

Electronic Supplementary Information

A novel generation of hybrid photochromic vinylidene-naphthofuran silica nanoparticles through fine-tuning of surface chemistry

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1. Experimental Section

Synthesis of naphthofuran **3**

7-Ethoxycarbonyl-1,2-dihydro-1-(2,2-diphenylvinylidene)-2,2-diphenylnaphtho-[2,1-b]furan: To a solution of ethyl 6-hydroxy-2-naphthoate **1** (200 mg; 0.92 mmol) and 1,1,4,4-tetraphenylbut-2-yn-1,4-diol **2** (1.0 eq) in chloroform (Merck; 15 mL), a catalytic amount of *p*-TSA was added. The solution was stirred at room temperature for 24 h. After that, water was introduced (40 mL) and then the organic phase was separated and the aqueous phase was extracted with chloroform (3×25 mL). Afterwards, the organic phase was dried with Na₂SO₄ (Merck), and the solvent was removed under reduced pressure resulting in an oil. Ethanol (Acros) was added affording a suspension of yellow crystals that were filtered. The final product **3** was purified by column chromatography (5% ethyl acetate (Merck)/petroleum ether (Merck)) and recrystallized with dichloromethane (Merck)/petroleum ether yielding white crystals (261 mg; 49%). **mp**: 192.2–195.3 °C. **IR** (KBr, cm⁻¹): 3058, 3026, 2981, 1712, 1626, 1468, 1275, 1240, 1185, 1099, 1022, 949, 928, 812, 765, 698, 649. **¹H NMR** (400 MHz, CDCl₃): 8.57 (s, 1H), 8.27 (d, *J*=8.76 Hz, 1H), 8.05 (d, *J*=8.76 Hz, 1H), 7.90 (d; *J*=8.84 Hz, 1H), 7.45-7.43 (m, 4H), 7.33-7.14 (m, 13H), 7.12 (m, 4H), 4.40 (q, *J*=7.10 Hz, 2H), 1.42 (t, *J*=7.12 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃): 202.63, 166.70, 159.47, 142.69, 136.21, 133.20, 132.09, 131.91, 129.13, 128.70, 128.43, 128.17, 128.01, 127.83, 127.36, 127.24, 126.97, 125.48, 122.17, 117.66, 114.18, 113.88, 113.27, 95.32, 60.98, 14.37. **EI-MS** (TOF) *m/z* (%): 570 (100), 493 (50), 464 (14), 420 (25), 403 (24), 379 (10), 375 (10). **HRMS** calculated for C₄₁H₃₀O₃: 570.2195. Found: 570.2194.

Synthesis of VNF-1

7-Hydroxymethyl-1,2-dihydro-1-(2,2-diphenylvinylidene)-2,2-diphenylnaphtho-[2,1-b]furan: LiAlH₄ (Sigma Aldrich; 65 mg; 1.72 mmol) was added to a solution of naphthofuran **3** (982 mg; 1.72 mmol) in anhydrous tetrahydrofuran (Sigma Aldrich) at room temperature. After 1 h, the solution was slowly added to water and then an aqueous solution of sodium hydroxide (Merck; 50 eq) was added. The mixture was stirred at room temperature for 24 h and then extracted with dichloromethane (20×10 mL). The organic phases were combined, dried with Na₂SO₄, and the solvent was removed under reduced pressure. The final product (**VNF-1**) was purified by recrystallization from dichloromethane/petroleum ether affording white crystals (74 mg; 81%). **mp**: 232.7–235.3 °C. **IR** (KBr, cm⁻¹): 3288, 3060, 3025, 2854, 1632, 1596, 1492, 1469, 1442, 1377, 1270, 1255, 1225, 1157, 1044, 1026, 958, 822, 762, 694, 644. **¹H NMR** (400 MHz, CDCl₃): 8.2 (d, *J* = 8.6 Hz, 1H), 7.8 (m, 2H), 7.47-7.43 (m, 5H), 7.29-7.20 (m, 13H), 7.14-7.04 (m, 4H), 4.79 (d, *J* = 5.8 Hz, 2H). **¹³C NMR** (100 MHz, CDCl₃): 202.73, 157.87, 142.94, 136.39, 136.04, 131.65, 129.98, 129.27, 128.70, 128.37, 128.11, 127.89, 127.71, 127.28, 127.24, 126.79, 122.63, 117.36, 114.71, 113.58, 112.72, 94.86, 65.41. **EI-MS** (TOF) *m/z* (%): 582 (100), 526 (18), 513 (19), 451 (52), 435 (42), 403 (15), 391 (13), 361 (34), 345 (27), 315 (30), 302 (18), 165 (17). **HRMS** calculated for C₃₉H₂₈O₂: 528.2089. Found: 528.2090.

