pH-Tunable Fluorescence and Photochromism of a Flavylium-Based MCM-41 Pigment

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Supporting Information

ABSTRACT: Incorporation of flavylium-derived chalcones in the cetyltrimethylammonium bromide-templated synthesis of mesoporous silica particles with no subsequent removal of the micellar phase leads to high luminescence (0.3 < ϕ < 0.5) and strong color-contrast photochromic pigments finely tunable over a large pH range (1 < pH < 11).

INTRODUCTION

The pH-driven chemical reaction network of flavylium compounds exhibits a diverse and rich photochemical variety, especially due to the appearance of photochromic systems. The photochromic effect arises mainly when trans-chalcone (Ct) molecules are irradiated, which produces cis-chalcone (Cc) species. Afterward, a cascade of reactions may lead to colored flavylium cations, as depicted in Scheme 1 in the case of 7-(N,N-diethylamino)-4′-hydroxyflavylium. All of this occurs in aqueous solutions, and it was already explored with detail in microheterogeneous systems, such as cetyltrimethylammonium bromide (CTAB) micelles, ionic liquids, and pluronic gels, for this particular compound. The fluorescence of the chalcone species, however, is rather elusive. Twisted intramolecular charge transfer-like processes occur in the excited states, which compete along with trans–cis photoisomerization, and therefore chalcone species are generally nonluminescent.

One of the challenges is indeed to immobilize these photochromic systems as pigments, abandoning solution-based photochromism, which hinders some potential applications typical of photochromic compounds. Incorporation in zeolites was already attempted, but no photochromic effects were observed as the flavylium cation was stabilized. Meanwhile, mesoporous silica materials have gained increasing attention in materials science because of their unique properties, such as, controlled pore structure, high pore volume, high surface area, and uniform pore size distribution, as well as the potential applications in catalysis, adsorption, sensing, optoelectronics, electrochromic devices, and in drug delivery. A study on mesoporous silica was recently carried out, wherein some photochromic effect was observed.

The chalcone was chemically grafted inside the pores of calcined silica, giving rise to photochemical reactions.

The covalently bonded chalcones in the MCM-41 particles bring the advantage of avoiding lixiviation of the samples when immersed in aqueous solutions, but until now the photochromic effect has shown rather low optical contrasts. Usually, these MCM-41 materials are used without the surfactant, which is eliminated by calcination or by solvent extraction. A new approach was therefore designed; the flavylium chalcone was incorporated in the micellar phase during the synthesis of MCM-41 by an easy single-step method, avoiding the surfactant removal. This method of inclusion has been much less explored, but previous work demonstrated that these surfactant–silica hybrid materials possess promising optical, sensing, and electrochemical properties. Because photochromism is indeed enhanced in CTAB micelles (as demonstrated previously) and they are an important ingredient for the formation of MCM-41 particles as templates, the calcination step is avoided and the chalcone species are directly incorporated in the CTAB micelles used for the synthesis of MCM-41. Unusual optical properties arise afterward, namely, high-fluorescence quantum yields and high-contrast photochromic effects, depending on the adjusted pH.

RESULTS AND DISCUSSION

The material MCM-41–Ct was prepared following literature procedures and by adding flavylium salt 7-(N,N-diethylamino)-4′-hydroxyflavylium.
no)-4′-hydroxyflavylium tetrafluoroborate in the CTAB solution according to Scheme S1. The concentration of the dye in the final material was estimated by UV–vis spectroscopy, extracting the dye from the material using a 0.2 M HCl aqueous solution, giving a value of 0.05% (w/w), leaving the silica powder colorless. The X-ray powder diffractionogram shows four well-defined basal reflections indexed to a hexagonal cell and typical of MCM-41 materials, a result also confirmed with transmission electron microscopy (TEM) imaging (Figure S3).

The resulting powder was obtained from solutions at pH ca. 10, which may be stored at room temperature in the dark for months with no loss of optical properties. At such basic conditions, ionized chalcone species should be predominant, namely, Ct− and Ct2−. These species are usually colored, but without significant photochromic or fluorescent properties because internal conversion processes completely dominate their excited-state properties in low-viscosity media.1,3 That is not the case with the powder here synthesized at pH ca. 10, where a very bright photoluminescence was observed upon irradiation with a UV-A light source (see Figure 1). A luminescence quantum efficiency of 46% was measured using the diffuse sphere absolute method25 with an average luminescence lifetime of 302 ns (see Table 1). This shows a situation in which nonradiative processes are greatly quenched, probably due to the relatively viscous environment of the MCM-41 channels filled with cylindrical CTAB micelles.

