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Supplementary Information

Surface modification of silica nanoparticles: a new strategy for the realization of self-organized fluorescence chemosensors

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1. Synthesis of compounds 1-8.

Pyridine-2-carboxylic acid (3-(triethoxysilyl-propyl)-amide (1a): Thionyl chloride (2.56 mL, 35.3 mmol) was slowly added by syringe to a 200 mL solution of picolinic acid (3.77 g, 30.7 mmol) and triethylamine (12.8 mL, 92 mmol) in CH_2Cl_2 at 0°C. The stirred reaction mixture was left at 0°C for 10 minutes and then allowed to warm at room temperature for about 40 minutes. After this time, the dark brown suspension was cooled again to about 0°C and a 150 mL solution of 3-aminopropyltriethoxysilane (10 mL, 42.7 mmol) in CH_2Cl_2 was added dropwise. The reaction mixture was allowed to warm to room temperature under stirring, and after 3 hours (TLC, CH_2Cl_2/MeOH 10:0.2) the solvent was removed by rotary evaporation. The crude product was purified by flash column chromatography (silica gel, CH_2Cl_2) to provide 4.26 g of **1a** (43%) as a dark brown oil. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 0.66 (t, J = 8.5 Hz, 2H, $NCH_2CH_2CH_2$-Si), 1.16 (t, J^3 = 7.0 Hz, 9H, $NCH_2CH_2CH_2$-Si-$(OCH_2CH_3)_3$), 1.71 (m, 2H, $NCH_2CH_2CH_2$-Si), 3.47 (q, 2H, J = 6.7 Hz, $NCH_2CH_2CH_2$-Si), 3.77 (q, J^3 = 7.0 Hz, 6H, $NCH_2CH_2CH_2$-Si-$(OCH_2CH_3)_3$); 7.41 (m, 1H, CH_{Py}); 7.83 (m, 1H, CH_{Py}); 8.18 (m, 2H, CH_{Py} e $NHCH_2CH_2CH_2$-Si); 8.53 (d, J = 4.6 Hz 1H, CH_{Py}). **^{13}C-NMR** (69.9 MHz, $CDCl_3$, 25°C) δ: 6.6 ($NCH_2CH_2CH_2$-Si), 18.1 ($NCH_2CH_2CH_2$-Si-$(OCH_2CH_3)_3$), 23.0 ($NCH_2CH_2CH_2$-Si), 58.1 ($NCH_2CH_2CH_2$-Si-$(OCH_2CH_3)_3$), 50.6 ($NCH_2CH_2CH_2$-Si), 122.2, 126.0, 137.3, 148.0, 150.0 (C_{Py}), 164.2 (C=O). **ESI-MS** (MeOH) m/z: 349 (100%, M+Na^+). **Elemental Analysis** for $C_{15}H_{26}N_2O_4Si$ (326.23 g/mol): calculated: C 55.19; H 8.03; N 8.58; found: C 54.24; H 7.73; N 8.41.

Pyridine-2-carboxylic acid propylamide (1b): 20 mL of a solution of thionyl chloride (0.71 mL, 9.7 mmol) in CH_2Cl_2 were slowly added to 70 mL of a solution of picolinic acid (0.80 g, 6.5 mmol) and triethylamine (1.49 mL, 14.7 mmol) in CH_2Cl_2 at 0°C. The stirred reaction mixture was left at 0°C for 10 minutes and then allowed to warm at room temperature for about 40 minutes. After this time, the dark brown suspension was recooled to about 0°C and 20 mL of a solution of propylamine (0.81 mL, 9.7 mmol) in CH_2Cl_2 were added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 3 hours (TLC, CH_2Cl_2 /EtOH 10:0.2). The reaction mixture was extracted with a Na_2CO_3(5%): brine 1/1 solution (3x200 mL) and with brine (3x100 mL), and the organic phase was dried over anhydrous Na_2SO_4. The solvent was removed by rotary evaporation to provide 1.056 g of **1b** (98%) as a dark brown oil. **^{1}H-NMR** ($CDCl_3$, 250 MHz) δ: 0.86 (t, 2H, J = 7.3 Hz, $NCH_2CH_2CH_3$), 1.53 (m, 2H, $NCH_2CH_2CH_3$), 3.31 (q, 2H, J = 7.3 Hz, $NCH_2CH_2CH_3$), 7.28 (m, 1H, CH_{Py}); 7.70 (m, 2H, CH_{Py} and $NHCH_2CH_2CH_2$), 8.30 (d, 1H, J = 4.6 Hz, H(pyr)). **ESI-MS** (MeOH/TFA 1%) m/z:

