

Supplementary Information for

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

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I. Spectroscopic instrumentation

UV/vis absorption spectra were recorded on a Cary5000 spectrophotometer from Agilent Technologies. Corrected emission spectra were obtained on a Fluorolog FL3-221 spectrofluorometer from Horiba Jobin-Yvon. The fluorescence quantum yields were determined by using quinine sulfate dihydrate in sulphuric acid (0.5 N) as a standard at $\lambda_{\text{exc}} = 325 \text{ nm}$ ($\Phi_F = 0.546$).

Photochromic reactions were induced *in situ* by a continuous irradiation Hg/Xe lamp (Hamamatsu, LC8 Lightningcure, 200 W) equipped with narrow band interference filters of appropriate wavelengths (Semrock FF01-335/7-25 for $\lambda_{\text{irr}} = 335 \text{ nm}$; FF01-575/25-25 for $\lambda_{\text{irr}} = 575 \text{ nm}$). The irradiation power was measured using a photodiode from Ophir (PD300-UV).

Differential extinction spectra $\Delta\text{Ext}(\lambda)$, shown in Fig. 2d (main text), were obtained from extinction spectra recorded before irradiation $\text{Ext}_0(\lambda)$ and after irradiation at 335 nm $\text{Ext}_{335\text{nm}}(\lambda)$, by means of the following equation: $\Delta\text{Ext}(\lambda) = \text{Ext}_{335\text{nm}}(\lambda) - \text{Ext}_0(\lambda)$

II. Synthetic protocols of silica-coated GNR samples

Synthesis of gold nanorods (GNR): The GNR were prepared by the “seed mediated growth method” devised by El-Sayed *et al.*^[1] Briefly, seed nanoparticles were obtained by the reduction of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ dissolved in an aqueous solution of cetyltrimethylammonium bromide (CTAB), with cold sodium borohydride (NaBH_4). The growth solution was prepared by dropwise addition of ascorbic acid in an aqueous solution of HAuCl_4 , CTAB, and AgNO_3 . A seed solution aged for 5 min was added to the growth solution, and the GNR growth was initiated. The color of the solution mixture changed from light pink to deep purple after incubation for 3 h at 27–30°C.

Synthesis of silica-coated gold nanorods (GNR- SiO_2): The coated silica-shell gold nanorods were prepared by a modified Stöber protocol.^[2] 3 mL of the previously prepared GNR dispersion was centrifuged at 6000 rpm for 10 min to remove the excess of CTAB surfactants. The precipitate was redispersed in 2 mL of deionized water and 20 μL of a 0.1 M aqueous NaOH solution were then added under vigorous stirring. After this step, 12 μL of tetraethylorthosilicate (TEOS) in methanol (20% v/v) were added under gentle stirring. The mixture was then allowed to react for 15 minutes (or 30 minutes), the resultant hybrid nanostructures were washed with two cycles of centrifugation and redispersed in water at the same volume. The silica thickness varies with reaction time (*cf.* Figure S1). Two samples were obtained: **GNR- SiO_2 (a)** and **GNR- SiO_2 (b)**, corresponding to 15 and 30 min of reaction time.