The next step toward the synthesis of a photochromic powder is the pH neutralization of Ct−/Ct2− species. The pristine powder was immersed in buffered aqueous solutions with a selected pH. The eventual lixiviation of the dye was monitored by UV–vis absorption spectroscopy (Figure S7). After centrifugation, new powders were obtained and pump-dried. As a result, at pH < 2, AH+ species were obtained, whereas at intermediate pH values in the range between 2.5 < pH < 4.5, it was possible to obtain the a priori desired Ct species. Figure 2 shows the light absorption spectra of the powder in the diffuse reflectance mode at different pH values.

The spectrum of acidic pHs shows absorption maxima at ca. 545 nm, which corresponds to the presence of AH+ cations. For pH values equal to 1.8 up to about 5, the spectra are dominated by a band centered at 440 nm, which is assigned to the Ct species. Therefore, predictably, those are the powders in which a photochromic effect would be prevalent.

Table 1. Photophysical Properties of MCM-41 Flavylium Systems Equilibrated at Different pH Values

| pH  | λ_ex max/nm | λ_em max/nm | ϕf/% | τ/ns |
|-----|-------------|-------------|------|------|
| 1.0 | 560         | 631         | 32   | 2.8  |
| 7.0 | 495         | 554         | 38   | 226  |
| 10.0| 495         | 559         | 46   | 302  |

Figure 1. Emission and excitation spectra of MCM-41 noncalcined powders with the pores filled with CTAB entrapping Ct2− species (top, equilibrated at pH = 10), Ct− species (middle, equilibrated at pH = 7), or AH+ species (bottom, equilibrated at pH = 1). Inset shows luminescence of the powders when exposed to a 360 nm light source.
At pH = 7.0, ionized chalcone species are still prevalent, and therefore the powder is photoluminescent. Interestingly, the excitation spectrum is very similar to that observed at pH = 10, although small changes in the emission spectrum give rise to a more “greenish” color with a slightly lower quantum efficiency (Figure 1 and Table 1). The hybrid material obtained from equilibration at pH < 2 gives rise to AH⁺ species and is also highly photoluminescent (Figure 1 and Table 1). The luminescence quantum efficiency is 32%, and the fluorescence decay has a lifetime of around 2.8 ns, in line with the typical photophysical properties of flavilium cations. The photoluminescence color shifts from green/yellow to pink, therefore it is possible to tune light emission in these pigments with simple pH adjustments.

The neutral Ct species are usually the photochromic active molecules of the flavilium chemical network. Results of Figure 2 already define the pH range in which photochromism may be active (between 2.5 and 6). The irradiation effects on powders equilibrated at pH = 2.7 are shown in Figure 3. After 5 min of irradiation at 445 nm \( (I_0 = 7.53 \times 10^{-8} \text{ einstein min}^{-1}) \), the color is developed, indicating the formation of AH⁺ (maximum absorption at 550 nm) as it is typical of these systems in aqueous solutions as well as in CTAB micelles, and an isosbestic point at 482 nm is observed, which is a requirement for a “two-species”-like photochromic effect.

\[
\text{Ct} \rightleftharpoons \text{AH}^+ \\
\Delta \nu
\]

The obvious advantage in this case is that the photochromic behavior is immobilized in the form of a pigment powder. The system may be characterized as a photochromic switch between Ct and AH⁺ species. Afterward, the system thermally reverts to its original state, therefore the original Ct species is fully recovered. The recovery process follows first-order kinetics, with \( t_{1/2} = 46 \text{ min (in CTAB micelles) and } t_{1/2} = 120 \text{ min}. \)

A significant photochromic effect (i.e., with significant color contrast) was observed in the pH range 2.6 < pH < 4.8 (Figure S6). The spectroscopic measurements at both irradiation and thermal re-equilibration show the same general features, with, nevertheless, different final colored states because at different pHs the AH⁺/A equilibrium determines the outcome. At pH = 4.8, the colored species have maximum absorption at 572 nm, a 22 nm shift compared to that at pH = 2.7, due to the fact that at this pH quinoidal base A predominates over AH⁺.

The hybrid photochromic powder is quite robust in terms of long-term photochemical stability. Without the presence of photochemical stabilizers, the system shows large reversibility. At pH = 2.7, on/off irradiation cycles (445 nm) were monitored by light absorption at 550 nm, and the contrast remains the same after three cycles within our experimental constraints (Figure 4).

