

Tunneling-current-induced light emission from chiral binaphthylene–perylenebiscarboxydiimide dimer

Y. Miyake¹, A. Fujiki¹, M. Kasaya-Akai¹, A. Saito^{1,2}, and Y. Kuwahara¹

¹ Department of Precision Science and Technology, Graduate School of Engineering, Osaka University, 2-1 Yamada-oka, Suita, Osaka 565-0871, Japan

² PRESTO, Japan Science and Technology Agency (JST), 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

E-mail: miyake@ss.prec.eng.osaka-u.ac.jp

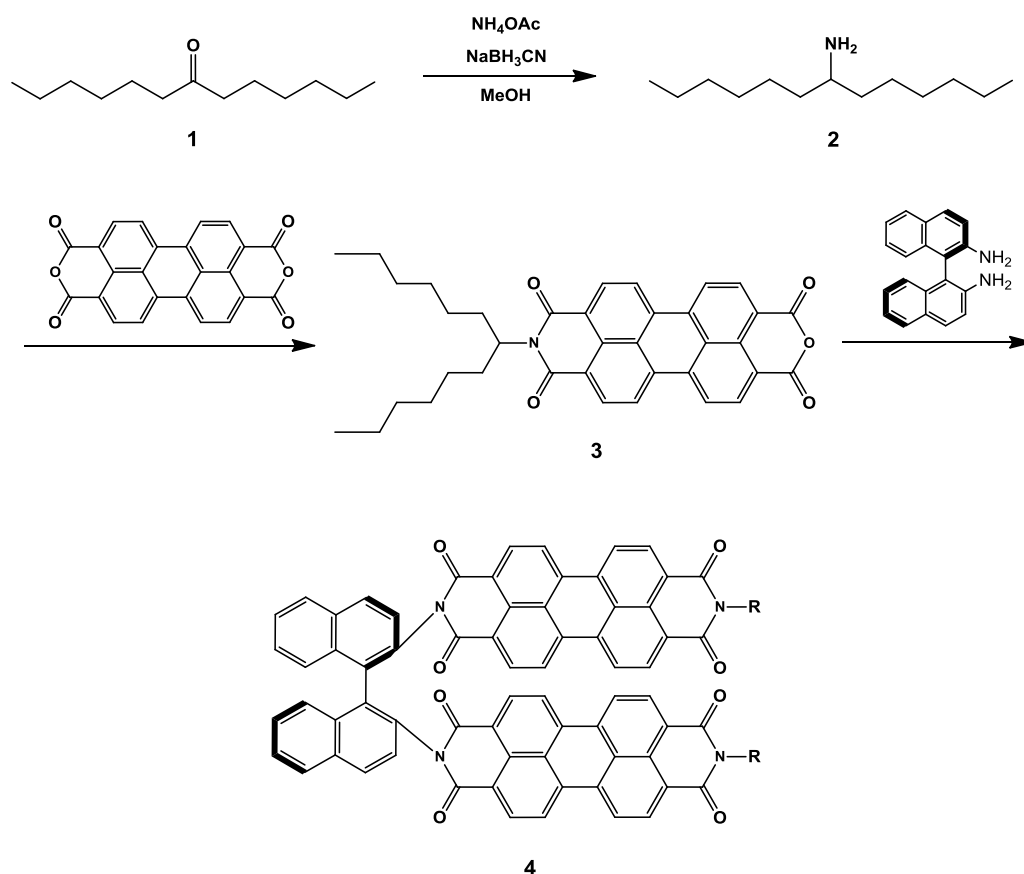
Chiral π -conjugated molecules and their self-organized structures have been attracted much attention for characteristic chiroptical behaviors such as dichroism (CD) and circularly polarized luminescence (CPL). Chiral molecular thin films and self-organized structures are expected to be potential candidates for chiroptical sensors and sources for circularly polarized light. [1] In this work, we have investigated the emission properties of chiral binaphthylene–perylenebiscarboxydiimide dimer (Scheme 1) thin films on the highly oriented pyrolytic graphite (HOPG) and the Au(111) surfaces using tunneling electrons from a scanning tunneling microscope (STM). The STM-induced light emission (STM-LE) analysis is a useful tool for characterizing the optical and electric properties of inorganic materials and organic molecules (Figure 1). So far, STM-LE has been utilized for analyzing achiral molecules. [2-4] The light emission from chiral molecules provides specific information about optical chirality of the molecules in the excited states. So, STM-LE analysis of chiral molecules can be a powerful tool for analyzing the excited state of chiral molecules on the surface. We adopt chiral binaphthylene–perylenebiscarboxydiimide dimer (**4**) for model compound chiral chromophore of light emission. Perylene diimides and the analogues show strong fluorescence. The central binaphthylene unit promotes chiral structure for the two perylene chromophore.

