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Photochromic-fluorescent-plasmonic nanomaterials: towards integrated three-component photoactive hybrid nanosystems

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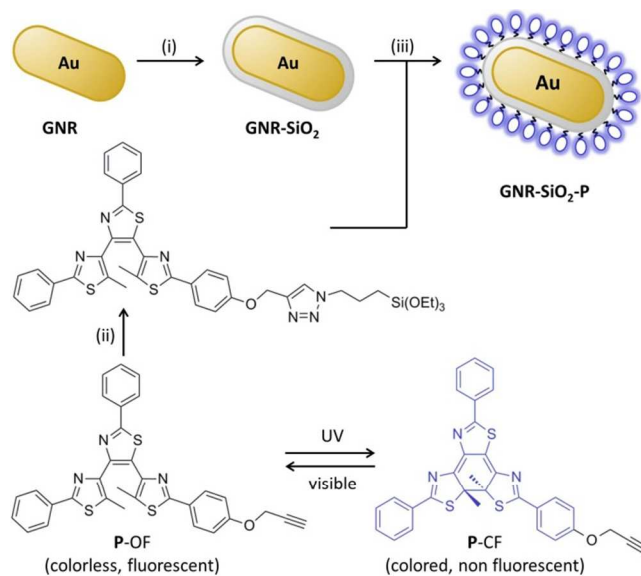
K. Ouhenia-Ouadahi,^a R. Yasukuni,^{a,c,d} P. Yu,^b G. Laurent,^a C. Pavageau,^a J. Grand,^c J. Guérin,^b A. Léaustic,^b N. Félidj,^c J. Aubard,^c K. Nakatani,^a and R. Métivier*^a

Silica-coated gold nanorods functionalized with grafted fluorescent and photochromic derivatives were synthesized and characterized. Spectroscopic investigations demonstrated that cross-coupled interactions between plasmonic, photochromic, and fluorescence properties play a major role in such nanosystems, depending on the thickness of the silica spacer, leading to multi-signal photoswitchability.

Hybrid systems showing coupling between plasmonic and organic units have recently generated numerous studies, with various innovative applications such as advanced sensing and biomedicine,^[1] allowed by an improved understanding of the enhancement mechanisms arising from the surface plasmon resonance (SPR) excitation of metallic nanoparticles. Such studies of hybrid metallic/organic materials, lying at the intersection of chemistry, physics and nanotechnology have been coined “molecular plasmonics”. Within this scope of research, the interplay between photophysical properties, such as fluorescence or photochromism, and surface plasmons have recently triggered great deal of interest. Concerning the coupling between plasmon and fluorescence, the control of the distance allows the fine tuning of the interaction, leading to quenched or enhanced fluorescence.^[2] In spite of fewer published reports, coupling plasmonic structures with photochromic molecules shows also appealing advantages.^[3] Several consequences of this coupling have been demonstrated: it can lead to a shift or distortion of the SPR under light irradiation, a decrease of the photochromic activity,^[4] an irreversibility of the photoreaction^[5] or an improvement of the photoswitching efficiency.^[6] The distance between the metallic nanoparticle and the photochromic molecule,^[3b,6a] and the overlap between the SPR and the electronic transition of the photochromic unit have been shown to play a major role in the coupling strength.^[7] Besides, combining photochromism and fluorescence in the same system is of great advantage for some applications such as optical data storage^[8] or high-resolution imaging.^[9] Molecular systems showing both photochromic and fluorescence properties can have several different structures:^[10] the photochromic molecule may be fluorescent itself;^[11] the photochromic and the fluorescent units may be covalently bonded,^[12] or both units may be non-covalently bonded.^[13]

In a hybrid system, the plasmonic unit plays a central role since it allows modifying the photochromic or fluorescence activity of the system. Many studies used spherical nanoparticles as the plasmonic unit because of their easy chemical synthesis or their commercial availability. However, using nanorods instead of nanospheres presents several advantages: (i) due to their anisotropic geometry, nanorods show two distinct SPR, (ii) as the longer axis increases, multipolar resonances are observed, giving rise to higher electromagnetic enhancement.^[14] Changing the aspect ratio of gold nanorods during the synthesis allows setting precisely the SPR spectral position within the visible-near infrared range.^[15]

Scheme 1. Synthesis of the silica-coated gold nanorods with surface-grafted photochromic and fluorescent derivatives.^a



^a (i) Stöber silica layer deposition; (ii) Cu(I)-catalyzed Huisgen cycloaddition; (iii) covalent surface grafting.

