Electronic Supplementary Information (ESI) for

Near-infrared (NIR) surface-enhanced Raman spectroscopy (SERS) study of novel functional phenothiazines for potential use in dye sensitized solar cells (DSSC)

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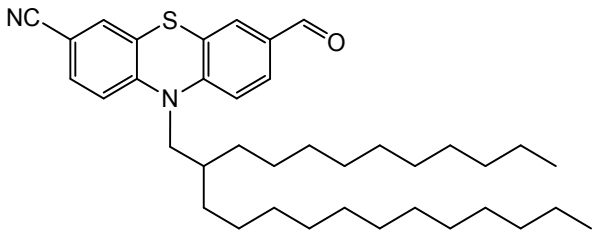
Experimental part

1) Syntheses

10-(2-Decyltetradecyl)-7-formyl-10*H*-phenothiazin-3-carbonitrile (A)[1]



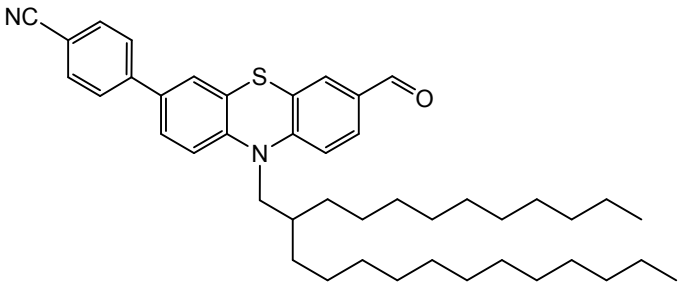
7
$C_{38}H_{56}N_2OS$
[588.93]

7-Bromo-10-(2-decyltetradecyl)-10*H*-phenothiazin-3-yl carbaldehyde[1] (3.01 g, 4.68 mmol) was dissolved in *N*-methylpyrrolidone (12 mL) in a Schlenk tube under nitrogen. Then, sodium carbonate (496 mg, 4.68 mmol), freshly dried potassium hexacyanoferrate(II) (431 mg, 1.17 mmol), palladium(II)acetate (10.55 mg, 47.00 µmol), and 1,1'-bis(diphenylphosphano)ferrocen (51.9 mg, 94.0 µmol) were successively added to the reaction mixture under nitrogen. The reaction mixture was heated to 125 °C (oil bath) for 20 h. After cooling to room temp a saturated aqueous solution of sodium sulfite was added to the reaction mixture. After extraction of the aqueous layer with dichloromethane (3 x 50 mL) the combined organic layer were dried with anhydrous magnesium sulfate and the solvents were removed under reduced pressure. The residue was purified by flash chromatography on silica gel (*n*-hexanes/ethyl acetate, R_f = 0.1-0.2) to furnish the product as a yellow oil (2.04 g, 74%).

^{1}H NMR (300 MHz, acetone-d_6) δ= 0.79 (t, *J* = 6.7 Hz, 6 H), 1.25 (m, 40 H), 1.87 (m, 1 H), 3.89 (d, *J* = 7.3 Hz, 2 H), 7.13 (d, *J* = 8.4 Hz, 1 H), 7.16 (d, *J* = 8.4 Hz, 1 H), 7.41 (d, *J* = 1.9 Hz, 1 H), 7.48 (dd, *J* = 8.5, 1.9 Hz, 1 H), 7.54 (d, *J* = 1.9 Hz, 1 H), 7.66 (dd, *J* = 8.5, 2.0 Hz, 1 H), 9.75 (s, 1 H). ^{13}C NMR (75 MHz, acetone-d_6) δ = 14.4 (CH_3)*, 23.4 (CH_2)*, 26.7 (CH_2)*, 30.1 (CH_2)*, 30.3 (CH_2)*, 30.35 (CH_2), 30.39 (CH_2)*, 30.42 (CH_2), 30.6 (CH_2)*, 31.85 (CH_2)*, 32.66 (CH_2)*, 35.4 (CH), 52.6 (CH_2), 107.4 (C_{quat}), 118.0 (CH), 118.3 (CH), 118.9 (C_{quat}), 125.74 (C_{quat}), 126.73 (C_{quat}), 129.1 (CH), 130.9 (CH), 131.4 (CH), 133.0 (CH), 133.5 (C_{quat}), 149.4 (C_{quat}), 150.6 (C_{quat}), 190.5 (CHO). *broadened signal by superposition. MS

(MALDI-TOF) calcd. for $C_{38}H_{56}N_2OS$ (*m/z*): 588.4; Found: 588.4 ([M^+]). IR $\tilde{\nu}$[cm^{-1}] = 2922 (s), 2850 (m), 2224 (w), 1690 (m), 1578 (m), 1462 (s), 1339 (s), 1196 (m), 885 (w), 817 (m), 721 (w). UV/VIS (CH_2Cl_2) λ_{max} (ε) [nm] = 258 (15000), 282 (46000), 384 (10000).

4-(10-(2-Decyltetradecyl)-7-formyl-10*H*-phenothiazin-3-yl)benzonitrile (B)



8
$C_{44}H_{60}N_2OS$
[665.03]

7-Bromo-10-(2-decyltetradecyl)-10*H*-phenothiazin-3-yl carbaldehyde[1] (2.70 g, 4.20 mmol) were dissolved in dimethoxymethane (30 mL) and distilled water (15 mL) in a Schlenk tube. The solution was deaerated with nitrogen for 1 h. Then pinacolyl 4-cyanophenyl boronate (1.16 g, 5.04 mmol), potassium carbonate (4.18 g, 30.2 mmol), and $Pd(PPh_3)_4$ (130 mg, 113 µmol) were added and the mixture was stirred at 100 °C under reflux for 20 h. After cooling to room temp brine was added and the solution was extracted with diethylether. The combined ethereal phases were dried with anhydrous magnesium sulfate and the solvents were removed under vacuo to give 2.46 g (88 %) of a yellow waxy product, Mp 50-54 °C.

^{1}H NMR (300 MHz, acetone-d_6) δ= 0.73 (t, *J* = 6.8 Hz, 6 H), 1.08-1.33 (m, 40 H), 1.90 (m, 1 H), 3.86 (d, *J* = 7.2 Hz, 2 H), 7.08 (d, *J* = 8.4 Hz, 1 H), 7.09 (d, *J* = 8.4 Hz, 1 H), 7.41 (d, *J* = 2.2 Hz, 1 H), 7.49 (dd, *J* = 8.5, 2.2 Hz, 1 H), 7.51 (d, *J* = 1.9 Hz, 1 H), 7.63 (dd, *J* = 8.4, 1.9 Hz, 1 H), 7.70 (m, 4 H), 9.72 (s, CHO). ^{13}C NMR (75 MHz, acetone-d_6) δ= 14.4 (CH_3)*, 23.4 (CH_2)*, 26.7 (CH_2), 26.8 (CH_2), 30.30 (CH_2)*, 30.31 (CH_2), 30.33 (CH_2), 30.36 (CH_2), 30.39 (CH_2)*, 30.43 (CH_2), 30.58 (CH_2), 30.60 (CH_2), 31.9 (CH_2)*, 32.7 (CH_2)*, 35.4 (CH), 52.5 (CH_2), 111.5 (C_{quat}), 117.2 (CH), 118.4 (CH), 119.4 (C_{quat}), 126.2 (C_{quat}), 126.4 (C_{quat}), 126.7 (CH), 127.4 (CH), 127.9 (2 CH), 128.9 (CH), 130.8 (CH), 132.8 (C_{quat}), 133.5 (CH), 135.0 (C_{quat}), 144.6 (C_{quat}), 145.6 (C_{quat}), 151.6 (C_{quat}), 190.5 (CHO). *broadened signal by superposition. MALDI-TOF MS calcd. for $C_{44}H_{60}N_2OS$ (*m/z*): 664.4; Found: 664.4 ([M^+]). Anal. calcd. for $C_{44}H_{60}N_2OS$ (665.0): C 79.47; H 9.09; N 4.21; Found: C 79.62; H 8.86; N 4.26. IR (neat) $\tilde{\nu}$ [cm^{-1}] = 2920 (s), 2851(m), 2224 (w), 1686 (m), 1603 (m), 1578 (m), 1466 (s), 1350 (w), 1281 (w), 1250 (w), 1196 (s), 920 (w), 820 (m), 812 (m), 719 (w). UV/VIS (CH_2Cl_2) λ_{max} (ε) [nm] = 293 (40000), 394 (12000).

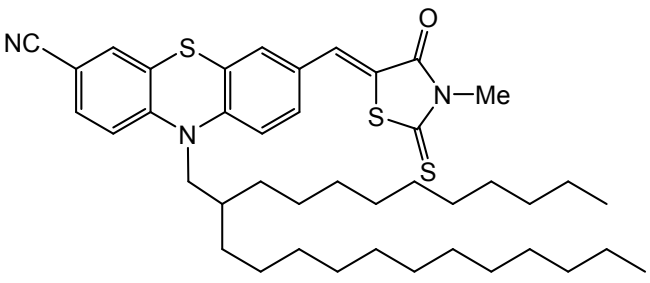
General Procedure for the synthesis of the phenothiazine chromophores 1-6

The corresponding aldehyde **A** or **B**, ammonium acetate and the methylene active compound **10**-**12** were placed in a 10 mL Schlenk tube and dichloromethane (1 mL) and acetic acid were added (for experimental details, see Table S1). The reaction mixture was then heated to reflux (oil bath temperature of 100 °C) for the times indicated. After cooling to room temp dichloromethane (10 mL) was added and the organic layer was extracted several times with brine until the pH of the washing solution was higher than 5. The combined aqueous layers were extracted once with dichloromethane (10 mL). The combined organic phases were dried (anhydrous magnesium sulfate), the solvents were removed in vacuo and the crude product was adsorbed on celite® and purified by flash chromatography on silica gel (*n*-hexane/acetone) (compounds **1**-**4**). Compounds **5** and **6** were purified by adsorptive filtration on silica with dichloromethane/acetic acid after removal of all soluble organic compounds with dichloromethane. All compounds were dried under high vacuum for 18 h.

Table S1: Experimental details of the syntheses of compounds **1-6**.

aldehyde [mg] (mmol)	**methylene active compound** [mg] (mmol)	**ammonium acetate** [mg] (mmol)	**conditions** (*T*,*t*)	**yield** [mg] (%)
300 (0.510) of **A**	82.6 (0.560) of 3-methylrhodanine	39 (0.51)	100 °C, 7 h	287 (78) of **1**
310 (0.472) of **B**	77.3 (0.519) of 3-methylrhodanine	98 (0.47)	95 °C, 3 h 80 °C, 16 h	319 (85) of **2**
205 (0.349) of **A**	66.4 (0.454) of 1,3-indandione	33 (0.42)	100 °C, 7 h	80 (32) of **3**
214 (0.320) of **B**	73.6 (0.500) of 1,3-indandione	41 (0.53)	100 °C, 4 h	71 (28) of **4**
226 (0.380) of **A**	83.0 (0.98) of cyano acetic acid	70 (0.91)	100 °C, 4 h	195 (78) of **5**
228 (0.340) of **B**	54.7 (0.640) of cyano acetic acid	45 (0.58)	RT, 14 h 100 °C, 3 h	190 (76) of **6**

(*Z*)-10-(2-decyltetradecyl)-7-((3-methyl-4-oxo-2-thioxothiazolidin-5-ylidene)methyl)-10H-phenothiazine-3-carbonitrile (1)



1

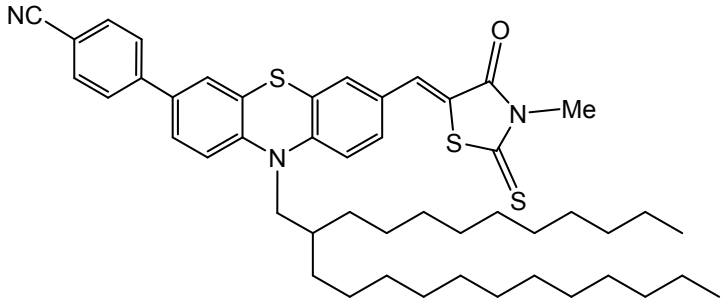
$C_{42}H_{59}N_3OS_3$

[718.13]

According to the GP and after flash chromatography (*n*-hexane/acetone) compound **1** (287 mg, 78%) was obtained as a red amorphous solid, Mp 80-81 °C.

^{1}H NMR (300 MHz, acetone-d_6) δ= 0.74 (t, J = 6.7 Hz, 6 H), 1.09 – 1.35 (m, 40 H), 1.88 (m, 1 H), 2.67 (s, J = 9.7 Hz, 1 H), 3.34 (s, 3 H), 3.86 (d, J = 7.2 Hz, 2 H), 7.10 (d, J = 8.6 Hz, 1 H), 7.12 (d, J = 8.6 Hz, 1 H), 7.24 (d, J = 2.1 Hz, 1 H), 7.36 (dd, J = 8.6, 2.1 Hz, 1 H), 7.40 (d, J = 1.9 Hz, 1 H), 7.48 (dd, J = 8.5, 2.0 Hz, 1 H), 7.51 (s, 1H). ^{13}C NMR (75 MHz, acetone-d_6) δ= 14.4 (CH_3)*, 23.4 (CH_2)*, 26.6 (CH_2)*, 26.7 (CH_2)*, 30.1 (CH_2)*, 30.31 (CH_2), 30.34 (CH_2), 30.38 (CH_2), 30.42 (CH_2)*, 30.5 (CH_2), 30.55 (CH_2), 30.58 (CH_2), 31.6 (CH_3), 31.8 (CH_2)*, 32.7 (CH_2), 35.4 (CH), 52.4 (CH_2), 107.2 (C_{quat}), 118.1 (C_{quat}), 118.5 (CH), 118.9 (CN), 122.2 (C_{quat}), 126.1 (C_{quat}), 126.4 (C_{quat}), 129.8 (C_{quat}), 130.4 (CH), 131.4 (CH), 131.6 (CH), 132.1 (CH), 133.0 (CH), 147.3 (CH), 149.5 (C_{quat}), 168.0 (C_{quat}), 194.1 (C_{quat}). *broadened signal by superposition. MS (MALDI-TOF) calcd. for $C_{42}H_{59}N_3OS_3$ (*m/z*): 717.4; Found: 717.5 ([M$^+$]). IR $\tilde{\nu}$ [cm^{-1}] = 2920 (m), 2851 (m), 2228 (w), 1711 (m), 1570 (m), 1464 (s), 1402 (m), 1344 (m), 1285 (s), 1254 (m), 1124 (m), 1101 (s), 912 (w), 820 (m), 806 (m). UV/VIS (CH_2Cl_2) λ_{max} (ε) [nm] = 264 (20000), 295 (28000), 359 (20000), 456 (29000).