Compound (**4**) was synthesized via a slightly modified method reported previously. [5] 1-hexylheptylamine (**2**) was obtained by the reaction between dihexyl ketone (**1**) and $\text{NH}_4\text{OAc}/\text{NaBH}_3\text{CN}$. [6,7] N-(1-hexylheptyl)perylene-3,4,9,10-tetracarboxyl-3,4-anhydride-9,10-imide (**3**) was prepared by the reaction between 1-hexylheptylamine (**2**) and excess perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) in DMF. The crude product of the reaction between 1-hexylheptylamine and PTCDA included symmetric dialkylated compound and asymmetric monoalkylated compound. Monoalkylated compound (**3**) was purified by column chromatography on a silica gel (eluent: chloroform). Chiral perylene diimide dimer (**4**) was synthesized via condensation reaction between binaphthyl diamine and (**3**). All compounds were identified using ^1H NMR, IR and elemental analysis. Cast films and spin coated films of compound (**4**) were prepared for STM-LE experiments.

In the present work, we will report surface morphology and STM-LE properties of chiral binaphthylene–perylenebiscarboxydiimide dimer (**4**) on the HOPG and the Au(111) surfaces.

References

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Scheme 1. Synthetic scheme of compound (*R*)-4 [R=CH (C₆H₁₃)₂].

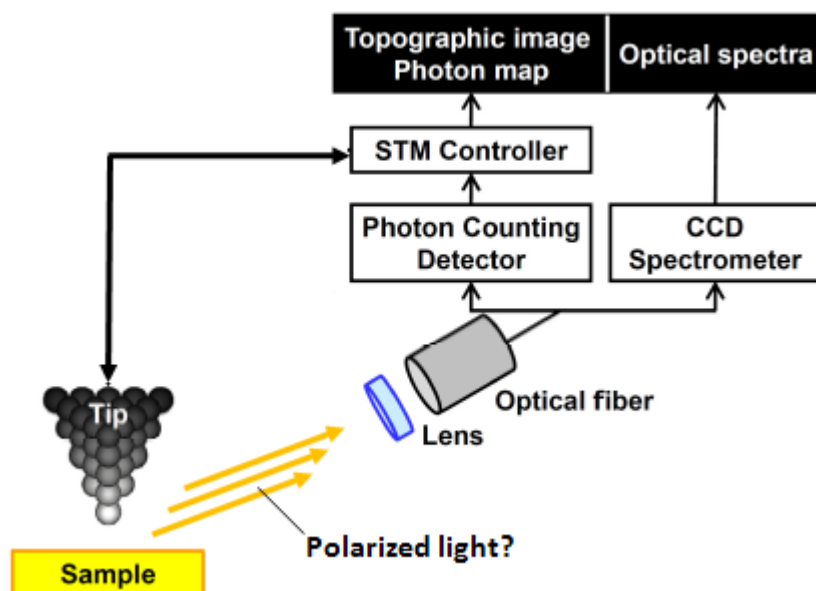


Figure 1. Schematic diagram of the photon detection system equipped with an STM under ambient condition.