165 (100%, $M+H^+$). **Elemental Analysis** for $C_9H_{12}N_2O$ (164.20 g/mol): calculated: C 65.83; H 7.37; N 17.06; found: C 65.53; H 7.49; N 16.77.

2-Chloro-N-pyridin-2-yl-methyl-acetamide (9): A 180 mL THF solution of chloroacetil chloride (4.00 mL, 50.3 mmol) was cooled to -70°C. To this stirred solution was added dropwise a solution of picolylamine (5.14 mL, 50.3 mmol) and TEA (7.00 mL, 50.3 mmol) in 20 mL of THF. The reaction mixture was allowed to warm at room temperature and the reaction monitored by TLC (EtOAc : MeOH 10/1). The reaction mixture was filtered and concentrated to about 2/3 of its initial volume without heating. 200 mL of ethyl acetate were added and the resulting organic phase was extracted with a $NaHCO_3$(5%):brine 1/1 solution and dried over Na_2SO_4. The solvent was removed by rotary evaporation at 20°C to afford 8.92 g of **19** (96%) as a light brown oil. **^{1}H-NMR**, ($CDCl_3$, 250 MHz) δ: 3.74 (s, 2H, (CO)C*H*$_2$Cl), 4.15 (d, J^3 = 5.5 Hz, 2H, (pyr)C*H*$_2$NH(CO)), H(pyr); 6.75 (m, 1H), 6.85 (d, J^3 = 7.5 Hz, 1H), 7.22 (m, 1H), 8.09 (d, broad, 2H, and CH_2N*H*(CO)). **^{13}C-NMR**, (69.9 MHz, $CDCl_3$, 25°C) δ: 42.23 ((CO)*C*H_2Cl), 44.27 ((pyr)*C*H_2(CO)), 121.11, 121.83, 136.25, 148.42, 156.02 (C_{arom}), 166.20 (*C*O). **GC-MS**, (80° C, 3 min.; 15° C / min.; 220° C, 15 min.): t_r 10.8 min. (100%). m/z: 184 $M^{+\cdot}$, 135 (100%), 107, 92.

N-(Pyridin-2-yl)-methyl-2-(3-triethoxysilyl-propylamino)-acetamide (2a): A 10 mL THF solution of APTES (4.73 mL, 20.2 mmol) and TEA (2.82 mL, 20.2 mmol) was added dropwise to a stirred 30 mL THF solution of **9** (3.74 g, 20.2 mmol) at -10°C. The reaction was allowed to warm at room temperature and monitored by TLC (ethyl acetate : methanol 10/1) and GC-MS (120° C, 3 min.; 15° C / min.; 270° C, 15 min, T_{inj} 270°C: tr(**2a**) 14.7 min). The reaction mixture was filtered and the solvent was evaporated under reduced pressure. The crude product was purified by flash chromatography (silica gel, ethyl acetate : methanol 10/1) to give **2a** (2.77 g, 37%) as light brown oil. **^{1}H-NMR**, ($CDCl_3$, 250 MHz) δ**:** 0.66 (t, J^3 = 8.5 Hz, 2H, $NCH_2CH_2CH_2$-Si), 1.21 (t, J^3 = 7.0 Hz, 9H, $NCH_2CH_2CH_2$-Si-(OCH_2CH_3)$_3$), 1.62 (m, J^3 = 8.5 Hz, J^3 = 6.75 Hz, 2H, $NCH_2CH_2CH_2$-Si), 2.63 (t, J^3 = 6.75 Hz, 2H, $NCH_2CH_2CH_2$-Si), 3.33 (s, 2H, (CO)C*H*$_2$NH), 3.81 (q, J^3 = 7.0 Hz, $NCH_2CH_2CH_2$-Si-(OCH_2CH_3)$_3$), 4.58 (d, J^3 = 5.5 Hz, (CO)NHC*H*$_2$-(pyr)), 8.32 (t, broad, J^3 = 5.5 Hz, (CO)N*H*CH_2-(pyr)), H(pyr); 7.17 (m, J^3 = 5.5 Hz, J^3 = 7.75 Hz, 1H), 7.26 (d, J^3 = 7.75 Hz, 1H), 7.64 (t, 7.5 Hz, 1H), 8.53 (d, J^3 = 4.75 Hz, 1H). **^{13}C-NMR**, (69.9 MHz, $CDCl_3$, 25°C) δ: 7.72 ($NCH_2CH_2CH_2$-Si), 18.14 ($NCH_2CH_2CH_2$-Si-(OCH_2CH_3)$_3$), 23.20 ($NCH_2CH_2CH_2$-Si), 44.05 ((CO)NH*C*H_2-(pyr)), 52.31, 52.62