(*Z*)-4-(10-(2-decyltetradecyl)-7-((3-methyl-4-oxo-2-thioxothiazolidin-5-ylidene)methyl)-10H-phenothiazin-3-yl)benzonitrile (2)

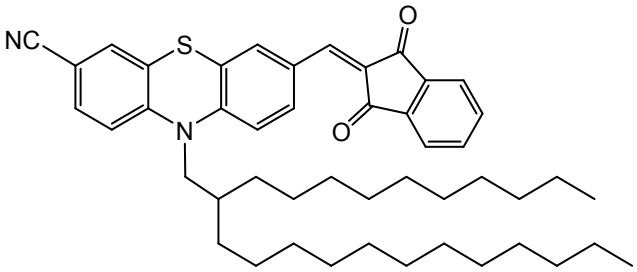


2
$C_{48}H_{63}N_3OS_3$
[794.23]

According to the GP and after flash chromatography (*n*-hexane/acetone) compound **2** (319 mg, 85%) was obtained as a violet amorphous solid, Mp 121-122 °C.

^{1}H NMR (300 MHz, CD_2Cl_2) δ= 0.79 (t, J = 6.7 Hz, 6 H), 1.09 – 1.35 (m, 40 H), 1.91 (m, 1 H), 3.40 (s, 3 H), 3.74 (d, J = 7.1 Hz, 2 H), 6.90 (d, J = 8.3 Hz, 1 H), 6.91 (d, J = 8.3 Hz, 1 H), 7.20 (d, J = 2.1 Hz, 1 H), 7.27 (dd, J = 8.6, 2.1 Hz, 1 H), 7.33 (d, J = 2.1 Hz, 1 H), 7.39 (dd, J = 8.4, 2.2 Hz, 1 H), 7.53 (s, 1 H), 7.60 (m, 4 H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ= 14.3 (CH_3)*, 23.1 (CH_2)*, 26.5 (CH_2)*, 29.75 (CH_2)*, 29.81 (CH_2)*, 29.99 (CH_2)*, 30.01 (CH_2), 30.05 (CH_2)*, 30.09 (CH_2), 30.3 (CH_2)*, 31.5 (CH_3), 31.7 (CH_2), 32.3 (CH_2)*, 35.1 (CH), 52.2 (CH_2), 111.0 (C_{quat}), 116.8 (CH), 117.3 (CH), 119.2 (C_{quat}), 120.9 (C_{quat}), 126.0 (C_{quat}), 126.35 (CH), 126.43 (C_{quat}), 126.8 (CH), 127.3 (C_{quat}), 128.3 (C_{quat}), 129.7 (CH), 131.2 (CH), 132.3 (CH), 133.0 (CH), 134.5 (CH), 144.3 (C_{quat}), 145.2 (C_{quat}), 148.1 (C_{quat}), 168.1 (C_{quat}), 193.7 (C_{quat}). *broadened signal by superposition. MS (MALDI-TOF) calcd. for $C_{48}H_{63}N_3OS_3$ (*m/z*): 793.4; Found: 793.4 ([M$^+$]). Anal. calcd. for $C_{48}H_{63}N_3OS_3$ [794.2]: C 72.59, H 8.00, N 5.29; Found: C 72.38, H 7.78, N 5.27. IR $\tilde{\nu}$ [cm^{-1}] = 2920 (m), 2851 (w), 2226 (w), 1705 (m), 1566 (m), 1475 (m), 1398 (m), 1356 (w), 1279 (s), 1223 (m), 1126 (m), 1099 (s), 835 (m), 795 (m), 713 (w). UV/VIS (CH_2Cl_2) λ_{max} (ε) [nm] = 280 (27000), 307 (28000), 358 (26000), 473 (28000).

10-(2-Decyltetradecyl)-7-((1,3-dioxo-1,3-dihydro-2H-inden-2-ylidene)methyl)-10H-phenothiazine-3-carbonitrile (3)

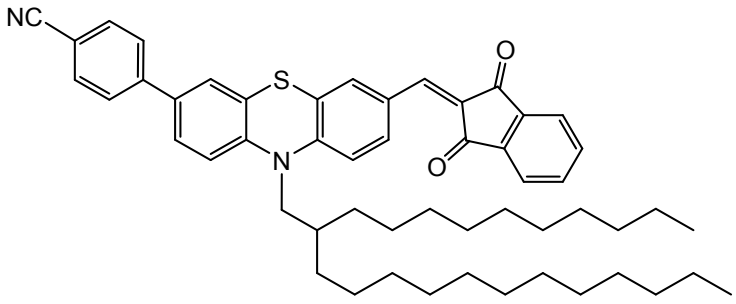


3
$C_{47}H_{60}N_2O_2S$
[717.06]

According to the GP and after flash chromatography (*n*-hexane/acetone) compound **3** (80 mg, 32%) was obtained as a red amorphous solid, Mp 91-94 °C.

^{1}H NMR (300 MHz, acetone-d_6) δ= 0.71 (t, *J* = 6,7 Hz, 6 H), 1.08 – 1.29 (m, 40 H), 1.88 (m, 1 H), 3.88 (d, *J* = 7.2 Hz, 2 H), 7.09 (d, *J* = 8.7 Hz, 1 H), 7.12 (d, *J* = 8.7 Hz, 1 H), 7.41 (d, *J* = 1.9 Hz, 1 H), 7.48 (dd, *J* = 8.5, 1.9 Hz, 1 H), 7.55 (s, 1 H), 7.81 (m, 4 H), 8.24 (dd, *J* = 8.8, 2.0 Hz, 1 H), 8.48 (d, *J* = 2.0 Hz, 1H). ^{13}C NMR (75 MHz, acetone-d_6) δ= 14.4 (CH_3)*, 23.4 (CH_2)*, 26.6 (CH_2)*, 26.7 (CH_2)*, 30.1 (CH_2)*, 30.31 (CH_2), 30.34 (CH_2), 30.38 (CH_2), 30.41 (CH_2)*, 30.55 (CH_2), 30.58 (CH_2), 31.77 (CH_2), 31.79 (CH_2), 32.7 (CH_2)*, 35.5 (CH), 52.5 (CH_2), 107.5 (C_{quat}), 117.7 (CH), 118.3 (CH), 118.9 (C_{quat}), 123.6 (CH), 123.8 (CH), 124.8 (C_{quat}), 126.7 (C_{quat}), 128.5 (C_{quat}), 130.0 (C_{quat}), 131.4 (CH), 132.9 (CH), 133.6 (CH), 136.2 (CH), 136.3 (CH), 136.5 (CH), 140.9 (C_{quat}), 143.3 (C_{quat}), 145.0 (CH), 149.0 (C_{quat}), 149.7 (C_{quat}), 189.8 C_{quat}), 190.2 (C_{quat}). *broadened signal by superposition. MS (MALDI-TOF) calcd. for $C_{47}H_{60}N_2O_2S$ (*m/z*): 716.4; Found: 716.5 ([M^+]). Anal. calcd. for $C_{47}H_{60}N_2O_2S$ [717.1]: C 78.73, H 8.43, N 3.91; Found: C 78.46; H 8.10, N 3.72. IR $\tilde{\nu}$ [cm^{-1}] = 2920 (m), 2851 (m), 2220 (m), 1722 (w), 1676 (m), 1557 (m), 1458 (s), 1412 (m), 1329 (m), 1252 (w), 1200 (s), 1155 (m), 1080 (m), 995 (m), 908 (w), 929 (w), 743 (m). UV/VIS (CH_2Cl_2) λ_{max} (ε) [nm] = 269 (38000), 303 (23000), 347 (19000), 478 (24000).

4-(10-(2-Decyltetradecyl)-7-((1,3-dioxo-1,3-dihydro-2H-inden-2-ylidene)methyl)-10H-phenothiazin-3-yl)benzonitrile (4)



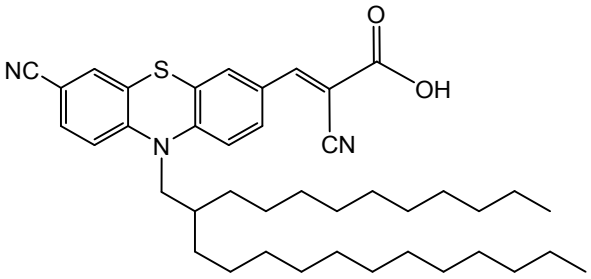
4
$C_{53}H_{64}N_2O_2S$
[793.15]

According to the GP and after flash chromatography (*n*-hexane/acetone) compound **4** (71 mg, 28%) was obtained as violet oil.

^{1}H NMR (600 MHz, acetone-d_6) δ= 0.69 (t, *J* = 6.7 Hz, 6 H), 0.95 – 1.29 (m, 40 H), 1.88 (m, 1 H), 3.82 (d, *J* = 7.2 Hz, 2 H), 6.99 (d, *J* = 8.7 Hz, 1 H), 7.04 (d, *J* = 8.6 Hz, 1 H), 7.36 (d, *J* = 2.2 Hz, 1 H), 7.47 (dd, *J* = 8.5, 2.2 Hz, 1 H), 7.53 (s, 1

H), 7.64 – 7.75 (m, 4 H), 7.75 – 7.84 (m, 4 H), 8.21 (dd, *J* = 8.8, 2.0 Hz, 1 H), 8.47 (d, *J* = 2.0 Hz, 1 H). ^{13}C NMR (150 MHz, acetone-d_6) δ= 14.4 (CH_3)*, 23.4 (CH_2)*, 26.65 (CH_2), 26.73 (CH_2), 30.10 (CH_2), 30.14 (CH_2)*, 30.3 (CH_2), 30.38 (CH_2), 30.42 (CH_2)*, 30.5 (CH_2)*, 30.56 (CH_2), 30.61 (CH_2), 31.8 (CH_2), 31.9 (CH_2), 32.7 (CH_2)*, 35.5 (CH), 66.1 (CH_2), 111.5 (C_{quat}), 117.0 (CH), 118.4 (CH), 119.4 (C_{quat}), 123.5 (CH), 123.7 (CH), 125.2 (C_{quat}), 126.3 (C_{quat}), 126.7 (CH), 127.3 (CH), 127.8 (C_{quat}), 127.9 (CH), 129.2 (C_{quat}), 133.5 (2 CH), 133.6 (CH), 135.0 (C_{quat}), 136.1 (CH), 136.2 (CH), 136.6 (CH), 140.8 (C_{quat}), 143.3 (C_{quat}), 144.5 (C_{quat}), 145.1 (C_{quat}), 145.4 (CH), 150.8 (C_{quat}), 189.9 (C_{quat}), 190.4 (C_{quat}). *broadened signal by superposition. MS (MALDI-TOF) calcd. for $C_{47}H_{61}N_3O_2S$ (*m/z*): 792.5; Found: 792.6 ([M^+]). Anal. calcd. for $C_{53}H_{64}N_2O_2S$ [793.1]: C 80.26, H 8.13, N 3.53; Found: C 80.02, H 8.01, N 3.59. IR $\tilde{\nu}$ [cm^{-1}] = 2920 (m), 2851 (w), 2226 (w), 1722 (w), 1678 (m), 1597 (w), 1562 (m), 1462 (s), 1411 (w), 1337 (m), 1198 (s), 1153 (m), 1083 (w), 997 (m), 812 (m), 735 (m). UV/VIS (CH_2Cl_2) λ_{max} (ε) [nm] = 270 (34000), 316 (27000), 504 (25000).

(*E*)-2-cyano-3-(7-cyano-10-(2-decyltetradecyl)-10H-phenothiazin-3-yl)acrylic acid (5)



5

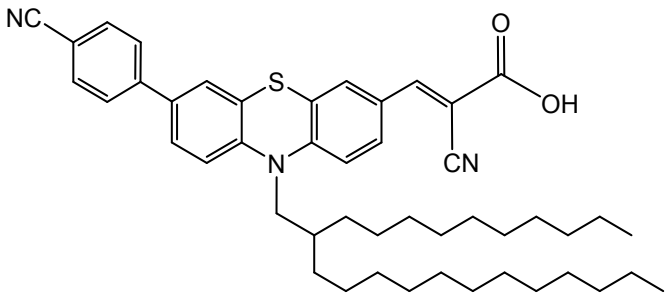
$C_{41}H_{57}N_3O_2S$

[655.98]

According to the GP and after flash chromatography (dichloromethane/acetic acid) compound **5** (195 mg, 78%) was obtained as a red amorphous solid, Mp 91-103 °C.

^{1}H NMR (600 MHz, acetone-d_6) δ = 0.74 (t, *J* = 7.1 Hz, 6 H), 1.10 – 1.43 (m, 40 H), 1.89 (m, 1 H), 3.90 (d, *J* = 7.3 Hz, 2 H), 7.14 (d, *J* = 8.6, 1 H), 7.16 (d, *J* = 8.7, 1 H), 7.41 (d, *J* = 1.9 Hz, 1 H), 7.49 (dd, *J* = 8.5, 1.9 Hz, 1 H), 7.78 (d, *J* = 2.1 Hz, 1 H), 7.91 (dd, *J* = 8.7, 2.1 Hz, 1 H), 8.06 (s, 1 H). ^{13}C NMR (150 MHz, acetone-d_6) δ = 14.4 (CH_3)*, 23.4 (CH_2)*, 26.7 (CH_2)*, 30.10 (CH_2), 30.11 (CH_2), 30.13 (CH_2)*, 30.31 (CH_2), 30.33 (CH_2), 30.37 (CH_2), 30.41 (CH_2), 30.42 (CH_2), 30.5 (CH_2), 30.6 (CH_2)*, 31.8 (CH_2)*, 32.7 (CH_2)*, 35.5 (CH), 52.5 (CH_2), 101.7 (C_{quat}), 107.6 (C_{quat}), 116.8 (C_{quat}), 118.2 (CH), 118.3 (CH), 118.8 (C_{quat}), 125.6 (C_{quat}), 126.4 (C_{quat}), 128.2 (C_{quat}), 130.8 (CH), 131.5 (CH), 132.5 (CH), 133.0 (CH), 149.1 (C_{quat}), 149.6 (C_{quat}), 153.5 (CH), 163.8 (C_{quat}). *broadened signal by superposition. MS (MALDI-TOF) calcd. for $C_{41}H_{57}N_3O_2S$ (*m/z*): 655.4; Found: 655.4 ([M^+]). Anal. calcd. for $C_{53}H_{64}N_2O_2S$ [656.0]: C 75.07, H 8.76, N 6.41; Found: C 75.35, H 9.04, N 6.19. IR $\tilde{\nu}$ [cm^{-1}] = 2920 (m), 2851 (w), 2224 (w), 1730 (w), 1690 (m), 1560 (m), 1464 (m), 1258 (m), 1258 (m), 1198 (m), 1090 (m), 1016 (s), 878 (w), 797 (s). UV/VIS (CH_2Cl_2) λ_{max} (ε) [nm] = 265 (19000), 299 (28000), 443 (19000).

(*E*)-2-cyano-3-(7-(4-cyanophenyl)-10-(2-decyltetradecyl)-10H-phenothiazin-3-yl)acrylic acid (6)



6

$C_{47}H_{61}N_3O_2S$

[732.07]

According to the GP and after flash chromatography (dichloromethane/acetic acid) compound **5** (190 mg, 76%) was obtained as violet-black crystals, Mp 82 °C.

