SUPPORTING INFORMATION

Wavelength selective caged surfaces: how many functional levels are possible?

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SYNTHETIC PROCEDURE

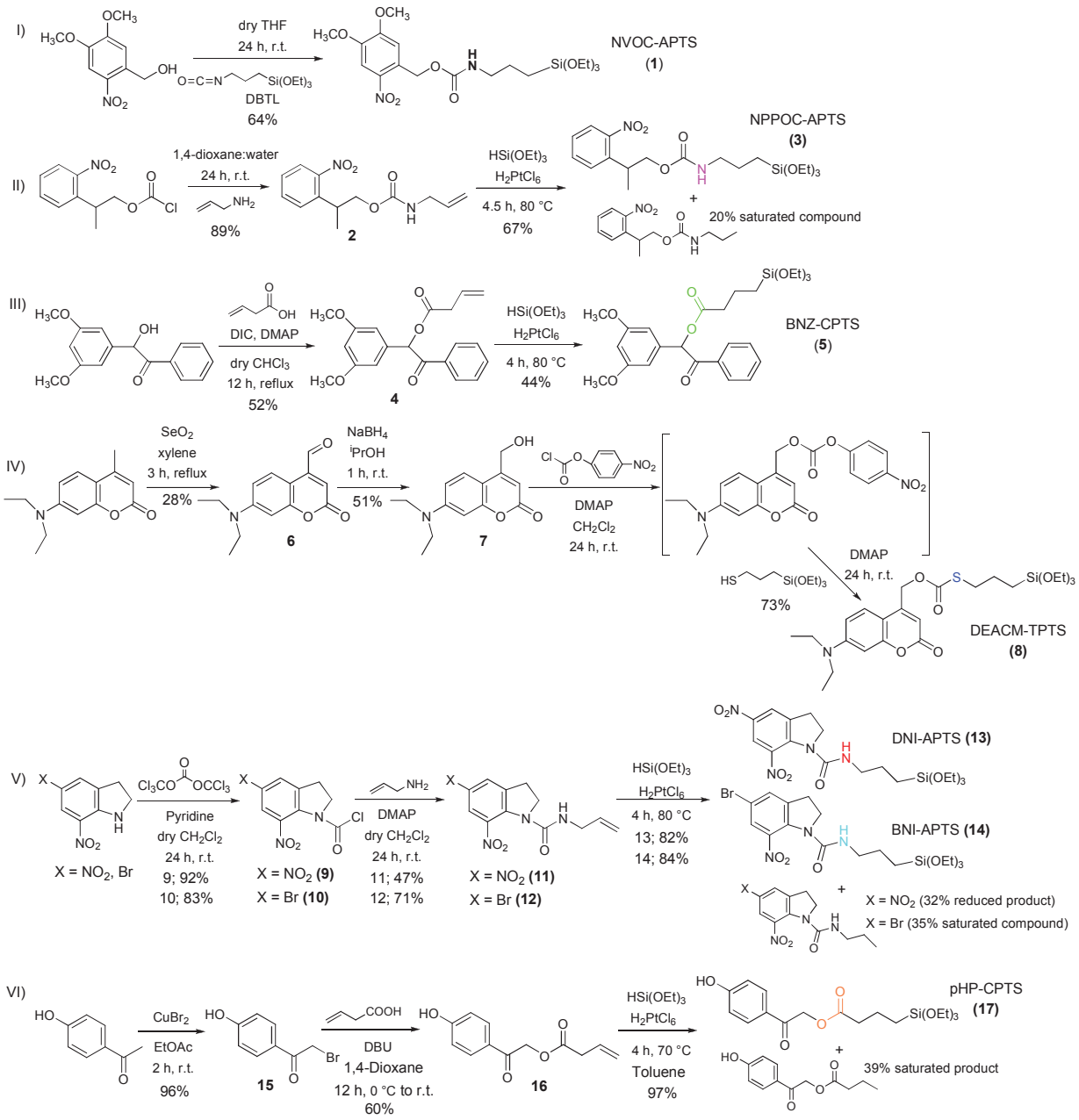
Materials

All reagents were, unless otherwise noted, used as purchased. Chemicals and solvents were purchased from Fluka Chemie AG (D-Taufkirchen, Germany), Fisher Scientific UK Ltd. (Loughborough, Leics. GB), Merck KGaA (Darmstadt, Germany), Sigma-Aldrich Chemie GmbH (Steinheim, Germany), and ABCR (Karlsruhe, Germany). Analytical thin-layer chromatography was performed on TLC plates (Alugram Sil G/UV254) from Macherey-Nagel (Düren, Germany). Preparative column chromatography was carried out using silica gel (60 Å pore size, 63-200 µm particle size) from Merck KGaA (Darmstadt, Germany). Silicon Wafers (100 orientation) were provided by Crystec (Berlin, Germany). Quartz substrates Suprasil with a thickness of 1 mm were purchased from Heraeus Quarzglas (Hanau, Germany).

