

Single-photon spectroscopy for energy conversion applications

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Single-molecule techniques are commonplace in the life sciences but receive surprisingly little attention in the context of the materials science in energy conversion, although they make an obvious frequency-domain complement to conventional time-domain spectroscopy [1]. Photon-correlation spectroscopy (PCS) considers the statistics of luminescence photons emitted by a single object and can reveal fundamental dynamics lost in ensemble spectroscopy, such as the spontaneous symmetry breaking in the excited state of the *c*3-symmetric Ir(ppy) OLED triplet emitter [2]. In multichromophoric systems like conjugated polymers, PCS reveals how the fluorescence quantum yield of P3HT is strongly suppressed by singlet-triplet annihilation [3]. By means of solvent-vapour annealing, mesoscopic aggregates of multiple single conjugated polymer chains can be grown to probe the transition from the single molecule to the bulk [4]. Even large aggregates of megadalton weight retain features of deterministic single-photon emission – photon antibunching [5]. As a corollary, counting the number of photons emitted at once offers a unique metric to quantify the number of chromophores present [6], as well as revealing the interactions between chromophores in the form of singlet-singlet and singlet-triplet annihilation [7].

A particularly appealing application of PCS lies in tracking photocatalytic processes such as the dehalogenation reaction by a photoexcited rhodamine radical [8]. The technique offers a real-time assessment of the “turnover number”, demonstrating that one single dye molecule can break over a hundred covalent bonds per second. Finally, single-molecule single-photon techniques are also useful in examining the underlying mechanisms of energy transfer phenomena. Whereas light harvesting from II-VI semiconductor nanocrystals to molecules generally occurs by FRET [9], surprisingly, energy transfer from perovskite nanocrystals does not [10]. Instead, strong electron-phonon coupling enables very efficient non-resonant energy transfer. When energy transfer occurs to a dye molecule, the nanocrystal biexciton emission is completely suppressed, but so is the molecular triplet state because energy transfer from the nanocrystal biexciton activates reverse intersystem crossing in the dye.

[1] Lupton & Vogelsang, *Appl. Phys. Rev.* 8, 041302 (2021); [2] Steiner *et al.*, *JPC Lett.* 6, 999 (2015); Steiner *et al.*, *PRL* 112, 137402 (2014); [4] Stangl *et al.*, *PNAS* 112, 5560 (2015); [5] Steiner *et al.*, *JACS* 139, 9787 (2017); [8] Haimerl *et al.*, *Chem. Sci.* 10, 681 (2019); [6] Hedley *et al.*, *Nature Comm.* 12, 1327 (2021); [7] Schröder *et al.*, *ACS Nano* 15, 18037 (2021); [9] Becker *et al.*, *Nature Mat.* 5, 777 (2006); [10] Hofmann *et al.*, *Nano Lett.* 19, 8896 (2019).