^{1}H NMR (600 MHz, acetone-d_6) δ= 0.73 (t, *J* = 6,7 Hz 6 H), 1.08 – 1.35 (m, 40 H), 1.89 (m, 1 H), 3.84 (d, *J* = 7.2 Hz, 2 H), 7.06 (d, *J* = 8.6 Hz, 2 H), 7.38 (d, *J* = 2.0, 1 H), 7.49 (dd, *J* = 8.5, 2.0 Hz, 1 H), 7.67 – 7.73 (m, 4 H), 7.76 (d, *J* = 1.9 Hz, 1 H), 7.86 (dd, *J* = 8.6, 1.9 Hz, 1 H), 8.03 (s, 1 H). ^{13}C NMR (150 MHz, acetone-d_6) δ = 14.4 (CH_3)*, 23.4 (CH_2)*, 26.70 (CH_2), 26.72 (CH_2), 30.11 (CH_2), 30.13 (CH_2)*, 30.3 (CH_2)*, 30.36 (CH_2), 30.39 (CH_2), 30.42 (CH_2)*, 30.5 (CH_2), 30.60 (CH_2), 30.62 (CH_2), 31.9 (CH_2)*, 32.7 (CH_2)*, 35.5 (CH), 52.3 (CH_2), 100.7 (C_{quat}), 111.5 (C_{quat}), 117.1 (C_{quat}), 117.4 (CH), 118.4 (CH), 119.4 (C_{quat}), 125.98 (C_{quat}), 126.04 (C_{quat}), 126.8 (CH), 127.3 (C_{quat}), 127.5 (CH), 127.9 (2 CH), 130.6 (CH), 132.5 (CH), 133.6 (2 CH), 135.1 (C_{quat}), 144.5 (C_{quat}), 145.3 (C_{quat}), 150.7 (C_{quat}), 153.7 (CH), 164.0 (C_{quat}). *broadened signal by superposition. MS (MALDI-TOF) calcd. for $C_{47}H_{61}N_3O_2S$ (*m/z*): 731.5; Found: 732.5 ([M+H]$^+$). Anal. calcd. for $C_{47}H_{61}N_3O_2S$ [732.1]: C 77.11, H 8.40, N 5.74; Found: C 77.28; H 8.70; N 5.64. IR $\tilde{\nu}$ [cm^{-1}] = 2922 (m), 2851 (m), 2224 (w),1684 (m), 1568 (m), 1464 (m), 1406 (w), 1343 (w), 1296 (w), 1276 (m), 1204 (s), 1173 (m), 883 (w), 814 (m), 718 (w), 694 (w). UV/VIS (CH_2Cl_2) λ_{max} (ε) [nm] = 265 (41000), 314 (66000), 462 (36000).

Synthesis of spherical gold nanoparticles [2]

Spherical gold nanoparticles were synthesized via a modified Turkevic route from $KAuCl_4$ (8 mg, 21.2 µmol) and trisodium citrate (10 mg, 38.8 µmol, molar ratio $KAuCl_4$: trisodium citrate = 1:1.8), which were dissolved in 40 mL Millipore water under vigorous stirring. The solution was heated in a microwave at 700 W for 2 min. The color changed from pale yellow to blue to red as the dispersion cooled to room temperature. The nanoparticles were characterized by TEM images which showed an average size of 36 ± 7 nm for the discrete gold nanoparticles (Fig. S1 in Supp. Info.). Besides gold, the elements C, Cu and O were detected in the accompanying EDX spectrum (Fig. S2 in Supp. Info.). Carbon and copper are stemming from the carbon-coated copper TEM-Grid, also carbon and oxygen originate from the citrate capping ligands around the nanoparticles. UV/Vis-spectroscopy confirmed the presence of the LSPR for the gold nanoparticles (Fig. S3 in Supp. Info.).

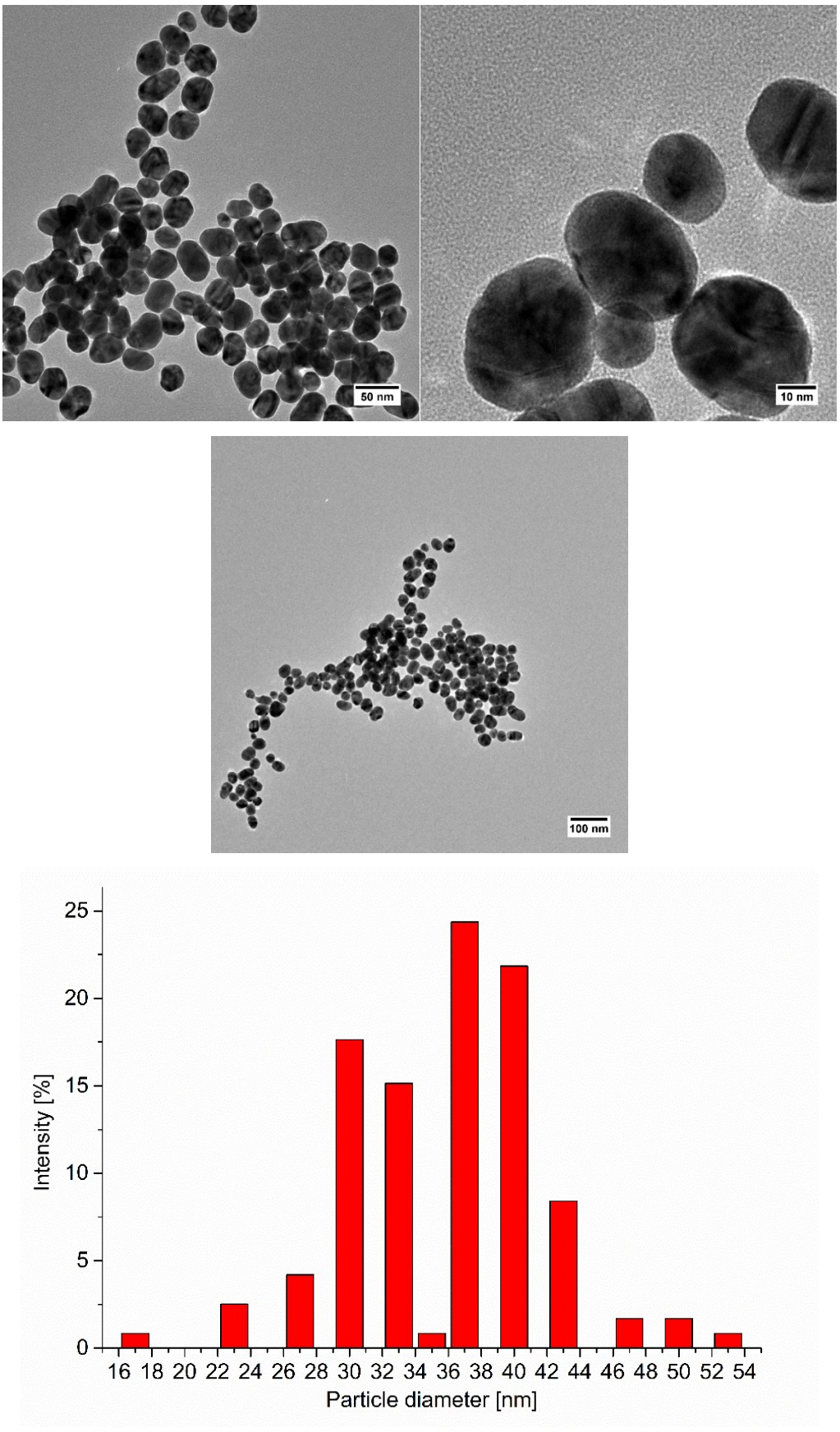


Figure S1 TEM images and size histogram of the synthesized Au-NPs. The size of 119 particles was measured by hand.

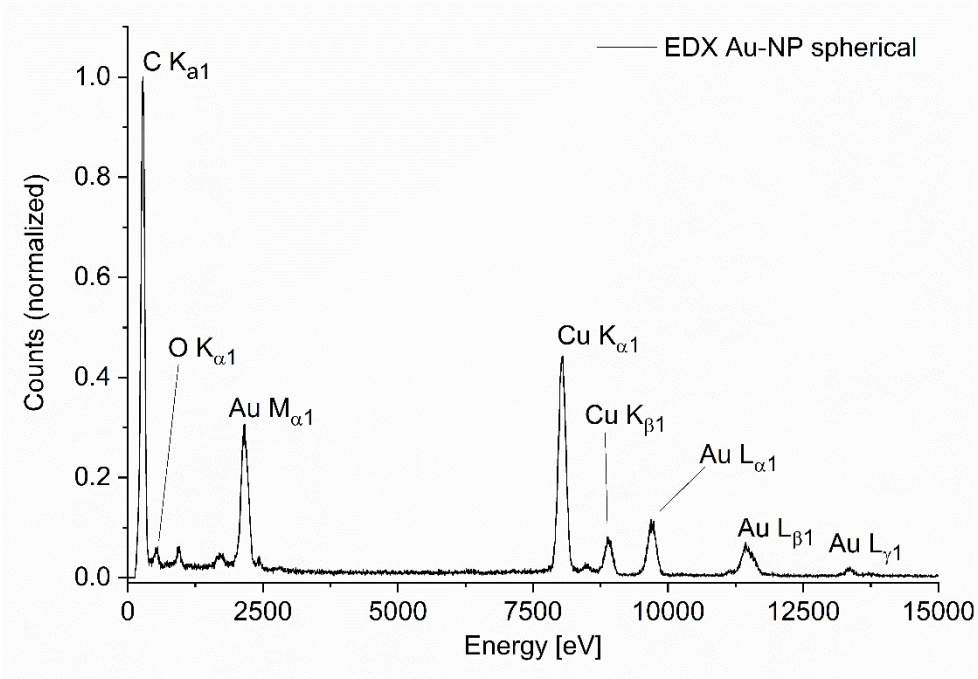
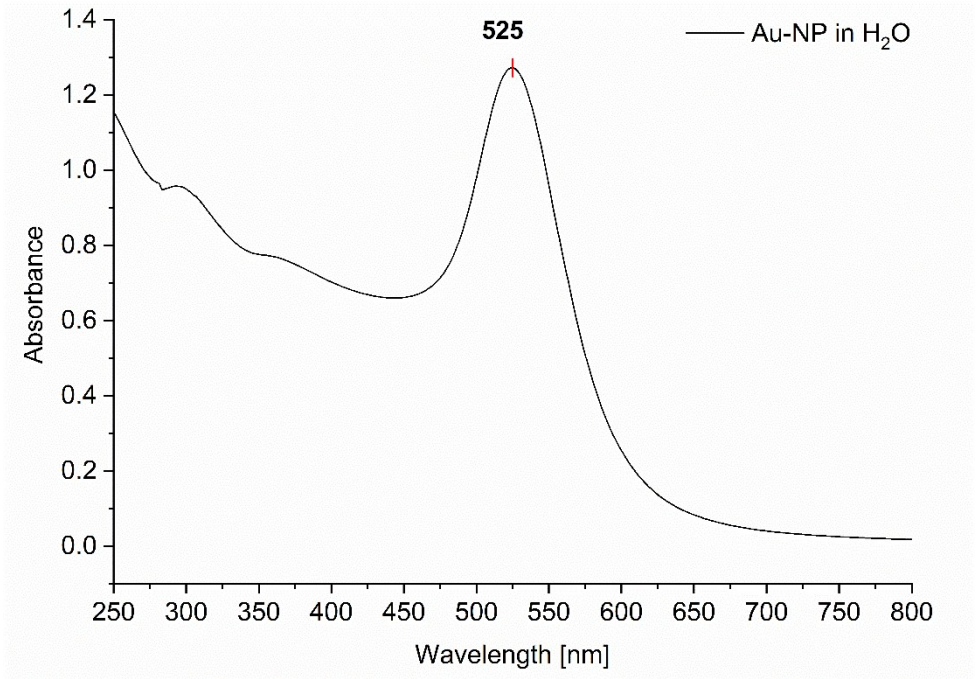


Figure S2 EDX spectrum of synthesized Au-NPs



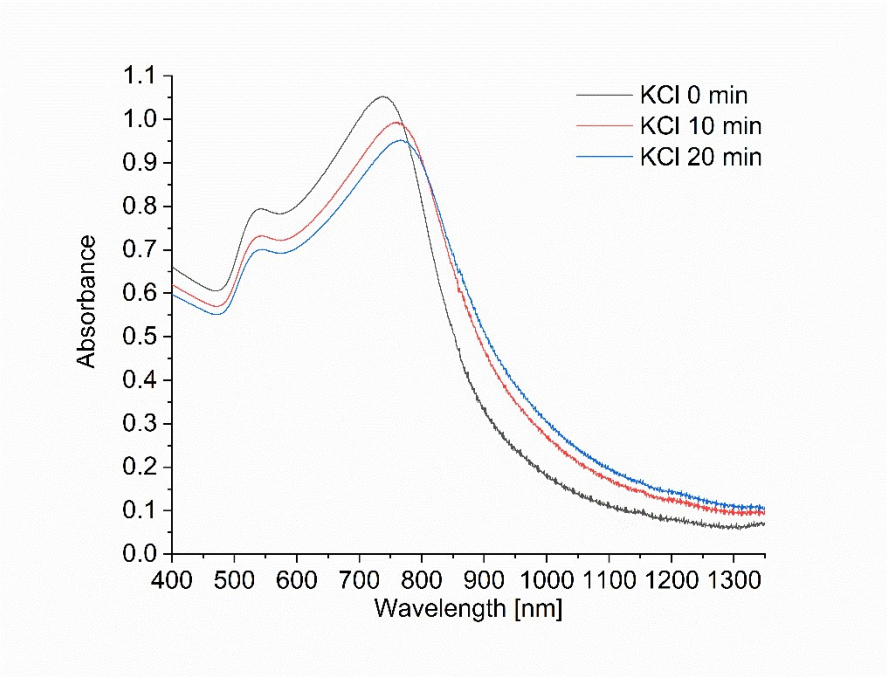
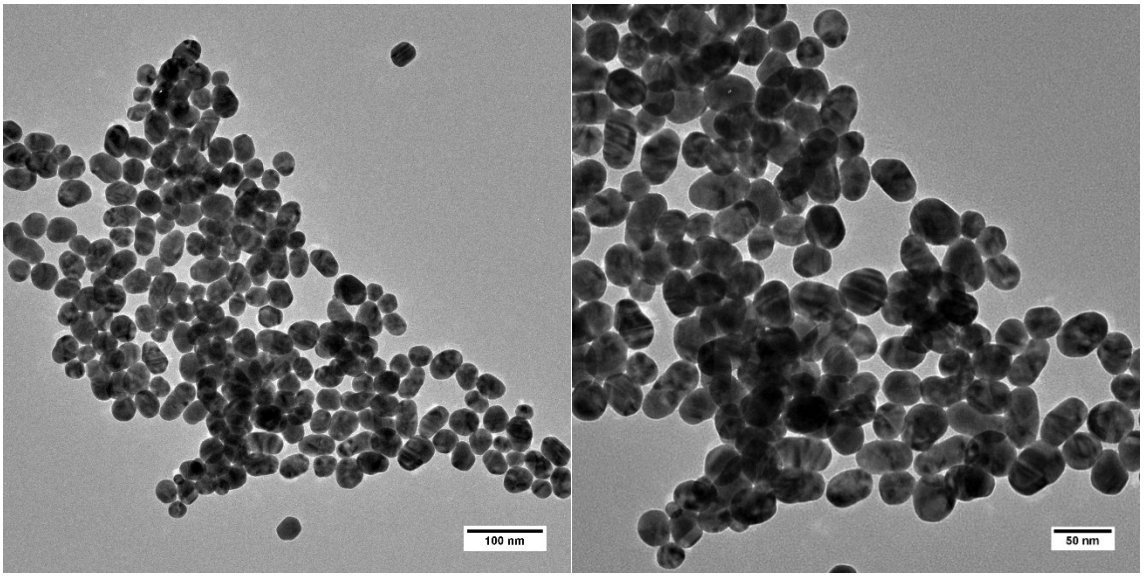


Figure S3 Top UV/vis spectrum of Au-NP/water dispersion. The band at 525 nm corresponds to the localized surface plasmon resonance (LSPR) band of the spherical gold nanoparticles [3]. **Bottom** Time dependent UV/vis/NIR absorption of Au-NPs in water/acetone (1:1 v:v) with KCl added.