Methods

Solution ^{1}H-NMR spectra were recorded on a Bruker Spectrospin 250 or 300 MHz. UV/VIS spectra were recorded with a Varian Cary 4000 UV/VIS spectrometer (Varian Inc. Palo Alto, USA).

Synthesis of Caged Organosilanes.



Scheme 1. Synthetic routes of the photosensitive silanes. Saturated compounds as by-products of the hydrosililation reaction are included.

3-Triethoxysilylpropyl-N-(4,5-dimethoxy-2-nitrobenzyloxycarbonyl)amine (NVOC-APTS) (**1**) was prepared as reported.[1]

2-(2-Nitrophenyl)propyl allylcarbamate (**2**) was obtained according to previously reported procedure.[2] $NaCO_3$ (0.96 g) was added to the solution of allyl amine (0.31 mL, 4.10 mmol) in 40 mL of 1,4-dioxane:water (1:1) at 0 °C, followed by the dropwise addition of 2-(2-nitrophenyl)propyl chloroformate (1.0 g, 4.10 mmol) in 4 mL of THF. After 20 minutes the ice bath was removed and the reaction mixture was stirring for 24 h. The solvents were removed in the rotary evaporator, 3 mL of water was added and the mixture was extracted with ethyl acetate (2x20 mL). The aqueous layer was acidified by addition of 5% HCl (10 mL) at 0 °C and extracted with ethyl acetate (3x40 mL). The extracts were dried over $MgSO_4$ and concentrated at reduced pressure to give an orange oil as the desired product **2** (0.96 g, 89%). ^{1}H NMR ($CDCl_3$): δ 7.71 (dd, *J* = 8.0 Hz, *J* = 1.1 Hz, 1H, Ar-H), 7.56 (td, *J* = 8.1 Hz, *J* = 1.3 Hz, 1H, Ar-H), 7.47 (dd, *J* = 8.0 Hz, *J* = 1.4 Hz, 1H, Ar-H), 7.32 (td, *J* = 8.0 Hz, *J* = 1.5 Hz, 1H, Ar-H), 5.71 (m, 1H, CH), 5.11 (m, 2H, CH_2), 4.69 (br d, 1H, NH), 4.16 (dq, *J* = 6.1 Hz, 2H, CH_2), 3.71 (m, 1H, CH), 3.71 (m, 2H, CH_2), 1.34 (d, *J* = 7.0 Hz, 3H, CH_3).

2-(2-Nitrophenyl)propyl 2-(triethoxysilyl)ethylcarbamate (NPPOC-APTS) (**3**). 2-(2-Nitrophenyl)propyl allylcarbamate (**2**) (0.5 g, 1.89 mmol) and triethoxysilane (3.5 mL, 18.92 mmol) were placed into a previously HMDS-passivated[3] dry, round-bottomed flask and heated to 80 °C under argon atmosphere. After addition of an isopropanolic H_2PtCl_6 solution (96 µL, 65 mM), the mixture was stirred for 5 hours at 80 °C and then allowed to cool. Excess of triethoxysilane was removed in vacuum, and the residue was taken up in dichloromethane and filtered through Celite500. The filtrate was concentrated under reduced pressure and determined to be **3** as a mixture with 20% of the saturated compound. Yield = 67%. ^{1}H NMR ($CDCl_3$): δ 7.73 (d, *J* = 7.5 Hz, 1H, Ar-H), 7.56 (td, *J* = 7.5 Hz, *J* = 1.1 Hz, 1H, Ar-H), 7.46 (d, *J* = 7.0 Hz, 1H, Ar-H), 7.35 (td, *J* = 8.5 Hz, *J* = 1.5 Hz, 1H, Ar-H), 4.83 (br d, 1H, NH), 4.16 (d, *J* = 6.1 Hz, 2H, CH_2), 3.80 (q, *J* = 7.0 Hz, 6H, 3xCH_2), 3.71 (m, 1H, CH), 3.19-2.90 (m, 2H, CH_2), 1.79-1.40 (m, 2H, CH_2), 1.34 (d, *J* = 6.9 Hz, 3H, CH_3), 1.21 (t, *J* = 7.0 Hz, 9H, 3xCH_3), 0.67 – 0.52 (m, 2H, CH_2).^{13}C NMR ($CDCl_3$): δ 156.1 (C), 150.7 (C), 137.5 (C), 132.6 (CH), 127.9 (CH), 127.3 (CH), 124.0 (CH), 68.6 (CH_2), 58.4 (CH_2), 43.3 (CH_2), 33.2 (C), 23.2 (CH_2), 18.0 (CH_3), 17.4 (CH_3), 7.5 (CH_2).