Synthesis of VNF-2

1-(2,2-Diphenylvinylidene)-(2,2-diphenyl-1,2-dihydronaphtho[2,1-b]furan-7-yl)methyl (3-(triethoxysilyl)propyl)carbamate: Brown Oil (85 %). $^1\text{H NMR}$ (400 MHz, CDCl_3): 8.25 (d, $J = 8.6$ Hz, 1H, H_{ar}), 7.81 (d, $J = 1.3$ Hz, 1H, H_{ar}), 7.79 (d, $J = 8.9$ Hz, 1H, H_{ar}), 7.42-7.51 (m, 5H, H_{ar}), 7.21-7.71 (m, 13H, H_{ar}), 7.11-7.17 (m, 4H, H_{ar}), 5.13-5.28 (m, 2H, ArCH_2O); 4.85-5.10 (bm, 1H, NH), 3.81 (q, $J = 7.0$ Hz, 6H, $3 \times \text{OCH}_2$), 3.10-3.26 (m, 2H, NCH_2), 1.59-1.70 (m, 2H, CH_2), 1.21 (t, $J = 6.9$ Hz, 9H, $3 \times \text{CH}_3$), 0.56-0.67 (m, 2H, SiCH_2); **ESI-MS**: calculated for $[\text{C}_{49}\text{H}_{49}\text{NO}_6\text{Si} + \text{H}]^+$ ($\text{M} + \text{H}^+$) 776.34. Found 776.38.

$^1\text{H NMR}$ spectrum of **VNF-2**:

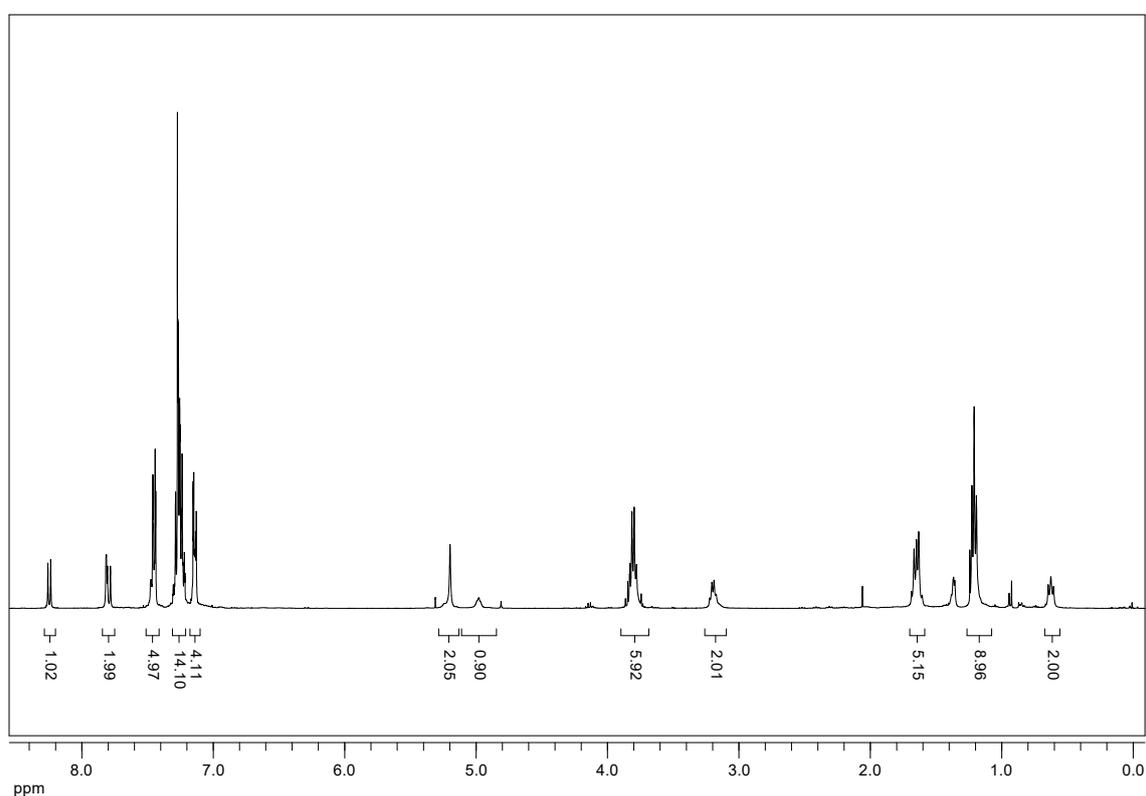


Figure S1. FTIR spectra of A) SiO_{2_w}, B) SiO_{2_w1} and C) SiO_{2_w2}-based nanomaterials in the 4000–400 cm⁻¹ range (obtained from diluted KBr pellets, 0.3 wt%).

