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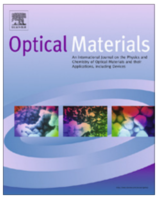

Beating photo-degradation in sum-frequency imaging of chiral organic media

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ABSTRACT

Sum-frequency generation from chiral bulk media holds the promise of a powerful tool in the investigation of biological as well as artificial materials containing optically active elements. Since this technique is based on a nonlinear optical effect, the high intensities of the illuminating light sources may induce spurious artifacts. Using simple conjugated chromophores, we demonstrate that multi-photon induced irreversible photolysis may be avoided while keeping undiminished levels of sum-frequency signals. In addition we show that the concurrent multi-photon induced luminescence may provide complementary means of imaging samples.

1. Introduction

Today, two-photon induced phenomena are widely used processes to optically probe matter, regardless of discipline. This is because they significantly improve the inherent spatial resolution of focused laser beams simply through their quadratic dependence on illumination intensity. In principle, the nature of the signal one detects is irrelevant provided it stems only from the initial excitation, and, indeed, two-photon induced fluorescence has revolutionized optical microscopy in biology and medicine for example [1]. In another field, two-photon fluorescence confocal microscopy was used to retrieve a high resolution 2D map of the concentration of monomer units in thin films of polyfluorenes over the sample's surface and was combined with the diffraction limited image of its circular dichroism to reveal the existence, distribution, and areas of domains of opposite helicities that form spontaneously in the polymer film during thermal annealing [2].

However, more information stands to be gained from the detection of quadratic optical signals such as second harmonic generation (SHG) since it can only occur if the medium is lacking inversion symmetry. SHG may also discriminate changes in the geometrical arrangement of molecular units while simultaneously providing high spatial resolution [3]. A further refinement of this idea consists in using two laser beams of different frequencies to exploit the process of sum-frequency generation (SFG), which includes combining IR and visible frequencies to use both vibrational and electronic transitions in the sample.

A special class of samples of interest are those comprising formally isotropic regions containing chiral molecules. Indeed, as Y.R. Shen has demonstrated, chiral species in solution are susceptible to give rise to detectable levels of IR-visible SFG bulk signals, operating either close to vibrational [4] or near electronic [5] resonances. The motivation behind bringing an optical non-linear phenomenon into play to probe dichroism is that it allows the use of longer wavelengths at which unwanted linear absorption and diffusion processes can be kept at a minimum.

SHG microscopy for imaging surface chirality has been demonstrated for the first time using the R-enantiomer of 1,1′-bi-2-naphthol (BN) [6]. Subsequently, thin layers of enantiomeric BN solutions containing micrometer sized silica beads have been used to prove that chiral imaging is in principle possible from bulk samples by scanning for SFG intensities [7]. More recently, the authors of the present work have tried to probe the potential of this latter technique for solid samples using the same BN molecule trapped in a sol–gel matrix [8]. It was thus found that the illuminating laser beams were able to induce various levels of photolysis in the chiral chromophores allowing both the photo-patterning and the imaging, i.e. the pattern-retrieval, in the same experimental SFG set-up.

In this work, we propose to investigate the possibilities allowed by the multi-photon induced fluorescence of BN and luminescence of the photo-products to confirm the two-photon like spatial resolution offered by image reconstruction from bulk SFG intensities.

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We further demonstrate that it is also possible to maintain high level of SFG signals while inducing hardly any photo-degradation in conjugated chiral chromophores thus proving that IR-visible SFG bulk imaging of a pre-existing inhomogeneous spatial distribution of chiral dyes in an otherwise isotropic medium is a realistic goal.

2. Photophysical vs. photochemical properties

The photophysical and photochemical properties of BN depend on the excitation wavelength, intensity but also on its environment. First, in solution, BN displays three absorption bands in the near UV: two weak bands exhibiting vibronic progressions with maxima at 335 nm and 275 nm and a strong featureless band at 230 nm. All three bands are very similar in appearance to the absorption bands of the corresponding monomer 2-naphthol which implies weak excitonic couplings between monomers and therefore pairs of close excited states of A1 and B1 symmetries, each absorption band resulting chiefly from the transition to the state allowed by electric dipole transition from the ground state. This interpretation is corroborated by theoretical studies at the Density Functional Theory level [9,10] which also imply a large dihedral angle between monomers in the ground state.

