Communication

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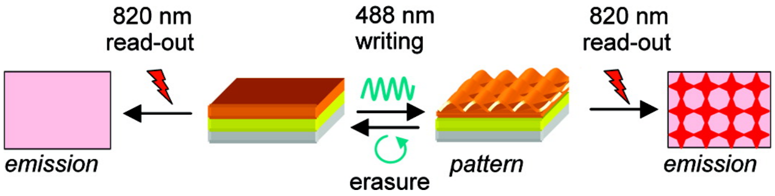

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Two-Photon Fluorescent Holographic Rewritable Micropatterning

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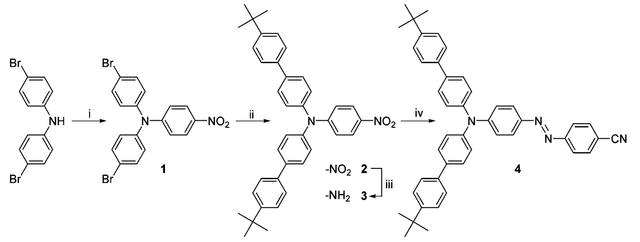
Holographic data storage[1] has recently attracted new interest with the use of organic photopolymerizable matrices[2] and photorefractive materials.[3] However photopolymerization produces undesirable matrix shrinkage while photorefractivity encounters progressive orientational relaxation of the photo-oriented chromophores. Another competing recording route to increase data storage density has been developed on the basis of the emission change induced in fluorescent photochromic materials through confocal illumination.[4] Unfortunately, the read-out process causes gradual erasure of the illuminated areas because of photoinduced back reaction of the bifunctional molecules even at very low irradiance.[5] Recently two-photon absorbing fluorescent materials have been used conjointly with photochromic dyes to reduce this back-reaction effect.[6] Yet all these materials are light sensitive, and high-density recording requires consuming pit-by-pit recording steps.

Surprisingly, the combination of both storage techniques, namely holography involving two-photon fluorescent systems, has never been envisaged to date even though it addresses all the performance limitations cited above. Such an innovative all-optical approach offers many attractive features. These features include rewritability, high photosensitivity dynamics owing to easily detectable changes in fluorescence, volumic recording, multiplexing possibilities, and the use of distinct conditions (wavelength,[5−7] polarization,[8] incidence angle[9]) to write and read-out the stored information.

We present herein bright fluorescent and stable 2D-photopatterns obtained by holography from new azo-based photochromic and two-photon fluorescent bilayer materials which provide nondestructive two-photon read-out and all-optical rewritability. When exposed to interferential illumination, azo derivatives undergo reversible photoinduced mass migration, and form time- and light-stable surface relief gratings (SRGs).[10] All the current SRG-forming systems require significant surface modulations to be locally measured by atomic force microscopy (AFM), which makes the read-out process tedious. On the contrary, introduction of fluorophores enables easier optical detection of weak events such as small peak-to-trough amplitudes.

As azoderivatives have proved to be strong emission quenchers of the investigated fluorophores through their $n\pi^*$ transition, physical separation of both fluorophores and azoderivatives was necessary. Thus, our system consists of a fluorescent lower layer covered with a nonfluorescent azo-based photochromic layer. In this way, the photostructurable azo-layer acts like a simple rewritable photomask modulating emission of the fluorescent layer. The read-out process, based on the fluorophore's two-photon excitation and emission monitoring, was subsequently performed under distinct polarization, wavelength, and power excitation conditions which ensures the azo photomask stability. To design such systems, the fluorescent and photochromic components must comply with stringent material processing and spectral requirements.

Scheme 1. General Synthesis of the Glass-Forming Fluorescent **2** and Photochromic **4** Compounds[a]



[a] Conditions: (i) 4-fluoro-1-nitrobenzene, K_2CO_3, DMSO, 140 °C, 12 h; (ii) 4-*tert*-butylphenylboronic acid, $Pd(PPh_3)_4$, toluene, 2 $mol{\cdot}L^{-1}$ Na_2CO_3, 80 °C, 20 h; (iii) $N_2H_4{\cdot}H_2O$, Pd/C 10%, reflux EtOH, 3 h; (iv) 4-nitrosobenzonitrile, room temp, 2 days.

First, these molecules must possess glass-forming properties to yield multilayered amorphous monomeric materials with excellent surface smoothness by successive vacuum thermal depositions.[11] Second, only the fluorophore must show two-photon up-converted fluorescence to avoid the erasure of the azo-SRG structure. Third, the resulting fluorescence modulation must be caused by partial reabsorption of the fluorophore's emitted light by the azolayer. The fluorophore emission must moderately overlap with the azolayer absorption. Finally, a large modulation of the fluorophore's emission is easily achieved if the azo layer can be efficiently photostructured. From our past expertise in azo-based monomeric materials, the best candidate appeared to be 4-[bis(4′-*tert*-butylbiphenyl-4-yl)amino)]-4′-cyanoazobenzene **4**.[12] Amid the various glass-forming fluorescent polar molecules we synthesized, the compound bis(4′-*tert*-butylbiphenyl-4-yl)-4-nitrophenylamine **2** fulfills all structural and spectral criteria.

We developed a novel synthetic strategy to generate the azo derivative **4**[12] directly from the nitro fluorophore **2** (Scheme 1). The formation of the key amino intermediate **3** provides modular access to a wide range of nonaggregating push−pull azo compounds which are of high interest in the studies on single molecule photoisomerization.[13]

Despite its large dipole moment ($\mu_{\text{calcd}} = 9.1$ D), compound **2** forms stable glassy films when evaporated under vacuum. Glass-transition temperature T_g was detected at 97 °C by differential scanning calorimetry without evidence of a melting peak until degradation occurred above 350 °C.

