Supporting Information

Tailoring Tautomerization of Single Phthalocyanine Molecules Through Modification of Chromophore Photophysics by the Purcell Effect of an Optical Microcavity

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Single-Molecule Detection in the Free Space and Inside a Microcavity

Figure S1a shows a fluorescence image acquired with a Gaussian laser mode and well-separated bright diffraction limited spots are observed from single PcS_4 molecules embedded in a thin PVA film. Once a single fluorescence molecule is in the excited state, it stays there for a finite time, which is on average equal to the fluorescence lifetime of the molecule, before it relaxes back to the ground state and can be excited again.[1] As a result, only one photon can be detected from the same molecule at a specific time. This temporal separation between two subsequent photon emission events from the same molecule is called photon antibunching.[2,3] Thus, direct proof of single-molecule emission is the observation of photon antibunching in the second-order intensity correlation function $g^{(2)}(\tau)$. Photon antibunching data can be observed with continuous wave (CW) or pulsed laser excitation.[1,3] The measured second-order photon correlation function obtained upon CW excitation from the bright spot indicated by the white arrow in Figure S1a is shown in red in Figure S1b. The clear photon antibunching dip with $g^{(2)}(\tau) = 0.35$ proves that the emission is from a single PcS_4 molecule. The photon antibunching result obtained under pulsed excitation, for another single PcS_4 molecule, is shown in blue in Figure S1b. In this case, the pulse at the lag time of zero is missing, which is a characteristic feature of single-molecule antibunching upon pulsed excitation.[3]

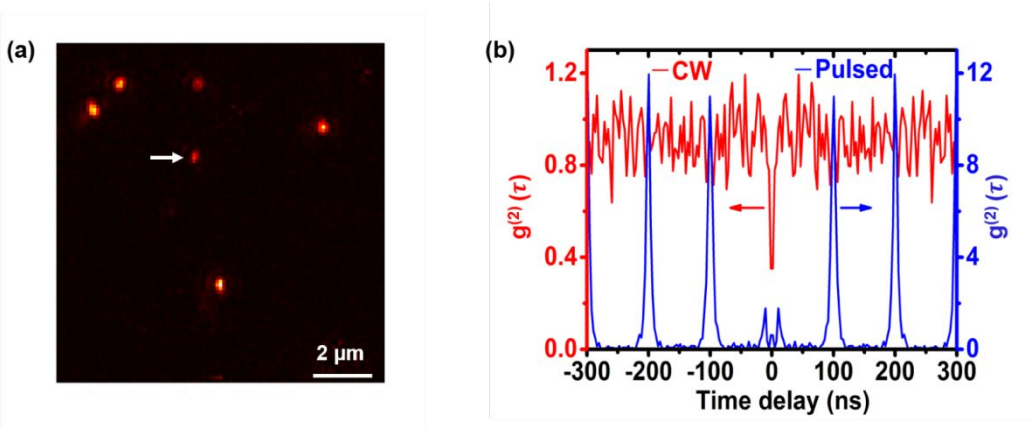

Figure S1. (a) Confocal microscopy image of single PcS_4 molecules embedded in PVA film. (b) Single PcS_4 molecule photon antibunching: the red curve shows the second order correlation function $g^{(2)}(\tau)$ measured from the single PcS_4 molecule indicated by the white arrow in Figure S1a, under continuous wave (633 nm laser) excitation and using the pulsed laser (640 nm) excitation (blue trace).

Antibunching of a single PcS4 molecule in a resonant microcavity is presented in Figure S2a. Figure S2b shows representative time-correlated single-photon counting histograms of single PcS_4 molecules embedded in PVA in free space (blue) and inside a resonant microcavity (green). The instrument response function (IRF) shown in black is used for the single exponential deconvolution fitting to evaluate the excited state lifetimes. The fits in Figure S2b give fluorescence lifetimes of 3.58 ns and 2.31 ns for molecules embedded in a thin PVA film in free space and inside a resonant microcavity, respectively.

