Synthesis of Sulfuric Macrocycles and a Rotaxane through Thiol-yne Click and Dithiol Coupling Reactions
Zhou, W.; Zheng, H.; Li, Y.; Liu, H.; Li, Y. Org. Lett. 2010, 12, 4078-4081.
Abstract:



A macrocycle and a rotaxane were constructed by virtue of the thiol-yne click reaction under the irradiation of light in high yield, which can proceed at ambient temperature and humidity under an air atmosphere. Two disulfide macrocycles were synthesized through a simple dithiol coupling reaction, which exhibited high stability and a weak assembly interaction with a dialkylammonium ion.

 Metalated Aziridines for Cross-Coupling with Aryl and Alkenyl Halides via Palladium Catalysis Nelson, J. M.; Vedejs, E. Org. Lett. 2010, 12, 5085-5087.
<u>Abstract:</u>



R = alkenyl, aryl

The palladium-catalyzed coupling of an aziridinylzinc chloride intermediate with alkenyl and aryl halides has been demonstrated. The method provides products with retention of aziridine stereochemistry. The utility of the coupling procedure is illustrated in the synthesis of structures related to L-furanomycin.

• Metal–Molecule–Metal Junctions in Langmuir–Blodgett Films Using a New Linker: Trimethylsilane

Pera, G.; Martín, S.; Ballesteros, L. M.; Hope, A. J.; Low, P. J.; Nichols, R. J.; Cea, P. *Chem. Eur. J.* **2010**, *16*, 13398-13405.

Abstract:



Herein trimethylsilane (TMS) is demonstrated to be an efficient binding group suitable for construction of metal-molecule-metal (M-mol-M') junctions, in which one of the metal 2 contacts is an atomically flat gold surface and the other a scanning tunnelling microscopy-(STM) tip. The molecular component of the M-mol-M' devices is an oligomeric phenylene ethynylene (OPE) derivative Me<sub>3</sub>Si C=C{C<sub>6</sub>H<sub>4</sub>C=C}<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>, featuring both Me<sub>3</sub>SiC=C and NH<sub>2</sub> metal contacting groups. This compound can be assembled into Langmuir-Blodgett (LB) films on Au-substrates by surface binding through the amine groups. Alternatively, low coverage (sub-monolayer) films are formed by adsorption from solution. In the case of condensed monolayers top electrical contacts are formed to STM tips through the TMS end group. In low coverage films, single molecular bridges can be formed between the gold surface and a gold STM tip. The similarity in the *I*–V response of a one-layer LB film and the single molecule conductance experiments reveals several points of critical importance to the design of molecular components for use in the construction of M-mol-M' junctions. Firstly, the presence of neighbouring  $\pi$  systems does not have a significant effect on the conductance of the M-mol-M' junction. Secondly, in the STM configuration, intermolecular electron hopping does not significantly enhance the junction transport characteristics. Thirdly, the symmetric behaviour of the I-V curves obtained, despite the different metal-molecule contacts, indicates that the molecule is simply an amphiphilic electron-donating wire and not a molecular diode with strong rectifying characteristics. Finally, the conductance values obtained from the amine/TMS-contacted OPE described here are of the same order of magnitude as thiol anchored OPEs, making them attractive alternatives to the more conventionally used thiol-contacting chemistry for OPE molecular wires.

 On/Off Switching of Perylene Tetracarboxylic Bisimide Luminescence by Means of Substitution at the N-Position by Electron-Rich Mono-, Di-, and Trimethoxybenzenes Flamigni, L.; Ventura, B.; Barbieri, A.; Langhals, H.; Wetzel, F.; Fuchs, K.; Walter, A. *Chem. Eur. J.* 2010, *16*, 13406-13416.
<u>Abstract:</u>



A series of perylene tetracarboxylic bisimides, substituted at the N-position with methoxyphenyl groups, have been synthesized together with model compounds and their photophysical properties have been investigated by means of steady-state and time-resolved spectroscopic techniques. The luminescence properties of the examined compounds vary remarkably with the substitution pattern, with emission quantum yields ranging from 1 to  $10^{-2}$ – $10^{-3}$ . The observed quenching of the luminescence is assigned to a photoinduced electron transfer (PET) from the electron-rich methoxybenzene unit to the perylene bisimide moiety. The radical anion of perylene bisimide has been detected by transient-absorption spectroscopy. The results could satisfactorily be explained by taking into consideration the redox potentials of the partners and the electron-releasing ability of

each methoxy group in relation to its position with respect to N. Quantum-chemical calculations were also performed.

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 Inflicting Controlled Nonthermal Damage to Subcellular Structures by Laser-Activated Gold Nanoparticles Krpetić, Z.; Nativo, P.; Sée, V.; Prior, I. A.; Brust, M.; Volk, M. Nano Lett. 2010, 10, 4549–4554.
<u>Abstract:</u>



We show that low-intensity laser irradiation of cancer cells containing endosomal gold nanoparticles leads to endosome rupture and escape of the nanoparticles into the cytosol without affecting the cells' viability. The low light intensity of our experiments allows us to rule out photothermal effects as the underlying mechanism, and we present results that suggest photoinduced radicals as the photogenerated active species. This nonthermal mechanism may also be important in the context of cell death at higher laser intensities, which had been reported previously.

 Donor–acceptor block copolymers for photovoltaic applications Sommer, M.; Huettner, S.; Thelakkat, M. J. Mater. Chem. 2010, 20, 10788-10797. <u>Abstract:</u>



Extensive research activities in polymer synthesis and device engineering have been devoted to the development of donor-acceptor (D–A) bulk heterojunction solar cells in the last years. In such devices, several photophysical processes occur all of which have to be optimized for efficient operation. First, excitons created upon light absorption need to reach the D/A interface within their exciton diffusion length (10– 20 nm), where they may dissociate into

holes and electrons. Subsequent charge transport and finally charge collection at the electrodes can occur, given that co-continous pathways of donor and acceptor domains are provided. Owing to the small exciton diffusion lengths and the required optical absorption length of 100–200 nm, vertically aligned pathways with a high aspect ratio of either phase should percolate through the film. The morphologies resulting from this ideal situation resemble those of vertically oriented microphase separated block copolymer thin films, and hence suggest the importance of D–A block copolymers for organic photovoltaics. Furthermore, the covalent bond between the donor and acceptor blocks is not only desired to improve morphology control, but also to enhance long term stability of the device. The potential of block copolymers with electronic functionality to microphase separate into well-defined microstructures with several tens of nanometers in size thus addresses the morphological requirements mentioned above. This article gives an overview of donor–acceptor block copolymers and summarises recent developments of this field.