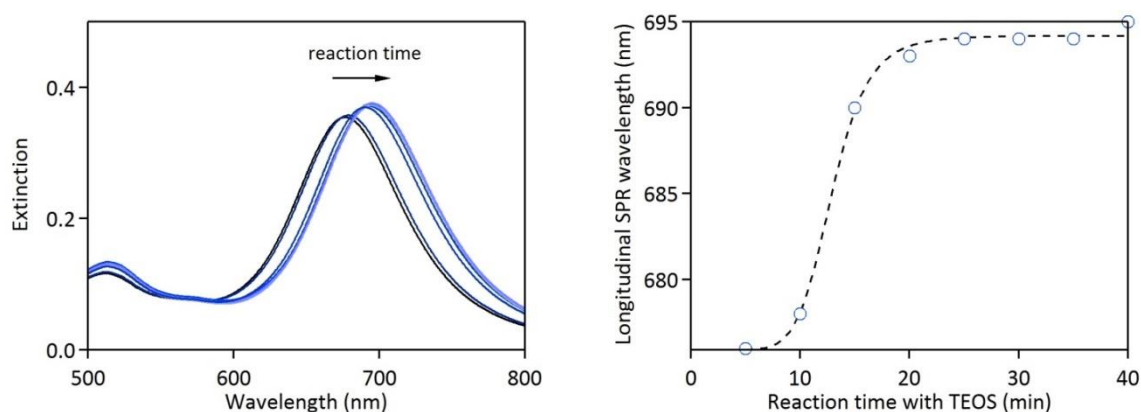


Figure S1. (a) Extinction spectra of GNR during the silica-coating process. (b) Plot of the longitudinal SPR as a function of the reaction time with TEOS.

III. Size distribution histograms

The size of the nanoparticles and the thickness of the silica-layer were examined using a Supra 40 Zeiss field emission scanning electron microscope (FESEM). Several hundreds of nanoparticles were examined in order to reach satisfactory statistics and plot histogram distributions (*cf.* Figure S2).

