

Photo-Induced Polymerization and Isomerization on Surface Observed by Scanning Tunneling Microscopy

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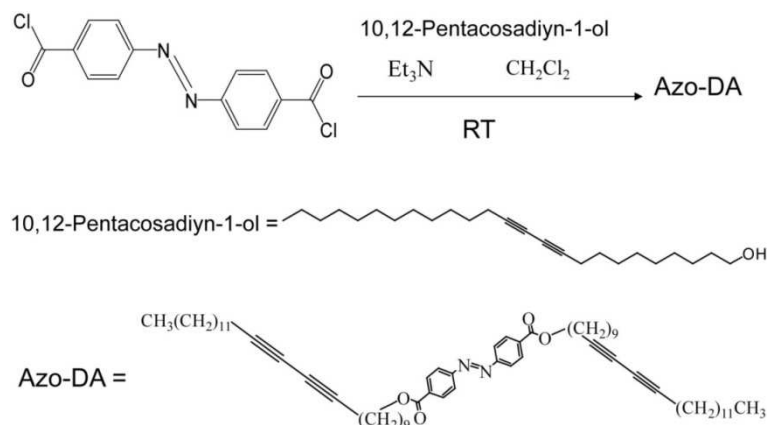
1. Synthesis of Azobenzene derivative

1.1 Materials and instruments

Azobenzene - 4, 4'-dicarboxyldichloride, 10, 12-Pentacosadiyn-1-ol and triethylamine (Et_3N) were purchased from TCI, toluene and phenyloctane were purchased from Acros Company, and all these materials were used without further purification. CH_2Cl_2 was bought from Peking Chemical Company and was dried by CaH_2 and distilled before experiment. Milli-Q-deionized water was used for all the experiments. ^1H NMR was recorded on an Advance Bruker 400M (400 MHz) spectrometer. Anal. Calcd was recorded on a FLASH EA1112 spectrometer.

1.2 Synthesis route and characterization method

The azobenzene derivative containing two symmetric diacetylene groups: Di (10, 12-Pentacosadiyn-1-yl) azobenzene-4, 4'-dicarboxylate (Azo-DA) was synthesized according to the synthesis route shown in Scheme S1. Azobenzene-4, 4'-dicarboxyl dichloride (42.58 mg, 0.139 mmol) and Et_3N (0.4 mL) were stirred in CH_2Cl_2 (10 mL), and 10, 12-Pentacosadiyn-1-ol (100 mg, 0.277 mmol) was added. The reaction was stirred at 20°C in the dark for two days. The mixture was diluted with 2 mL 1N HCl and extracted with CH_2Cl_2 (2×15 mL). The combined organic extracts were dried over MgSO_4 and solvents were removed in vacuo to give a light grey solid. Purification by column chromatography (silica gel, CH_2Cl_2) gave the desired Azo-DA (87.76 mg, 66%) as a white solid. ^1H NMR (400 MHz; CDCl_3 , 30°C) δ 7.53-7.01 (t, 8H), 4.34-4.31 (s, 4H), 2.49- 2.27 (m, 8H), 1.85-1.05 (m, 68H), 0.9 (m, 6H). Anal. Calcd for $\text{C}_{64}\text{H}_{94}\text{N}_2\text{O}_4$: C, 80.50; H, 9.85; N, 2.94. Found: C, 80.72; H, 9.80; N, 2.92.



Scheme S1. Synthesis route of Azo-DA.

2. Light system used for irradiation experiment

254 nm UV light was obtained from a 254 nm low pressure mercury lamp (10W) without any filter, 365 nm UV light was obtained from Xenon lamp (PLS-SXE 300, 50W) with 365 nm glass filter (Figure S1a), and visible light was obtained from Xenon lamp (PLS-SXE 300, 50W) with 435 nm filter (Figure S1b). And all these light system were bought from Peking Perfect Company (CHN). During the irradiation process, the temperature of the sample was kept between 20 °C to 25 °C, the lamp was at a distance of 25 cm from the sample. And all of the irradiation experiments as well as STM investigation were operated in the dark place.

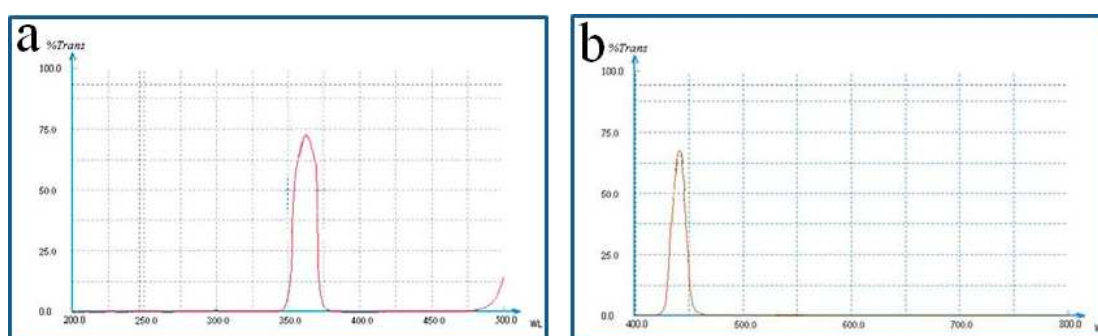


Figure S1. Spectra of Xenon lamp with filter (a) $\lambda_{\text{max}} = 365$ nm and (b) $\lambda_{\text{max}} = 435$ nm.