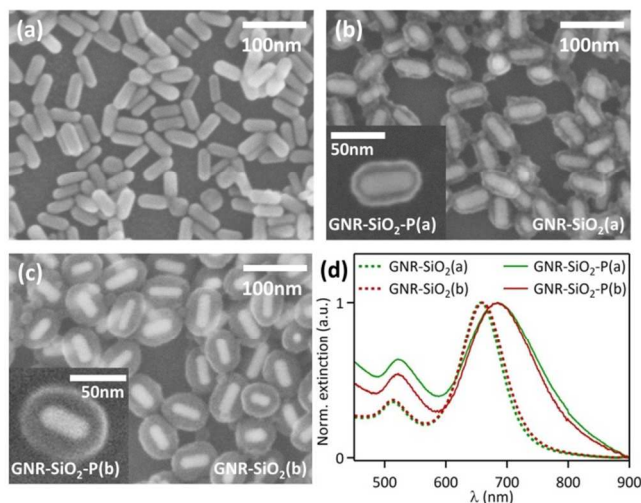
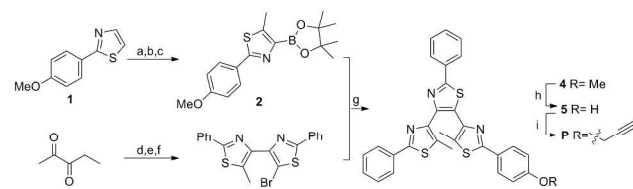


Figure 1. SEM images of (a) the GNR cores, and the silica-coated GNR (b) **GNR-SiO₂(a)** and (c) **GNR-SiO₂(b)**, corresponding respectively to silica-layers of 8 ± 1 nm and 16 ± 1 nm. Insets: SEM images of the corresponding hybrid nanosystems incorporating grafted **P** molecular derivatives. (d) Extinction spectra of the hybrid nanosystems in acetonitrile solution.

In this work, we describe a three-component hybrid system based on functionalized gold nanorods (GNR) showing plasmonic, photochromic and fluorescence properties. To the best of our knowledge, it is the first time that an all-in-one system is designed, built and characterized to obtain up to five different signal outputs: two visible light scattering resonances from the GNR core, UV and visible light absorption and blue fluorescence emission from the surrounding molecular species.

Scheme 1 presents the final hybrid nanostructure which is composed of three different parts. The GNR core is coated with a silica shell. The role of the shell is double. On one hand, the silica coating is used as a spacer between the molecules and the metallic particle which is a crucial parameter for the plasmon and fluorescence / photochromism coupling.^[2,3b,6a] On the other hand, the silica shell is a convenient platform allowing further covalent bonding of functionalized molecules. The GNR were prepared by the “seed mediated growth method” devised by El-Sayed *et al.*,^[16] and further coated with a silica shell through a modified Stöber protocol (Scheme 1, step i, see details in SI).^[17] The thickness of the silica layer can be efficiently varied with the silica precursor reaction time. Two samples were obtained: **GNR-SiO₂(a)** and **GNR-SiO₂(b)**, corresponding to 15 and 30 min of reaction time, respectively. Representative scanning electron microscopy (SEM) of the GNR before coating, **GNR-SiO₂(a)** and **GNR-SiO₂(b)** samples are displayed on Figure 1(a-c). In both cases, the average length and diameter of the GNR are respectively 50 ± 2 nm and 20 ± 2 nm (see SI).[†] When the GNR are dispersed in acetonitrile, the longitudinal (resp. transversal) SPR is located at 650 nm (resp. 510 nm). The silica coating is almost uniform around the GNR, even if a more accurate analysis reveals slightly smaller thickness at their extremities. The average value of the silica shell thickness has been measured over hundreds of particles to be 8 ± 1 nm and 16 ± 1 nm for **GNR-SiO₂(a)** and **GNR-SiO₂(b)**, respectively. After silica coating, the longitudinal SPR peaks are red-shifted by 15 nm for **GNR-SiO₂(a)** and 20 nm for **GNR-SiO₂(b)** (see SI),[†] which is attributed to the increasing of the refractive index of the surrounding medium.^[18]