1-(3,5-Dimethoxyphenyl)-2-oxo-2-phenylethyl 3-butenoate (**4**): 3',5'-Dimethoxybenzoin (obtained according to the literature)[4] (490 mg, 1.8 mmol), *N,N´*-dicyclohexylcarbodiimide (520 mg, 2.5 mmol), and 4-dimethylaminopyridine (DMAP) (22 mg, 0.18 mmol) were dissolved in anhydrous chloroform (20 mL). The mixture was heated and then 3-butenoic acid

was added (196 mg, 2.16 mmol). The reaction was kept under reflux for 12 h. Ethyl acetate was added, and the mixture was washed with 10% HCl (20 mL) and aqueous bicarbonate solution. The organic layer was dried over $MgSO_4$, filtered, and concentrated. The residue was purified by flash chromatography (hexane:AcOEt, 1:1) to give 320 mg (yield = 52%) of **4** as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.94 (d, *J* = 7.1 Hz, 2H, Ar-H), 7.51 (d, *J* = 7.5 Hz, 1H, Ar-H), 7.40 (t, *J* = 7.4 Hz, 2H, Ar-H), 6.76 (s, 1H, CH), 6.59 (d, *J* = 2.2 Hz, 2H, Ar-H), 6.42 (s, 1H, Ar-H), 6.07 – 5.83 (m, 1H, CH), 5.25- 5.18 (m, 2H, CH_2), 3.79 (d, *J* = 16.1 Hz, 6H, 2xCH_3), 3.43 – 3.02 (m, 2H, CH_2).

1-(3,5-Dimethoxyphenyl)-2-oxo-2-phenylethyl-4-(triethoxysilyl)butanoate (BNZ-CPTS) (**5**). Product **4** (1.19 g, 3.5 mmol) and triethoxysilane (6.8 mL, 35 mmol) were placed into a previously HMDS-passivated[3] dry, round-bottomed flask and heated under an argon atmosphere to about 80 °C. After the addition of an isopropanolic H_2PtCl_6 solution (50 µL, 0.027 mg/µL), the mixture was allowed to react for 4 h at 80 °C and then cooled to room temperature. Excess triethoxysilane was removed in vacuum. The crude was purified by a previously HMDS-passivated flash chromatography (hexane: ethyl acetate, 3.2:0.8) with a R_f of 0.42. Fractions were concentrated and the silane **5** was obtained as a brown oil (0.76 g, 44 %). ^{1}H NMR ($CDCl_3$): δ 7.94 (d, *J* = 8.2 Hz, 2H, Ar-H), 7.62 – 7.33 (m, 3H, Ar-H), 6.75 (s, 1H, CH), 6.59 (s, 2H, Ar-H), 6.41 (s, 1H, Ar-H), 3.76- 3.85 (m, 12H, 3xCH_2 and 2xCH_3), 2.54-2.49 (m, 2H, CH_2), 1.85-1.77 (m, 2H, CH_2), 1.23 (t, *J* = 7.1 Hz, 9H, 3xCH_3), 0.68-0.73 (m, 2H, CH_2). ^{13}C NMR ($CDCl_3$): δ 194.0 (C), 172.9 (C), 161.2 (C), 135.7 (C), 134.7 (C), 133.4 (CH), 128.8 (CH), 106.6 (CH), 101.1 (CH), 79.5 (CH), 58.4 (CH_2), 55.4 (CH_3), 36.8 (CH_2), 18.3 (CH_3), 17.9 (CH_2), 10.0 (CH_2).

7-(Diethylamino)-2-oxo-2H-chromene-4-carbaldehyde (**6**) was obtained according to previously reported procedure.[5] Selenium (IV) dioxide (1.10 g, 10 mmol) was added to a solution of 7-(diethylamino)-4-methyl-coumarin (2.06 g, 8.9 mmol) in xylene (25 mL, mixture of isomers). The reaction mixture was heated under reflux with vigorous stirring for 3 hours. The brown mixture was allowed to cool to room temperature and a second portion of selenium (IV) oxide (1.10 g, 10 mmol) was added. The system was refluxed again during 3 hours. Then, the solvent was removed carefully under reduced pressure. The dark-brown residual oil was dissolved in acetone and the dark solid was filtered off. The obtained dark-orange solid after concentrating was purified by column chromatography using hexane:acetone (4:1). The appropriate fractions were collected and the solvents were removed to give a yellow solid as

the product **6** (620 mg, 28%). ^{1}HNMR ($CDCl_3$): δ 10.03 (s, 1H, CHO), 8.30 (d, *J* = 9.2 Hz, 1H, Ar-H), 6.60 (dd, *J* = 9.2 Hz, *J*= 2.6 Hz, 1H, Ar-H), 6.51 (d, *J* = 2.6 Hz, 1H, Ar-H), 6.46 (m, 1H, Ar-H), 3.43 (q, *J* = 7.1 Hz, 4H, 2xCH_2), 1.22 (t, *J* = 7.1 Hz, 6H, 2xCH_3).

