GIANT AMPLIFICATION OF FLUORESCENCE PHOTOSWITCHING IN ORGANIC NANOPARTICLES WITH FEW PHOTONS

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Controlling or switching the optical signal of a very large collection of molecules with the minimum of photons represents an extremely promising concept, from both fundamental and practical points of view. The development of photoresponsive nanodevices based on such an ***"amplified photoswitching effect"*** may find innovative applications, for instance, in the field of biocompatible nanophotoswitches for super-resolution imaging.

In this scope, we have prepared organic nanoparticles, based on a novel dyad molecule **PF** (Fig. 1a), advantageously combining photochromic and fluorescent moieties, designed to achieve an efficient fluorescence quenching by intramolecular Förster resonance energy transfer (FRET) when **PF** is in the closed form (CF).[1] The **PF** nanoparticles represent a state-of-the-art system, showing strong red emission in the open-form (OF) (Φ_F = 0.65), reversible fluorescence photoswitching upon UV-visible light irradiation, complete ON-OFF contrast, excellent photostability and fatigue-resistance. Most interestingly, upon UV irradiation, **PF** nanoparticles exhibit a complete fluorescence quenching even at very low OF→CF conversion yield: only 1% of **PF**(CF) molecules is enough to turn OFF the entire nanoparticles (Fig. 1b). This fascinating ***"giant fluorescence quenching"*** originates from a particularly efficient long-range intermolecular FRET within each nanoparticle, leading to the quenching of more than 400 fluorescent molecules, for only one molecule converted. In other words, one single UV photon induces the quenching of several dozens of **PF** molecules. Additionally, microscopy studies on individual nanoparticles demonstrated the emergence of a threshold effect during the fluorescence recovery upon the CF→OF reaction. No fatigue effect was observed over more than 100 UV-vis cycles on single nanoparticles (Fig. 1c-e).

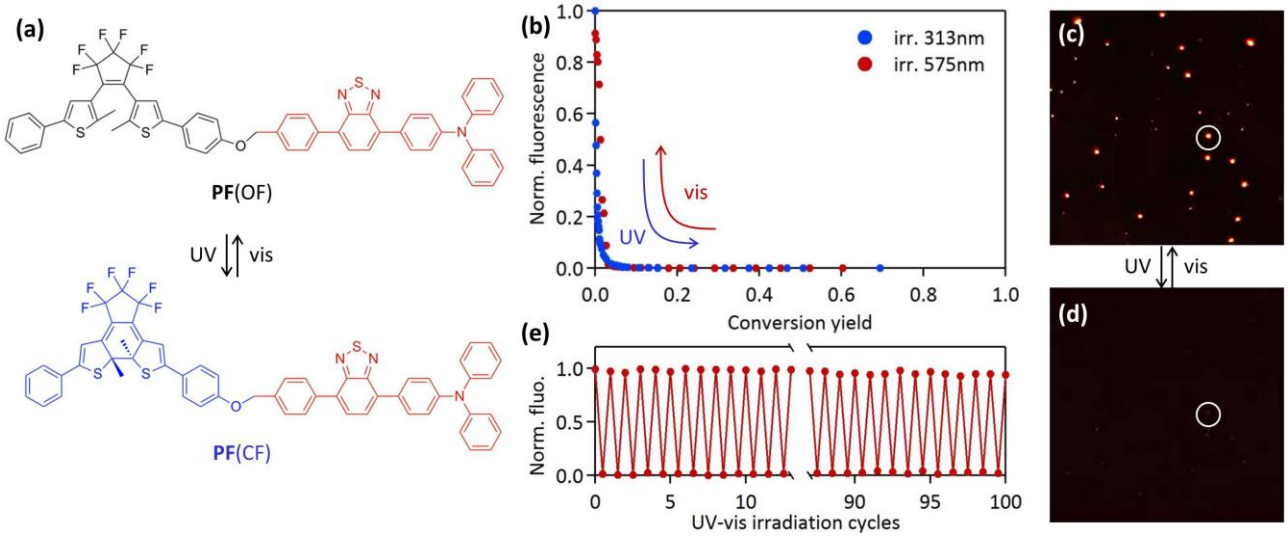

Fig. 1. *(a) Photochromism of the **PF** dyad molecule. (b) Giant amplification of fluorescence photoswitching of **PF** nanoparticles upon UV and visible irradiation. (c,d,e) Complete ON-OFF contrast and excellent fatigue resistance of individual **PF** nanoparticles.*

[1] (a) Fukaminato, T. *Photochem. Photobiol., C* **2011**, *12*, 177; (b) Métivier, R.; Badré, S.; Méallet-Renault, R.; Yu, P.; Pansu, R.B.; Nakatani, K. *J. Phys. Chem. C*, **2009**, *113*, 11916; Ouhenia-Ouadahi, K.; Métivier, R.; Nakatani, K. *et al. Photochem. Photobiol. Sci.*, **2012**, *11*, 1705.