### CONCLUSIONS

Hybrid mesoporous silica particles enclosing a flavilium system were synthesized. The optical properties can be adjusted by pH, showing remarkable photoluminescent brightness and high quantum efficiencies. These pigments also show high-contrast photochromic effects, thus enabling for the first time the production of solid-state flavilium-based photochromic systems with high reversibility.

### EXPERIMENTAL SECTION

**Materials.** 7-(N,N-Diethylamino)-4’-hydroxyflavilium tetrafluoroborate was available from previous studies. All other chemicals used were of analytical grade. Solutions were...
prepared using Millipore water. The pH of solutions was adjusted by addition of HCl, NaOH, or the universal buffer of Theorell and Stenhagen. CTAB and sodium silicate solution were purchased from Aldrich.

Synthesis of MCM-41 Containing Ct of 7-(N,N-Diethylamino)-4'-hydroxyflavilium (See Scheme S1). The material was prepared from a gel with the molar composition SiO2:0.29 Na2O:0.50 CTAB:150 H2O, and then the pH was readjusted to 10.0. After further stirring for 30 min, the mixture was transferred to a powder X-ray diffractometer with a Cu Ka (λ = 1.5418 Å) radiation source (30 kV, 15 mA). Measurements were step-scanned in 0.02° 2θ steps in the 1−12° range, with a scan speed of 0.5°/min. The textural characterization was obtained from physical adsorption of nitrogen at 77 K, using a Micrometrics ASAP 2010 V4 instrument. The Brunauer−Emmett−Teller surface area was calculated using the relative pressure data in the range 0.04−0.2. The total pore volume, Vp, was evaluated on the basis of the amount adsorbed at a relative pressure of about 0.97. The pore size distributions were obtained from the adsorption branches of the isotherms, applying the Barrett−Joyner−Halenda method with the modified Kelvin equation and a correction for the statistical film thickness of the pore walls. The statistical film thickness was calculated using the Harkins−Jura equation, in the p/p0 range of 0.1−0.95. Thermogravimetric analyses were performed using TA Instruments SDT 2960 simultaneous differential scanning calorimetry−thermogravimetric analysis (TGA) at a heating rate of 10 °C min−1 from room temperature to 700 °C. The mesoporous silica was also characterized by TEM using a Hitachi H8100 TEM. The samples were supported on a carbon-coated copper grid.

Preparation of the Samples at Different pH Values (See Scheme S2). The materials were stirred and then equilibrated at room temperature overnight in buffered water solutions at specific pH values. The suspensions were centrifuged, decanted, and finally dried under vacuum. Typically, 40.0 mg of the material was suspended in 5 mL of the appropriate buffered solution.

Measurements. pH values were measured with a MeterLab pHM240 pH meter from Radiometer Copenhagen. Diffuse reflectance UV−vis spectra were acquired in a Shimadzu UV-2501PC equipped with an integrating sphere. The powdered samples were smashed between two quartz lamellae, and the spectra were run using an identical BaSO4-filled support as the blank. The remission function, F(R), was calculated using the Kubelka−Munk equation for optically thick samples. Irradiation experiments were carried out in a spectrophotometer (Spex Fluorolog 3.22) equipped with a 150 W Xe-Hg lamp as the light source and using maximum slit width, with the following conditions: λsw = 445 nm and I0 = 7.53 × 10−6 einstein min−1.

Fluorescence spectra were recorded on a SPEX Fluorolog-3 Model FL3-22 spectrophotometer, and luminescence quantum efficiencies were measured by the absolute method with an Integrated Sphere. This method was checked by measuring the fluorescence quantum yield of a solution of Rhodamine 6G in ethanol, giving 96.6%, which compares very well with the value reported in the literature (95% in ref 27).

Time-resolved fluorescence decays were acquired by the time-correlated single-photon counting technique using two different home-built equipment. The samples were excited at 370 nm using a nanoled (IBH). The electronic start pulses were shaped in a constant fraction discriminator (Canberra 2126) and directed to a time to amplitude converter (TAC, Canberra 2145). The emission wavelength was selected by a monochromator (Oriel 77250) imaged in a fast photomultiplier (9814B Electron Tubes Inc.). The phase modulation signal was shaped as before and delayed before entering the TAC as stop pulses. The analogue TAC signals were digitized (ADC, ND582) and stored in a multichannel analyzer installed in a PC (1024 channels).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.6b00381.

Additional characterization data and figures (powder XRD pattern, TGA curve, and TEM images), details and figures about luminescence, and irradiation measurements and lixiviation during pH adjustment (PDF).

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Notes

The authors declare no competing financial interest.
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