However, accounts become more controversial after BN has been promoted to an excited state and several phenomena have been invoked to explain the resulting luminescence, depending on the situation. Indeed, in addition to BN fluorescence with maximum emission in the vicinity of 360 nm, a red shifted luminescence at wavelengths above 450 nm with a maximum around 550 nm has been attributed to phosphorescence [11] in presence of small amounts of dibromopropane but has been assigned to various photochemical products resulting from proton transfers and condensation reactions involving the two alcohol functions in a recent racemization study [12]. During our previous investigations of SFG imaging with BN as a guest in sol–gel matrices [8], we had detected the same red luminescence and, faced with the irreversibility of the phenomenon, had attributed it to UV induced chemical changes of the chromophore rather than emission from the triplet excited state.

Since our objectives here are to probe the perspectives offered by IR-visible SFG microscopy as a general technique and since we merely use BN as a generic chiral chromophore because it is readily available and shows good solubility in many solvents, we are first concerned with its luminescence properties in order to determine wether they are specific to this compound or wether they are quite common phenomena. We have thus proceeded to measure absorption and fluorescence spectra for different aromatic compounds starting with the monomeric, and hence achiral, naphthalene moving on to the monovalent alcohols phenol and 2-naphthol, and finally on to the dimeric and chiral BN as well as two bridged relatives of it that have been shown to be more resistant to racemization in recent vapor deposition experiments [13]. The spectra were recorded in a UV–vis spectrometer (Horiba Jobin Yvon FL3-22) from $2.5 \cdot 10^{-5}\,\mathrm{mol\,L^{-1}}$ solutions of CH_2Cl_2 and are shown in Fig. 1 (excitation at 250 nm). Obviously, the absorption and the emission spectra are red shifted as the number of the aromatic cycles increases but dimerization or functionalization do not substantially affect them.

We now turn to the more controversial aspect of UV resistance of these molecules. For this purpose, we have used a modified commercial microscope (Olympus IX71) to record the evolution of the luminescence of each compound under UV radiation (330–385 nm) from a mercury lamp (Osram HBO 103W/2). All the samples simply consisted in an unweighted amount of powder of the compound used as purchased, smeared onto a glass plate

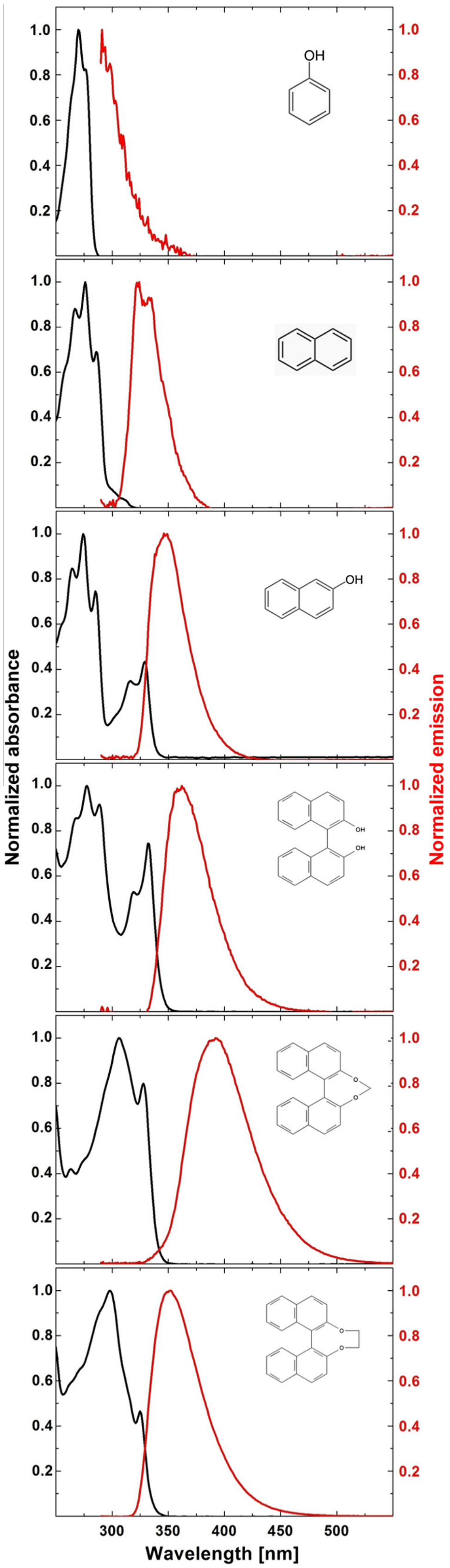

Fig. 1. Normalized absorbance (black curves) and fluorescence after excitation at 250 nm (red curves) recorded (Horiba Jobin Yvon spectrometer) in dichloromethane (2.5×10^{-5} M) for the compounds shown as insets. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)