

## Supplementary Information for:

### Bifunctional Catechol Based Linkers for Modification of TiO<sub>2</sub> Surfaces

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#### Preparation and Modification to TiO<sub>2</sub> Nanoparticles

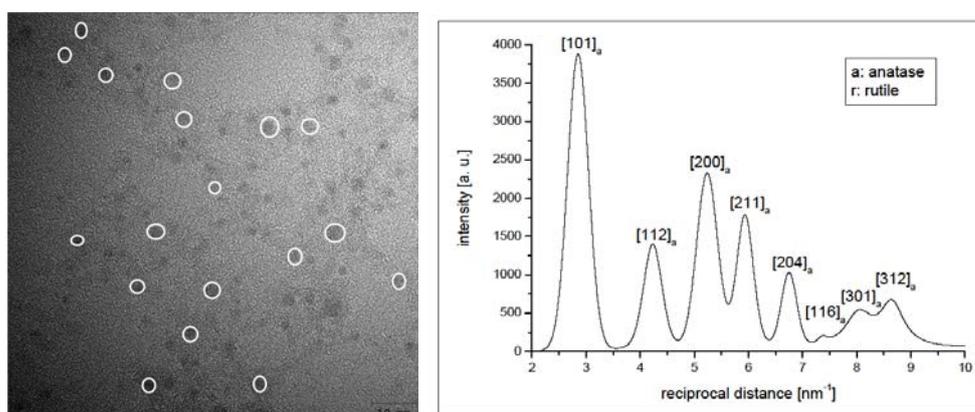


Figure S1. a) TEM image of used TiO<sub>2</sub> NPs and b) radial profile of selected area electron diffraction ring pattern.

Figure S1a shows the transmission electron microscope (TEM) image of the TiO<sub>2</sub> nanoparticles in water used for the modifications and S1b shows the radial profile of a selected area electron diffraction ring pattern (SAED).

#### Purification of peptide - dopamine derivative 3

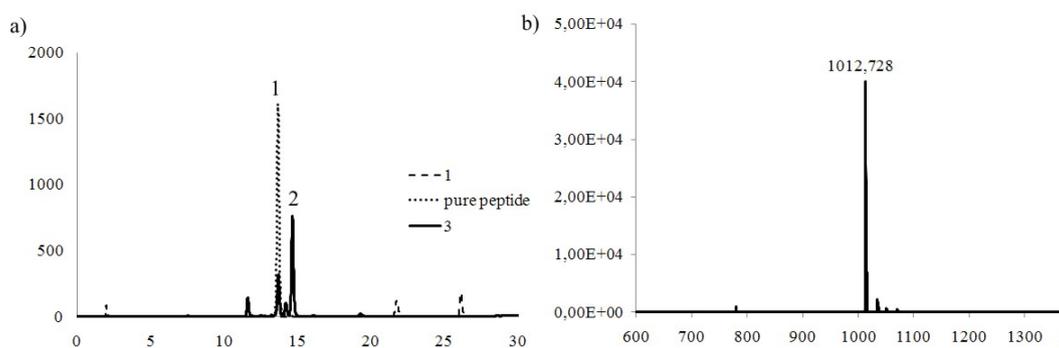


Figure S2. a) HPLC chromatogram of peptide-dopamine maleimide **1** reaction mixture: Peak 1 is pure peptide and peak 2 is the synthesised linker peptide compound **3** and b) Maldi chromatogram of peak 2.

Figure S2 displays the HPLC chromatogram of the peptide-dopamine maleimide reaction mixture. The expected mass of 1012.2 gmol<sup>-1</sup> is shown in the Maldi chromatogram of S2b.

### TEM image of the peptide TiO<sub>2</sub> NP-3 cut out of gel

In Figure S3, EDXS and TEM measurements cut of the gel were shown, which confirms that lane 3 cut out if the gel were the modified TiO<sub>2</sub> NPs.