7-(Diethylamino)-4-(hydroxymethyl)-2H-chromen-2-one (**7**) was synthesised according to a reported protocol.[6] Product **6** (620 mg) was dissolved in isopropanol (50 mL) and then sodium borohydride (1.5 eq.) was added. The solution was stirred for 1 h at room temperature and the reaction was followed by thin layer chromatography (TLC). Once product **6** can not be noticed ethyl acetate (100 mL) and water (150 mL) were added. The red solution was extracted with ethyl acetate (2x100 mL). The combined organic extracts were washed with water and brine (saturated sodium chloride) and dried over anhydrous sodium sulfate. Removal of the solvent under reduced pressure gave a dark-brown oil. Column chromatography using hexane:acetone (3:1) as the eluent afforded desired alcohol **7** (320 mg, 51%). ^{1}HNMR ($CDCl_3$): δ 7.32 (d, *J* = 8.9 Hz, 1H, Ar-H), 6.60 (dd, *J* = 8.9 Hz, *J*= 2.6 Hz, 1H, Ar-H), 6.51 (d, *J* = 2.6 Hz, 1H, Ar-H), 6.25 (m, 1H, Ar-H), 3.40 (q, *J* = 7.1 Hz, 4H, 2xCH_2), 1.20 (t, *J* = 7.1 Hz, 6H, 2xCH_3).

O-(7-(Diethylamino)-2-oxo-2H-chromen-4-yl)methyl S-3-(triethoxysilyl)propyl carbonothioate (DEACM-TPTS) (**8**). Product **7** was dissolved in dry dichloromethane (40 mL). 4-dimethylaminopyridine (0.53 g, 4.3 mmol) and 4-nitrophenylchloroformate (0.462 g, 2.3 mmol) were added and the yellow solution was stirred at room temperature. After 18 h stirring the formation of the carbamate intermediate was confirmed by ^{1}H NMR, with the observed shift of the signals attributed to Ar-$\underline{CH_2}$-O from 4.83/4.84 ppm in alcohol **7** to 5.22 ppm in the carbamate. 4-DMAP (0.258 g, 2.11 mmol), 3-(mercaptopropyl) triethoxysilane (0.582 mL, 2.4 mmol) and triethylamine (1.35 mL, 9.69 mmol) were then added to the stirring solution. After 24 h at room temperature, dichloromethane was evaporated. The obtained orange crude was purified by chromatography using HMDS-passivated silica gel[3] as support and dichloromethane:ethyl acetate (1:0.2, R_f 0.33) as eluent. The residual yellow solid (0.82 g, 73%) was the desired product **8**. ^{1}H NMR ($CDCl_3$): δ 7.25 (d, J = 7.5 Hz, 1H, Ar-H), 6.56 (d, J = 9.0 Hz, 1H, Ar-H), 6.49 (d, J = 2.5 Hz, 1H, Ar-H), 6.11 (br s, 1H, NH), 5.30 (d, J = 3.5 Hz, 2H, CH_2), 3.81 (q, J = 7.0 Hz, 6H, 3xCH_2), 3.40 (q, J = 7.0 Hz, 4H, 2xCH_2), 2.94 (dd, J = 8.4 Hz, 15.8, 2H, CH_2), 1.76 (m, 2H, CH_2), 1.36 – 1.14 (m, 15H, 5x CH_3), 0.78 – 0.64 (m, 2H, CH_2). ^{13}C NMR ($CDCl_3$): δ 172.5 (C), 155.7 (C), 150.7 (C), 150.5 (C), 124.6 (CH), 122.6 (C), 108.9 (C), 106.4 (CH), 61.8 (CH_2), 58.7 (CH_2), 45.0 (CH_2), 43.1 (CH_2), 18.2 (CH_3), 14.6 (CH_2), 12.6 (CH_3), 7.9 (CH_2).

5,7-Dinitroindoline-1-carbonyl chloride (**9**) and *5-bromo-7-nitroindoline-1-carbonyl chloride* (**10**) were prepared as previously reported.[7]