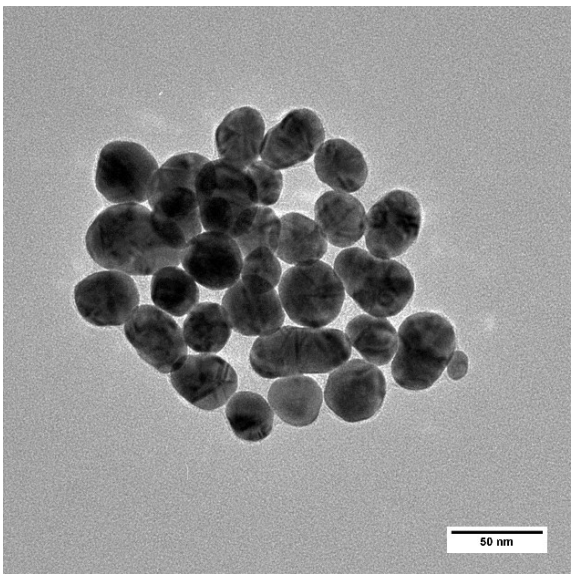


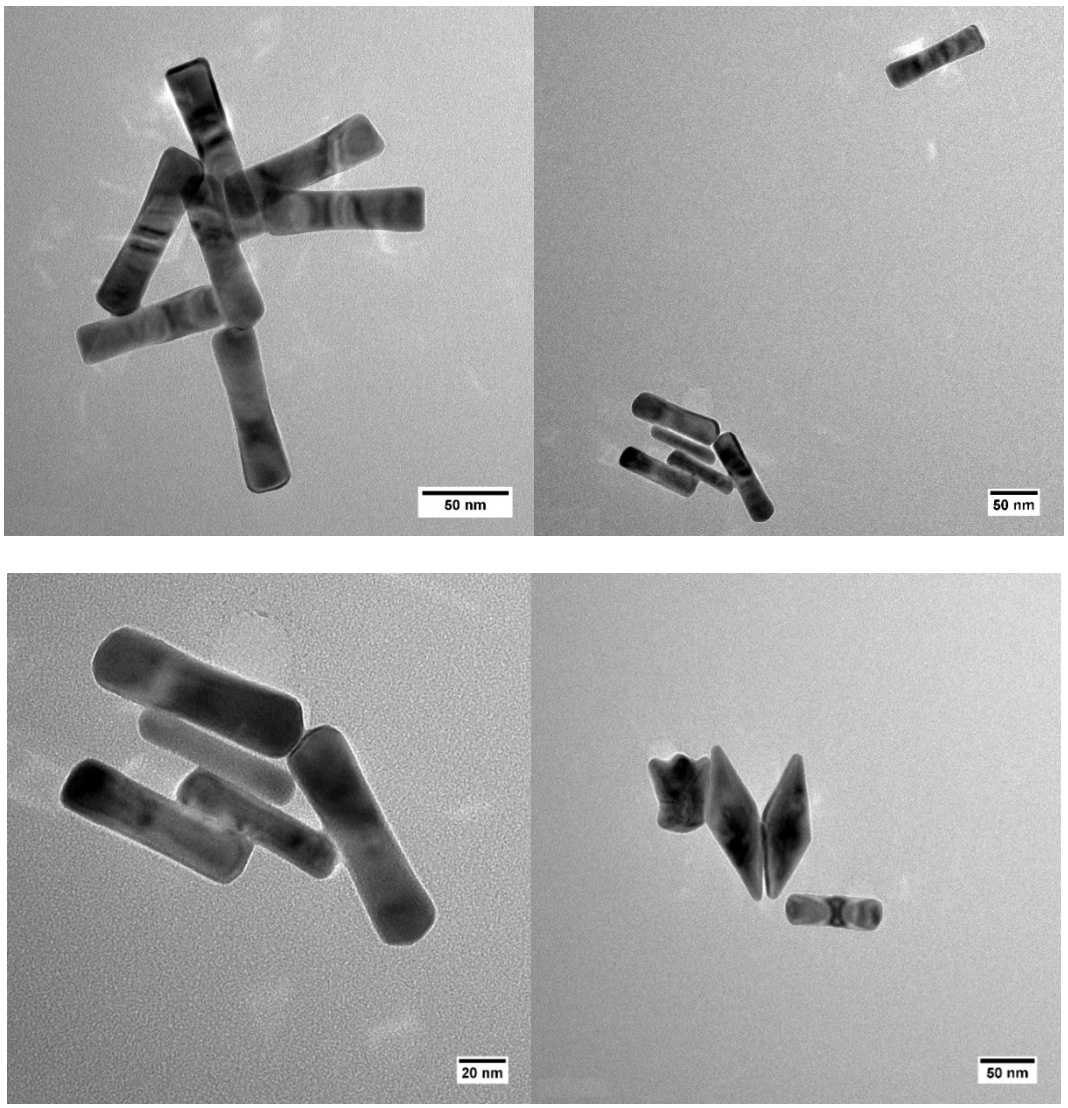
Figure S4 TEM images of the synthesized Au-NPs after the addition of acetone (to a 1:1 v:v mixture) to the of aqueous Au-NP dispersion.

Synthesis of gold nanorods [4]

Gold nanorods were prepared using a seedless synthesis with dopamine as a reducing agent. 5 mL of cetyltrimethylammonium bromide (CTAB, 50 mmol/L in water) were mixed in a 25 mL beaker with 500 µL of an aqueous dopamine solution (500 mmol/L) and stirred for 10 min. After that, 5 mL of an aqueous $KAuCl_4$ solution (1 mmol/L) was added and the resulting solution stirred for 10 minutes. After this time 100 µL of $AgNO_3$ (200 mmol/L) and 500 µL of an aqueous dopamine solution (500 mmol/L) were added. In the last step the stirring rate was set to 1200 RPM and 10µL of an ice-cold $NaBH_4$ solution (10 mmol/L) was added in one step. The stirring was stopped and the reaction solution kept for several hours at room temperature. The solution changed colour from white over pale red to deep red. For purification, the solution was filtered and then centrifuged two times (10 min, 8000 RPM) and re-dispersed in 11 mL water. The Au-concentration of the dispersion were c = 0.53 mmol/L.

We would also like to mention, that literature states, that the amount of silver nitrate has an important influence on the aspect ratio of gold nanorods (see Fig. 9 in ref. [5]). Since we wanted to shift the LSPR near the excitation wavelength of the used Raman laser, it was necessary to use higher amounts of $AgNO_3$ and CTAB.

The particles were characterized by TEM images which showed an average size of 89 ± 13 nm for the nanorod length and 21 ± 6 nm for the nanorod width (Fig. S5 in Supp. Info.)



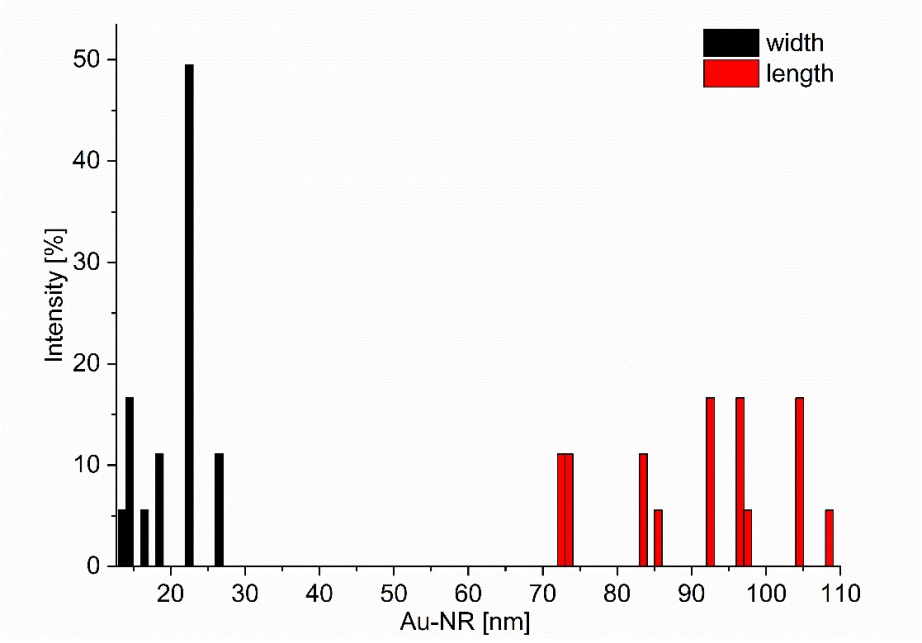


Figure S5 TEM images and size histogram of the synthesized Au-NRs. TEM images show nanorods from three different spots on the TEM grid. The size of 18 particles was measured by hand.

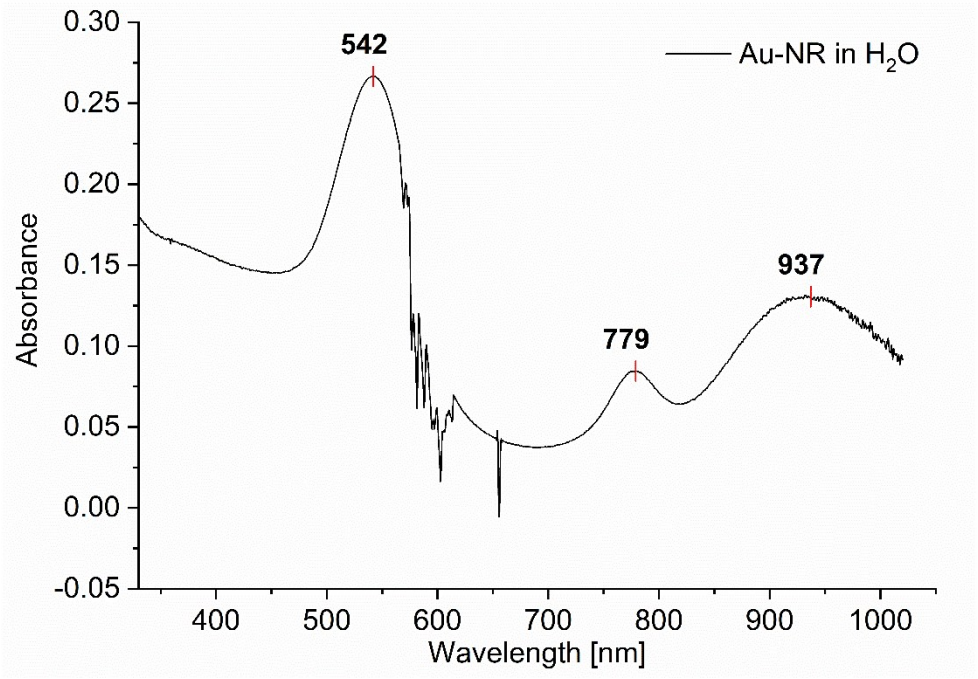


Figure S6 UV/Vis spectrum of Au-NR/water dispersion. The peak at 542 nm refers to the transverse axis, the peak at 937 nm a peak to the longitudinal axis. At 779 nm a small peak for gold nanoprisms occured (see Fig. S5), where the reaction was not completed to nanorods.

We would like to mention, that the form and the size distribution of the Au-NRs are in good accordance to a report by Zubarev *et al*.[4] who prepared different sizes for shifting the Au-SPR. Zubarev *et al*. reported for their largest Au-NRs a length of 97 ± 16 nm and a width of 20 ± 5 nm. A comparison of our TEM images with the ones by Zubarev *et al.* shows similar shaped Au-NRs with a high aspect ratio and with the same slight bone shape for our and his nanorods. In comparison to the literature on bone shaped nanorods, our synthesized nanorods are clearly more rod than bone shaped.[6]

Comparison Raman spectra solvent/ Raman spectra solvent and phenothiazine dye (PD) 1

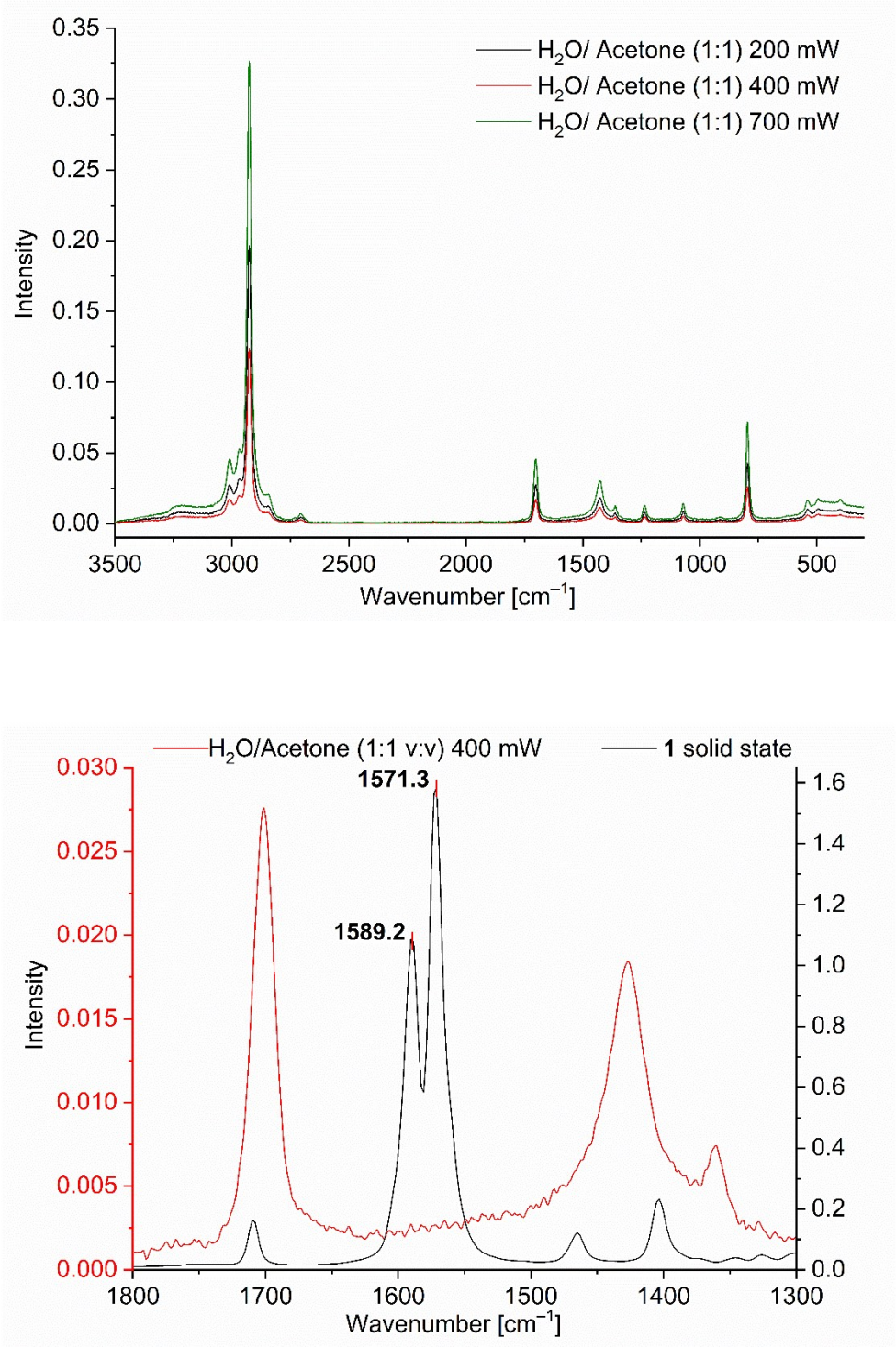


Figure S7 Top Raman spectrum of an H_2O/acetone (1:1 v:v) mixture at 200, 400, 700 mW Laser output. **Bottom** Comparative overlay of the Raman spectrum of PD **1** (solid state, black) and of the H_2O/acetone (1:1 v:v) mixture in the spectral region between 1800-1300 cm^{-1}