The strong similarities between the absorption and emission properties of compound **2** in toluene solution and thin film indicate the absence of intermolecular aggregations in the solid state, which guarantees materials with high optical quality (Figure 1).

As required, the emission spectrum of **2**, peaking at 601 nm in thin film (574 nm in toluene) overlaps with the absorption spectrum of the azo film **4** showing two maxima at 328 and 483 nm (see

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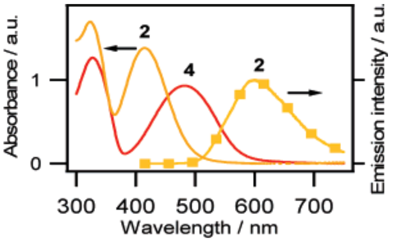

Figure 1. UV−vis absorption (—) and normalized emission spectra (−■−) of thin evaporated film **2** and film **4** (200 nm thick).

Table 1. UV−Visible Spectroscopic Data of Compounds **2** and **4**

	λ_{max}^{abs} (nm)[a]	λ_{max}^{em} (nm)[a,b]	Φ_f [a]	τ/ns[a]
2	408 (415), 324 (324)	574 (601)	0.12[c] (0.15)[d]	2.84[e] (∼2)
4	478 (483), 329 (328)			

[a] Data measured in toluene solution (thin film). [b] λ_{exc} = 445 nm. [c] Determined from coumarine 540A solution in EtOH as a fluorescence standard (Φ_f = 0.38). [d] λ_{exc} = 407 nm based on integration sphere measurements. [e] λ_{exc} = 330 nm, χ^2 = 1.14.

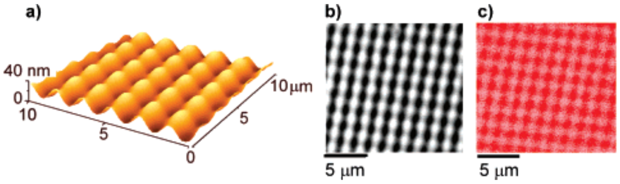

Figure 2. Crossed SRGs recorded on a bilayer thin film **4**/**2**: (a) AFM 3D-imaging; (b) one-photon transmission imaging at 488 nm with black spots corresponding to azo hills; (c) TPF imaging at 820 nm excitation (emission range 580−750 nm) with red areas featuring the brightest spots.

Table 1). The large Stokes shift up to 170 nm and the strong fluorescence exhibited by the nitro compound **2** at room temperature have been assigned to the strongly twisted and consequently decoupled dibiphenylamino group.[14]Bilayer thin films **4**/**2** were fabricated by successive vacuum depositions of fluorophore **2** and photochrome **4** onto precleaned 0.17 mm-thick glass cover-slips (l.6 × 10^{-5} mbar). By adjusting the amount of material to be evaporated and the final setpoint temperature, we obtained fluorescent and photochromic layers with similar thicknesses of 200 nm.

The bicomposite film **4**/**2** was subsequently exposed to two p-polarized interfering argon-ion laser beams (488 nm) of equal intensity (15 mW·cm^{-2}) using a Lloyd interferometer setup. After 15 min, the film was rotated 90° and the previously exposed area was subjected for a further 15 minute period to the same interference fringe pattern. AFM measurements showed two series of gratings crossed at a right angle with a 40 nm deep modulation and a spatial period Λ equal to 1.82 μm in accordance with Bragg's law $\lambda = 2\Lambda \sin\theta$ (λ and θ represent the irradiation wavelength and the beam incidence angle respectively: $\lambda = 488$ nm, $\theta = 7.5°$) (Figure 2).

Fluorescence imaging of the emissive lower layer **2** was investigated by two-photon fluorescence (TPF) microscopy in a reflection mode. Since the patterned upper azo layer **4** is exposed first toward the microscope objective, only the emitted light (and not the absorbed light) gets modulated. In fact, only compound **2** presents a significant two-photon absorption cross-section δ_{2PA} valued to 150 GM (1 GM = 10^{-50} cm^4·s·photon^{-1}·molecules^{-1}) as determined by femtosecond Z-scan technique at 820 nm in toluene solution. In contrast, δ_{2PA} for the azo compound **4** is close to zero because no signal was detected beyond the background level noise (<50 GM). Thus, use of a two-photon excitation at 820 nm confines the excitation density within the fluorophore layer and considerably improves the spatial resolution without recording undesirable fluorescence or affecting the azo-pattern.

Detection of the emitted light above 580 nm revealed a regular fluorescent pattern. Sizes of the fluorescent micrometric spots and upper azo periodic 3D-structure correspond well with each other. As expected, the black spots observed in one-photon transmission at 488 nm and featuring the azo "hills" become optically the less luminous ones (pink spots). After a 1-year storage under ambient light exposure, the fluorescent gratings show no change in the emission signal and prove to be perfectly stable.

Grating erasure has been successfully tested by exposing the photopatterned bilayer film for 30 min under uniform circularly polarized light of an argon-ion laser working at 488 nm (60 mW·cm^{-2}). Complete disappearance of the SRG structure has been observed by AFM measurements, as well as its full recovery after reiterated exposure to interferential illumination.

In conclusion, two-photon fluorescence micropatterning by using holographic photochromism has been demonstrated for the first time. The use of uncoupled photochromes and fluorophores, holographic recording, and nondestructive near-infrared read-out conditions has appeared as an effective strategy to generate stable and rewritable photopatterns. These studies open up a new way of recording optical information which is applicable to various organic systems.

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Supporting Information Available: Experimental procedures for compounds **1**−**4**, equipment description for thin film fabrication photostructuration, and TPA measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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