Submolecular-scale control of phototautomerization

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Photochemistry plays a central role in fundamental natural and artificial reactions such as photosynthesis, photocatalysis, or phototautomerization. Here, we demonstrate that using a tunable light source focused on a scanning tunneling microscope (STM) tip we drive and control the rate of a free-base phthalocyanine (H_2Pc) phototautomerization with sub-molecular precision, providing a path to pilot the intrinsic reactivity of the molecule with an external controllable stimulus. In addition, we probe the excited state of the molecule, which drives the tautomerization, by recording tip-enhanced photoluminescence (TEPL) spectra and maps where varying patterns for non-resonant and resonant excitation conditions are observed. These TEPL maps reflect different atomic-scale coupling between the localized plasmonic fields and the transition dipole moment of the molecule [1] influenced by the hydrogen switching process. Such sub-nanometric control can be used to study other photochemical processes with nearly atomic precision and will be beneficial for site-selective photochemistry potentially providing access to previously unavailable chemical compounds [2].

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