Photoactivated Covalent Bonding of Organic Molecules on an Insulator Surface

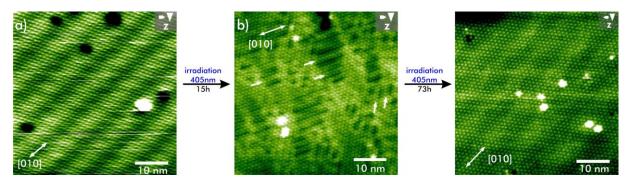
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Controlled surface functionalization is crucial for future technologies like molecular electronics. In order to increase the stability and functionality of self-assembled structures, covalent linking of organic molecules is a most promising approach.

Thermally induced covalent bonding on metallic and insulating substrates has been demonstrated in impressive ways [1, 2]. The downside of this approach is that the same external stimulus is used for the deposition as well as for the covalent linking of the molecules. In order to gain further control, photochemical linking provides an elegant method to separate the two functionalization steps.

Photopolymerization of bulk C60 Fullerene has been described in literature and the reaction mechanism has been assigned to a [2+2]-cycloaddition [4]. In this work, we study the photopolymerization of C60 on CaCO₃(10.4). C60 is known to form well-ordered monolayer islands on calcite [3]. We examined these C60 islands with non-contact atomic force microscopy before and after irradiation with a laser (Fig.1). Interestingly, the molecular structure is changed significantly upon irradiation, which is ascribed to the formation of a two-dimensional, polymeric network. The successful photoreaction was confirmed by a change in the C60 superstructure and a change in intermolecular distances (see Fig.1).



- Fig. 1: Monolayer islands of C60 on the calcite (10.4) surface; a) Before irradiation a hexagonal arrangement and a moiré pattern can be seen; b) After irradiation, the moiré pattern has vanished and polymerized domains become visible, as indicated by the white arrows.
- [1] Grill, L. Dyer, M. Lafferentz, L. Persson, M. Peters, M. V.; Hecht, S. *Nature nanotechnology* **2007**, *2*, 687-691.
- [2] Kittelmann, M. Rahe, P. Nimmrich, M. Hauke, C. M. Gourdon, A.; Kühnle, A. ACS nano 2011, 5, 8420–8425.
- [3] Rahe, P., Lindner, R., Kittelmann, M., Nimmrich, M., Kühnle, A., *Physical chemistry chemical physics* **2012**, *14*, 6544–6548.
- [4] Zhou, P., Dong, Z., Rao, A. M., Eklund, P. C., *Chemical Physics Letters* **1993**, *211*, 337–340.