Tunable emissive thin films through ICT photodisruption of nitro-substituted triarylamines[†]

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UV-assisted photocleavage in the solid state of orange emitting nitro-substituted triarylamines leads to the appearance of blue emission following photodisruption of the ICT state.

Fluorescence photoswitching in the solid state¹ has stirred great attention for a decade due to its numerous applications in non-destructive data storage,² high resolution optical imaging,³ and (bio)chemical sensing.⁴ Most of the approaches developed to date turn on or off emission through various quenching mechanisms such as photoinduced electron transfer and electronic energy transfer, creating large contrast in emission intensity.⁵ Conversely, phototuning of the emission color has rarely been exploited despite the large demand of multicolor emitting displays. These latter are actually commonly elaborated from blends of various fluorophores exhibiting distinct emitting ranges and emission quantum yields. This requires delicate balance between the components, which implies time-consuming modification of the composition until the targeted performances in terms of color wavelength and brightness are achieved.⁶ Color tuning by photoirradiating materials made of a single component would appear as an attractive alternative since repetitive fabrication procedures would be spared. This has been obtained with silver nanoparticles embedded in zeolithe scaffolds whose size-related emission wavelength could be varied according to the irradiation dose.⁷ Surprisingly to our knowledge, this approach has not been explored in organic materials. In this case, color changes entail unimolecular photochemical reactions generating new species with distinct emission spectra and fluorescence quantum yields.

We want herein to report on an original strategy consisting of the photodisruption of a radiative intramolecular charge transfer (ICT), which creates higher-energy emissive entities upon UV irradiation. In this way, tuning of orange to green blue fluorescence could be achieved in monolithic thin films by using light only.

We synthesized in the past a series of bulky push-pull fluorescent triarylamines whose emission energy could be varied in the solid state as a function of the electron-withdrawing group.⁸ Among them, the nitro compound appeared

particularly attractive when located in the *ortho* position of a benzyl group since it efficiently phototransforms under UV irradiation into a nitrosobenzaldehyde homologue with distinct electronic transitions.⁹ To this aim, we devised the nitroaminobenzyl ester derivative **2** obtained through a Hartwig-Buchwald aromatic coupling between 5-bromo-2-benzylnitroethanoate and bis(4'-tert-butylbiphenyl-4-yl)amine **1** (Scheme 1).

The UV-vis absorption spectrum of compound 2 in cyclohexane solution is dominated by two bands located in the visible and UV range at around 400 nm and 324 nm, respectively (Fig. 1, Table 1). From previous theoretical calculations, these two bands involved strongly permitted electronic transitions with large oscillator strengths f from the amino-located HOMO, to the nitro-centered LUMO (f = 0.452) and the biphenyl-centered LUMO+1 (f = 0.602), respectively (see ESI, Fig. S1[†]). Low-fluence excitation in the UV or visible band of 2 in cyclohexane produced stable yellow fluorescence around 510 nm. When intense irradiation $(260 \text{ m W cm}^{-2})$ was performed at 365 nm in the sole UV band which involved amino-biphenyl centered $n\pi^*$ transitions, blue emission peaking at 375 nm started appearing (Fig. 1). This spectral change was accompanied by the simultaneous decrease of the CT band both in absorption and emission, featuring an electronic disruption between the amino and the nitro groups.

The presence of clear isosbestic points suggested the clean phototransformation of the nitrotriarylamine into a product which was actually identified to be the bis(4'-tert-butyl-biphenyl-4-yl)amine 1 from column chromatography separation and further ¹H NMR analyses. This was confirmed by the spectral match between an amino solution and the photo-irradiated solution as well as by MALDI-TOF measurements which showed after irradiation a new peak at m/z = 433.27 corresponding to the amine. The conversion rate ρ was valued to be 71% while the photoconversion quantum yield $\Phi_{\rm r}$ was



Scheme 1 Structure of compounds 2-4 and photolysis pathway under UV irradiation.