Scheme 2. Synthesis of the photochromic compound **P**^a



^a(a) NBS/DMF, rt, 94%; (b) LDA/Mel/THF, -78°C to rt, 92%; (c) BuLi/-PrOB(pin)/Et₂O, -78°C to rt, 96%; (d) Br₂, 0°C; (e) benzothioamide/MeOH, reflux; (f) NBS/DMF, 80°C, 48% (in three steps); (g) CsF/Pd(PPh₃)₄/dioxane, reflux, 95%; (h) BBr₃/CH₂Cl₂, -78°C to rt, 81%; (i) propargyl bromide/Cs₂CO₃/acetone, reflux, 84%.

The photochromic and fluorescent diarylethene **P** (Scheme 1) was chosen as an organic derivative to be combined to silica-coated GNR. **P** was prepared by the synthetic route outlined in Scheme 2. Boronic ester **2** was synthesized in 3 steps in high yield from 2-(4-methoxyphenyl)thiazole. Suzuki coupling with **3** provided **P** after deprotection of methoxy group and propargyl grafting (see details in SI).[†] The functionalization procedure of the silica-coated GNR was modified from the one developed for coating mesostructured silica shells on CTAB-stabilized inorganic nanocrystals.^[19] In the present case, the incorporation of the diarylethene onto the silica shell was realized by one-pot covalent grafting as illustrated in Scheme 1. **P** was linked by the well-known Cu(I)-catalyzed Huisgen 1,3-dipolar cycloaddition reaction^[20] to one equivalent of 3-azidopropyltriethoxysilane (Scheme 1, step ii). After 12 hours, the mixture was added to the silica-coated gold nanorod suspension (**GNR-SiO₂(a)** or **GNR-SiO₂(b)**) without prior purification (Scheme 1, step iii) with 3 equivalents of acetic acid. After 12h at room temperature, the resulting hybrid nanostructures were purified by several centrifugation steps with acetonitrile. The effect of the grafting of **P** is shown in Figure 1d. Comparing the extinction spectra of **GNR-SiO₂-P(a)** (resp. **GNR-SiO₂-P(b)**) with the extinction spectra of **GNR-SiO₂(a)** (resp. **GNR-SiO₂(b)**), a red shift along with a broadening of both longitudinal and transversal SPR are observed. This effect can be attributed to a variation of the local refractive index due to the grafting of **P** molecules at the surface of the silica shell.

The absorption spectrum of the diarylethene molecule **P-OF** in acetonitrile is plotted on Figure 2a, with absorption maxima at 277 nm and 317 nm. When irradiated at 335 nm, the solution turns from colorless to blue, indicating the **P-OF**→**P-CF** reaction. A well-defined absorption band of **P-CF** appears in the visible range ($\lambda_{\max} = 588$ nm), together with changes in the UV range ($\lambda_{\max} = 271$ nm and 331 nm). The reversibility of the photochromic reaction is fully achieved under irradiation at 575 nm.^[21] Figures 2b and c, respectively, show the extinction spectra of colloidal suspension of hybrid samples **GNR-SiO₂-P(a)** and **GNR-SiO₂-P(b)** in acetonitrile, before and after irradiation at 335 nm. In both cases the total extinction of the hybrid system increases at 350 and 600 nm, and decreases around 300 nm. These spectral modifications are directly attributed to the absorption of the grafted **P-CF**.

Figure 2d shows differential extinction spectra ΔExt , obtained by subtracting extinction spectra recorded after and before irradiation at 335 nm (see SI).[†] These ΔExt spectra are useful to identify the photochromic contribution during the irradiation process and discriminate the possible modification of the SPR. On the ΔExt spectrum of the photochromic compound **P** in acetonitrile solution (Fig. 2d, blue dashed curve), which is used as a reference, positive bands at 350 and 600 nm (resp. a negative one at 300 nm) are observed, corresponding to spectral regions where the **P-CF** absorption is higher (resp. lower) than the **P-OF** absorption. Interestingly, the ΔExt spectrum of the **GNR-SiO₂-P(a)** sample displayed on Figure 2d (green curve) exhibits many differences from