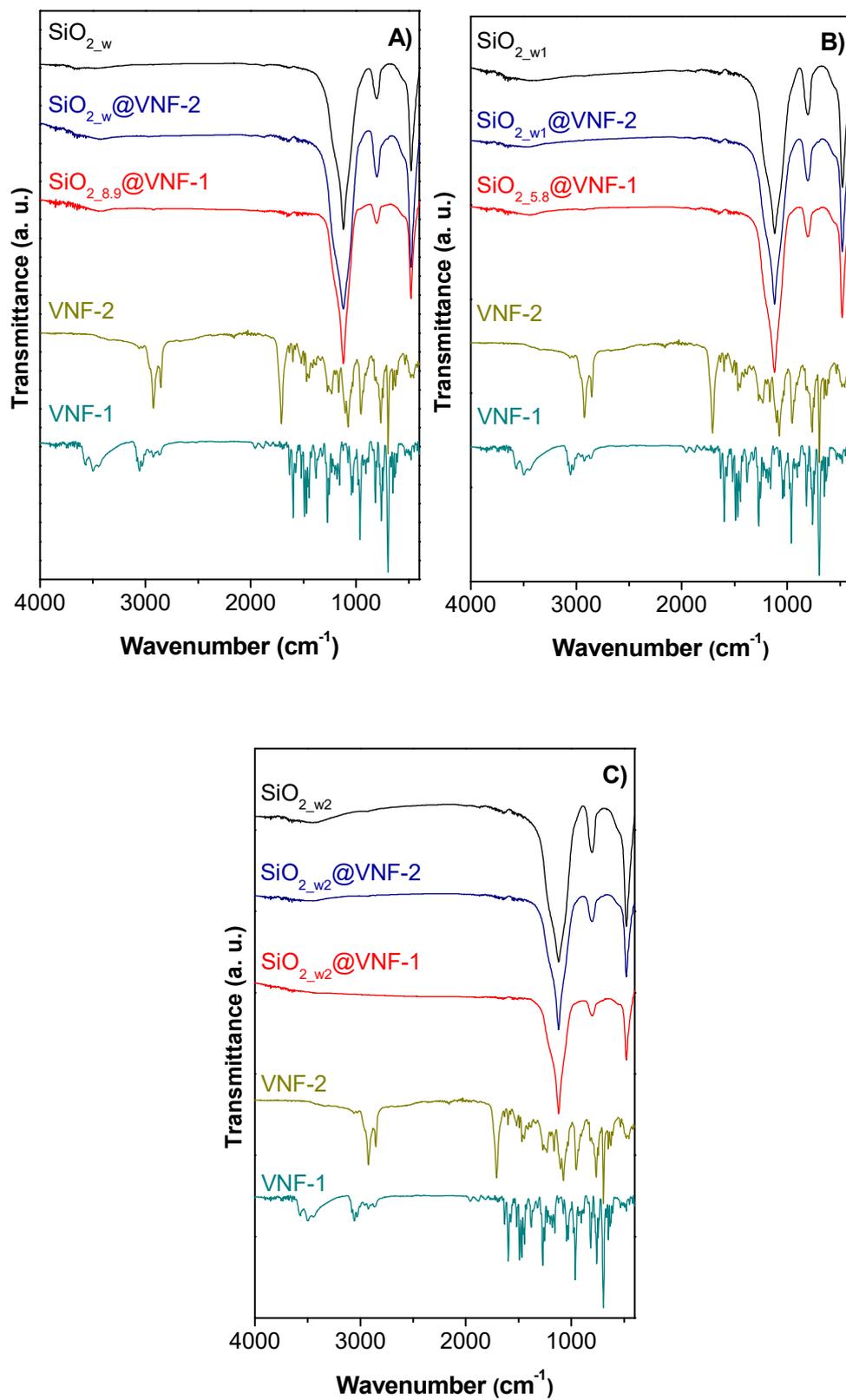


Figure S2. Photographs of the $\text{SiO}_2\text{-}_w\text{@VNF-1}$, $\text{SiO}_2\text{-}_w\text{@VNF-2}$, $\text{SiO}_2\text{-}_{w1}\text{@VNF-2}$, $\text{SiO}_2\text{-}_{w2}\text{@VNF-2}$ and $\text{SiO}_2\text{-}_m\text{@VNF-2}$ hybrid nanomaterials: before and after being irradiated with UV ($\lambda = 365 \text{ nm}$) during 10 min, at room temperature.