SERS studies with spherical gold nanoparticles and KCl

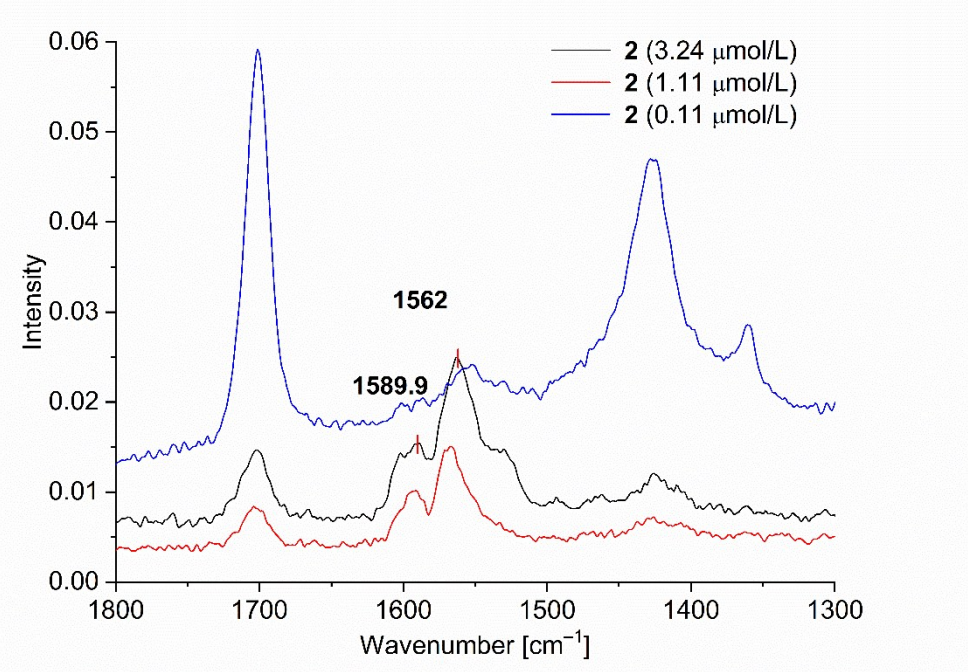
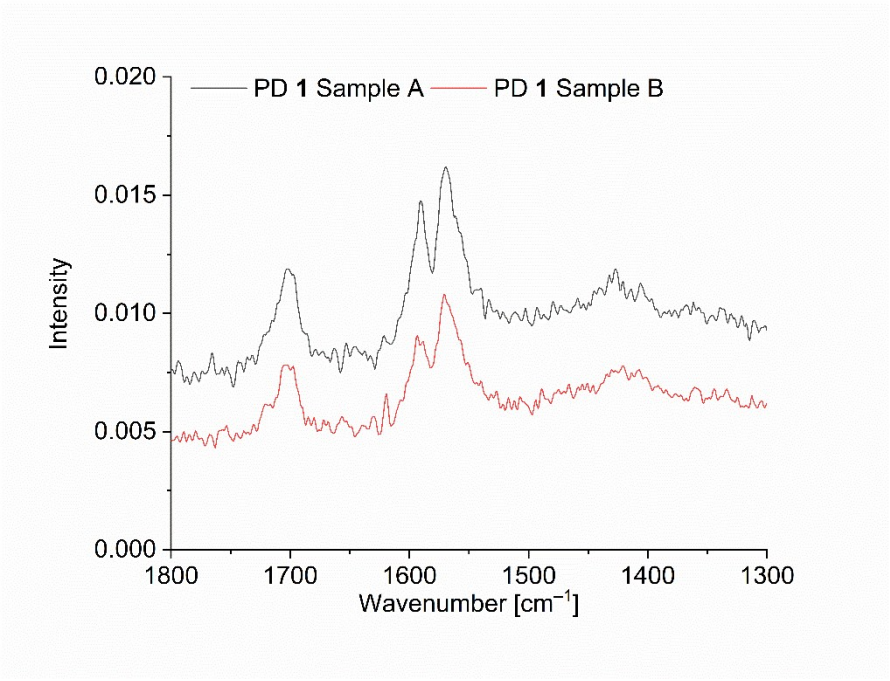
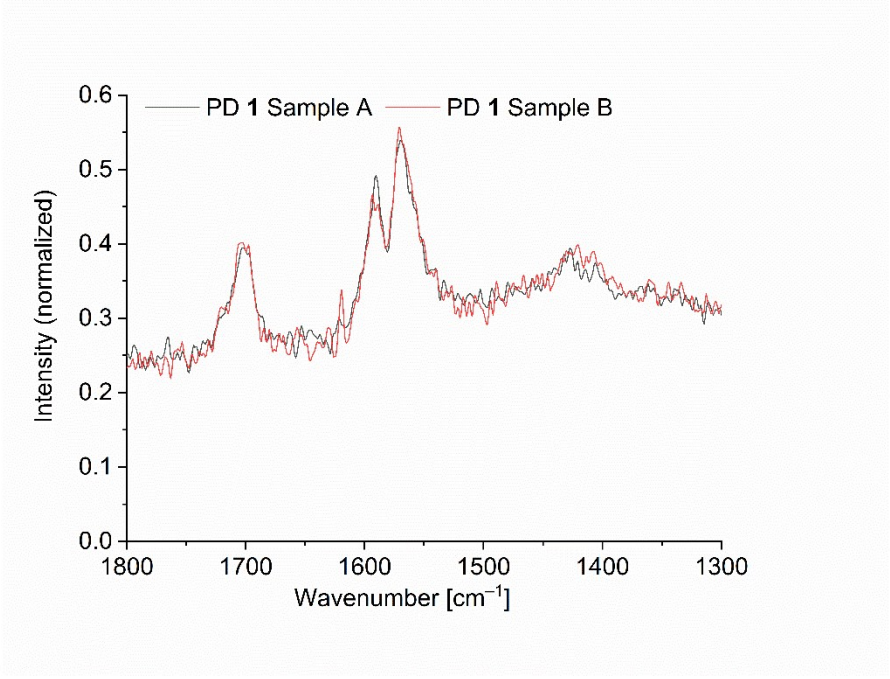


Figure S8 SERS studies (200 mW) for PD **2**@Au-NP at 3.24, 1.11 (both 200 mW) and 0.11 µmol/L (700 mW) in H_2O/acetone (1:1 v:v) + 10 mg KCl added to 3 mL of the dispersion.

In SERS measurement the reproducibility and uniformity of SERS signals is an aspect which is often discussed. Literature defines uniformity of SERS signals as the absence of variation in signal intensity.[7] In the liquid state Raman spectral uniformity is a critical aspect since it strongly depends on the Brownian motion of the molecules.



(a)



(b)

Figure S9: PD **1** (*c* = 1.11 µM) measured twice with the same settings in the presence of Au-NPs after KCl induced agglomeration (same conditions as in all other SERS measurements). a) not normalized b) normalized (highest solvent signal set to 1)

Normalizing both spectra negates the intensity differences through the Brownian motion and shows, that the measurements were reproducible and that the SERS signals are uniform. It also shows, that the molecule movement and movement of the agglomerating Au-NP has an influence on the overall signal intensities. SERS signal enhancements are reproducible.

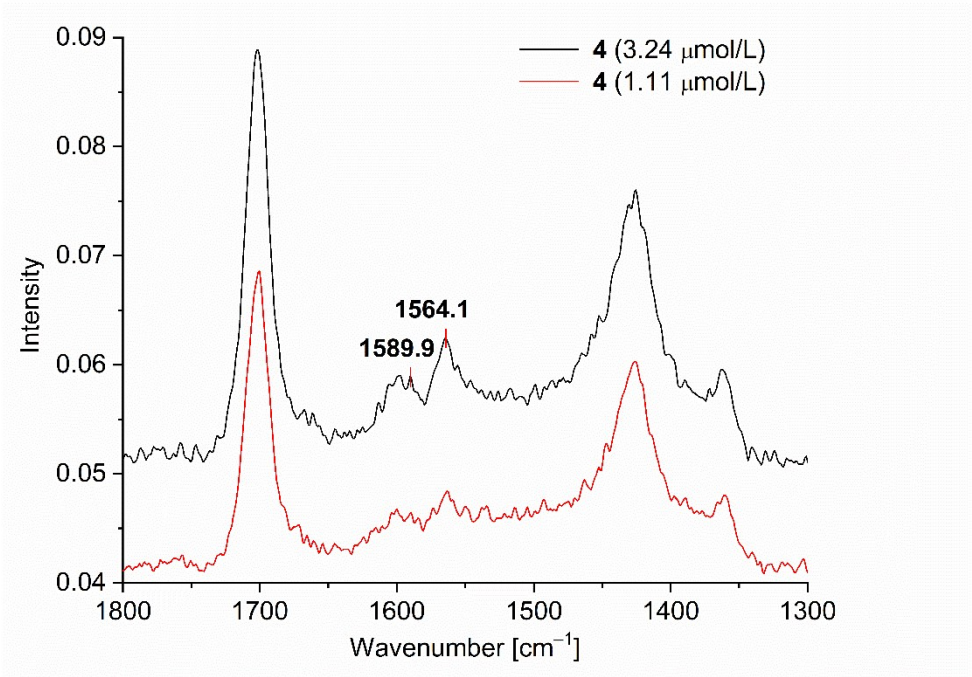


Figure S10 SERS studies for PD **4**@Au-NP at 3.24 (500 mW), 1.11 (700 mW) μmol/L in H_2O/acetone (1:1 v:v) + 10 mg KCl added to 3 mL of the dispersion.

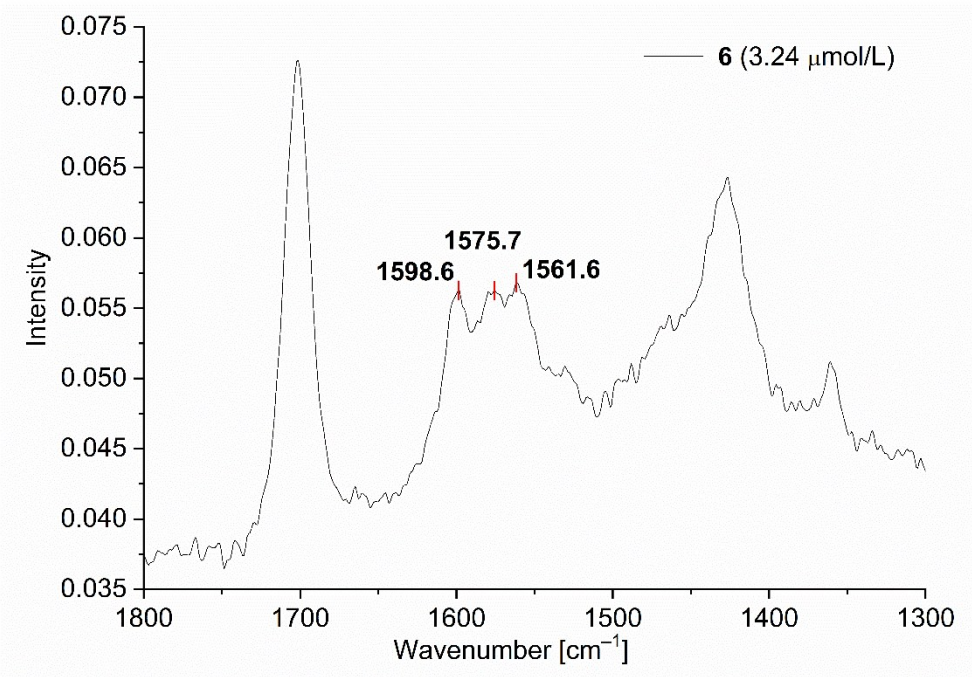
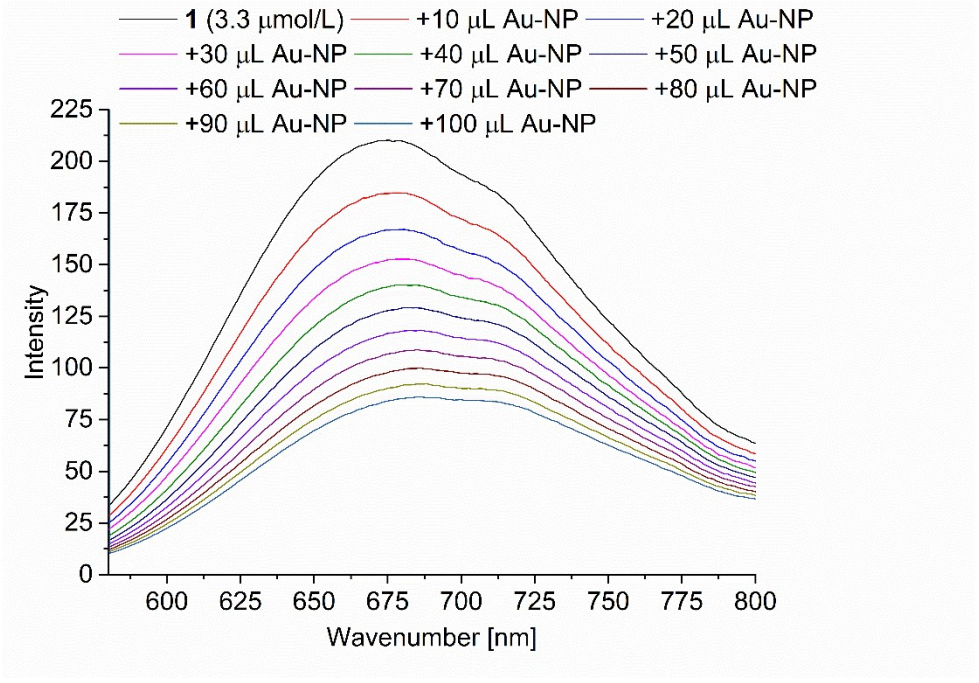
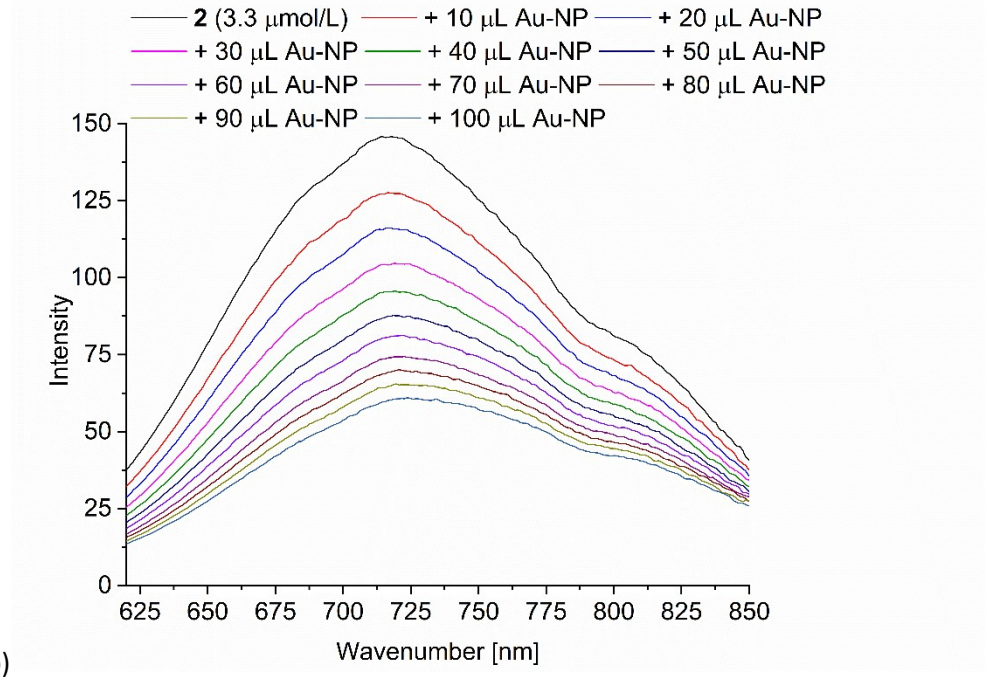


Figure S11 SERS studies for PD **6**@Au-NP at 3.24 μmol/L (500mW) in H_2O/acetone (1:1 v:v) + 10 mg KCl added to 3 mL of the dispersion.