the one of **P** in solution. For wavelengths below 400 nm, both spectra look similar, meaning that there is only a photochromic contribution at these wavelengths. Between 400 – 550 nm and 650 – 900 nm, the ΔExt spectrum of the sample **GNR-SiO₂-P(a)** is below the **P** curve. These two different areas correspond to the transversal and longitudinal SPR of the GNR core, and indicate a negative contribution of the SPR. Contrarily, in the 550 – 650 nm region, the ΔExt spectrum of **GNR-SiO₂-P(a)** is higher than the **P** curve, and denotes a positive contribution of the SPR. These observations can be analyzed as a combination of several SPR changes: decrease of the SPR intensities, broadening and wavelength shift of the SPR bands. Moreover, this experimental effect was completely reversible under irradiation at 575 nm. As this behavior occurs reversibly upon light irradiation of the hybrid system, which induces the **P-OF**→**P-CF** (UV) or **P-CF**→**P-OF** (visible) photochromic reactions, it clearly demonstrates a direct interaction between the plasmonic GNR core and the surrounding photochromic molecules, leading to a very sensitive photo-control of the SPR properties.^[22] The ΔExt spectrum of the **GNR-SiO₂-P(b)** sample plot on Figure 2d (red curve) is exactly overlaying the one of **P** in solution (dashed blue curve). In this case, there is no modification of the position, the shape nor the intensity of the SPR bands upon irradiation. This behavior shows the absence of coupling between the plasmon of the core and the photochromic molecules. The difference of behavior between the two samples is attributed to the thickness of the silica shell, which is larger in the case of **GNR-SiO₂-P(b)** than **GNR-SiO₂-P(a)** (16 ± 1 nm vs 8 ± 1 nm, respectively, as mentioned above). Indeed, many previous studies have already emphasized that the distance between plasmonic structures and photoactive molecules is a critical parameter to observe coupling between the two parts.^[3b,6a] The observed phenomena and the difference between samples **GNR-SiO₂-P(a)** and **GNR-SiO₂-P(b)** clearly confirm the existence of a distance-dependent coupling between the GNR and the photochromic organic derivatives.

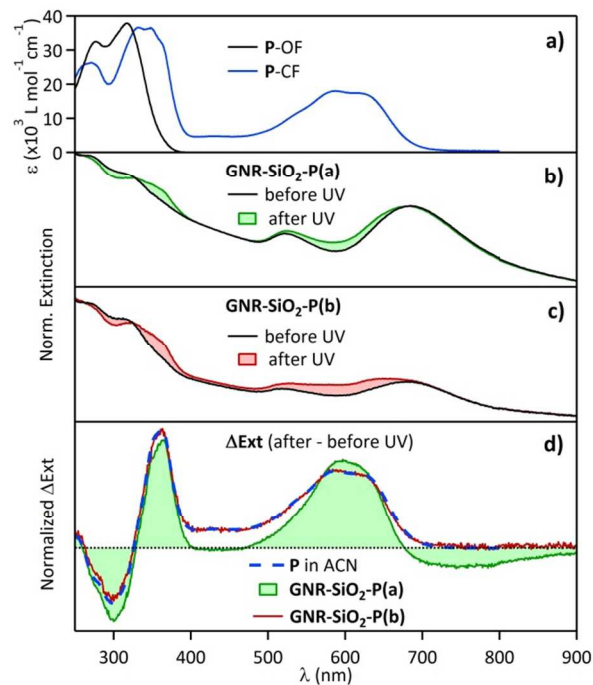


Figure 2. (a) Absorption spectra **P-OF** and **P-CF** molecules in solution. (b, c) Extinction spectra of **GNR-SiO₂-P(a)** and **GNR-SiO₂-P(b)**, respectively, before and after irradiation at 335 nm. (d) Extinction difference spectra of the samples obtained after

subtraction of the corresponding extinction spectra after and before irradiation at 335 nm. All spectra were recorded in acetonitrile.

