Femtosecond fluorescence dynamics of a proton transfer dye interacting with silica-based nanomaterials

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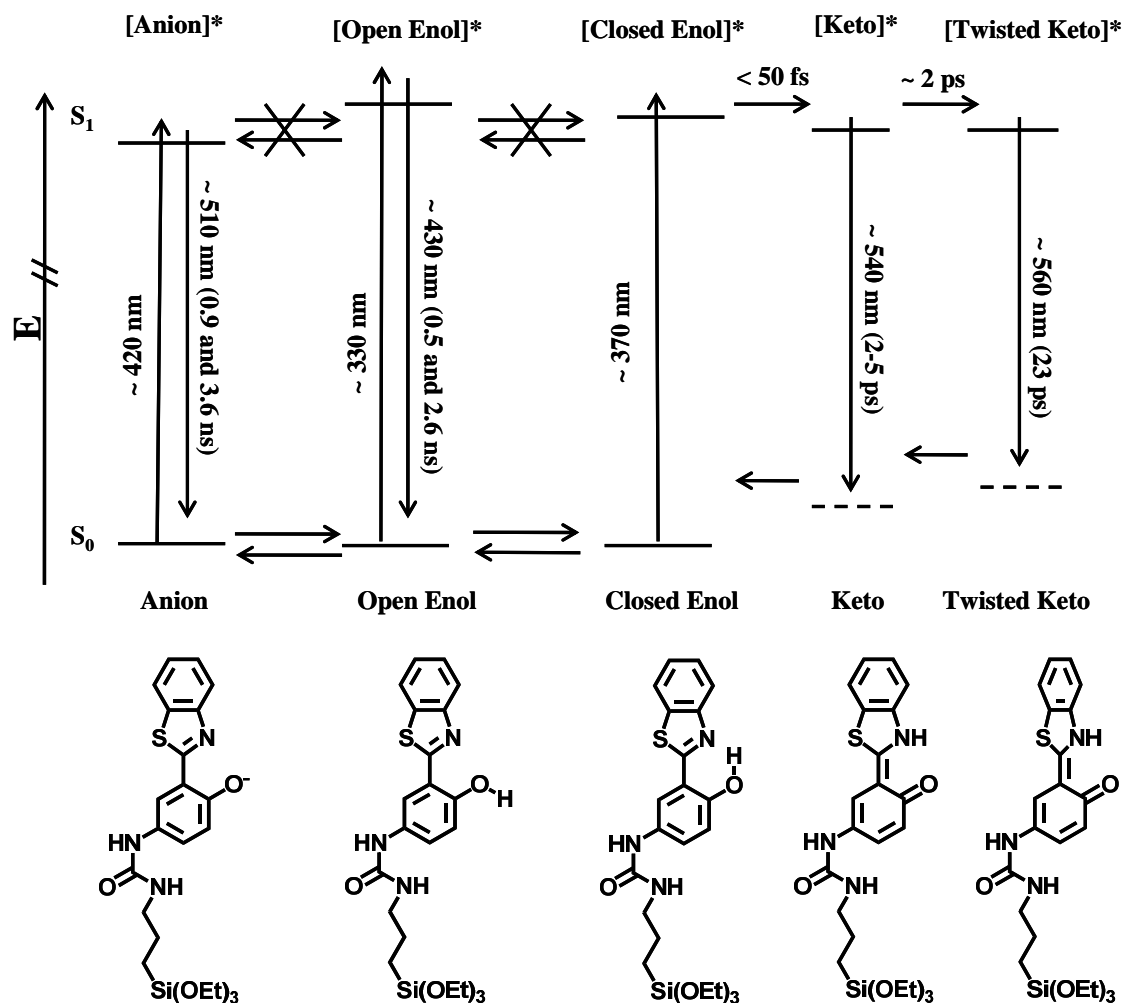
SI Scheme 1. Relevant photophysical data of the photoreactions involved in HBTNH2 in acetonitrile solutions. After excitation of the closed enol conformer, an excited state intramolecular process occurs in less than 50 fs to produce the keto structure. This keto one can emits in 2-5 ps and twists in ~ 2 ps to give a twister conformer, which relax to the electronic ground state by fluorescence in 23 ps. Finally, we suggest that the proton in the keto tautomers is transferred back to the initial closed enol structure in a thermal process. In addition to that, optical excitations of the so called open enol from where the OH group of the dye has established intermolecular H-bonds with the solvent molecules, and of the anion strcture where the proton has shifted to the solvent produce excited open