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Fig. 1 Evolution of the absorption (left) and emission spectra (right) of compounds 2 and 4 in cyclohexane solution $(2 \times 10^{-5} \text{ mol } \text{L}^{-1})$ under irradiation at 365 nm (260 mW cm⁻²).

 Table 1
 Photophysical and thermal properties of compounds 2–4

	$\lambda_{\max}^{abs}/nm^a$	$\lambda_{\max}^{em}/nm^{ab}$	$\Phi_{ m f}{}^{ac}$	$T_{\rm g}/^{\circ}{\rm C}^d$
1	325	361, 375 (sh)	0.71	_
2	399 (416), 321 (322)	508 (578)	0.25	69
3	396 (415), 321 (324)	506 (601)	0.22	96
4	400 (422), 317 (319)	525 (598)	0.31	101
a Doto	manurad in avalahayana	solution (thin film)	b 1 _ /	100

^{*a*} Data measured in cyclohexane solution (thin film). ^{*b*} $\lambda_{exc} = 400$ nm. ^{*c*} Determined from POPOP and coumarine 540A as fluorescence standards. ^{*d*} Measured by DSC with a 10 °C min⁻¹ thermal gradient.

calculated to be 3.0×10^{-4} from kinetics analyses in cyclohexane solutions at the CT absorption and emission maxima.

This photofragmentation was additionally accompanied by the release of a non-fluorescent nitrosobenzaldehyde derivative issued from the UV-reactive nitrobenzyl unit. This was evidenced by ¹H NMR spectroscopy with a peak characteristic of the benzaldehyde proton at $\delta = 9.51$ ppm, and by UV-vis absorption spectroscopy with a large band typical of nitrosobenzaldehyde derivatives centered around 490 nm. A new peak at 1.91 ppm featuring the possible formation of acetic acid could also be observed. However nitrobenzyl units when connected to an amino moiety have been reported to slowly react.^{9d} This was confirmed by TDDFT computations which showed that the reactive state, issued from the HOMO-5 \rightarrow LUMO transition in compound 2, exhibits low absorption probability $(f = 9 \times 10^{-4}; \text{ see ESI, Fig. S1}^{\dagger})$ compared to the nitrobenzyl unit devoid of amino substituent (f = 0.017). These results tend to support that this second reactivity, generating the formation of a nitrosobenzaldehyde derivative, may rather take place in a fast ulterior step following the photodisruption of 2.

To assess the real participation of the methylacetate moiety to the photofragmentation process, we varied the substituent in the *ortho* position relative to the nitro group. Two model compounds **3** and **4** bearing no additional substituent and an ester unit respectively were synthesized and displayed very similar photophysical properties (Table 1).

Clearly, compound 2 converts faster and more efficiently into the diarylamino photofragment compared to 3 and 4 (Table 2, Fig. 1; see ESI, Fig. S2 \dagger). Apparently there are no

 Table 2
 Photoconversion characteristics of compounds 2–4^a

Cpd	2	3	4
$rac{ ho (\%)^b}{arPsi_{ m r}}$	$71.0 \\ 3.0 \times 10^{-4}$	$15.4 \\ 3.5 \times 10^{-5}$	24.2 7.0×10^{-5}
^a In cyclohe	exane solution (2 \times	10^{-5} mol L ⁻¹) irradi	iated at 365 nm

 (260 mW cm^{-2}) . ^b Obtained after the same time of irradiation (20 min).

obvious electronic or steric reasons accounting for the 3's and 4's inferior reactivity. Furthermore, TDDFT theoretical calculations revealed for these latter compounds very similar energy levels. We thus explored the hydrogen abstractability from the benzyl unit as a possible accelerating factor. To this aim, we performed irradiation of 2 in the presence of a drop of 1,4-cyclohexadiene known for its large hydrogen transfer ability.¹⁰ The rate of photofragmentation was considerably enhanced and the reaction quantum yield Φ_r in neat 1,4-cyclohexadiene was found to be almost ten times $(\Phi_{\rm r} = 2.8 \times 10^{-3})$ as high as in cyclohexane while its photoconversion rate ρ reached 88% (see ESI, Fig. S5†). This tends to suggest that proton abstraction from the $n\pi^*$ excited state is a key step in the photofragmentation process. To gain preliminary insight into the nature of the excited state, we looked at the reactivity of 2 in toluene and acetonitrile.

