# Supplementary Information

## A Slowing Down of Proton Motion from HPTS to Water Adsorbed on MCM-41 Surface

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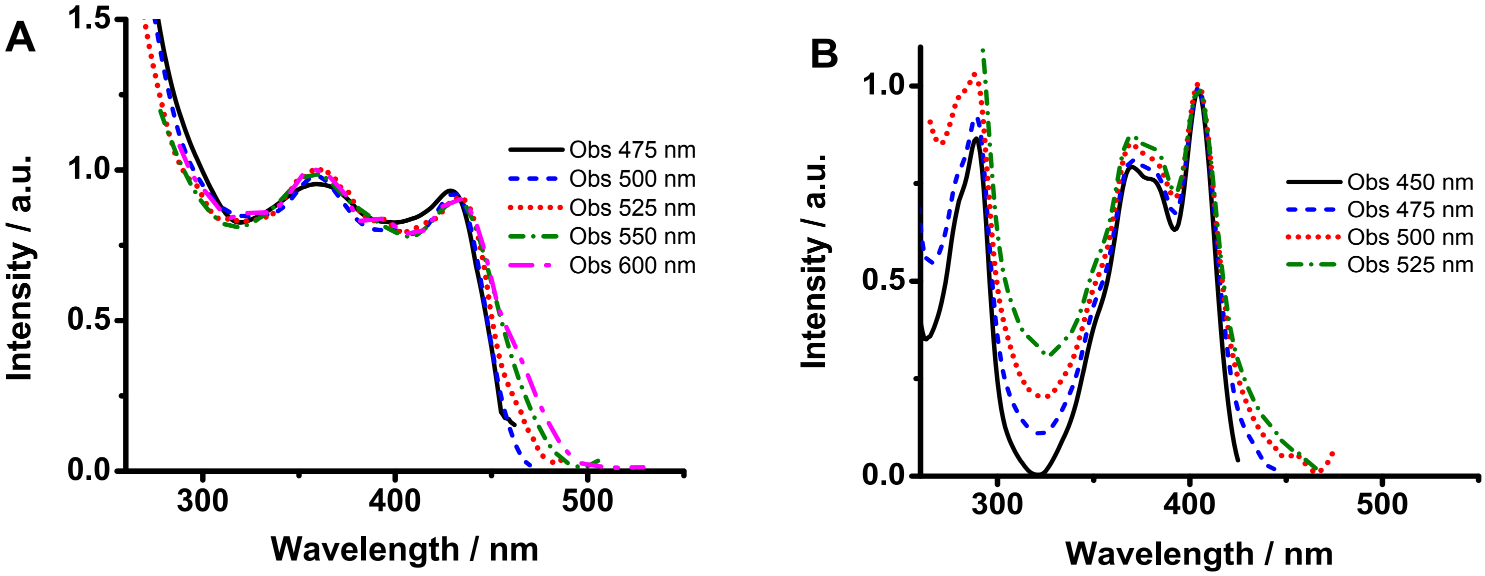


**Figure S1**. Excitation and absorption spectra of (A) HPTS and (B) HPTS/MCM-41 in solid-state. The observation wavelengths are given in the inset.