enol and anion (phenolate type) species that are not in equilibrium at the excited state, contrary to the situation at the ground state. Both return to the electronic ground state by fluorescence in 0.5 and 2.6, and 0.9 and 3.6 ns, respectively. Note that the relative energy levels of S0 and S1 are not in scale.
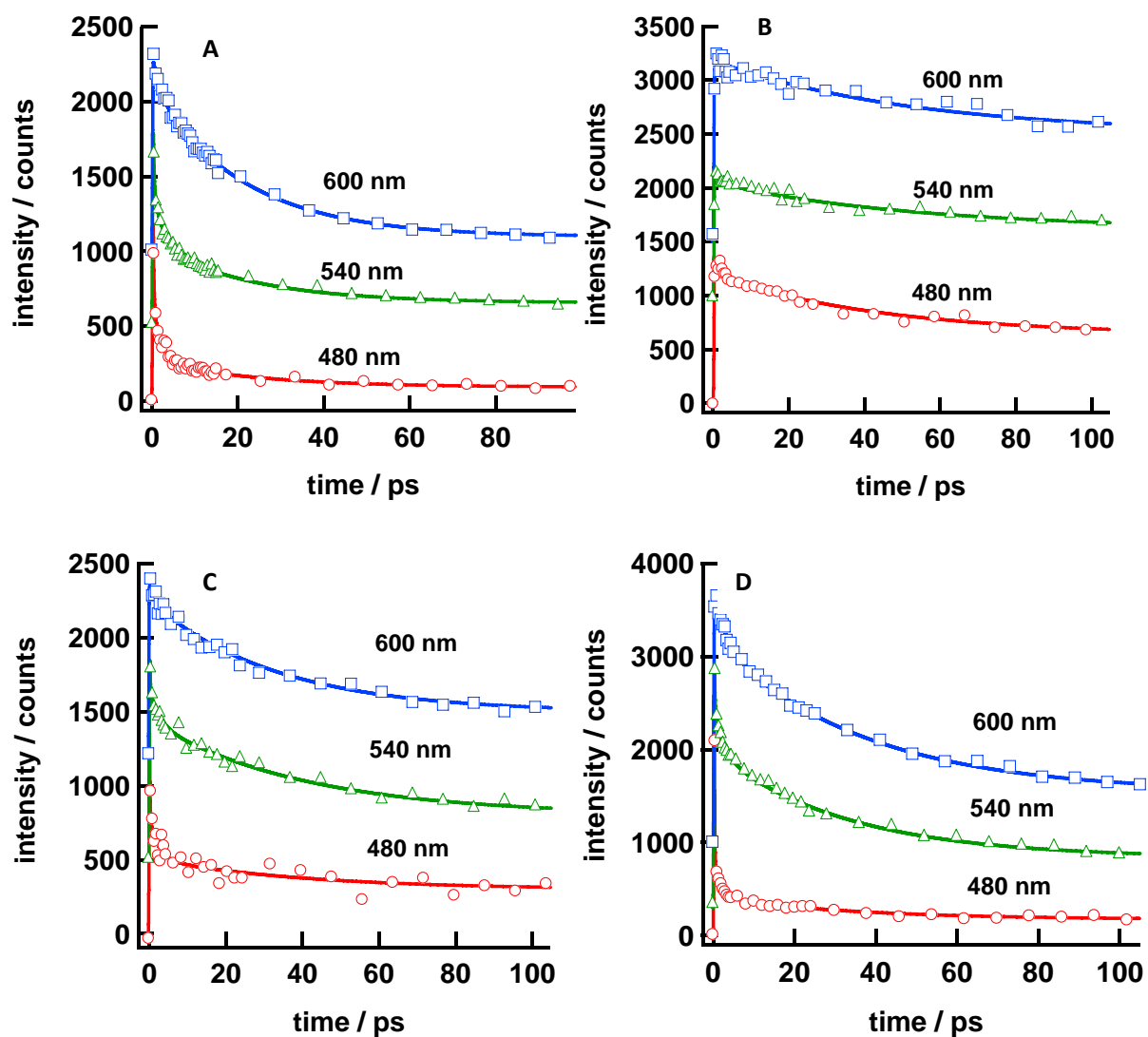
SI Figure 1. Fluorescence up-conversion transients of (A) HBTNH2, (B) HBTNH2-(Al)MCM-41, (C) HBTNH2-MCM-41 and (D) HBTNH2-Si in acetonitrile solution at three selected emission wavelengths (as indicated). The solid lines represent the nonlinear least square fits, and the relevant parameters of the multi-exponential fits (τ_i and a_i) are given in tables 1 and 2 in the main manuscript.
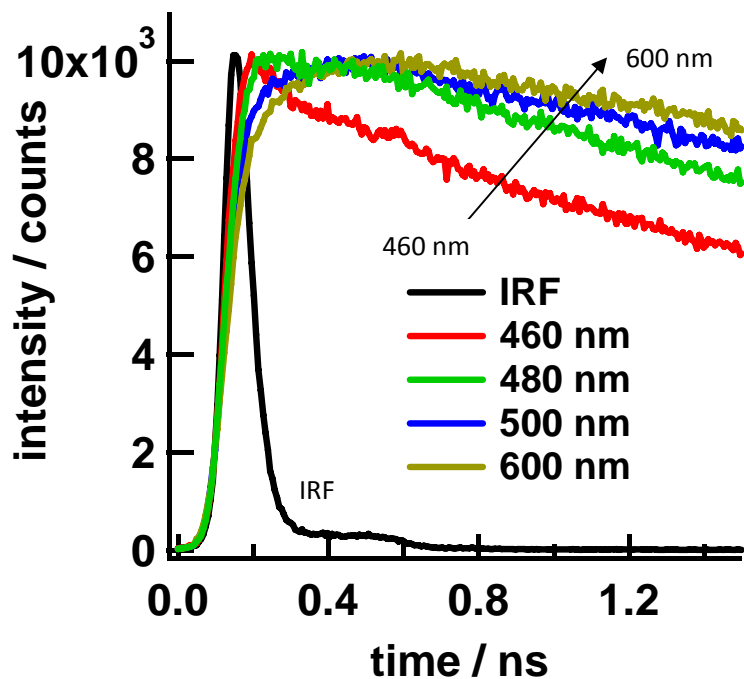
SI Figure 2. Representative time-correlated single-photon counting emission decays of HBTNH2 in acetonitrile solution in presence of KOH (at the indicated wavelengths). The excitation wavelength was 371 nm. The IRF (~ 80 ps) was measured as scattered laser light from a Ludox solution.

SI. Table 1A: Fluorescence lifetimes (τ_i) and relative contributions (a_i) in the emission decays of HBTNH2 in acetonitrile. The data were obtained by using a bi-exponential function to fit the signal from the time-correlated single-photon counting measurements upon excitation at 371 nm and gating the enol emission band (see Figure 1B).

λ/nm	τ_1/ps	a_1 %	τ_2/ns	a_2 %
435	0.5	5	2.6	95
445	0.5	6	2.6	94
460	0.5	6	2.6	94
480	0.5	9	2.6	91

SI Table 1B: Fluorescence lifetimes (τ_i) and relative contributions (a_i) in the emission decays of HBTNH2 in acetonitrile. The data were obtained by using a multi-exponential function to fit the signal from the time-correlated single-photon counting measurements upon excitation at 371 nm and gating the anion and keto emission bands (see Figure 1B).

λ/nm	τ_1/ps	a_1 %	τ_2/ns	a_2 %	τ_3/ns	a_3 %
510	23	45	0.9	15	3.6	40
530	23	65	0.9	10	3.6	25
550	23	90	0.9	7	3.6	3
640	23	98	0.9	2	-	-