

Reversible trans–cis photoisomerization of ALD/MLD-fabricated azobenzene-based inorganic-organic thin films

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We report the successful incorporation of photoresponsive azobenzene molecules through atomic/molecular layer deposition (ALD/MLD) in inorganic-organic thin films. Together with azobenzene-4, 4'-dicarboxylic acid as the organic precursor we use diethyl zinc (DEZ) as the inorganic precursor for our hybrid thin films of the $(\text{Zn-O-C}_{14}\text{H}_9\text{N}_2\text{-O}_4)_k$ type. The fabrication route developed for the hybrid films was then combined with the diethylzinc/ H_2O ALD process for ZnO in order to grow $[(\text{ZnO})_m(\text{Zn-O-C}_{14}\text{H}_9\text{N}_2\text{-O}_4)_{k=1}]_n$ superlattice structures where single azobenzene layers are sandwiched between thin crystalline zinc oxide blocks. The ratio of the ALD-ZnO and MLD-(Zn-O-C₁₄H₉N₂-O₄-) cycles was varied between 199:1 and 1:1. The kinetics of the trans-cis-trans photoisomerization were studied by alternate exposures to UV radiation and visible light ($\lambda > 450$ nm). Our inorganic-organic hybrid and superlattice structures were found to be photoreactive upon 360 nm irradiation. This observation confirms that switching processes with photochromic compounds, such as azobenzene, can be implemented in inorganic-organic thin films prepared by the ALD/MLD technique. This underlines the exciting new possibilities provided by the ALD/MLD technique for preparing novel light-sensitive materials.

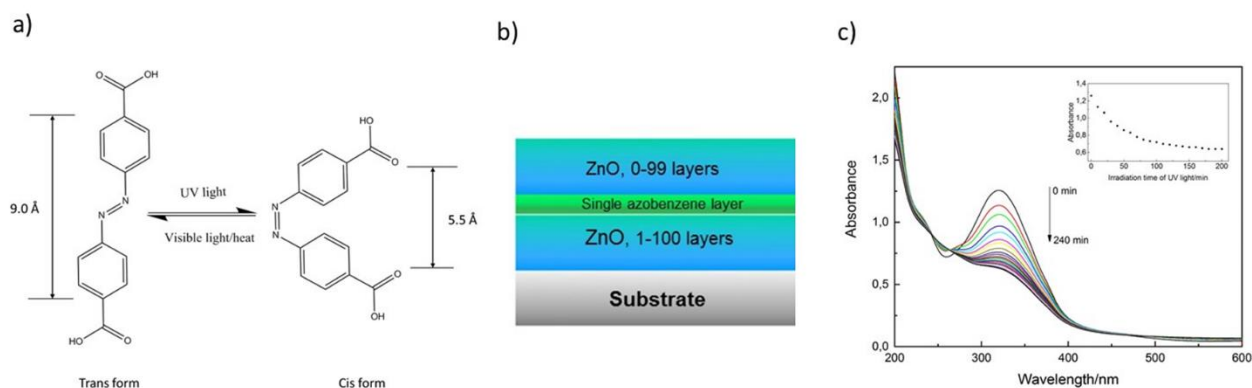


Figure 1. (a) A schematic of reversible change of conformation between the more stable Trans isomer and its less stable cis isomer of azobenzene-4, 4'-dicarboxylic acid upon light irradiation. (b) Layered structure of a superlattice film of $[(\text{ZnO})_m(\text{Zn-O-C}_{14}\text{H}_9\text{N}_2\text{-O}_4)_{k=1}]_n$ with different ratio of the ALD-ZnO and MLD-(Zn-O-C₁₄H₉N₂-O₄-) cycle. (c) Variation in the UV-visible spectra of the hybrid film with irradiation time by UV light. The inset shows the photoisomerization kinetics for the sample.