Electronic Supplementary Information (ESI)

Probing Single-Molecule Electron-Hole Transfer Dynamics at a Molecule-NiO Semiconductor Nanocrystalline Interface

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**Fig. S1** AFM topography image (A) and height profile (B) of dispersed NiO nanoparticles on cover glass surface. Steady-state excitation spectra (C) and fluorescence spectra (D) of \( m \)-ZnTCPP (1 µM) and \( m \)-ZnTCPP bound to NiO (10 µM) in ethanol.

The excitation spectra (Fig. S1C) show the typical intense Soret band (at 420 nm) corresponding to a transition from the ground-state to higher excited states and Q-bands (at 560 and 600 nm) corresponding to the higher vibrational mode Q(1,0) and the lowest energy vibrational mode Q(0,0), respectively, of the \( S_0 \rightarrow S_1 \) transition of regular porphyrins as reported previously\(^1, 2\) and the spectra is almost not altered upon the adsorption to the NiO NPs indicating that no significant aggregation occurred during adsorption. The Fluorescence spectra at excitation wavelength 532 nm (Fig. S1D) of \( m \)-ZnTCPP in ethanol showed a strong fluorescence with emission maximum at 615 and
660 nm, typical for regular porphyrins. When attached to NiO NPs, however, the emission was strongly quenched, which is attributed to the significant deactivation of the porphyrin singlet excited state via charge transfer pathways.

Fig. S2 Typical single-molecule fluorescence emission trajectories of \( m \)-ZnTCPP on ZrO\(_2\) NP surface and corresponding single-molecule fluorescence decays derived from the total photocount trajectories.

References: