



# Confinement effect on ultrafast events of a salicylideneaniline derivative within mesoporous materials



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## ABSTRACT

We report on femtosecond (fs) studies of HBA-4NP interacting with MCM41, Al-MCM41 and SBA15 materials, and discuss the dynamics of caged monomers and J-aggregates. For MCM41 and Al-MCM41 composites, and upon excitation at 380 nm (monomers region) the ultrafast dynamics (250 fs and 2.5 ps for HBA-4NP/MCM41, 350 fs and 3.5 ps for HBA-4NP/Al-MCM41) is slower than that observed in solution due to aggregates formation inside the material pores. While exciting at 410 nm, we got a slower behaviour. However, for HBA-4NP/SBA15 composites, with a low loading, where the caged monomers are the main guests, we recorded faster dynamics (200 fs and 2 ps) independently on the pumping wavelength. These results show how the properties of mesoporous materials, especially its pore size and Al-doping, affect the nature of the formed composites and their ultrafast photodynamics.

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## 1. Introduction

Silica-based materials are being used in important scientific and technology fields such as catalysts [1–3], photonics [4–6], and medicine [7–10], to cite a few of them. Porous silica materials, like zeolites and mesoporous materials, are widely used as host to encapsulate organic molecules, dyes and drugs [11–18]. However, the use of zeolites, hinders the encapsulation of large molecules due to their small pore size (~1 nm). The replacement of zeolites by mesoporous silica materials known as M41S, allowed to overcome such limitation [1]. The versatility of these M41S materials, especially that of the hexagonal structure like MCM41, lies in the simplicity of the synthetic approaches, which allow their easy modification and functionalization, leading to more controlled structural properties, such as tunable pore size (1–20 nm) and presence of specific reaction centers [1,19,20]. Moreover, this kind of materials is characterized by a high surface area, a homogeneous and ordered distribution of pores and a high thermal, chemical and mechanical stability [21–23]. As a result, they are being used in many applications for efficient adsorption and separation processes, catalysis and molecular confinement [1–3,5,24–28].

Understanding the intimate interactions between caged molecules (guests) and the used silica-based materials (hosts) is paramount to get better composites for a specific application, and helps to elucidate the reaction mechanisms involved in the formed complexes. It is well known that trapped guests within hosts exhibit physical and chemical behaviors different from those observed in solution [11–18,28–33]. For example, it has been observed for the dye studied here, (E)-2-(2-hydroxybenzylidene) amino-4-nitrophenol (HBA-4NP), that in solution and upon UV-excitation it undergoes an ultrafast excited-state intramolecular proton-transfer (ESIPT) reactions coupled to a twisting process [34]. The twisting motion, together with the short fluorescence lifetime in solution and the presence of a strong electro-acceptor group (–NO<sub>2</sub>) make this dye an interesting new compound to explore confined ultrafast dynamics within silica-base materials. Thus, encapsulating HBA-4NP in these hosts, such as NaX, NaY, MCM41, Al-MCM41 and SBA15 materials, its fluorescence intensity increases as a result of the restriction, specific and nonspecific interactions with the silica framework [30,31]. In addition to that, we observed molecular aggregation. The trapped dye molecules are in form of monomers, H- and J-aggregates, which undergo an ESIPT reaction at S<sub>1</sub> with the formation of keto (K) type phototautomers [30,31]. These species exhibit interesting spectroscopic and dynamical properties, making these composites of great interest for possible

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applications in nanophotonics. Moreover, depending on the morphological and chemical properties of the host, the relative populations and photobehavior of these species can be modulated. For example, caged K monomer shows different fluorescence lifetime in NaX and NaY zeolites (~6 ns) that in mesoporous materials (~2 ns), and both are much longer than that observed in DCM solutions (14 ps). These changes are also reflected at the ultrafast regime. Thus, we have reported on femtosecond (fs) studies of HBA-4NP in solution and within NaX and NaY zeolites, observing that the ultrafast processes are also affected by the confinement of these hosts [34]. The dynamics is slower than that in DCM, and is excitation-wavelength dependent, reflecting host-guest and guest-guest specific and nonspecific interactions [34]. However, ultrafast observation of this kind of interactions using mesoporous materials with different pore sizes is not yet elucidated to get a bigger and precise picture, despite the reported ps-study [31].

Herein, we report on the ultrafast photodynamics of HBA-4NP interacting with MCM41, Al-MCM41 and SBA15 materials in dichloromethane (DCM) suspensions. We found that the dynamics strongly depends on the properties of the used host materials, and on the excitation wavelength. For MCM41 and Al-MCM41 complexes, the observed times (250–350 fs and 2.5–3.5 ps) are slower than in a DCM solution (100 fs and 1.2 ps). The slowing down is more pronounced in Al-MCM41 host due to a larger J-aggregates formation promoted by the Al-atoms presence in the silica framework. Both dynamics of MCM41 and Al-MCM41 complexes exhibit changes with the excitation wavelength, observing the slowest ones when exciting at 410 nm (J-aggregates region). On the other hand, for SBA15 host, the dynamics (180 fs and 2.0 ps) is similar to that in solution. This is due to low encapsulation ability (40% loading) and its larger pore size (6 nm) not allowing robust confinement. For the global picture, we compare the dynamics observed here with the obtained in DCM, triacetin (TAC) (highly viscous medium), and within NaX and NaY zeolites, previously reported [34]. Our results give new insights into the photobehaviour of HBA-4NP/mesoporous complexes, and thus can help in the design of new nanophotonics devices (nanosensors, nano-LEDs) based on this kind of materials, and for a better understanding of the interaction of aromatic reactants when using them in catalysis and drugs delivery as supports and vehicles.

## 2. Experimental section

The synthesis of (E)-2-((2-hydroxybenzylidene)amino-4-nitrophenol) (HBA-4NP) was described in a previous report [30]. Dichloromethane (DCM, spectroscopic grade 99.9%, Scharlab), and MCM41, Al-MCM41 and SBA15 materials (purity < 99%, Sigma-Aldrich), were used as received. HBA-4NP/mesoporous materials were prepared by adding 100 mg of dried mesoporous material (5 h at 270 °C) to 10 mL of DCM containing  $\sim 2 \times 10^{-3}$  M of HBA-4NP, and stirred at room temperature for 24 h. To remove the dye molecules loosely adsorbed on the external surface of the host, the obtained material was washed three times with DCM. Finally, the composites were dried under vacuum at room temperature. The loading of the samples was calculated knowing the absorption intensities of HBA-4NP in the parent DCM solution and in the supernatant phase after the first washing process. We obtained loading (%) 85, 95 and 40 for MCM41, Al-MCM41 and SBA15 materials, respectively.

Femtosecond time-resolved emission transients were collected using fluorescence up-conversion technique [34]. The system consists of a fs-Ti:sapphire oscillator (MaiTai HP, Spectra Physics) coupled to a second harmonic generation setup. The oscillator pulses (90 fs, 250 mW, 80 MHz) were centered at 760 and 820 nm, and doubled in an optical setup using a 0.5 mm BBO crystal to

generate a pumping beam at 380 and 410 nm, respectively. The polarization of the excitation was set to magic angle with respect to the fundamental gating beam. The samples, in the form of a fine powder in a DCM solution, have been placed in a 1-mm thick rotating quartz cell. The fluorescence was focused with reflective optics into a 1-mm BBO crystal and gated with the remaining fundamental fs-beam. The excitation light (380 and 410 nm) scattered from the sample was blocked by a cut off filter (YL12, CDP Systems) placed after the first collecting mirror. No photodegradation was detected during the experiments. To analyse the fs-transients, a multiexponential function convoluted with the instrument response function (IRF ~170 fs) was used to fit the up-converted emission signals. The errors for the calculated time constants were lower than 15%, and the experiments were performed at 293 K.

## 3. Results and discussion

### 3.1. Steady-state observation

To begin with, we briefly discuss the recently reported steady-state spectral behaviour of HBA-4NP within MCM41, Al-MCM41 and SBA15 [31]. The UV–visible absorption and emission spectra are different from those observed in pure DCM, suggesting the presence of different dye structures both at the ground and excited states (Fig. S1 in SI) [31]. For the absorption spectra, we observed three bands having intensity maxima at 310, 360 and 410 nm assigned to encapsulated H-aggregates, monomers and J-aggregates, respectively [31]. We have shown that the formation and stability of these species depend on the pore size and chemical composition (doping metal) of the used materials [31]. For example, in Al-MCM41 complexes, J-aggregates (410 nm-band) are more predominant than in MCM41 ones due to Al-doping of the host framework (Fig. S1 in SI) [35,36]. However, for SBA15 ones, we observed a weaker absorption intensity at 410 nm, which is explained in terms of its different structural properties not allowing a favourable dye encapsulation, and thus a lower aggregates formation (Fig. S1 in SI). The presence of monomers and aggregates is also reflected in the emission spectra where the bands have different spectral positions at their intensity maxima: 500, 505 and 475 nm for MCM41, Al-MCM41 and SBA15, respectively (Fig. S1 in SI). According to our previous report, the maxima of the emission intensity of monomers, J- and H- aggregates are 465, 485 and 530 nm, respectively [31]. Note that encapsulated monomers and aggregates species experience an ESIPT reaction at the  $S_1$  state, producing a (K) type phototautomer [30,31]. It is well known that MCM41 with and without Al-atoms, and SBA15 have a narrow pore distribution centered on 2.5 and 6 nm, respectively. However, both materials also contain a small proportion of microporous of 0.8–1 nm. The HBA-4NP size (length = 1.1 nm and width = 0.5 nm) and the relatively larger population of the mesoporous pores suggest that the dye encapsulation occurs mainly in this type of pores. Therefore, the discussion of the photobehavior of trapped HBA-4NP will be based on the difference between mesoporous diameters and BET surface areas, in addition to the nature of the host composition.

### 3.2. Femtosecond time-resolved fluorescence observation

To elucidate the early dynamics of HBA-4NP interacting with mesoporous materials in DCM suspensions, we recorded femtosecond (fs) emission transients upon excitation at 380 and 410 nm, and observing at different emission wavelengths.

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