Fluorescence studies after the addition of Au-NP dispersion

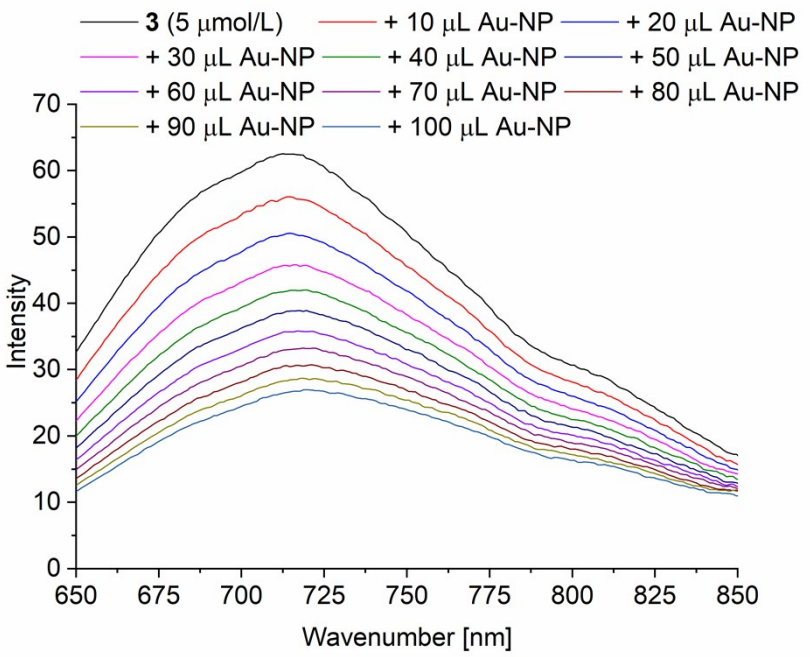


(a)

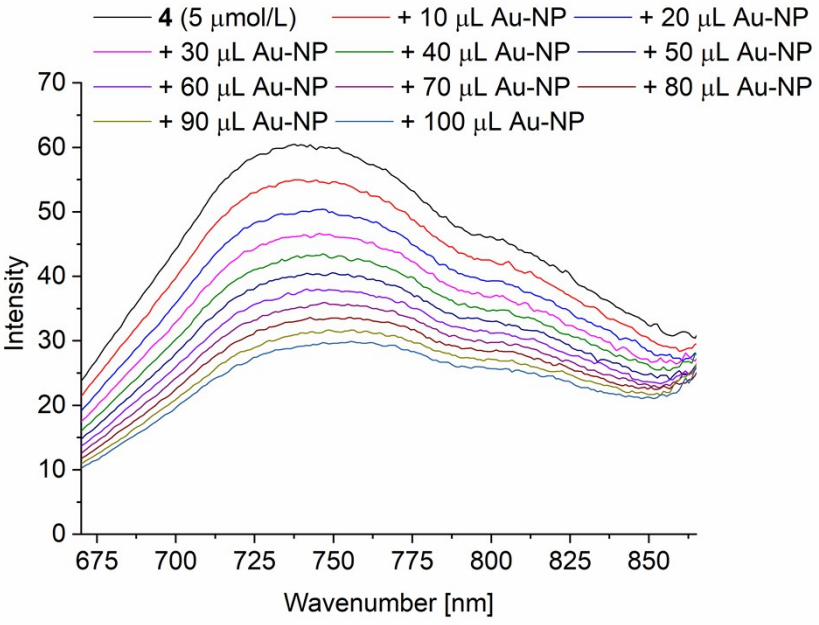


(b)

Figure S12 a)-b) Fluorescence spectra of PD **1** and PD **2** (c = 3.3 μmol/L) with the stepwise addition of 100 μL Au-NP dispersion (excitation wavelength a) 450 nm b) 465 nm).



(a)



(b)

Figure S13 a)-b) Fluorescence spectra of PD **3** and PD **4** (c = 5 µmol/L) with the stepwise addition of 100 µL Au-NP dispersion (excitation wavelength a) 466 nm b) 494 nm). Concentrations were higher than for PD **1** and **2** and **5** and **6** due to lower fluorescence intensities.

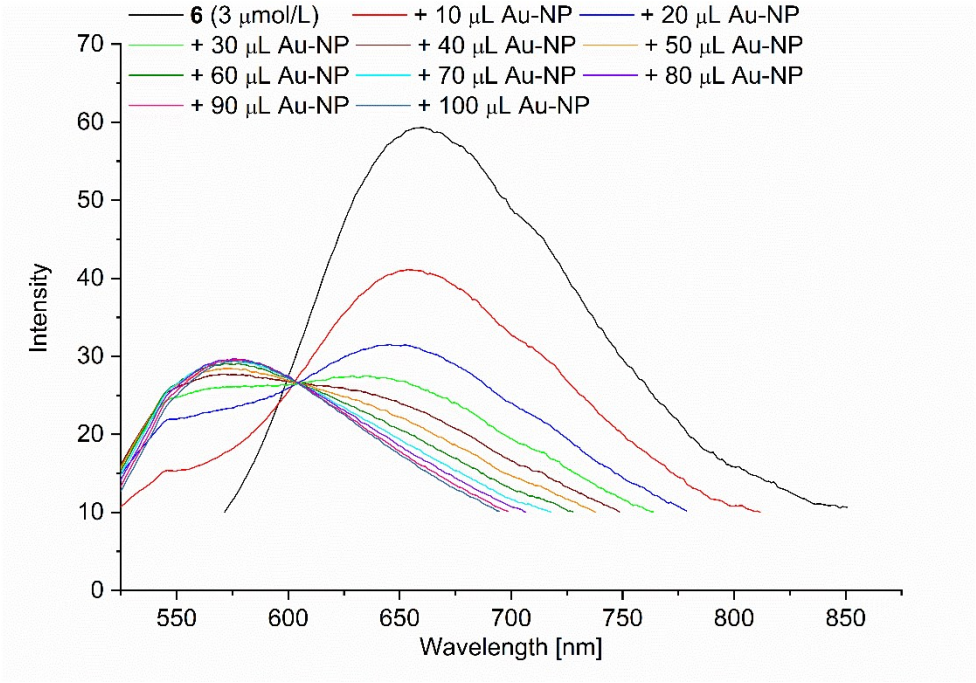
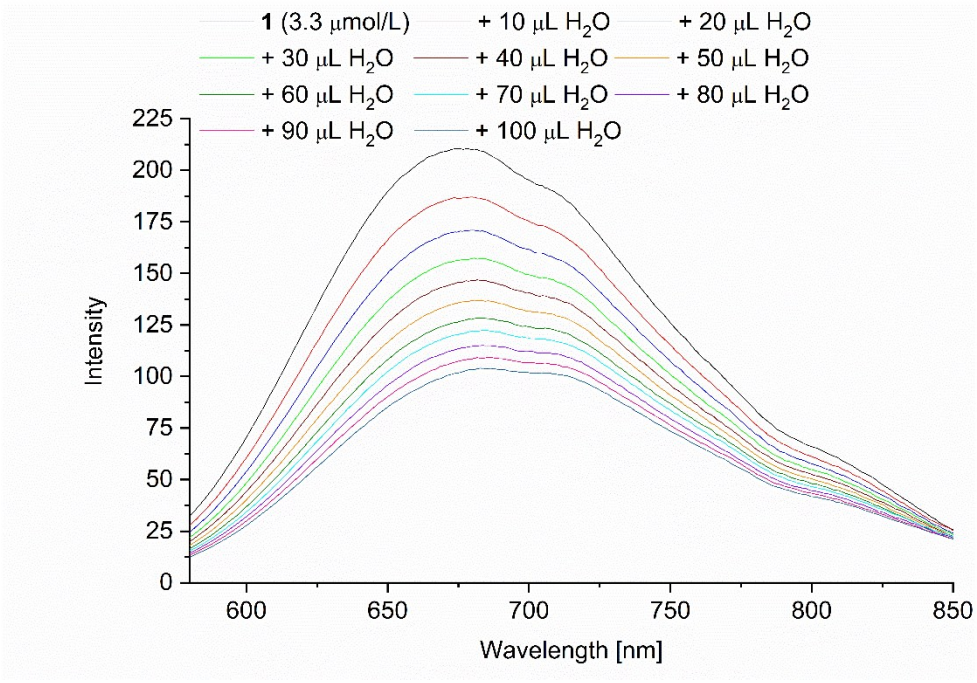
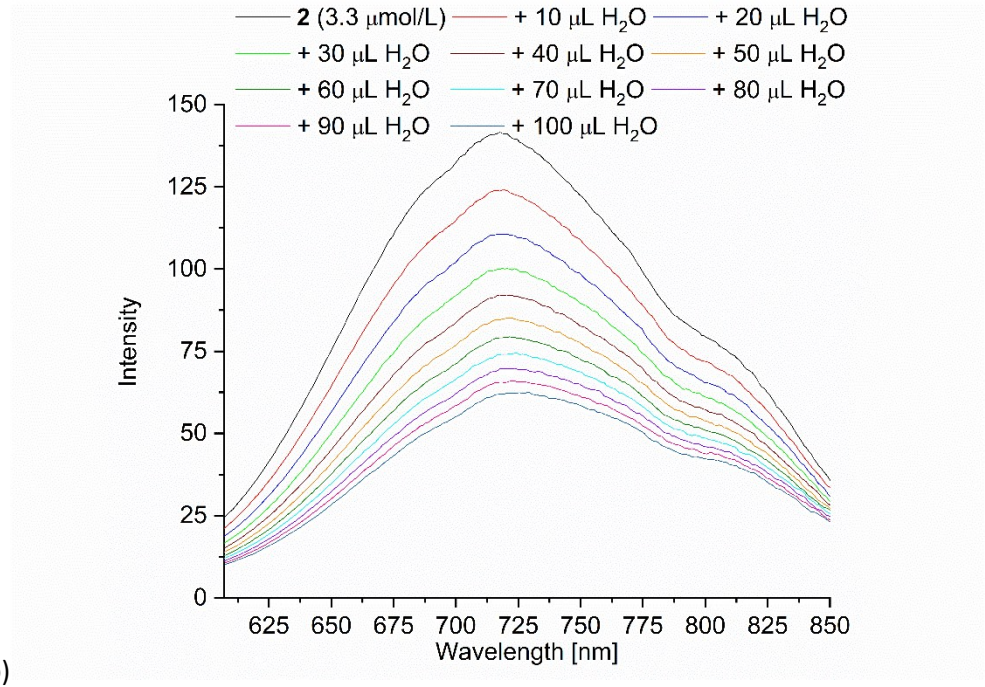


Figure S14 Fluorescence spectra of PD **6** (c = 3 µmol/L) with the stepwise addition of 100 µL Au-NP dispersion (excitation wavelength = 470 nm).

Fluorescence studies after the addition of water

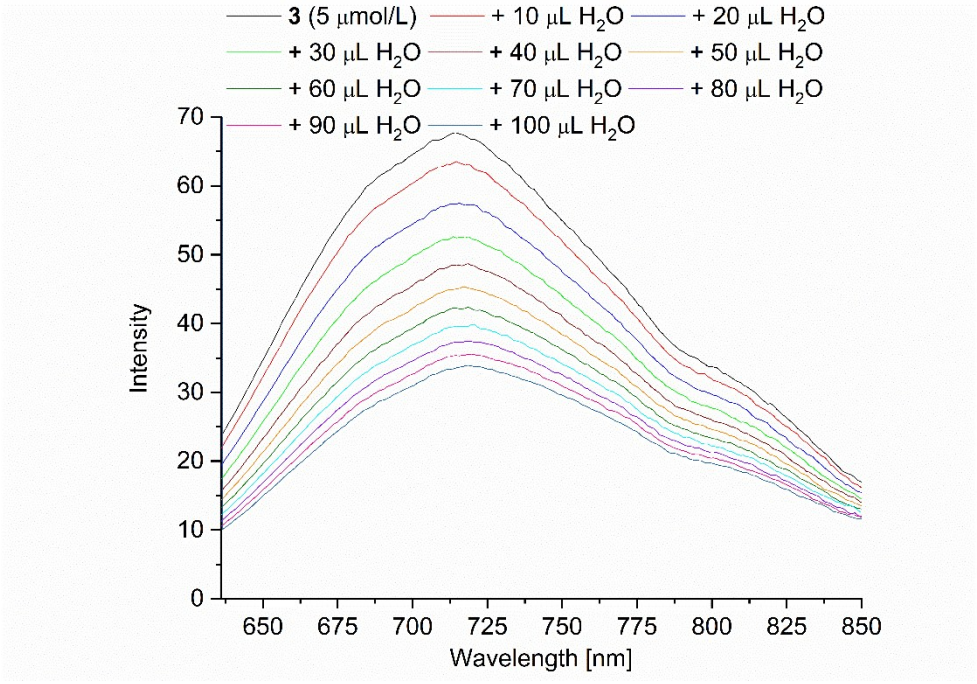


(a)