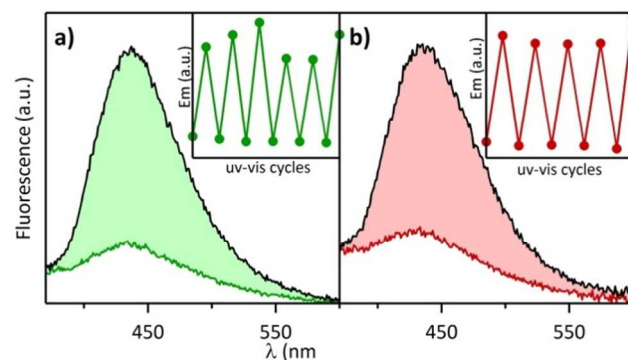


Figure 3. Fluorescence spectra of (a) **GNR-SiO₂-P(a)** and (b) **GNR-SiO₂-P(b)** hybrid samples in acetonitrile colloidal suspension before irradiation (black curve) and after irradiation at 335 nm (green and red curves). Insets: irradiation cycles at 335 nm and 575 nm.

Experiments have been conducted to evaluate the fluorescence properties of our hybrid nanosystems. In acetonitrile solution, photochromic compound **P** actually shows fluorescence emission in its open form (**P-OF**), and not in its closed form (**P-CF**).^[21] As expected, the hybrid nanosystems **GNR-SiO₂-P(a)** and **GNR-SiO₂-P(b)** are also fluorescent, revealing the emissive properties of the grafted **P-OF** molecules at the surface of the silica-coated GNR. The emission spectra were recorded in acetonitrile colloidal suspension and show a broad band peaking at 435 nm. Under irradiation at 335 nm, the **P-OF**→**P-CF** reaction is induced, leading to a significant decrease of the fluorescence emission (80-85% of the initial fluorescence level in both cases) which is fully recovered under irradiation at 575 nm (**P-CF**→**P-OF** reaction), as evidenced in Figure 3. Several complete cycles can be achieved without any significant fatigue effect (Figure 3, insets). This behavior is similar whatever the considered sample. Based on these results, fluorescence quantum yields (Φ_F) have been measured to be 0.038 and 0.048 respectively for samples **GNR-SiO₂-P(a)** and **GNR-SiO₂-P(b)**. These values clearly show that both samples are slightly more fluorescent than the free **P** molecule ($\Phi_F = 0.016$ in acetonitrile)^[21] with a more pronounced fluorescence in the case of the sample **GNR-SiO₂-P(b)**, probably due to local field enhancement in the presence of GNR. Again, this result highlights the important role of the silica shell for modulating plasmonic-fluorescence interaction and, following, the fluorescence emission of the hybrid system.

In conclusion, we designed, synthesized and characterized multi-component hybrid nanosystems composed of a plasmonic GNR core functionalized by molecules displaying both photochromic and fluorescence properties. Accurate control of the distance between the plasmonic core and the photoactive organic counterparts has been achieved by means of a silica shell, yielding evidences of plasmon-photochromism coupling on one side and plasmon-fluorescence interaction on the other side. Although these two effects have already been studied separately, our study represents, to the best of our knowledge, the first attempt to build a three-component hybrid system showing both couplings in the same composite nanostructure. Moreover the fluorescence signal is tightly related to the photochromic state of the molecules, ensuring complete cross-talks between the three properties. All in all, our new system shows a three-component structure with multiple light-responsive signatures. Up to five output signals can be exploited and switched by light in

the present case: (i) light absorption of the colorless state of the photochromic molecules (P-OF), (ii) light absorption of the colored state (P-CF), (iii) fluorescence emission of the molecules, (iv) light scattering of the traversal and (v) longitudinal SPR of the GNR. Finally, we have demonstrated that all these cross-interactions can be tuned and optimized by a proper engineering of the architecture of the system. We believe that such “colored-fluorescent-plasmonic nanophotoswitches” are extremely promising in the field of smart and integrated photo-controllable nanodevices, and we are currently investigating their detailed optical properties down to the single particle level by means of appropriate microscopy and spectroscopy methods.

Notes and references

^a Laboratoire PPSM, ENS-Cachan, CNRS, 61 av Président Wilson, 94235 Cachan cedex, France. Email: metivier@ppsm.ens-cachan.fr

^b ICMMO, Université Paris-Sud, Bât 410, 15 rue Georges Clemenceau, 91405 Orsay cedex, France

^c Laboratoire ITODYS, Univ Paris Diderot, Sorbonne Paris Cité, 15 rue J-A de Baïf, 75205 Paris Cedex 13, France

^d Present address: Laboratoire CSPBAT, Univ. Paris 13, 74 rue Marcel Cachin, 93017 Bobigny cedex, France

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