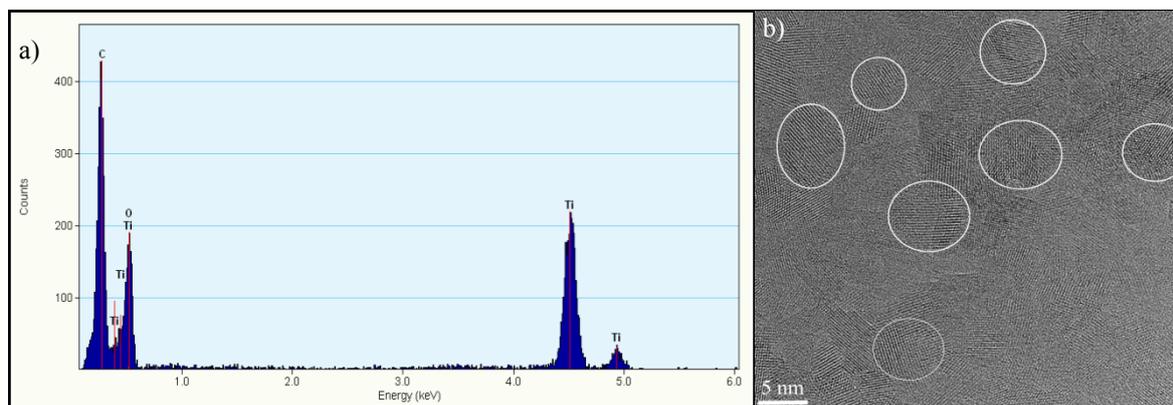
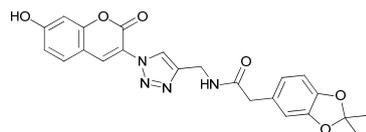


Figure S3. a) EDXS diagram showing presence of TiO<sub>2</sub> NPs and b) TEM image of the modified TiO<sub>2</sub> NP with peptide linker compound (NP-3).

### Cu catalysed Huisgen cycloaddition between 3-azidocoumarin and dopamine alkyne **2** in solution

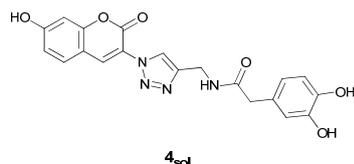
#### 2-(2,2-Dimethylbenzo[d][1,3]dioxol-5-yl)-N-((1-(7-hydroxy-2-oxo-2H-chromen-3-yl)-1H-1,2,3-triazol-4-yl)methyl)acetamide



3-Azidocoumarin (50 mg, 0.246 mmol) and **2** (60 mg, 0.246 mmol) were dissolved in water/ethanol (v/v = 1:1, 6 mL). 1 M freshly prepared solution of sodium ascorbate (49  $\mu$ L, 0.0492 mmol) was added followed by the addition of copper (II) sulfate pentahydrate 7.5 % in water (41  $\mu$ L, 0.0123 mmol). The reaction mixture was stirred overnight in the dark at room temperature. Ethanol was removed and the residue was diluted with water (5 mL), cooled in ice, and the precipitate was collected by filtration. After washing the precipitate with cold water (10 mL), it was dried under vacuum to afford 53 mg of pure 2-(2,2-dimethylbenzo[d][1,3]dioxol-5-yl)-N-((1-(7-hydroxy-2-oxo-2H-chromen-3-yl)-1H-1,2,3-triazol-4-yl)methyl)acetamide as brown oil.

Yield: 47%. <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>, δ): 10.9 (br, 1H, NH), 8.58 (s, 1H, Triazole H), 8.36 (s, 1H, Olefine H), 7.74 (d, *J* = 8.5 Hz; 1H, Ar H), 6.64-6.92 (m, 5H, Ar H), 4.38 (s, 2H, CH<sub>2</sub>), 3.34 (s, 2H, CH<sub>2</sub>), 1.60 (s, 6H, C(CH<sub>3</sub>)<sub>2</sub>); FAB-MS (*m/z* (%)): 511 (45), 449 (100) [M]<sup>+</sup>, 293 (25), 214 (32), 163 (73), 136 (80), 123 (32), 107 (30), 91 (23).