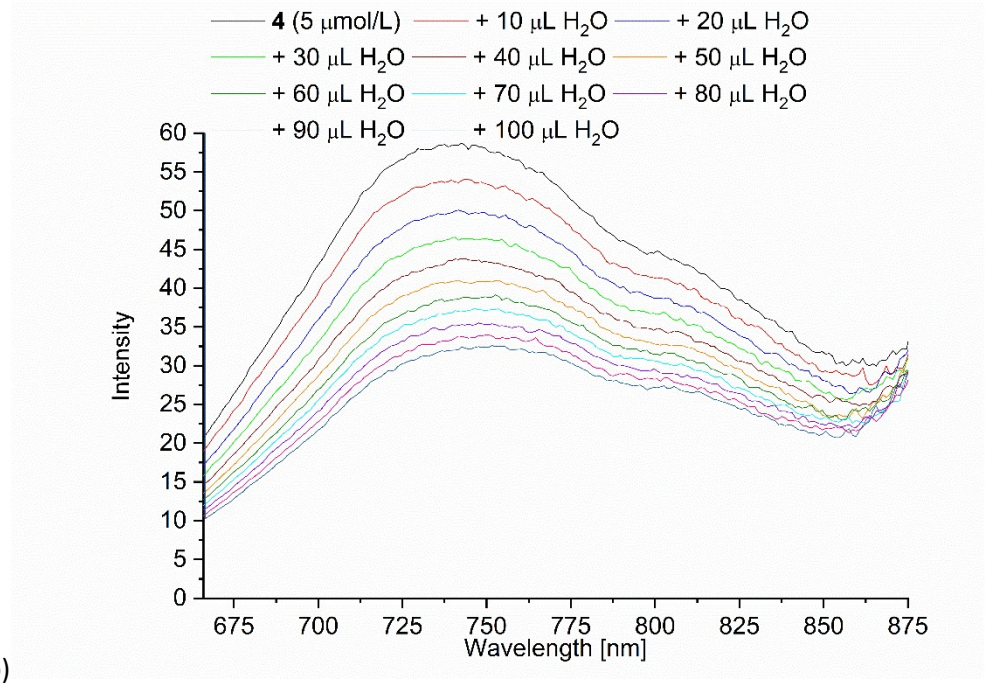


(b)

Figure S15 a)-b) Fluorescence spectra of PD **1** and PD **2** (c = 3.3 µmol/L) with the stepwise addition of 100 µL H_2O (excitation wavelength a) 450 nm b) 465 nm).



(a)



(b)

Figure S16 a)-b) Fluorescence spectra of PD **3** and **4** (c = 5 µmol/L) with the stepwise addition of 100 µL H_2O (excitation wavelength a) 466 nm b) 494 nm). Concentrations were higher than for PD **1** and **2** and **5** and **6** due to lower fluorescence intensities.

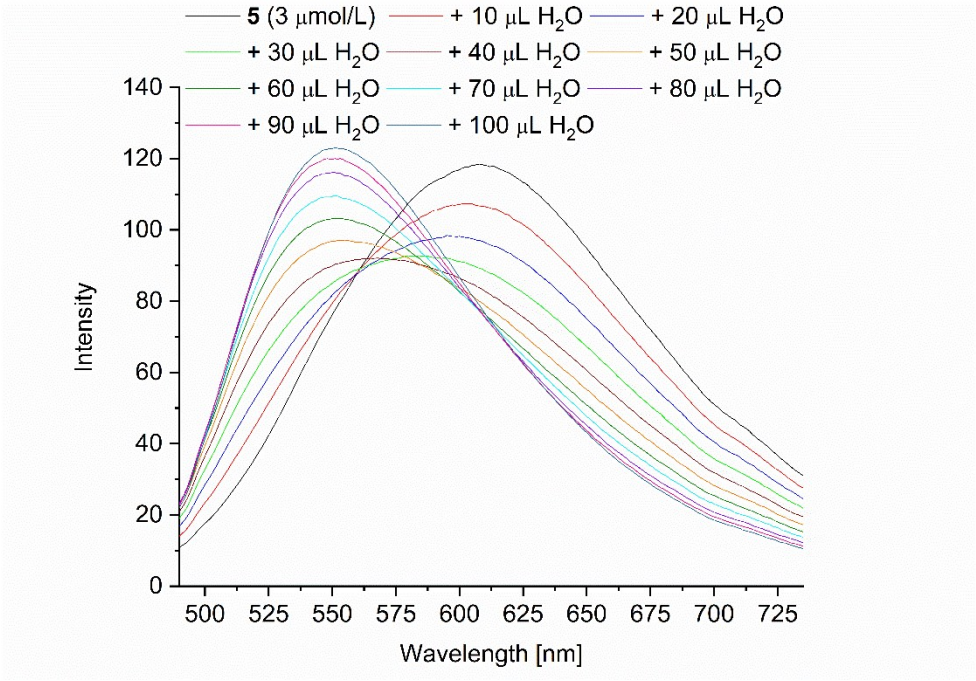


Figure S17 Fluorescence spectra of PD **5** (c = 3.3 µmol/L) with the stepwise addition of 100 µL H_2O (excitation wavelength = 428 nm).

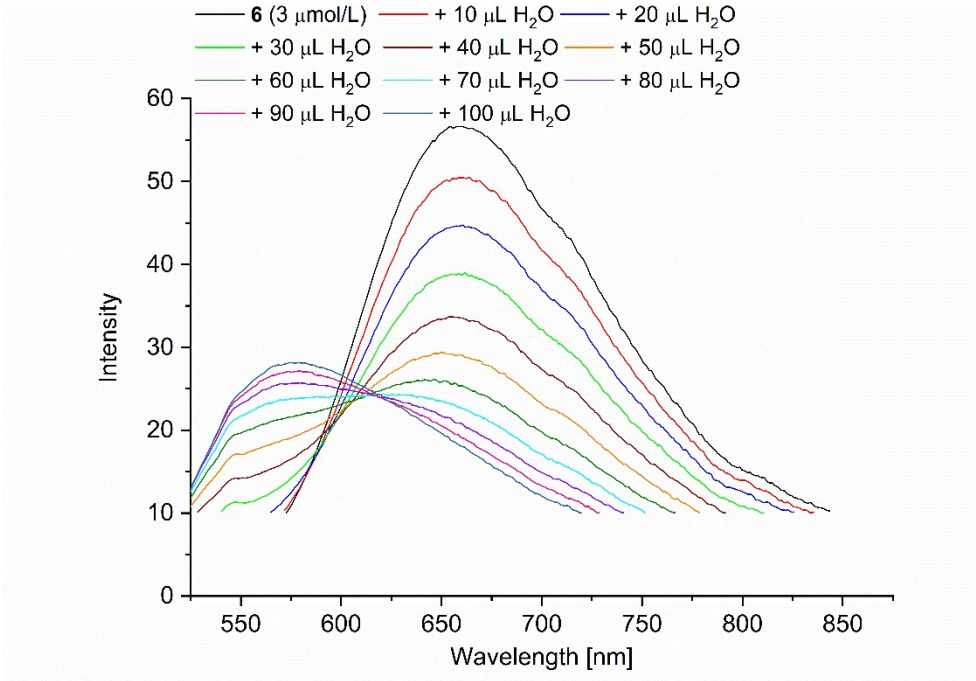


Figure S18 Fluorescence spectra of PD **6** (c = 3 µmol/L) with the stepwise addition of 100 µL H_2O (excitation wavelength = 470 nm).

SERS studies with gold nanorods

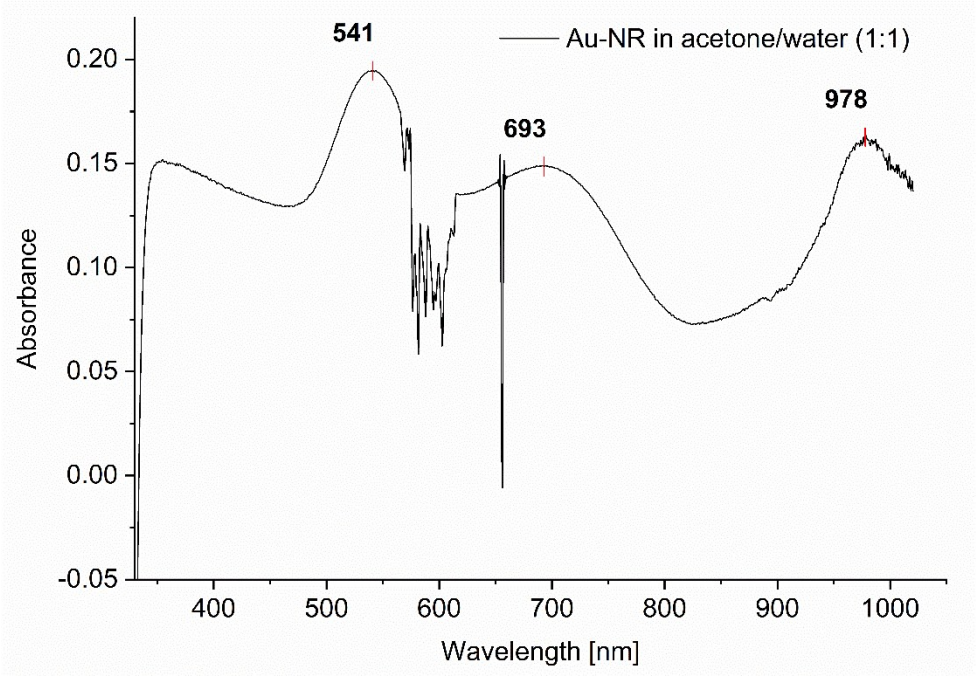


Figure S19 UV/Vis spectrum of Au-NRs in water/acetone (1:1 v:v)

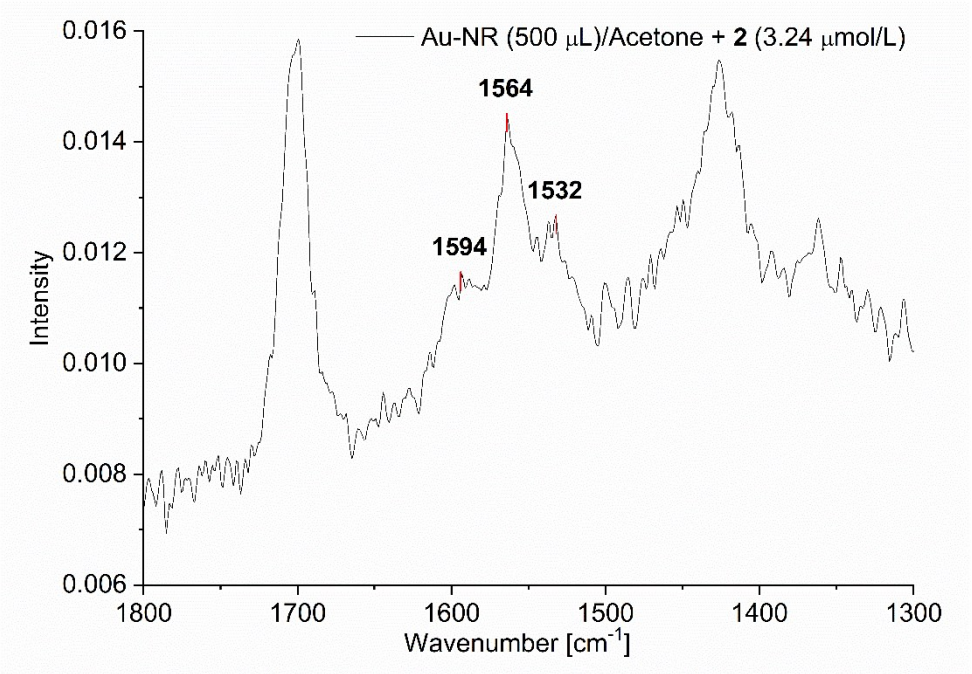


Figure S20 SERS studies (200 mW) for PD **2**@Au-NR at 3.24 µmol/L in H_2O/acetone (1:1 v:v) (section between 1800-1300 cm^{-1}).

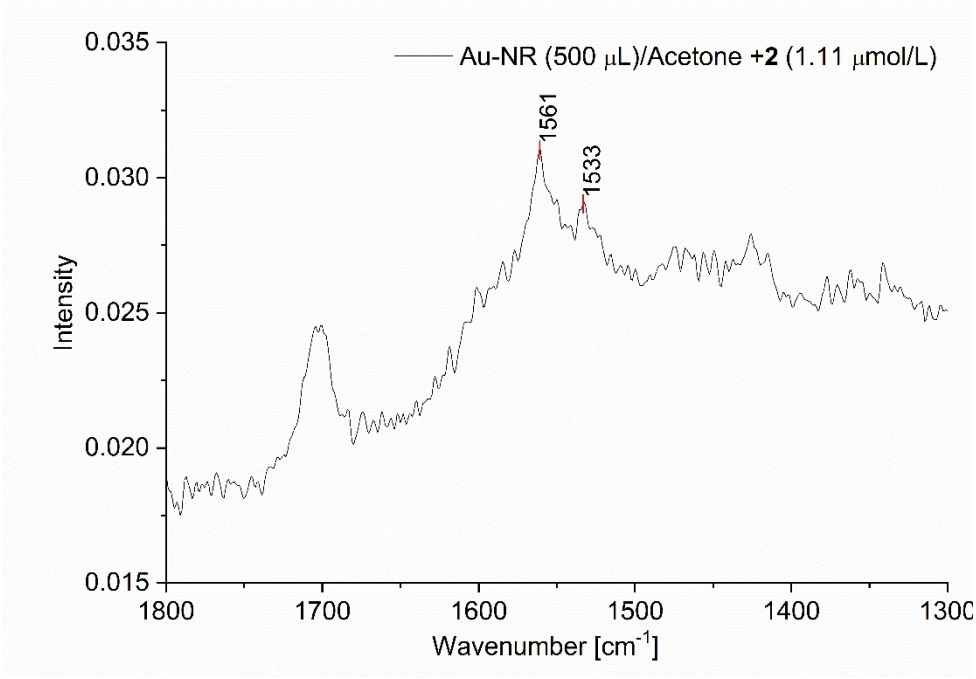


Figure S21 SERS studies (200 mW) for PD **2**@Au-NR at 1.11 µmol/L in H_2O/acetone (1:1 v:v) (section between 1800-1300 cm^{-1}).