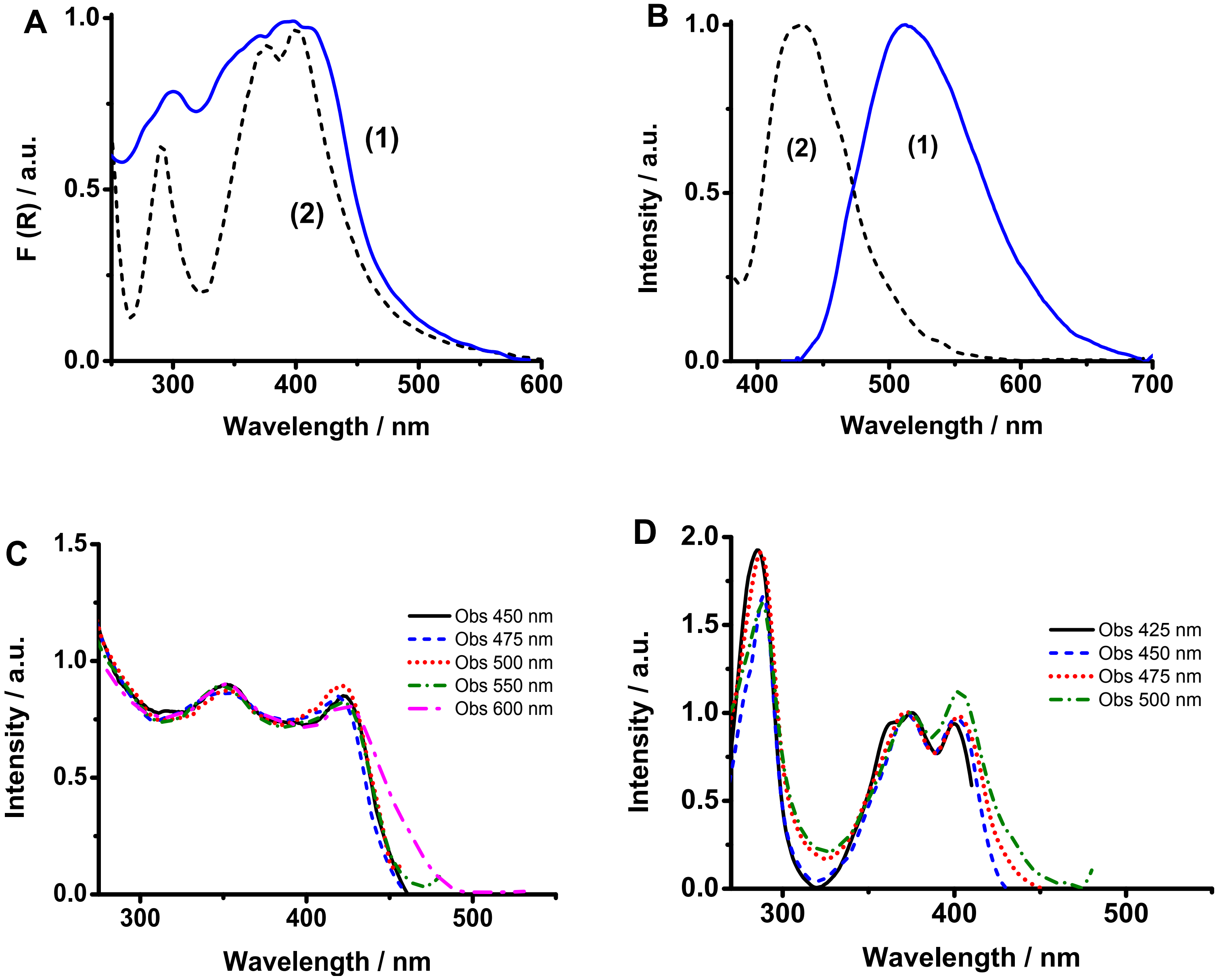


**Figure S2**. (A) Normalized (to the intensity maximum) Uv-visible diffuse transmittance and (B) fluorescence spectra of HPTS (solid line) and HPTS/MCM-41 (dashed line) in DCM suspensions. F(R) is the Kubelka-Munk function. $F(R)= ((1-R)^2/2R)$, where R is the diffuse reflectance from the sample. For emission the excited wavelength was 370 nm. Excitation and absorption spectra of (C) HPTS and (D) HPTS/MCM-41 in DCM suspensions. The observation wavelengths are given in the inset.

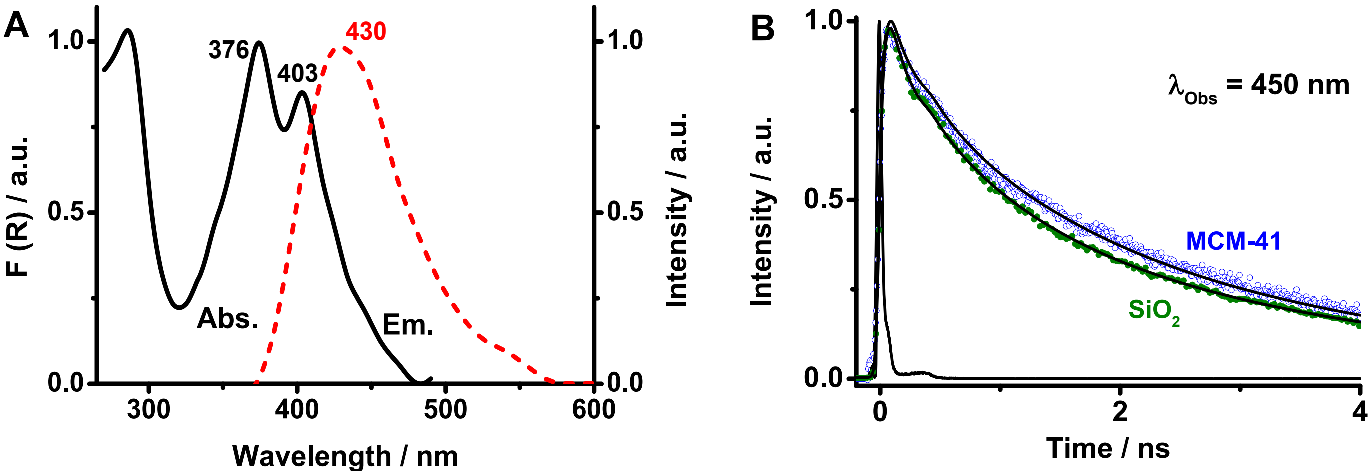


**Figure S3.** A) Normalized (to the maximum intensity) Uv-visible diffuse transmittance and fluorescence spectra of HPTS/SiO2 (HPTS 10-5 M) in DCM suspension. F(R) is the Kubelka-Munk function. F(R)= $((1\text{-R})^2/2\text{R})$, where R is the diffuse reflectance from the sample. For emission the excited wavelength was 370 nm. B) Magic-angle emission decays of HPTS (10-5 M) with MCM-41and SiO2 in DCM suspension excitation at 350 nm. The samples were observed at 450 nm. The solid lines are from the best-fit using a multiexponential function.

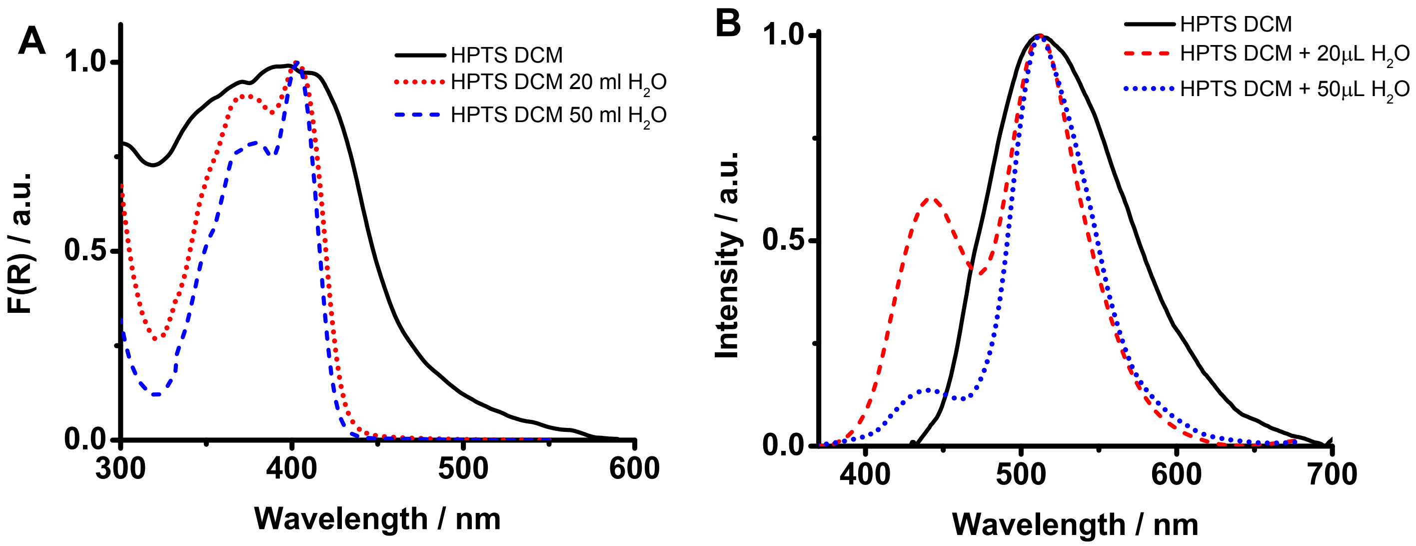


**Figure S4**. (A) Normalized (to the intensity maximum) Uv-visible diffuse transmittance and (B) fluorescence spectra of HPTS in DCM suspensions (solid line) and in presence of different amounts of water (20 and 50 μL). F(R) is the Kubelka-Munk function. F(R)= $((1\text{-R})^2/2\text{R})$, where R is the diffuse reflectance from the sample. For emission, the excited wavelength was 370 nm.

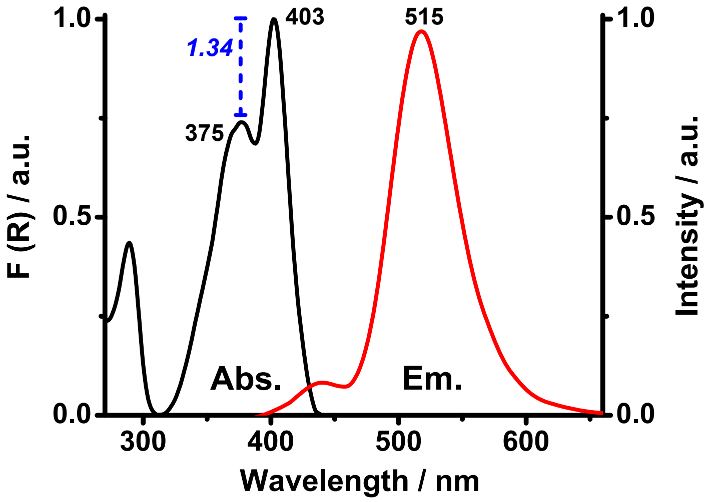


**Figure S5.** Normalized (to the intensity maximum) Uv-visible diffuse transmittance and fluorescence spectra of HPTS/MCM-41(hydrated) in DCM suspension. F(R) is the Kubelka-Munk function. F(R)= ((1-R)²/2R), where R is the diffuse reflectance from the sample. For emission, the excited wavelength was 370 nm.

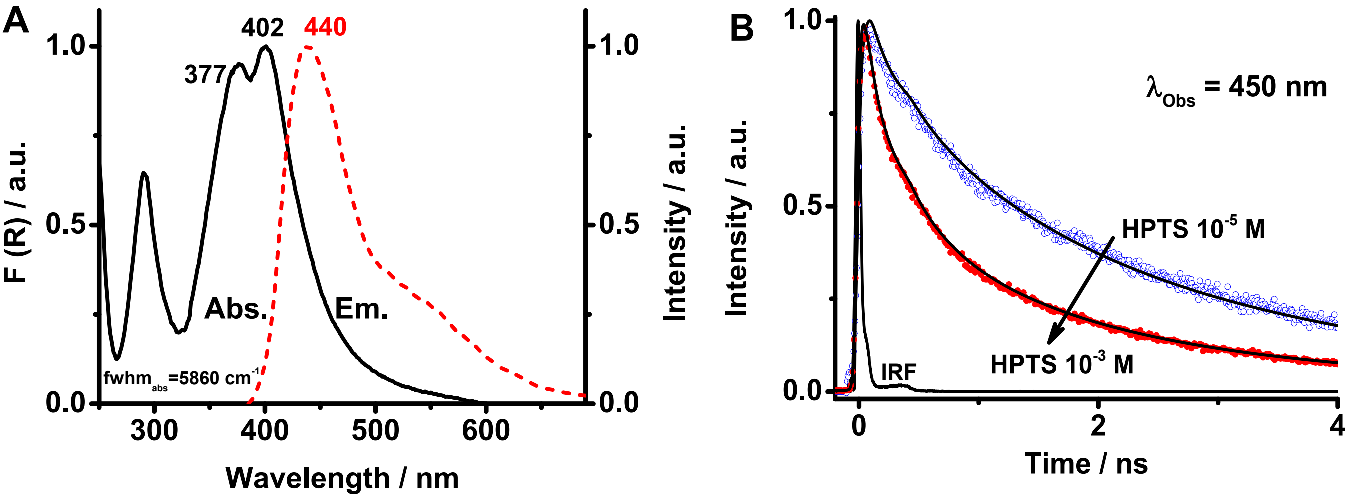


**Figure S6.** A) Normalized (to the maximum intensity) Uv-visible diffuse transmittance and fluorescence spectra of HPTS/MCM-41 concentrated (HPTS 10-3 M) in DCM suspension. F(R) is the Kubelka-Munk function. F(R)= ((1-R)²/2R), where R is the diffuse reflectance from the sample. For emission the excited wavelength was 370 nm. B) Magic-angle emission decays of HPTS/MCM-41 in DCM suspension to different concentrations excitation at 350 nm. The samples were observed at 450 nm. The solid lines are from the best-fit using a multiexponential function.

