

Direct Synthesis of Vinylene-Linked Conjugated Polymers by Selective Methyl/Methylene C-H Activation on Gold Surfaces

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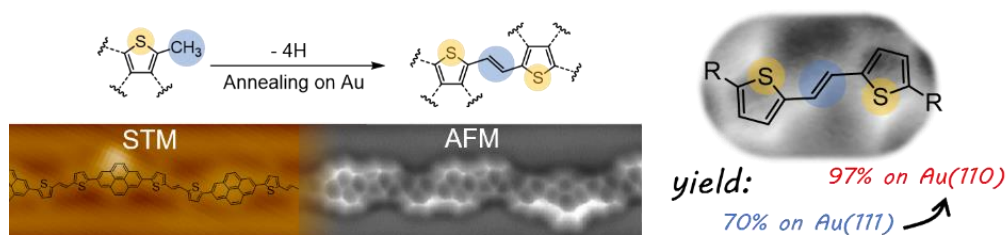
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Vinylene (C=C) linkage facilitates the distribution of highly conjugated electrons along the polymer chain, thereby playing a crucial role in the development of conductive polymers for promising applications in organic electronics. Directly connecting two methyl groups to construct a vinylene linkage would streamline the synthesis process considerably, reducing the number of reaction steps required. However, reactions through alkyl groups normally form C-C single bonds as linkages. Achieving vinylene bonds via further dehydrogenation remains a significant challenge. Here, we demonstrate the successful synthesis of vinylene linkages by selectively activating methyl/methylene C-H bonds using the predesigned monomers bearing methylthiophenes on Au(111) and Au(110) surfaces. Non-contact atomic force microscopy confirms the formation of vinylene linkage by bond-resolved imaging on both surfaces, achieving a vinylene linkage yield of 97%. Density functional theory calculations and control experiments reveal that the strong adsorption of the thiophene ring on the gold substrate effectively reduces the energy barriers for methyl and methylene C-H dissociation, enabling the two-step dehydrogenation for the formation of vinylene-linked polymers with up to 27 units. Our findings present a novel strategy for polymerization or oligomerization via vinylene linkages on surfaces.



Reference

[1] Q. Zheng, et al. *Angew.* **accepted**.