N-Allyl-5,7-dinitroindoline-1-carboxamide (**11**) and *N-allyl-5-bromo-7-nitroindoline-1-carboxamide* (**12**) were synthesised according to a reported protocol.[7-8] Allyl amine (0.28 mL, 3.68 mmol) was added dropwise to the stirred solution of 5,7-dinitroindoline-1-carbonyl chloride (1.00 g, 3.68 mmol) and 4-dimethylaminopyridine (1.12 g, 9.20 mmol) in anhydrous CH_2Cl_2. The mixture was stirred overnight at room temperature and then washed with 3% HCl solution (2x40 mL) and 3% $NaHCO_3$ solution (2x40 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated. The crude was chromatographed on silica gel (EtOAc:petroleum ether, 1:1) to get **11** as a yellow solid (0.51 g, 47% yield). Similar procedure was followed in order to obtain N-allyl-5-bromo-7-nitroindoline-1-carboxamide (**12**) product. The stoichiometry relation of 5-bromo-7-nitroindoline-1-carbonyl chloride:allyl amine:4-DMAP used was 1:10:10. Compound **12** was obtained as an orange solid after purification by chromatography (0.76 g, 71%). ^{1}H NMR of **11** ($CDCl_3$): δ 8.61 (m, 1H, Ar-H), 8.18 (m, 1H, Ar-H), 5.87 (m, 1H, CH), 5.24 (m, 2H, CH_2), 5.07 (br d, 1H, NH), 4.28 (t, *J* = 8.4 Hz, 2H, CH_2N), 3.94 (m, 2H, CH_2-NH), 3.37 (t, *J* = 8.4 Hz, 2H, CH_2). ^{1}H NMR of **12** ($CDCl_3$): δ 7.80 (m, 1H, Ar-H), 7.45 (m, 1H, Ar-H), 5.88 (m, 1H, CH), 5.20 (m, 2H, CH_2), 4.76 (br d, 1H, NH), 4.16 (t, *J* = 8.7 Hz, 2H, CH_2N), 3.92 (m, 2H, CH_2-NH), 3.25 (t, *J* = 8.7 Hz, 2H, CH_2).

5,7-Dinitro-N-(3-(triethoxysilyl)propyl)indoline-1-carboxamide (DNI-APTS) (**13**) and *5-Bromo-7-nitro-N-(3-(triethoxysilyl)propyl)indoline-1-carboxamide* (BNI-APTS) (**14**). Silanization of the ureas **11** and **12** was carried out following same synthetic strategy as used in the synthesis of **3**; resulting in a 68% mixture with the reduced compound for product **13** (yield= 82%) and in a 65% mixture for product **14** (yield= 84%). ^{1}H NMR of **13** ($CDCl_3$): δ 8.61 (m, 1H, Ar-H), 8.18 (m, 1H, Ar-H), 4.90 (br d, 1H, NH), 4.25 (t, *J* = 8.6 Hz, 2H, CH_2N), 3.86 (q, *J* = 7.0 Hz, 6H, 3xCH_2), 3.35 (m, 4H, 2xCH_2), 1.79-1.51 (m, 2H, CH_2), 1.23 (t, *J* = 7.0 Hz, 9H, 3xCH_3), 0.75 – 0.65 (m, 2H, CH_2). ^{13}C NMR of **13** ($CDCl_3$): δ 155.3 (C), 144.0 (C), 142.9 (C), 142.4 (C), 137.2 (C), 123.4 (CH), 120.5 (CH), 59.2 (CH_2), 51.5 (CH_2), 43.0 (CH_2), 28.2 (CH_2), 23.2 (CH_2), 18.6 (CH_3), 11.2 (CH_2).^{1}H NMR of **14** ($CDCl_3$): δ 7.80 (m, 1H, Ar-H), 7.45 (m, 1H, Ar-H), 4.13 (t, *J* = 8.4 Hz, 2H, CH_2N), 3.74 (q, *J* = 7.0 Hz, 6H, 3xCH_2), 3.27 (m, 4H, 2xCH_2), 1.81-1.42 (m, 2H, CH_2), 1.24 (t, *J* = 7.0 Hz, 9H, 3xCH_3), 0.76 – 0.62 (m, 2H, CH_2). ^{13}C NMR of **14** ($CDCl_3$): δ 155.6 (C), 139.1 (C), 132.9 (C), 132.4 (C), 131.9 (C), 121.4

(CH), 118.5 (CH), 58.7 (CH_2), 51.3 (CH_2), 44.0 (CH_2), 28.0 (CH_2), 23.2 (CH_2), 18.5 (CH_3), 10.5 (CH_2).

α-Bromo-4-hydroxyacetophenone (**15**) was obtained as previously reported.[9]

