals distance. Preliminary results showed promising mechanosensitivity indicated by oscillations of more than one order of magnitude in the conductance response upon increasing the electrode-to-electrode distance.

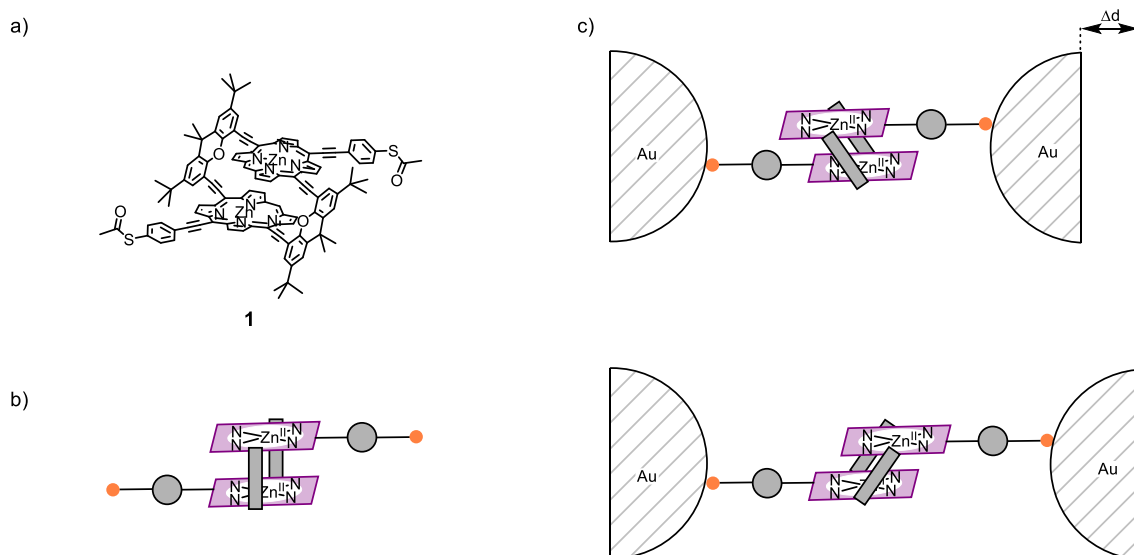


Figure 1: Schematic representation of the target compound **1** between two gold electrodes in a MCBJ setup (left) and outlined working principle of the mechanosensitivity of the latterly interlocked porphyrin-cyclophane (right).

- [1] Abbassi, M. E.; Zwick, P.; Rates, A.; Stefani, D.; Prescimone, A.; Mayor, M.; Zant, H. S. J. van der; Dulić, D., *Chemical Science*, **2019**, 10 (36), 8299 – 8305.
- [2] Zwick, P.; Weiland, K. J.; Malinčik, J.; Stefani, D.; Häussinger, D.; Zant, H. S. J.; Dulić, D.; Mayor, M., *The Journal of Organic Chemistry*, **2019**, accepted manuscript.