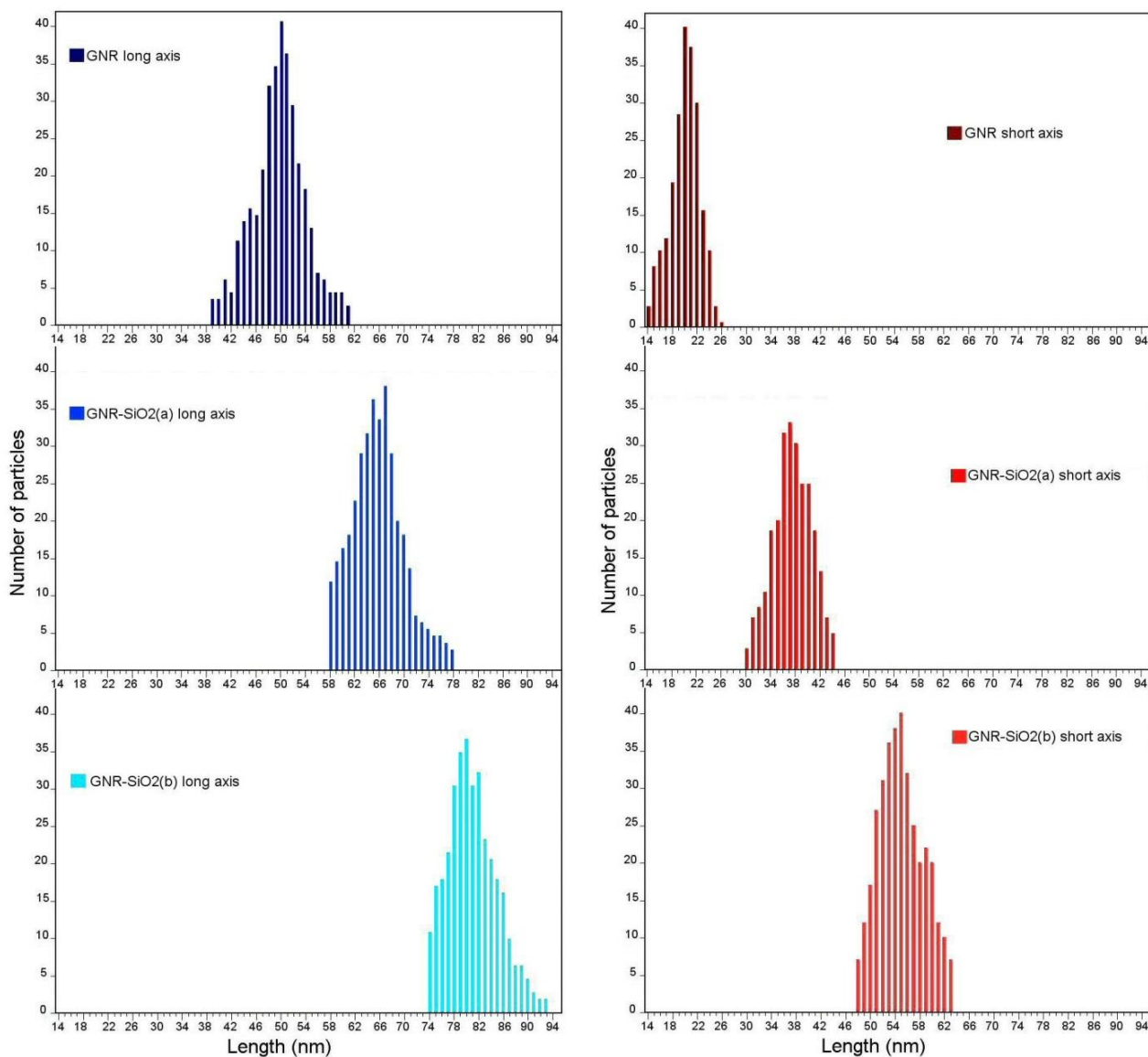


Figure S2. Long axis (left) and short axis (right) dimensions of silica-free GNR (top), **GNR-SiO₂(a)** (middle), and **GNR-SiO₂(b)** (bottom).

IV. Organic syntheses and characterizations

¹H NMR and ¹³C NMR were taken on either Bruker AM 360 (360 MHz), AM 300 (300 MHz) or AM (250 MHz) or JEOL ECS 400 (400 MHz) spectrometer and calibrated to the residual solvent peaks (CDCl₃, 7.24 ppm and 77 ppm). The data are reported as chemical shift (ppm). Solvents and reagents are used as received unless otherwise stated. Elemental analyses were performed by Service de Microanalyse, ICSN, 91198, Gif sur Yvette, France.

2-(4-methoxy-phenyl)-4-Bpin-5-methyl-thiazole (2) was prepared in three steps as follows:

(1) To a DMF (50 mL) solution of 2-(4-methoxy-phenyl)-thiazole (**1**)^[3] (5.00 g, 26.18 mmol) was added NBS (5.00 g, 28.10 mmol) in one portion and the mixture was stirred overnight at rt. To the pale brown solution was added water (ca. 200 mL) and metabisulfite (Na₂S₂O₅, ca. 0.5 g). After ca. 30 min of stirring the precipitate was filtered, washed with water and vacuum dried. 2-(4-methoxy-phenyl)-5-bromothiazole, obtained as an off-white crystalline solid (6.64 g, 94%), was pure enough for the following step without further purification. ¹H NMR (300 MHz, CDCl₃): δ = 7.78 (d, *J*=8.8 Hz, 2H), 7.65 (s, 1H), 6.94 (d, *J*=8.8 Hz, 2H), 3.84 (s, 3H).

(2) 2-(4-methoxy-phenyl)-4-bromo-5-methyl-thiazole : 2-(4-methoxy-phenyl)-5-bromo-thiazole (1.350 g, 5 mmol) was dissolved in dry THF (30 mL) and cooled to -78°C. Then, LDA (4 mL, 2M) was added slowly and the solution was stirred ca. 20 min. at that temperature before MeI (0.5 mL, 8 mmol) was introduced. The mixture was allowed to warm to rt overnight and quenched with aqueous NH₄Cl solution (40 mL, 1M). After addition of diethyl ether (20 mL), organic phase was collected, and aqueous phase was extracted twice with diethyl ether (20 mL). Combined organic phase was washed with brine (40 mL) and dried over Na₂SO₄. After removal of solvents, column chromatography (SiO₂, CH₂Cl₂) of the residue gave 2-(4-methoxy-phenyl)-4-Br-5-Me-2-phenylthiazole as a white crystalline solid (1.312 g, 92%). ¹H NMR (360 MHz, CDCl₃): δ = 7.79 (d, *J* = 8.6 Hz, 2H), 6.91 (d, *J* = 8.6 Hz, 2H), 3.83 (s, 3H), 2.40 (s, 3H).