2-(4-Hydroxyphenyl)-2-oxoethyl but-3-enoate (**16**) was prepared by esterification of **5** with 3-butenic acid in the presence of 1,8-diazabycyclo[5.4.0.]undec-7-ene (DBU). Butenoic acid (0.42 mL, 4.80 mmol) was added to a solution of α-bromo-acetophenone (1.05 g. 4.80 mmol) in 1,4-dioxane (100 mL), which was cooled to 0 °C. Then the addition of DBU (0.81 mL, 5.40 mmol) was followed dropwise for 10 min. The reaction mixture was allowed to reach room temperature and after that the mixture was stirred overnight. Thin layer chromatography (TLC) indicated that the reaction was complete. Mixture was filtered and solvent was removed in vacuo. The crude product was purified by silica gel column chromatography using as eluent dichloromethane:ethyl acetate (10:1). After collection of appropriate fractions for the product, the solvent was concentrated to give a white solid as the product **16** (630 mg, 60%). ^{1}H NMR ($CDCl_3$): δ 7.78 (dt, *J* = 8.8 Hz, *J* = 2.0 Hz, 2H, Ar-H), 7.13 (br d, 1H, OH), 6.88 (dt, *J* = 8.8 Hz, *J* = 2.0 Hz, 2H, Ar-H), 5.96 (m, 2H, CH), 5.32 (s, 2H, CH_2), 5.24 (m, 2H, CH_2), 3.30 (dt, *J* = 6.9 Hz, *J* = 1.4 Hz, 2H, CH_2).

2-(4-Hydroxyphenyl)-2-oxoethyl-4-(triethoxysilyl)butanoate (pHP-CPTS) (**17**). Product **16** (267 mg, 1.21 mmol) was dissolved in 4 mL of toluene and placed into a previously HMDS-passivated[3] dry, round-bottomed flask and heated under an argon atmosphere to about 70 °C. Then, triethoxysilane (2.23 mL, 12.1 mmol) was added to the solution. After the addition of isopropanolic H_2PtCl_6 solution (62 μL, 65 mM), the mixture was stirred for 5 hours at 70 °C and then allowed to cool down. Excess of triethoxysilane was removed in vacuum, and the residue was taken up in toluene and filtered through Celite500. The filtrate was concentrated under reduced pressure to give product **17** in a 61% mixture with the reduced compound (450 mg, 97%). ^{1}H NMR ($CDCl_3$): δ 7.86 (m, 2H, Ar-H), 7.07 (m, 2H, Ar-H), 6.90 (br d, 1H, OH), 5.29 (s, 2H, CH_2), 3.84 (m, 6H, 3xCH_2), 2.52 (m, 2H, CH_2), 1.94-1.72 (m, 2H, CH_2), 1.22 (m, 6H, 3xCH_2), 0.80 – 0.68 (m, 2H, CH_2). ^{13}C NMR ($CDCl_3$): δ 190.8 (C), 173.2 (C), 159.1 (CH), 130.1 (C), 119.6 (CH), 115.7 (CH), 65.6 (CH_2), 59.2 (CH_2), 36.5 (CH_2), 18.1 (CH_3), 13.1 (CH_2), 10.1 (CH_2).

Passivation of Glassware

Glass reaction vessels used for silanization were previously passivated either by leaving them in a desiccator overnight under vacuum and in the presence of HMDS or by wetting the glass surface with pure HMDS, washing with THF and drying in the oven. This step avoids undesired reactant consumption during surface silanization due to the condensation of the triethoxysilane groups with the free Si-OH groups at the surface of the glass reactors.

Substrate Cleaning

Quartz and silicon slides 1 x 2.5 cm^2 were cut and cleaned by soaking them in Piranha solution (H_2SO_4 (conc.)/H_2O_2 (30%) 5/1) overnight and subsequent rising with MilliQ-water and drying in vacuum at 90 ºC for 1 hour.

Surface Modification

A 1% w/v solution of the photosensitive silane in THF with 5-20 µl of 1 N NaOH (aq.) was stirred between 30 min and 1 hour. The solution was filtrated through a 0.2 µm pore-size PTFE filter in the reaction vessel, and clean substrates were immersed in it. After reaction, the substrates were rinsed with THF and Milli-Q water and baked for 1 h at 90 ºC in a vacuum oven and stored in the dark. Experiments with increasing catalyst concentration and deposition times were performed to obtain layers with a maximum density of functional groups (as revealed by UV spectroscopy). Before further application, all substrates were sonicated in THF for 3 min, washed with Milli-Q water and dried under N_2 stream.

Fig A.: Spectra of the irradiation sources: (a) LUMOS 43 (Atlas Photonics Inc.), (b) Polychrome V system (TILL Photonics GmbH, Gräfelting, Germany)

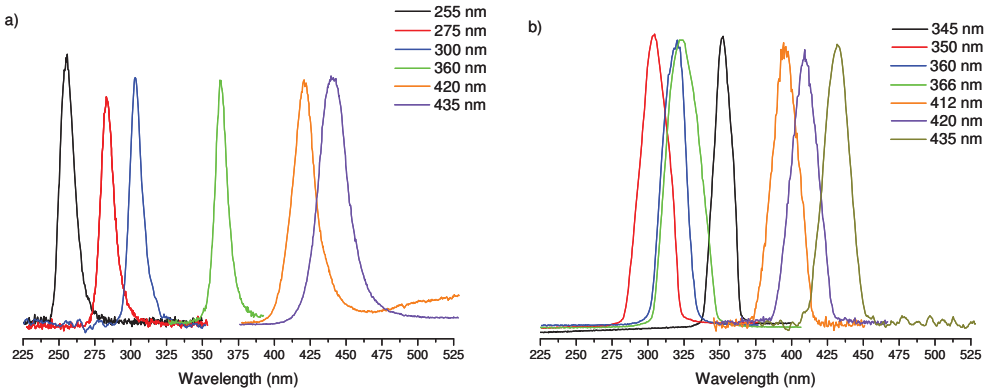


Figure B. Normalized UV-Vis spectra of caged surfaces with different chromophores before and after full exposure at 255 nm.