Photoclevage was actually considerably slowed down in more polar solvents. The photoconversion rate ρ in toluene and acetonitrile solutions of 2 subjected to similar irradiation conditions dropped to 21% and 11%, respectively. Preliminary femtosecond transient absorption experiments have evidenced strong stabilization of the nitro-amino ICT excited states in polar solvents. These low-energy CT states may thus partly quench upon energy transfer the aminobiphenyl-centered $n\pi^*$ excited state responsible for the photocleavage reaction in apolar solvent, hence the reaction proceeds in a more sluggish way. Such an assumption is supported by the absence of reactivity for all compounds when directly irradiated in the visible in their CT bands (see supra) despite their large oscillator strength ($f \sim 0.42$ –0.45). We thus suspect that the nature of the excited state responsible for the photofragmentation may also evolve with the solvent polarity.

The photoreaction was not limited to solutions and could successfully be performed in glassy thin films (glass transition temperatures T_g around 70–100 °C) obtained from spin-coating a 2 wt% chloroform solution on glass substrates and subsequent drying under vacuum. Special focus was given to thin films made of **2** owing to its faster reaction in solution. A thin film of **2** was placed at the focal plane of a confocal fluorescence microscope and irradiated in the UV range with a bandpass filter centered at 360 nm (bandwidth 40 nm) for 15 min (Fig. 2). Snapshots recorded with a color camera at various time intervals displayed a pronounced fluorescence evolution from orange to green and finally bright blue. After transformation, the film could be addressed by using low UV irradiance without causing further photochemical transformation.

Use of a diaphragm allowed us to print a blue emissive spot which contrasted with the non-irradiated orange fluorescent surroundings (here represented as a shell; inset Fig. 2). The emission spectra were recorded *in situ* for each area with a



Fig. 2 (A) Fluorescence snapshots of thin film **2** irradiated under a microscope with a 360 nm bandpass filter: (a) before, (b) after 10 min, (c) after 20 min of irradiation. (B) Emission spectra recorded (1) before and (2) after irradiation at 343 nm. Inset: blue-emitting irradiated area surrounded by an unexposed orange-emitting area.

spectrometer coupled to the microscope through an optical fiber. Maximum of emission was detected at 563 nm before irradiation and underwent a hypsochromic shift to 496 nm with a shoulder at 453 nm after irradiation in correlation with the colors observed previously. We checked the stability of the photoreacted area under ambient light and temperature conditions, which did not change after months of storage.

In conclusion, the strategy of emission color tuning based on the photodisruption of radiative intramolecular charge transfers opens up an innovative and simple approach toward the modulation of color in the solid state by using light only. This has been demonstrated through the investigation of a series of yellow orange emitting push-pull triarylamine compounds which could be cleaved into green blue fluorescent diarylamine species in solution and non-doped thin films. The high propensity of the excited state to abstract hydrogen atoms may evoke the participation of a $n\pi^*$ triplet excited state,¹⁰ which may be highly favored by the presence of a nitro group.^{11,12} Substitution of the nitro group with another strong electron-accepting group like dicyanovinylene indeed provoked no photolysis reaction. Ultra-fast spectroscopy and electrochemical experiments are currently being conducted to address the complex underlying mechanism as well as the spin multiplicity of the involved excited state. This reactivity unexplored to date should attract much attention since nitro compounds are commonly subjected to intense light irradiation when used as photosensitizers in radical photopolymerization¹² or as dopants in organic solar cells to form charge transfer complexes absorbing in the near-infrared range.13

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