(3) 2-(4-methoxy-phenyl)-4-Br-5-Me-2-phenylthiazole (1.136 g, 4 mmol) was dissolved in dry diethyl ether (60 mL) and cooled to -78°C before dropwise addition of nBuLi (2 mL, 2.5 M). Stirring was continued for ca. 1h30 at -78°C before addition of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (ca. 1 mL, 5 mmol). The mixture was allowed to warm slowly to rt overnight and quenched with aqueous NH₄Cl solution (40 mL, 1M). Then, diethyl ether (20 mL) was added and organic phase separated. Aqueous phase was extracted twice with diethyl ether (20 mL), combined organic phase was washed with brine (40 mL) and dried over Na₂SO₄. Removal of solvents gave 2-(4-methoxy-phenyl)-4-Bpin-5-methyl-thiazole (**2**) as an off-white solid (1.270 g) in 96% yield and used as such for the coupling reaction. ¹H NMR (250 MHz, CDCl₃): δ = 7.88 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 3.82 (s, 3H), 2.69 (s, 3H), 1.35 (s, 12H).

5-bromo-5'-methyl-4,4'-bi-(2-phenyl)-thiazole (3) was synthesized in three steps as follows:

(1) 1,4-dibromopentane-2,3-dione: under stirring, Br₂ (5.1 mL, 100 mmol) was slowly added to 2,3-pentanedione (5.2 mL, 50 mmol) at rt during 0.5 h. After 1 h of stirring, air was flushed into the mixture to remove HBr. The resulting brown oil was a mixture of several isomers but was used without further purification.

(2) Thiobenzamide (5.50 g, 40 mmol) was dissolved in MeOH (60 mL) and crude 1,4-dibromopentane-2,3-dione (5.20 g, 20 mmol) was added. The solution was stirred at rt for ca. 20 min. before the solution was refluxed overnight. After cooling down to rt, the precipitate was filtered and washed with small amount of MeOH and vacuum dried. 5-methyl-4,4'-bi-(2-phenyl)-thiazole was obtained as a sand-colored crystalline solid (3.40 g, 51%). ¹H NMR (360 MHz, CDCl₃): δ = 8.02 (d, *J* = 7.9 Hz, 2H), 7.96 (d, *J* = 7.9 Hz, 2H), 7.90 (s, 1H), 7.44 (m, 6H), 2.97 (s, 3H).

(3) After complete dissolution of 5-methyl-4,4'-bi-(2-phenyl)-thiazole (1.92 g, 5.75 mmol) in DMF (30 mL) at ca. 70°C, NBS (1.15 g, 6.47 mmol) was added portionwise and stirred at that temperature overnight. Once cooled to rt, water (ca. 100 mL) was added, followed by Na₂S₂O₅, (ca.0.5 g). After 20 min. of stirring at rt, the solid was filtered, washed with water and then redissolved in CHCl₃ (ca. 50 mL) before addition

of EtOH (96%, 30 mL). Removal of most CHCl_3 under vacuum led to an off-white crystalline solid, which was filtered, washed with some EtOH (96%) and vacuum dried to give 5-bromo-5'-methyl-4,4'-bi-(2-phenyl)-thiazole (**3**) as an off-white crystalline solid (2.24 g, 94%). ^1H NMR (300 MHz, CDCl_3): δ = 7.98-7.90 (m, 4H), 7.45-7.38 (m ; 6H), 2.69 (s, 3H).

Compound 4:

2 (0.730 g, 2.2 mmol), **3** (0.826 g, 2 mmol), CsF (0.760 g, 5 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (0.120 g, 0.10 mmol) were purged three times by alternating vacuum and Argon. Then, similarly purged dioxane (40 mL) was introduced and the mixture was refluxed under Ar overnight. At room temperature, CHCl_3 (ca. 40 mL) followed by H_2O (20 mL) were added and stirred vigorously for few min. Then, the organic phase was separated and the aqueous phase was extracted twice with CHCl_3 (ca. 20 mL). Combined organic phase was washed with brine (40 mL) and dried over Na_2SO_4 . **4** was obtained after column chromatography (SiO_2 , CH_2Cl_2 to 10% EtOAc) as an bluish crystalline solid (1.020 g, 95%).