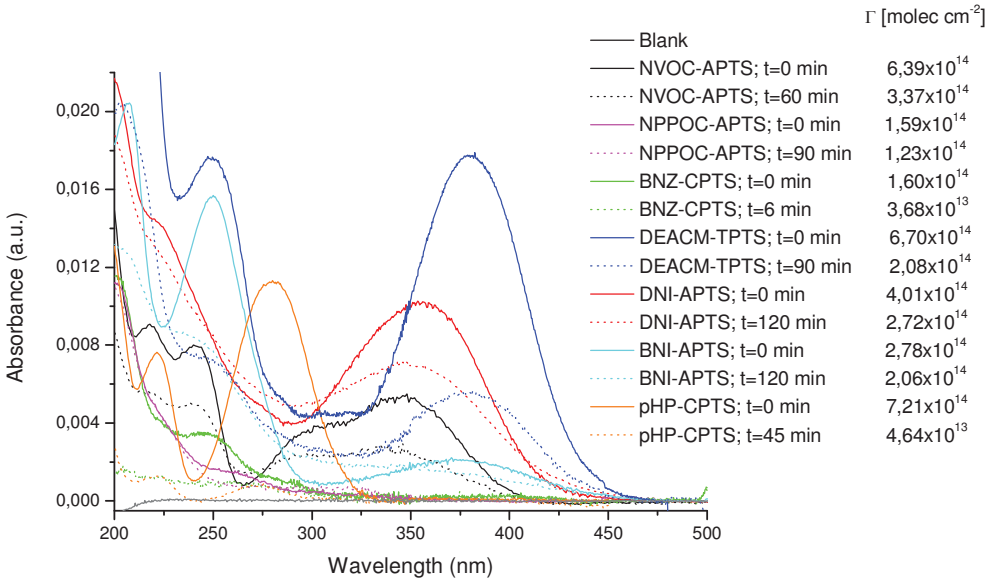


Figure C. Conversion (%) of the photocleavage of DNI-APTS (**13**) at the surface upon irradiation at 358 nm in absence and presence of a water containing solvent.

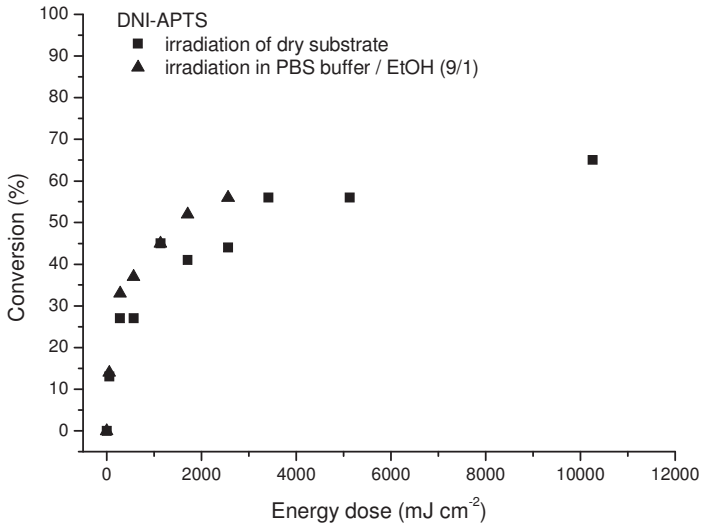


Table A. Calculated values of the product $\varepsilon_\lambda \phi$ for the caged organosilanes obtained by fitting the experimental conversion data following reference.[10]

Cages	$\lambda_{irradiation}$ (nm)	a_{dir} [(a)] ($J^{-1}cm^2$)	$\varepsilon_\lambda \phi$ [(b)] ($M^{-1}cm^{-1}$)	ε_λ [(c)] ($M^{-1}cm^{-1}$)
NVOC (**1**)	255	1.52	310	3203
	275	2.67	504	1295
	300	2.14	370	2245
	345	2.52	380	2555
	360	0.67	97	2241
	412	0.34	43	69
	420	0.005	0.61	30
	435	0.002	0.30	14
NPPOC (**3**)	255	5.73	1167	3779
BNZ (**5**)	255	40.44	8239	5949
	275	21.18	4001	2829
	300	6.96	1206	1185
	350	1.77	263	72
	360	0.40	65	25
DEACM (**8**)	255	2.54	517	4603
	275	0.72	136	1098
	300	0.40	69	1123
	345	0.90	135	3494
	360	0.52	75	6194
	412	1.00	126	1811
	420	0.02	2.2	783
	435	0.008	0.91	105