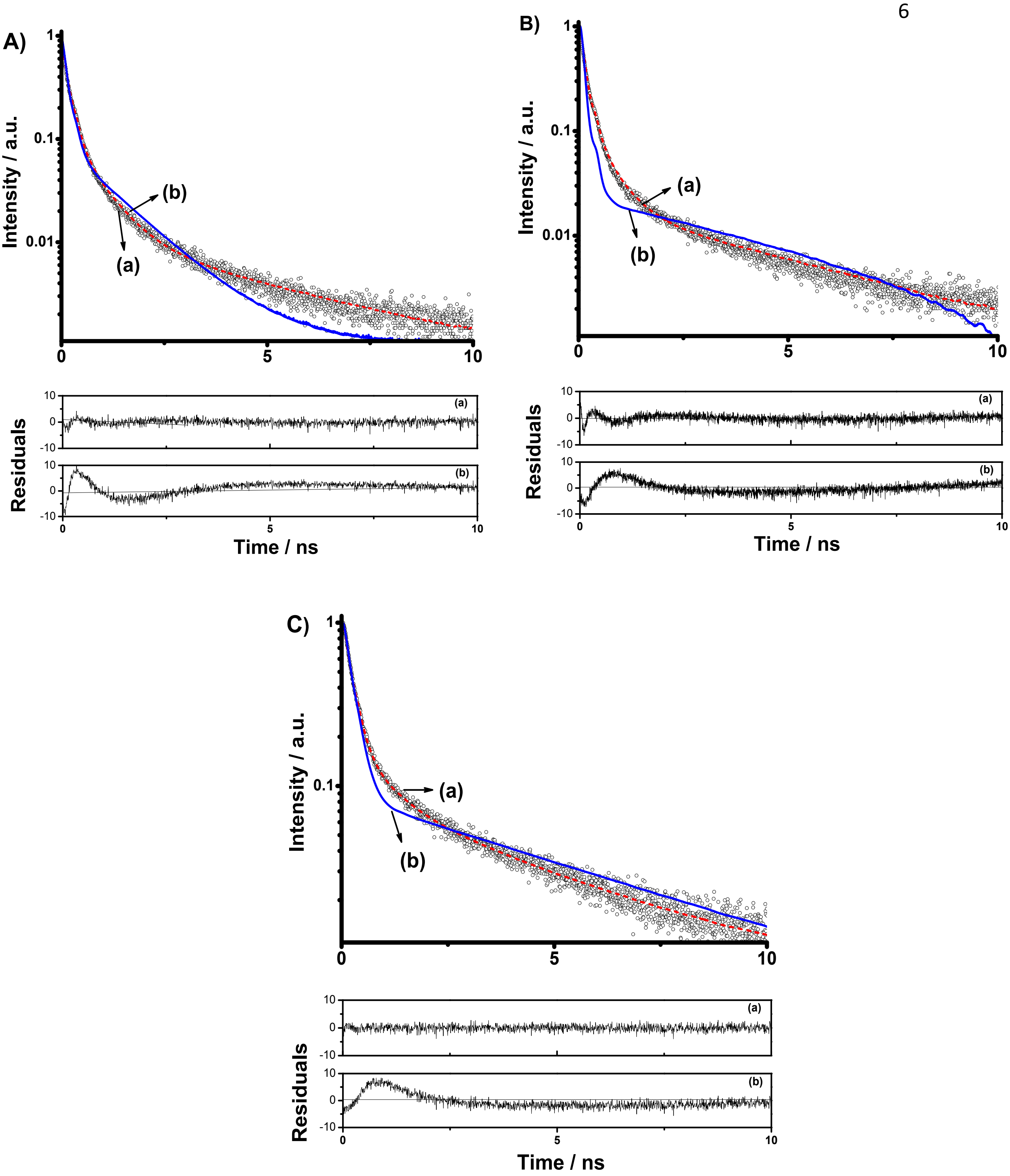


**Figure S7.** Magic-angle emission decays of HPTS (A) in bulk water, (B) in DCM suspensions with 1% of water and (C) interacting with MCM41 in presence of water. The samples were excited at 370 nm and observed at 430 nm. The fits (dashed and solid lines) show the results using (a) 3- and (b) 2-exponential models from which the former is more accurate.

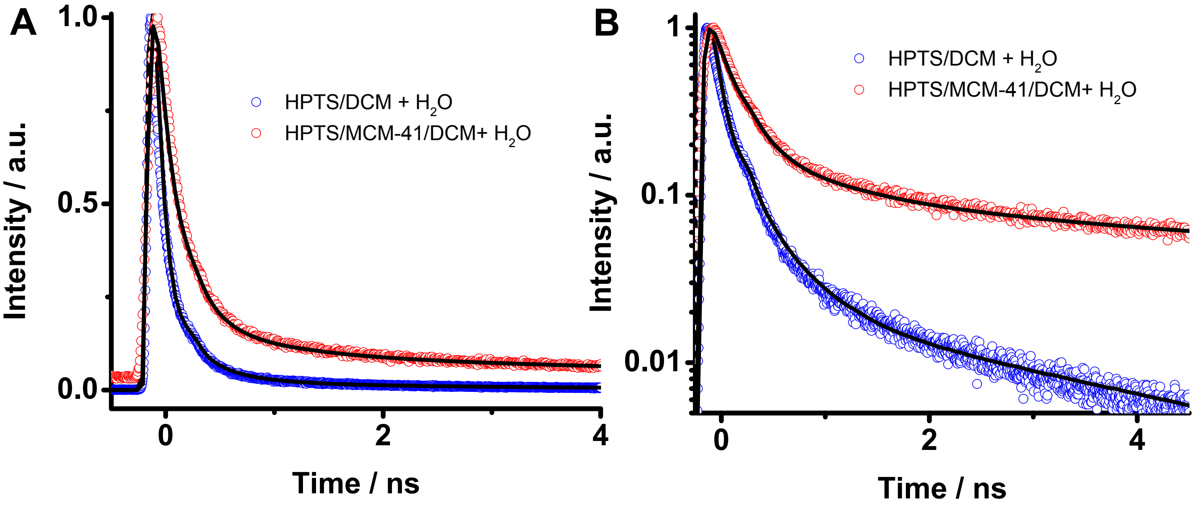


**Figure S8.** Magic-angle emission decays of HPTS and HPTS/MCM-41 in DCM suspension in presence of water in (A) linear and (B) logarithmic scale. The samples were excited at 370 nm and observed at 430 nm. The solid lines are from the computer fit using the GR model.