### Deprotection of 2-(2,2-Dimethylbenzo[d][1,3]dioxol-5-yl)-N-((1-(7-hydroxy-2-oxo-2H-chromen-3-yl)-1H-1,2,3-triazol-4-yl)methyl)acetamide **4<sub>sol</sub>**

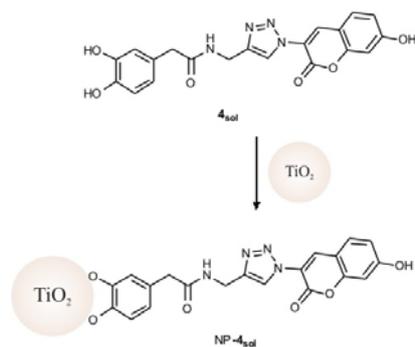


2 mL degassed chloroform, 0.596 mL TFA and 0.0238 mL water were added to the solution of acetamide (50.0 mg, 0.204 mmol) under argon and the mixture was stirred for 3 h at room temperature. The solvents were evaporated under reduced pressure to give title product as brown oil.

Yield: quantitative. <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>, δ): 8.35 (t, *J* = 5 Hz, 1H; NH), 6.61-6.66 (m, 2H, Ar H), 6.49 (dd, *J* = 2 Hz, 1H; Ar H), 3.82-3.84 (m, 2H, NHCH<sub>2</sub>), 3.22 (s, 2H, ArCH<sub>2</sub>), 3.08 (t, *J* = 3 Hz, 1H, CH); <sup>13</sup>C NMR (400 MHz, DMSO-d<sub>6</sub>, δ): 170.57, 162.26, 156.17, 154.48, 144.79, 143.70, 135.91, 130.82, 126.77, 119.60, 119.26, 116.35, 115.18, 114.14, 110.26, 102.03, 41.50, 40.33; FAB (*m/z* (%)): 409 (35) [M]<sup>+</sup>, 408 (18) [M<sup>+</sup> - H]; HRMS (FAB) calcd for C<sub>20</sub>H<sub>17</sub>N<sub>4</sub>O<sub>6</sub> [M + H]<sup>+</sup>: 409.1070; found: 409.1150; FT-IR (ATR): 3066, 1605, 1515, 798, 633 cm<sup>-1</sup>.

### Modification of the NP with coumarin-dopamine

0.50 mg TiO<sub>2</sub> NP dissolved in 200 μL H<sub>2</sub>O and coumarin dopamine **4<sub>sol</sub>** (30 mg, 0.074 mmol) were mixed over night (Scheme S1). After five seconds, a charge transfer from orange to brown was visible. Before performing UV-Vis measurements, the modified NPs were purified by centrifugation (three times) and the residue was dissolved in DMSO (Figure S4).



Scheme S1. Modification of TiO<sub>2</sub> with **4<sub>sol</sub>**.

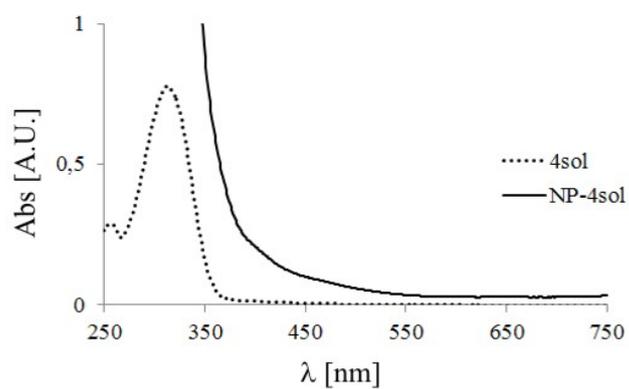


Figure S4. UV-Vis spectrum of the **4** and NP-**4<sub>sol</sub>**.

### DLS Data for NP-4 conjugates

Table S1. DLS measurements of click reaction on TiO<sub>2</sub> NPs.

Sample	Radius [nm]
NP-2	20.0 ± 3.18
NP-4	102 ± 1.92