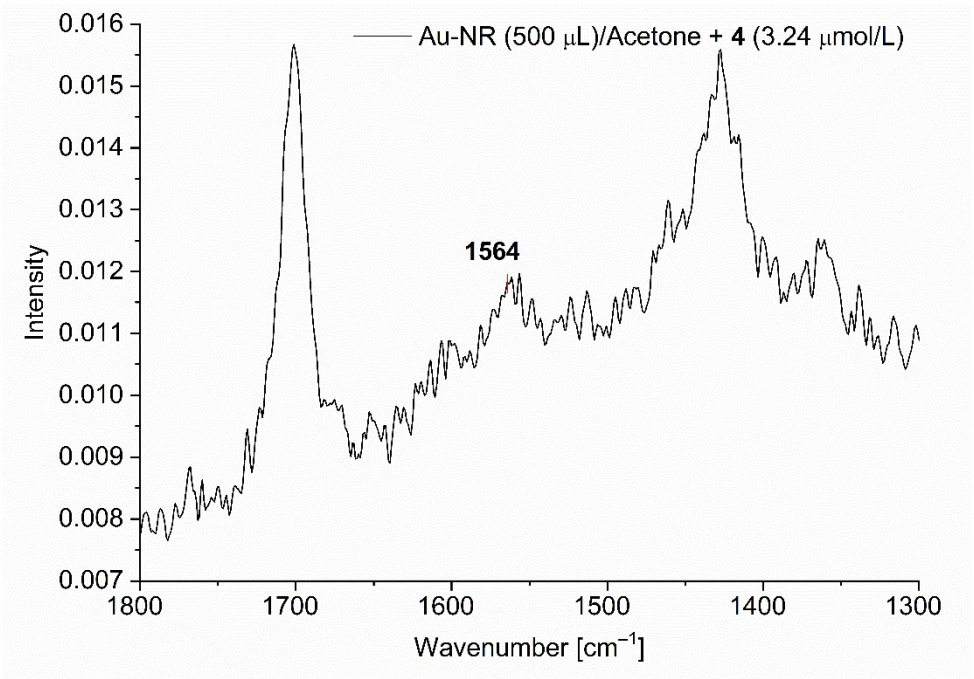


Figure S22 SERS studies (200 mW) for PD **4**@Au-NR at 3.24 µmol/L in H_2O/acetone (1:1 v:v) (section between 1800-1300 cm^{-1}).

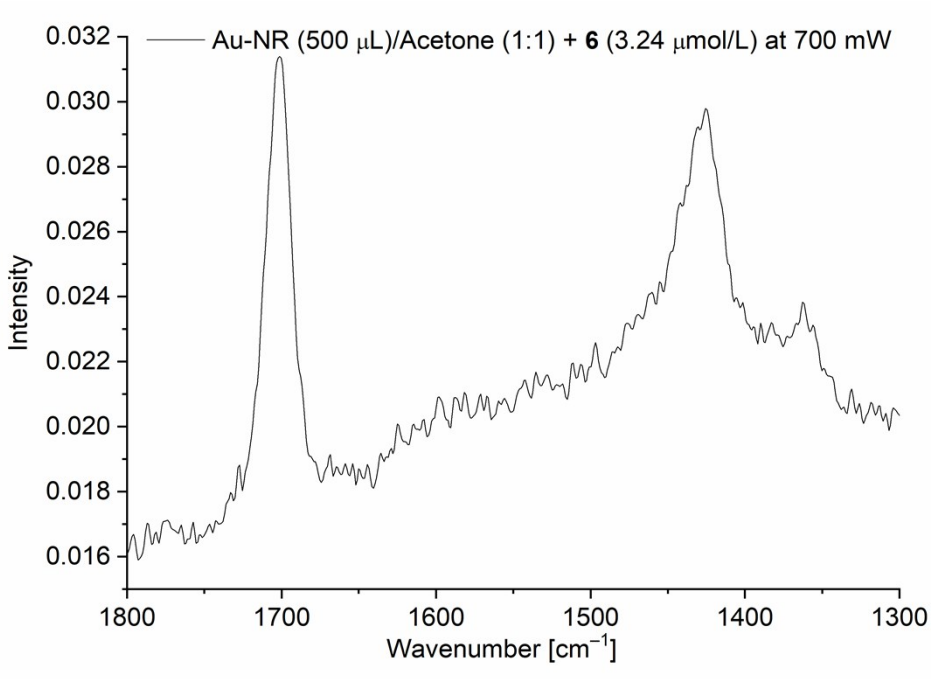
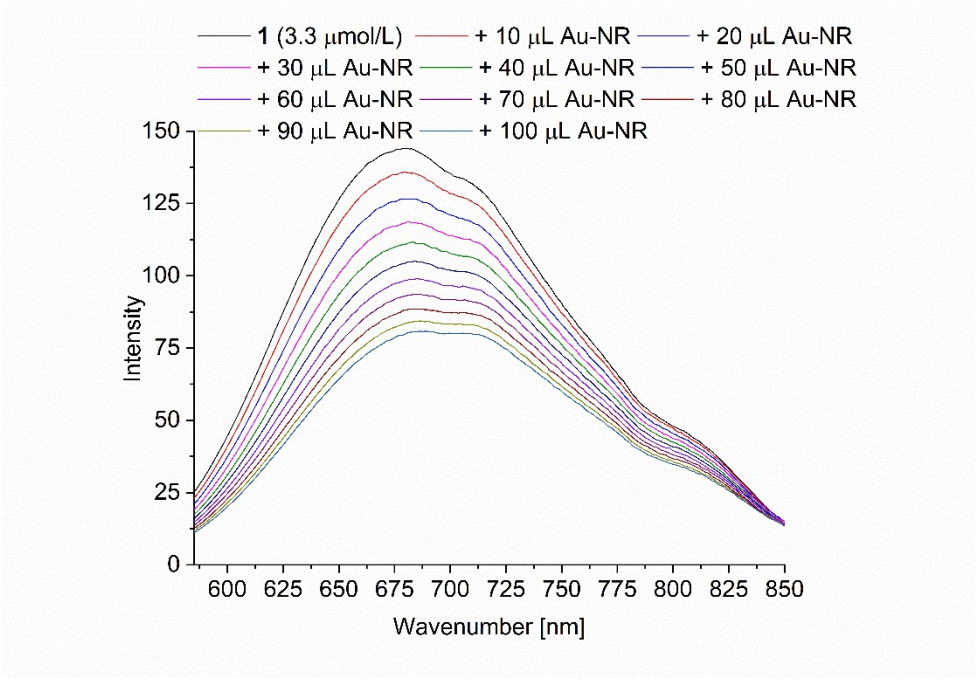
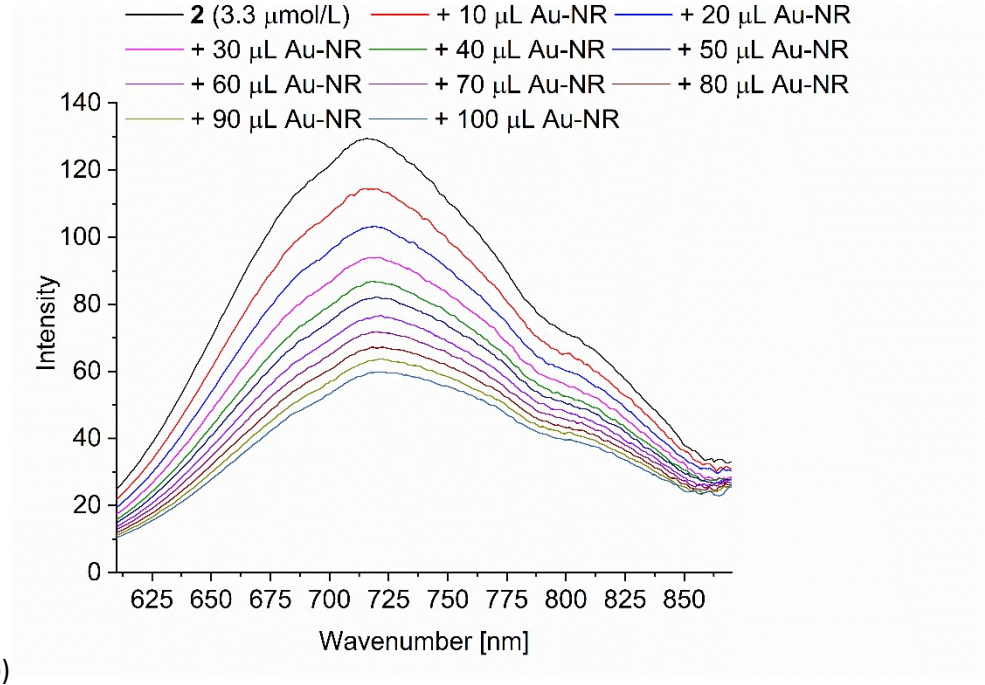


Figure S23 SERS studies (700 mW) for PD **6**@Au-NR at 3.24 µmol/L in H_2O/acetone (1:1 v:v) (section between 1800-1300 cm^{-1}).

Fluorescence studies after the addition of Au-NR dispersion

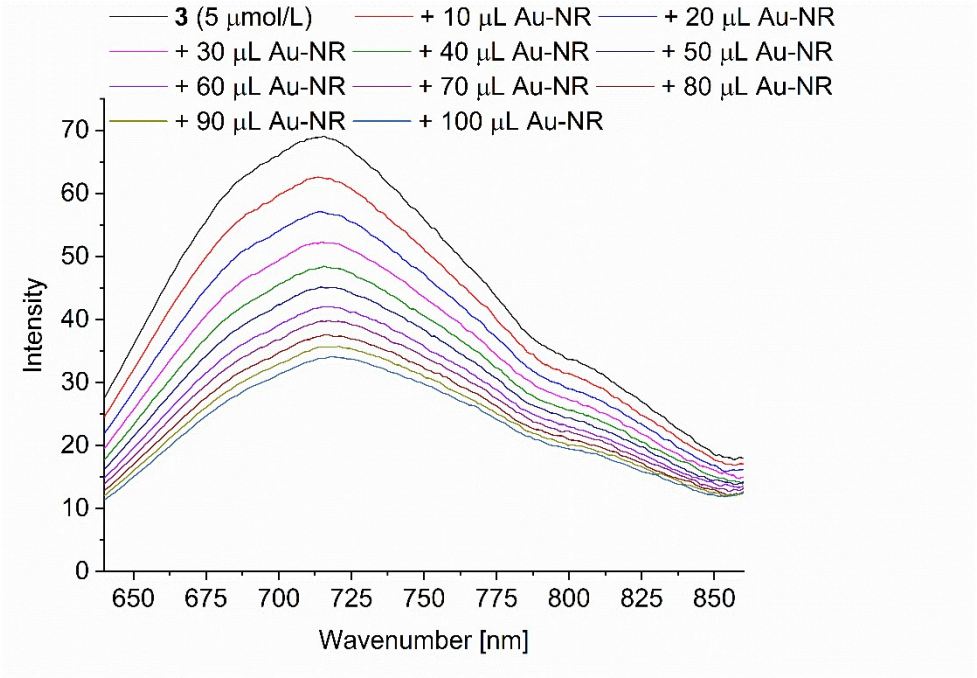


(a)

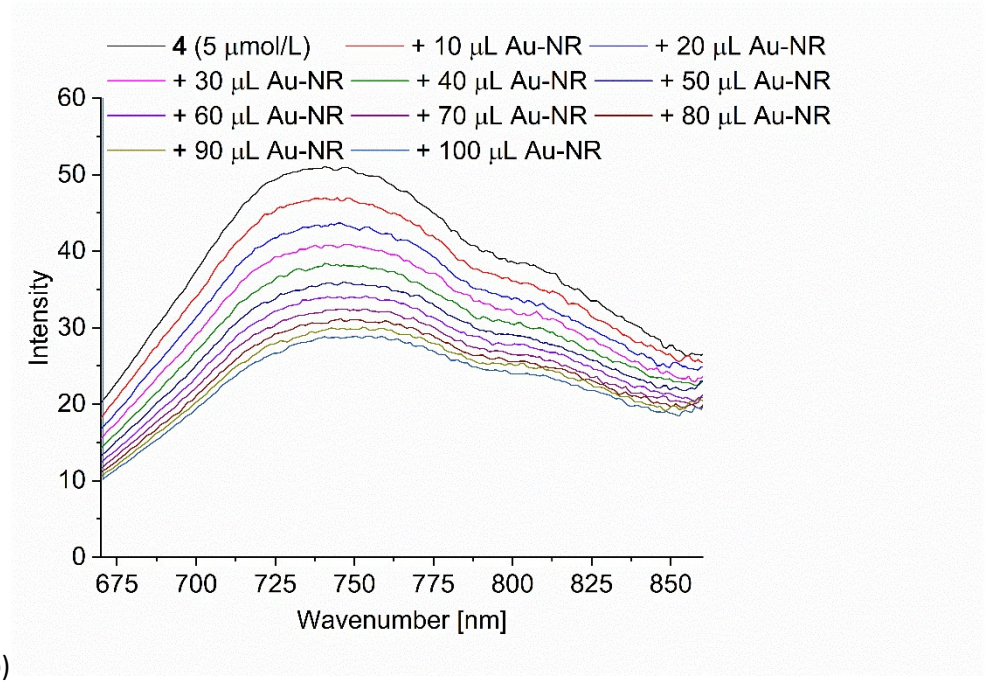


(b)

Figure S24 a)-b) Fluorescence spectra of PD **1** and **2** (c = 3.3 µmol/L) with the stepwise addition of 100 µL Au-NR dispersion (excitation wavelength a) 450 nm b) 465 nm).



(a)



(b)

Figure S25 a)-b) Fluorescence spectra of PD **3** and **4** (c = 5 µmol/L) with the stepwise addition of 100 µL Au-NR dispersion (excitation wavelength a) 466 nm b) 494 nm). Concentrations were higher than for PD **1** and **2** and **5** and **6** due to lower fluorescence intensities.

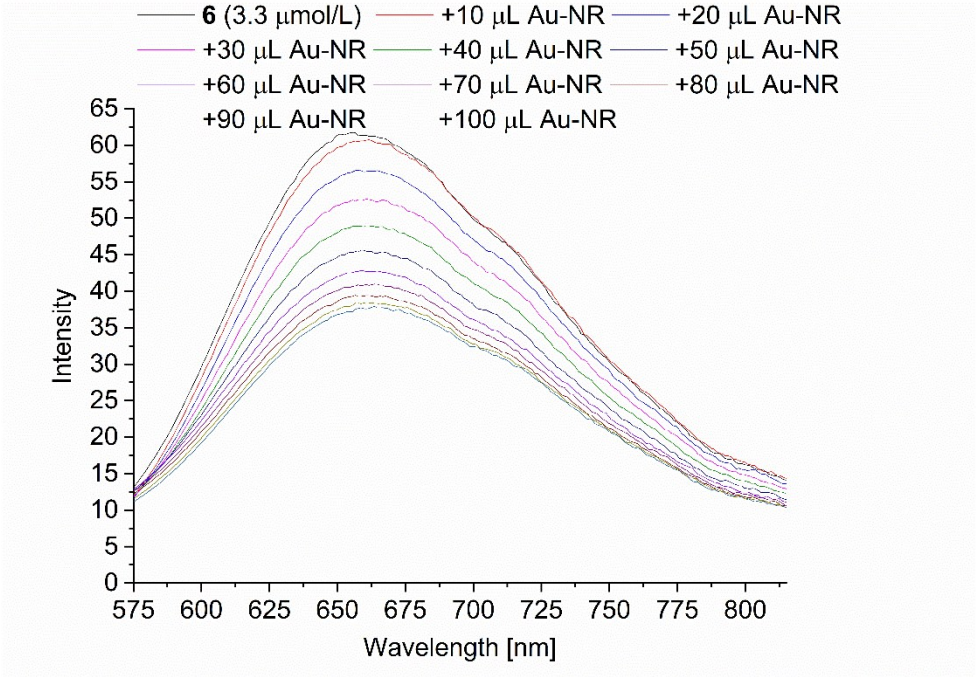


Figure S26 Fluorescence spectra of PD **6** (c = 3 μmol/L) with the stepwise addition of 100 μL Au-NR dispersion (excitation wavelength = 470 nm).

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