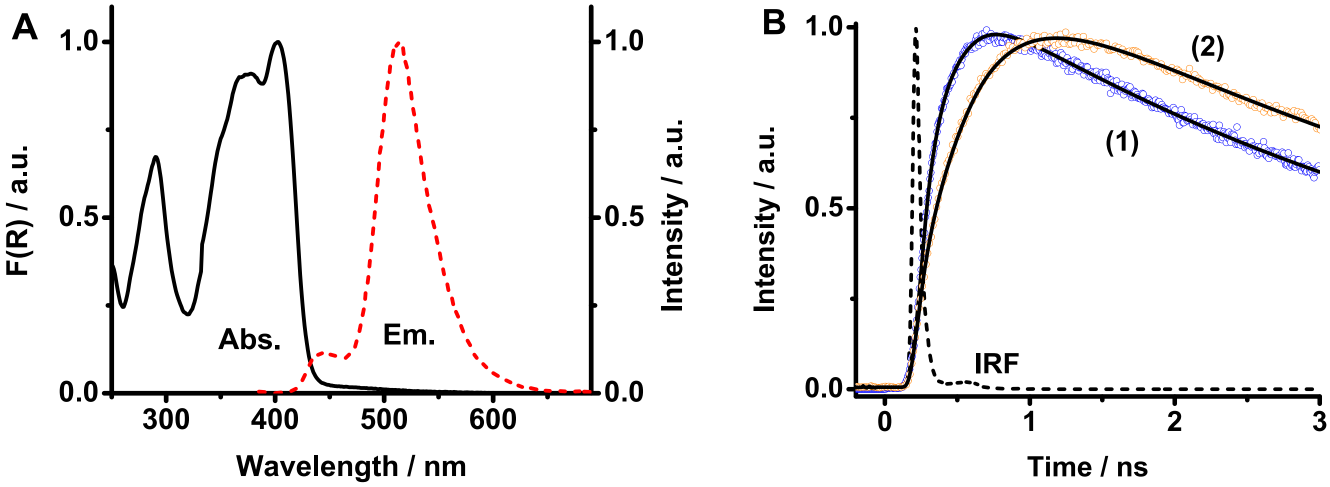


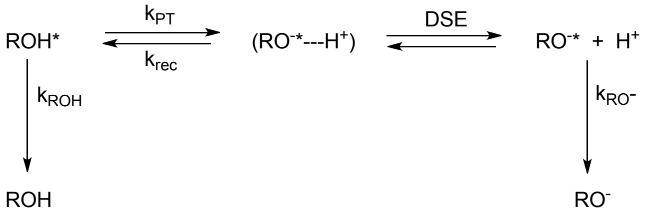
**Figure S9.** A) Normalized (to the maximum intensity) Uv-visible diffuse transmittance and fluorescence spectra of HPTS/MCM-41(dry) in DCM suspension with 20 μL of $D_2O$. F(R) is the Kubelka-Munk function. F(R)= ((1-R)$^2$/2R), where R is the diffuse reflectance from the sample. For emission the excited wavelength was 370 nm. B) Magic-angle emission decays of HPTS/MCM-41 in DCM suspension containing (1) $H_2O$ and (2) $D_2O$ upon excitation at 370 nm. The samples emission was observed at 550 nm. The solid lines are from the best-fit using a multiexponential function.

**Table S1.** Values of time constants ($\tau_i$) and normalized (to 100) pre-exponential factors ($a_i$) obtained from the fit of the emission ps-ns decays of HPTS, HPTS ($10^{-3}$ M) with MCM-41 and HPTS ($10^{-5}$ M) with $SiO_2$ in DCM suspension. The excitation of the samples was at 350 nm and observation as indicated. The estimated errors for the obtained values are 15-20 %.

| **Sample** | **$\lambda_{Obs}$/nm** | **$\tau_1$ / ps** | **$a_1$** | **$\tau_2$ / ps** | **$a_2$** | **$\tau_3$ / ns** | **$a_3$** |
|---|---|---|---|---|---|---|---|
| **HPTS/DCM (suspension)** | 450 | **120** | 40 | **600** | 32 | **2.2** | 28 |
| | 470 | **120** | 43 | **600** | 39 | **2.2** | 18 |
| | 500 | **120** | 46 | **600** | 37 | **2.2** | 17 |
| | 525 | **120** | 48 | **600** | 32 | **2.2** | 20 |
| | 550 | **120** | 50 | **600** | 32 | **2.2** | 18 |
| | 575 | **120** | 54 | **600** | 31 | **2.2** | 15 |
| | 600 | **120** | 56 | **600** | 30 | **2.2** | 14 |
| **HPTS $10^{-3}$/MCM-41 (suspension)** | 400 | **50** | 60 | **320** | 29 | **2.5** | 11 |
| | 410 | **50** | 58 | **320** | 28 | **2.5** | 12 |
| | 430 | **50** | 57 | **320** | 26 | **2.5** | 17 |
| | 450 | **50** | 51 | **320** | 25 | **2.5** | 24 |
| | 470 | **60** | 46 | **350** | 17 | **2.5** | 27 |
| | 490 | **65** | 48 | **380** | 19 | **2.4** | 23 |
| | 510 | **70** | 60 | **490** | 24 | **2.2** | 16 |
| | 525 | **80** | 60 | **530** | 24 | **2.2** | 16 |
| | 550 | **100** | 62 | **580** | 24 | **2.2** | 14 |
| | 575 | **100** | 61 | **580** | 26 | **2.2** | 13 |
| | 600 | **120** | 57 | **600** | 28 | **2.2** | 15 |
| | 620 | **120** | 55 | **600** | 29 | **2.2** | 16 |