((CO)CH_2NH) and N$CH_2CH_2CH_2$-Si), 58.13 (NCH$_2$CH$_2$CH$_2$-Si-(OCH_2CH_3)$_3$), 121.53, 122.01, 136.47, 148.95, 157.06, 171.99 (C_{arom}). **GC-MS**, (120° C, 3 min.; 15° C / min.; 270° C, 15 min, T_{inj} 270°C): t_r 14.7 min. (100%). m/z: 369 $M^{+\cdot}$, 234, 188 (100%), 144. **Elemental Analysis** per $C_{17}H_{31}N_3O_4Si$ (369.53 g/mol): calculated: C 55.25; H 8.46; N 11.37; found: C 53.61; H 8.46; N 11.55.

N-(Pyridin-2-yl)-methyl-2propylamino-acetamide (2b): A 20 mL THF solution of propylamine (0.28 mL, 3.35 mmol) and TEA (0.47 mL, 3.35 mmol) was added dropwise to a stirred 30 mL THF solution of **9** (0.62 g, 3.35 mmol). The reaction mixture was allowed to warm at room temperature and stirred for about 24 h, monitored by TLC (CH_2Cl_2/MeOH/NH_3 10/1/0.03). The reaction mixture was filtered and the solvent was evaporated under reduced pressure. The crude product was purified by flash chromatography (silica gel, CH_2Cl_2/MeOH/NH_3 10/1/0.03) to give **2b** (0.20 g, 30%) as brown oil. **^{1}H-NMR**, ($CDCl_3$, 250 MHz) δ**:** 1.02 (t, J^3 = 7.5 Hz, 3H, NCH$_2$CH$_2$$CH_3$), 1.60 (m, J^3 = 7.1 Hz, J^3 = 7.3 Hz, 2H, NCH$_2$CH_2CH$_3$), 2.25 (s, 1H, NHCH$_2$CH$_2$CH$_3$), 2.70 (t, J^3 = 7.1 Hz, 2H, NCH_2CH$_2$CH$_3$), 3.46 (s, 2H, (CO)CH_2NH), 4.69 (d, J^3 = 5.5 Hz, (CO)NHCH_2-(pyr)), 8.30 (s, (CO)NHCH$_2$-(pyr)), H(pyr); 7.28 (m, J^3 = 0.8 Hz, J^3 = 5.0 Hz, 1H), 7.29 (d, J^3 = 9.0 Hz, 1H), 7.72 (t, J^3 = 7.5 Hz, 1H), 8.64 (d, J^3 = 4.3 Hz, 1H). **^{13}C-NMR**, (69.9 MHz, $CDCl_3$, 25°C) δ: 11.65 (NCH$_2$CH$_2$$CH_3$), 23.10 (NCH$_2$$CH_2CH_3$), 44.33 ((CO)NH$CH_2$-(pyr)), 52.03, 52.45 ((CO)CH$_2$NH) and NCH$_2$CH$_2$CH$_3$), 121.99, 122.36, 136.80, 149.25, 157.09, 171.87 (C_{arom}). **ESI-MS** (MeOH) m/z: 208.08 (100%, M+H^+). **Elemental Analysis** per $C_{11}H_{17}N_3O$ (207.14 gr/mol): calculated: C 63.74; H 8.27; N 20.27; found: C; H; N.