3. Sample preparation for STM investigation

3.1 self-assembled structure of Azo-DA

Azo-DA was dissolved in toluene with a concentration of less than 1 μ M. A drop of this solution was deposited on a freshly cleaved surface of highly oriented pyrolytic graphite (HOPG grade ZYB, Advanced Ceramics Inc., Cleveland, USA). After the solvent was completely evaporated (about 30 minutes), the sample was studied by STM.

3.2 Photo induced polymerization of Azo-DA

Azo-DA was dissolved in toluene with a concentration of less than 1 μ M. A drop of this solution was deposited on a freshly cleaved surface of HOPG. After the solvent was completely evaporated, the sample was subjected immediately to sufficient irradiation with UV light at 254 nm for 15 min. and then STM investigation was performed.

3.3 Photo induced isomerization of Azo-DA after polymerization

After imaging the structure of the irradiated sample (254 nm) by STM, some 1-phenyloctane was added into the irradiated sample, about 15 minutes later, it was irradiated by UV light at 365 nm for 30 min, then STM investigation was performed immediately. Next, the studied sample was exposed under visible light at 435 nm for 15 min. Then STM characterization was investigated again. One thing we want to mention is that 1-phenyloctane was added to the sample in order to keep the liquid environment during the irradiation process.

4. UV-Vis spectra of Azo-DA and polymerized Azo-DA

Perkin L950 (USA) spectrometer was used to record the UV-Vis spectra.

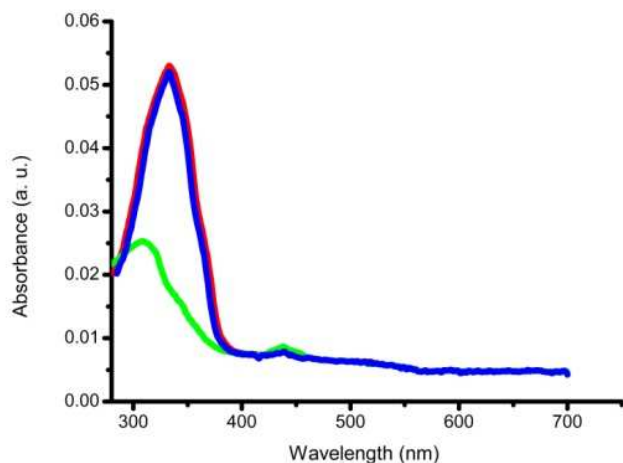


Figure S2 UV-Vis spectra of Azo-DA ($c=6\times 10^{-6}$ M) in 1-phenyloctane: Before (*trans*-Azo-DA, red); after UV light irradiation at 365 nm for 8 min (*cis*-Azo-DA, green); and after subsequent visible light irradiation at 435 nm for 12 min (*retrans*-Azo-DA, blue).

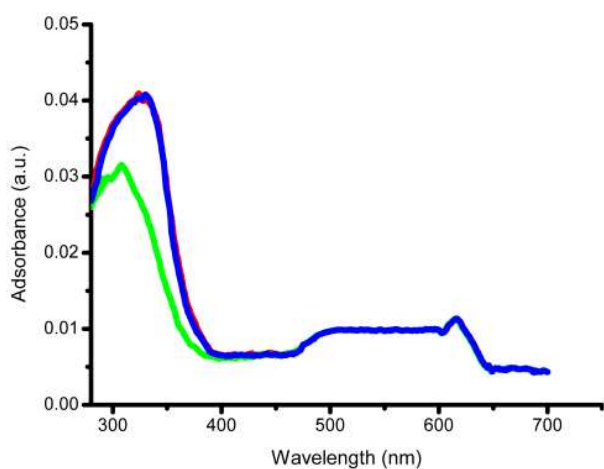


Figure S3 UV-Vis spectra of polymerized Azo-DA (Azo-poly(DA)) ($c=4\times 10^{-6}$ M) in 1-phenyloctane: Before (*trans*-Azo-poly(DA), red); after UV light irradiation at 365 nm for 10 min (*cis*-Azo-poly(DA), green); and after subsequent visible light irradiation at 435 nm for 15 min (*retrans*-Azo-poly(DA), blue).