| **Sample** | **$\lambda_{Obs}$/nm** | **$\tau_1$ / ps** | **$a_1$** | **$\tau_2$ / ns** | **$a_2$** |
|---|---|---|---|---|---|
| **HPTS $10^{-5}$/$SiO_2$ (solid)** | 410 | **320** | 38 | **2.3** | 62 |
| | 440 | **320** | 35 | **2.3** | 65 |
| | 450 | **320** | 32 | **2.3** | 68 |
| | 470 | **320** | 32 | **2.3** | 68 |
| | 490 | **320** | 30 | **2.3** | 70 |
| | 500 | **320** | 30 | **2.3** | 70 |

## Reversible Diffusion Model



According to Scheme, the proton dissociation ($k_{PT}$), leads to formation of the contact ion pair ($RO^{-*}\cdots H^+$), whereas recombination ($k_{rec}$) re-form the excited acid. Separation of a ($RO^{-*}\cdots H^+$) from the contact radius, a, to infinity is described by the transient solution of the Debye-Smoluchowski equation (DSE). The DSE model has been described in detailed by numerous studies.[1-3] The DSE solution is determined by several parameters:

a) The potential of interaction, V(r), between $RO^{-*}$ and $H^+$ is assumed to be the Coulomb potential, which is governed by the Debye radius:

$$V(r) = -R_D / r \qquad (1.1)$$

$$R_D = e^2 \left| z_{RO^-} z_{H^+} \right| / (\varepsilon k_B T) \qquad (1.2)$$

where z are ionic charges of the proton (1 charge = 1 $H^+$) and anion (4 charge = 1$RO^-$ and 3$SO_3^-$), e is the electronic charge, ε is the dielectric constant of the solvent, T temperature absolute and $k_B$ is the Boltzmann constant.

b) The contact distance of the ion pair, a, which is the center-to-center distance between both species. “a” and “A” are the minimum and maximum distance which both species due is in contact for that the protonic transfer process can occur. (a = 6.8 Å and A depends on the medium).[4]

c) The relative diffusion constant (D) of the proton and base, which we assume to be independent of the interparticle separation r.

$$D = D_{RO^-} + D_{H^+} \qquad (1.3)$$

$D \approx D_{H^+}$; due to that the 99 % of the mobility will be given by the water molecules.

The asymptotic long-time florescence tail amplitude and the time dependence of the ROH* from of a reversible photoacid are given by:

$$I_f^{ROH}(t) \cong \frac{\pi a^2 k_a \exp[-V(a)]}{2 k_{PT} (\pi D t)^{d/2}} \qquad (1.4)$$

where $\tau_f$ is the excited-state lifetime of the $RO^-$, *d* is the dimensionality of the relevant problem. This equation shows that the tail amplitude depends on several parameters and that its time depends on the dimensionality of the system.

We estimate the diffusion coefficient of the deuterion ($D_{D+}$) on the HPTS/MCM-41 systems in presence of deuterated water, from the ratio between the diffusion coefficient of the proton ($D_{H+}$) and $D_{D+}$ in bulk water, and the $D_{H+}$ value (2.4 x $10^{-5}$ $cm^2/s$) when the water is confined within mesoporous material[5, 6]

The ratio in bulk water is equal to:

$$(D_{H+}=9.5x10^{-5}\ cm^2/s)/(D_{D+}=6x10^{-5}\ cm^2/s) = 1.58$$

therefore, the value $D_{D+}$ of the deuterated water within mesoporous materials can be assumed as:

$$(D_{D+}) = (D_{H+}=2.4x10^{-5})/\ 1.58 = 1.5x10^{-5}\ cm^2/s$$

## References

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6. A. A. Milischuk and B. M. Ladanyi, *J. Chem.Phys.*, 2011, **135**, 174709.