^1H RMN (300 MHz, CDCl_3): δ = 8.06-8.03 (m, 2H), 7.86 (d, J = 8.7 Hz, 2H), 7.81-7.77 (m, 2H), 7.46-7.32 (m, 3H), 7.34-7.32 (m, 3H), 6.93 (d, J = 8.7 Hz, 2H), 3.84 (s, 3H), 2.49 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ = 167.19, 164.27, 164.02, 161.19, 147.72, 146.59, 143.44, 133.86, 133.77, 133.09, 131.45, 130.28, 129.79, 129.72, 129.04, 128.86, 128.00, 126.77, 126.64, 126.47, 114.36, 55.58, 12.81, 12.41. ESI-HRMS (m/z) [MH] $^+$: calcd: 538.1076; found: 538.1087. Elemental analysis calcd (%) for $\text{C}_{30}\text{H}_{23}\text{N}_3\text{OS}_3$: C 67.01, H 4.31, N 7.81; found : C 66.33, H 4.30, N 7.56.

Compound 5:

To a dry CH_2Cl_2 (20 mL) solution of **4** (0.362 g, 0.673 mmol) cooled at -78°C was added BBr_3 (3.6 mL, 1M in CH_2Cl_2) with stirring and allowed to warm slowly to rt overnight. Ca. water (20 mL) was introduced and the mixture was vigorously stirred during ca. 20 min before addition of CHCl_3 (40 mL). Aqueous phase was extracted twice with CHCl_3 (40 mL) and combined organic phase was washed with brine (30 mL) and dried over Na_2SO_4 . After removal of solvents, the oily residue was triturated with EtOH (ca. 10 mL) and the solid formed was filtered and vacuum dried to give **5**. EtOH (0.31 g, 81% yield), which was used for the next step without further purification.

^1H NMR (300 MHz, CDCl_3): δ = 8.04-8.00 (m, 2H), 7.75-7.68 (m, 4H), 7.45-7.41 (m, 3H), 7.30-7.19 (m, 3H), 6.86 (d, J = 8.7 Hz, 2H), 2.58 (s, 3H), 2.13 (s, 3H).

Compound P:

5.EtOH (0.263 g, 0.46 mmol), Cs_2CO_3 (0.180 g, 0.55 mmol) and propargyl bromide (0.11 mL, 80% in toluene) in acetone (15 mL) were refluxed until TLC showed no more **4** was present (ca. 4h). Once cooled to rt, the solid was filtered off, washed with acetone and the filtrate was evaporated to dryness. Column chromatography of the residue (SiO_2 , CH_2Cl_2) afforded a thick oil, which was then triturated with hexane (ca. 20 mL) to give **P** as an off-white solid (0.220 g, 84% yield).

^1H NMR (250 MHz, CDCl_3): δ = 8.06-8.02 (m, 2H), 7.87 (d, J = 8.8 Hz 2H), 7.81-7.76 (m, 2H), 7.46-7.43 (m, 3H), 7.34-7.31 (m, 3H), 7.00 (d, J = 8.8 Hz, 2H), 4.73 (d, J = 2.5 Hz, 2H), 2.53 (t, J = 2.5 Hz, 1H), 2.48 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (90 MHz, CDCl_3): δ = 166.88, 163.71, 163.66, 158.85, 147.66, 146.38, 143.41, 133.70, 133.61, 132.90, 131.51, 130.06, 129.48, 128.84, 128.64, 127.85, 127.77, 127.33, 126.54, 126.24, 115.17, 78.13, 75.82, 55.85, 12.63, 12.19. ESI-HRMS (m/z) [MH] $^+$: calcd: 562.1076; found: 562.1060. Elemental analysis calcd (%) for $\text{C}_{32}\text{H}_{23}\text{N}_3\text{OS}_3 \cdot 0.3\text{H}_2\text{O}$: C 67.77, H 4.19, N 7.41; found : C 67.63, H 4.10, N 7.34.

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