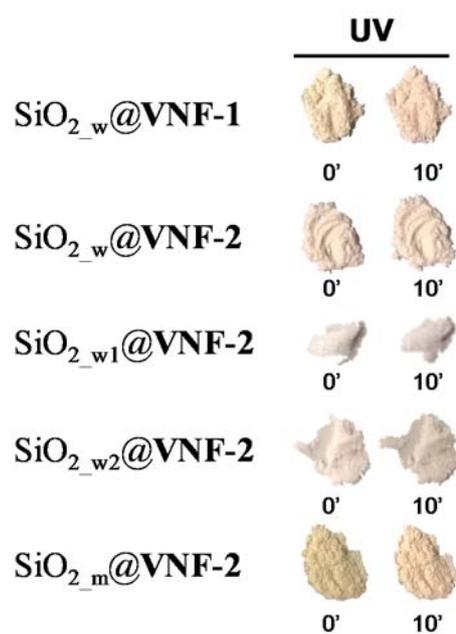


Figure S3. CIELab colorimetric parameters (L^* , a^* and b^*) of the ●) $\text{SiO}_2\text{-}_m\text{@VNF-1}$, ■) $\text{SiO}_2\text{-}_w1\text{@VNF-1}$ and ▲) $\text{SiO}_2\text{-}_w2\text{@VNF-1}$ hybrid nanomaterials: before (⊗, ⊠ and ⊡) and after being UV-irradiated during 5 min (●, ■ and ▲), at room temperature.

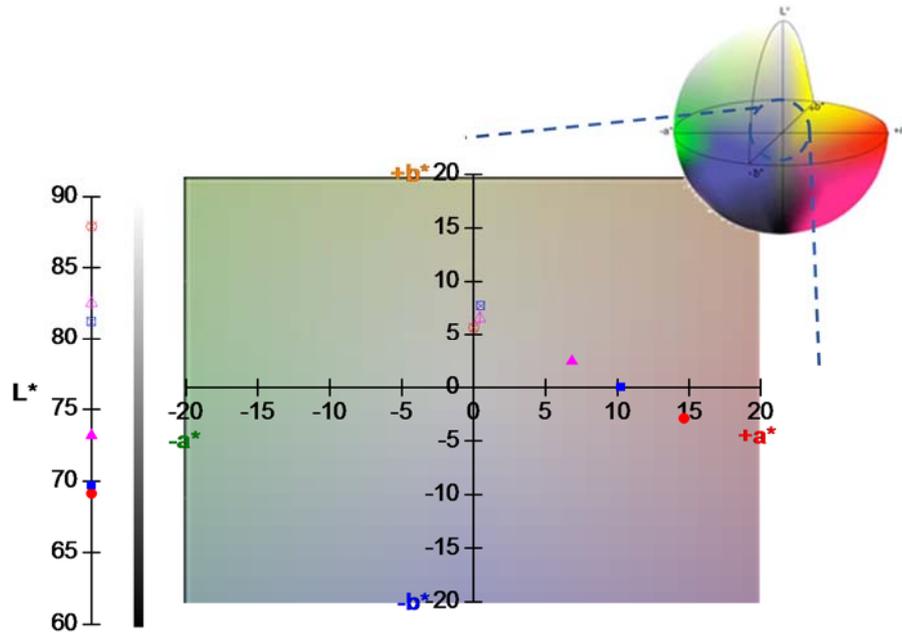


Figure S4. UV-Vis absorption spectra of A) $\text{SiO}_2_{\text{w1}}@\text{VNF-1}$ and B) $\text{SiO}_2_{\text{w2}}@\text{VNF-1}$ hybrid nanomaterials during the thermal bleaching process after being irradiated with UV ($\lambda = 365$ nm) for 1 min (black line: before UV irradiation; red line: after UV irradiation). Bi-exponential fit of the thermal bleaching curve of C) $\text{SiO}_2_{\text{w1}}@\text{VNF-1}$ and D) $\text{SiO}_2_{\text{w2}}@\text{VNF-1}$, measured at $\lambda = 565$ nm, in the dark, at room temperature (blue: measured data; black: bi-exponential model fitting).