DNI (**13**)	255	2.89	589	3613
	275	1.17	221	1341
	300	0.98	170	2725
	358	0.88	128	7478
	360	0.58	84	8147
	412	1.88	237	372
	420	0.01	1.09	365
	435	0.002	0.27	98
BNI (**14**)	255	1.89	385	11868
	366	0.63	89	2231
	360	0.33	47	2148
pHP (**17**)	255	2.65	540	4225
	275	7.30	1379	5487
	300	8.51	1473	305

(a) Values extracted from the fits to the plots conversion *versus* energy dose for the different protecting groups and wavelengths with the equation $y = 1-\exp(-a_{dir}\, x)$.

(b) Data calculated according to the equation $a_{dir}=1/f_{EJ}\,[\ln(10)\,\varepsilon_\lambda\,\phi]$, where f_{EJ} is the conversion factor from Einstein to Joule, as previously reported.[10]

(c) Absorption coefficients of the chromophores IN SOLUTION at the corresponding wavelength

Table B. Reported photolysis quantum yields for different cages.

Caging group	Caged functionality	ϕ	λ_{max}[nm] (ε [M^{-1} cm^{-1}])
NVOC (carbamate)	Amine	≈0.023[11]	350 (2499)
NPPOC (carbonate)	Carboxylic acid	≈0.4[12]	355 (331)
BNZ (carboxyl)	Carboxylic acid	≈0.64[13]	247 (6388)
DEACM (phosphate ester)	Phosphate	≈0.20[14]	385 (7805)
DNI (amide)	Carboxylic acid	≈0.50[15]	358 (7478)
BNI (amide)	Carboxylic acid	<0.01[15]	366 (2231)
pHP (phosphate ester)	Phosphate	≈0.77[16]	280 (4733)

REFERENCES

(1) Stegmaier, P.; Alonso, J. M.; del Campo, A. *Langmuir* **2008**, *24*, 11872.
(2) Bhushan, K. R.; DeLisi, C.; Laursen, R. A. *Tetrahedron Letters* **2003**, *44*, 8585.
(3) del Campo, A.; Boos, D.; Spiess, H. W.; Jonas, U. *Angew Chem Int Edit* **2005**, *44*, 4707.
(4) Blanc, A.; Bochet, C. G. *J. Org. Chem.* **2002**, *67*, 5567.
(5) Ito, K.; Maruyama, J. *Chemical & Pharmaceutical Bulletin* **1983**, *31*, 3014.
(6) Schonleber, R. O.; Bendig, J.; Hagen, V.; Giese, B. *Bioorganic & Medicinal Chemistry* **2002**, *10*, 97.
(7) Hassner, A.; Yagudayev, D.; Pradhan, T. K.; Nudelman, A.; Amit, B. *Synlett* **2007**, 2405.
(8) Helgen, C.; Bochet, C. G. *J. Org. Chem.* **2003**, *68*, 2483.
(9) Durden, D. A.; Juorio, A. V.; Davis, B. A. *Analytical Chemistry* **1980**, *52*, 1815.
(10) Woll, D.; Walbert, S.; Stengele, K. P.; Albert, T. J.; Richmond, T.; Norton, J.; Singer, M.; Green, R. D.; Pfleiderer, W.; Steiner, U. E. *Helv Chim Acta* **2004**, *87*, 28.
(11) Goeldner, M.; Givens, R. *Dynamic Studies in Biology: Phototriggers, Photoswitches and Caged Biomolecules* **2005**, *Wiley, VCH*, Weinheim.
(12) Walbert, S.; Pfleiderer, W.; Steiner, U. E. *Helv. Chim. Acta* **2001**, *84*, 1601.
(13) Sheehan, J. C.; Wilson, R. M.; Oxford, A. W. *J. Am. Chem. Soc.* **1971**, *93*, 7222.
(14) Eckardt, T.; Hagen, V.; Schade, B.; Schmidt, R.; Schweitzer, C.; Bendig, J. *J. Org. Chem.* **2002**, *67*, 703.
(15) Adams, S. R.; Kao, J. P. Y.; Tsien, R. Y. *J. Am. Chem. Soc.* **1989**, *111*, 7957.
(16) (a) Givens, R. S.; Jung, A.; Park, C. H.; Weber, J.; Bartlett, W. *J. Am. Chem. Soc.* **1997**, *119*, 8369(b) Park, C. H.; Givens, R. S. *J. Am. Chem. Soc.* **1997**, *119*, 2453.