Representative fluorescence intensity time traces of single PcS_4 molecules, recorded with the same binning time (10 ms), are shown in Figure S2c-d. To characterise the intermittency and the length of the time intervals in which a molecule resides in a dark-state or a bright-state, we define a threshold: when the detected signal is above a threshold (the black dashed lines in Figure S2c and d) of twice the background signal the molecule is ON (t_{on}) and below it is OFF times (t_{off}).

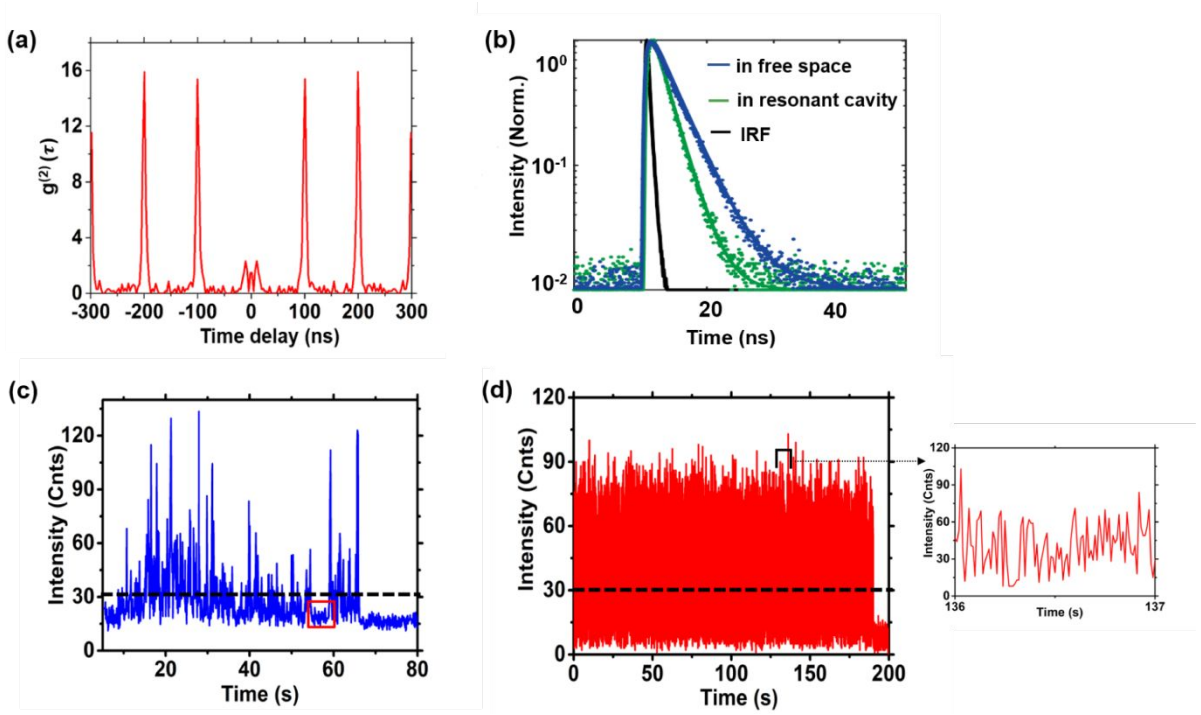

Figure S2. (a) Photon antibunching measured for single PcS_4 molecule in a resonant microcavity, using the pulsed laser (640 nm) excitation. (b) Fluorescence decays of a single PcS_4 molecule embedded in PVA in free space and for another molecule inside a resonant microcavity are shown in blue and green traces, respectively. The blue and green curves are single exponential fits to the fluorescence decays. The black curve shows the instrument response function (IRF). The fittings give excited-state lifetimes of 3.58 ns and 2.31 ns for a single PcS_4 molecule embedded in PVA in free space and inside a resonant microcavity, respectively. The error, i.e., the width of the 95% margin for both decays, is 0.04 ns. (c) Fluorescence intensity time trace of a single PcS_4 molecule embedded in a thin PVA film. (d) Fluorescence intensity time trace of a single PcS_4 molecule embedded in the PVA matrix and placed inside the resonant microcavity.

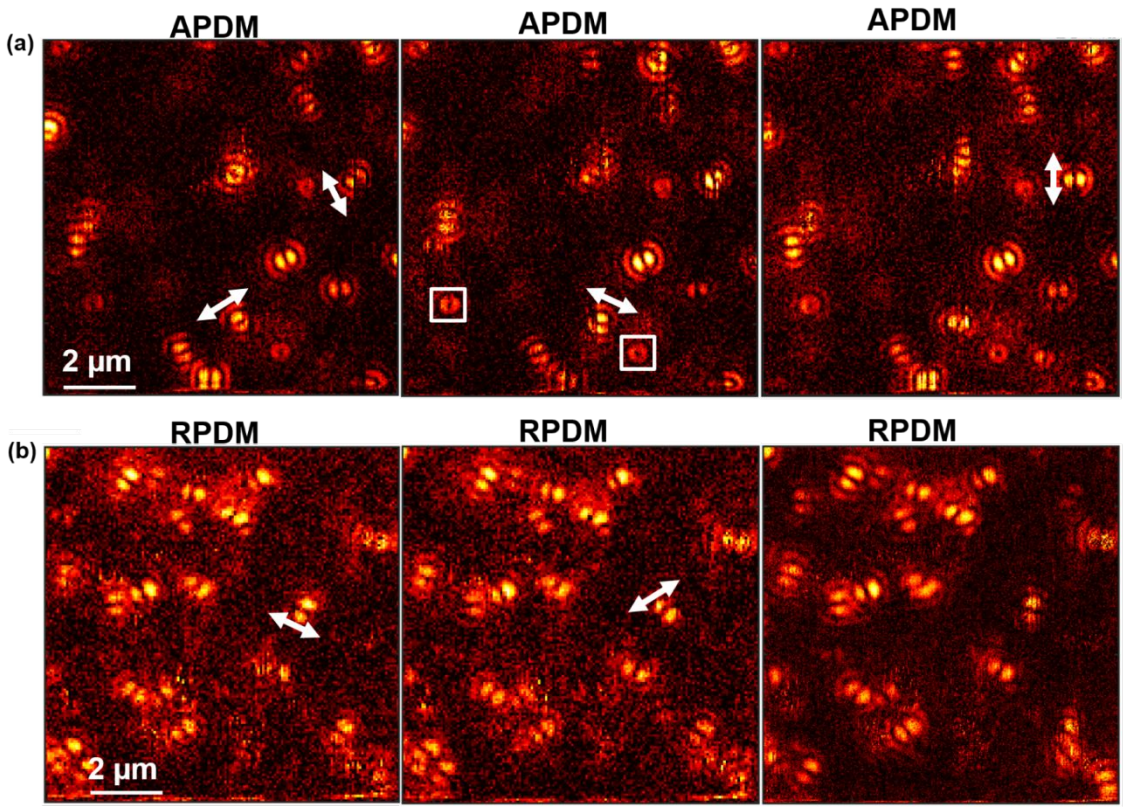

Figure S3. Series of successive confocal fluorescence images of single PcS_4 molecules embedded in PVA acquired with azimuthal (APDM) and radial (RPDM) polarization in free-space (a) and in a resonant λ/2-microcavity (b). Molecules that show double lobe pattern and a reorientation of the transition dipole moment are marked with double-headed arrows, whereas those that do show fast tautomerization (ring-like pattern) are marked with white rectangles.

Figure S4a shows the calculated intensity distribution of the electric field component in the focus (NA = 1.46) of the APDM and the RPDM in free space. The APDM mode has only in-plane component, whereas the RPDM consists of both in-plane and longitudinal components.[4] When the APDM and the RPDM modes are focused inside the λ/2 cavity, the in-plane components of RPDM and APDM have maximum electromagnetic field intensity in the center of the cavity (Figure S4b, the first and the last panels). In contrast, the longitudinal component of RPDM has a maximum intensity at the cavity mirrors and a minimum in the center (Figure S4b, the middle panel).[5] Thus, when we image the change of the transition dipole moment of single PcS_4 molecules inside a microcavity, we observe only double lobe patterns in the case of both the APDM and the RPDM excitations (Figure 3, main text).

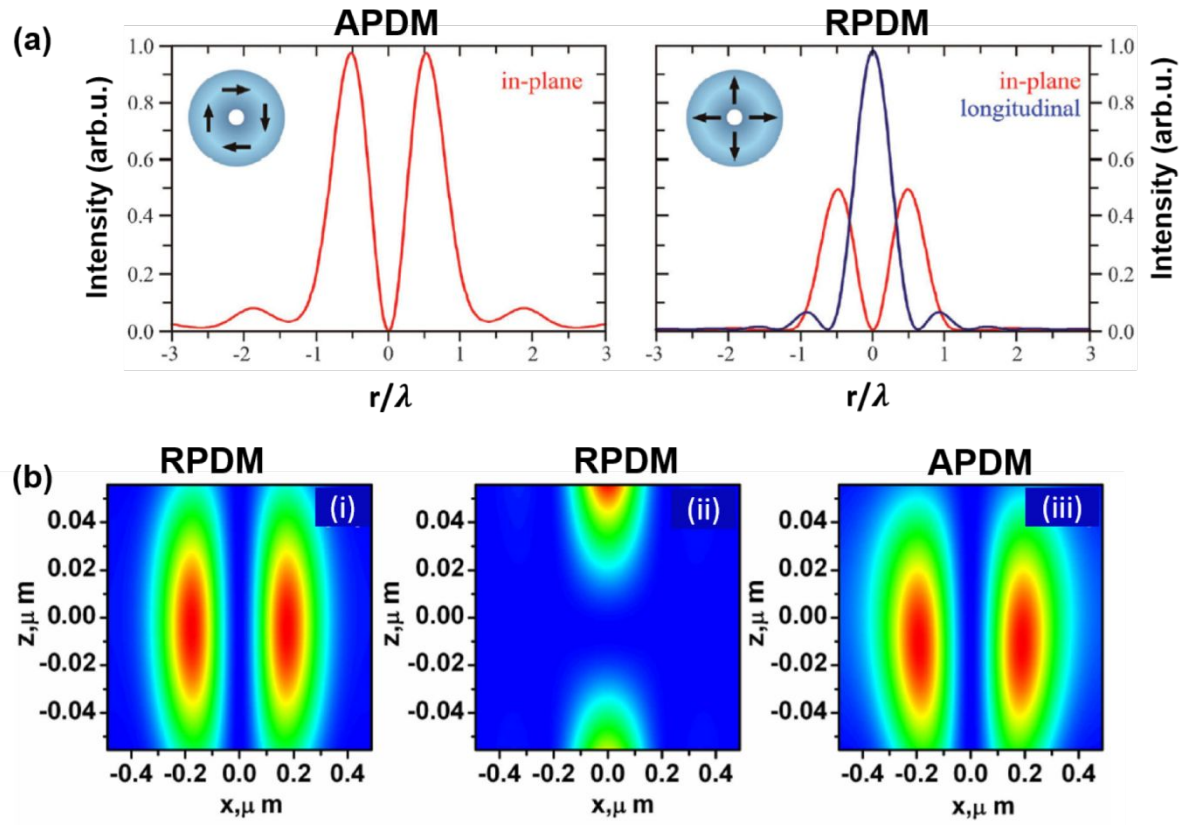

Figure S4. (a) The calculated field intensity distribution of the azimuthal polarized (APDM) and the radial polarized doughnut mode (RPDM) in free space. Adopted from ref. 4. Copyright (2011) Royal Society of Chemistry. (b) Electromagnetic field distribution of APDM and RPDM focused in λ/2 region of microcavity: RPDM in-plane (i), RPMD longitudinal (ii), and APDM in-plane (iii). Adopted from ref 5. Copyright (2008) Optical Society of America.

References

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