3-(Dansylamido)-propyl-triethoxysilane (3a): A solution of dansylchloride (0.90 g, 3.3 mmol) in CH_2Cl_2 (20 mL) was added to a solution of 3-aminopropyltriethoxysilane (APTES, 0.80 mL, 3.4 mmol) and triethylamine (0.60 mL, 4.3 mmol) in the same solvent (20 mL). The mixture was stirred at room temperature for 2 h monitoring the reaction by TLC (toluene/ethyl acetate 1:1). The solvent was evaporated under reduced pressure and the crude product was purified by flash chromatography (silica gel, toluene/ethyl acetate 1:1) to afford 1.51 g (99%) of **3a** as a yellow-bright green oil. **^{1}H-NMR** (250 MHz, $CDCl_3$, 25°C) δ (ppm): 0.53 (t, J = 8.1 Hz, 2H, NCH$_2$CH$_2$CH_2-Si), 1.15 (t, J^3 = 7.0 Hz, 9H, NCH$_2$CH$_2$CH$_2$-Si-(OCH$_2$CH_3)$_3$), 1.55 (m, 2H, NCH$_2$CH_2CH$_2$-Si), 2.86 (s 6H, N(CH_3)$_2$), 2.98 (q 2H, J^3 = 5.0 Hz, NCH_2CH$_2$CH$_2$-Si), 3.71 (q, J^3 = 7.0 Hz, 6H, NCH$_2$CH$_2$CH$_2$-Si-(OCH_2CH$_3$)$_3$); 5.84 (t, J = 5.6 Hz, 1H, NHCH$_2$CH$_2$CH$_2$-Si), 7.16 (d, J = 7.4 Hz, 1H, CH_{DNS}), 7.53 (q, J = 7.5 Hz, 2H, CH_{DNS}), 8.30 (d, J = 7.5 Hz, 2H,

CH_{DNS}), 8.46 (d, J = 8.6 Hz, 1H, CH_{DNS}), 8.53 (m, J = 7.5 Hz, 1H, CH_{DNS}). **^{13}C-NMR** (62.9 MHz, $CDCl_3$, 25 °C) δ (ppm): 7.42 ($NCH_2CH_2CH_2$-Si), 18.3 ($NCH_2CH_2CH_2$-Si-(OCH_2CH_3)$_3$), 23.1 ($NCH_2CH_2CH_2$-Si), 45.7 ($NCH_2CH_2CH_2$-Si), 58.3 ($NCH_2CH_2CH_2$-Si-(OCH_2CH_3)$_3$), 115.2 ($N(CH_3)_2$), 119.2, 123.2, 125.3, 128.3, 129.0, 129.5, 129.9, 130.2, 135.5, 151.8 (C_{DNS}). **ESI-MS** (MeOH) m/z: 477 (100%, M+Na^+). **Elemental analysis** for $C_{21}H_{34}N_2O_5SSi$ (412.58 g/mol): calculated: C 55.48; H 7.54; N 6.16; S 7.05; found: C 55.58; H 7.59; N 6.15; S 6.93.

5-Dimethylamino-naphthalene-1-sulfonic acid propylamide (3b): 50 mL of a CH_2Cl_2 solution of dansylchloride (270 mg, 1.0 mmol) were added to a stirred 50 mL cooled (0°C) solution of propylamine (0.21 mL, 4.6 mmol) in CH_2Cl_2. The reaction was allowed to warm at room temperature and monitored by TLC (CH_2Cl_2). The reaction mixture was extracted with a Na_2CO_3(10%): brine 1/1 solution and the organic phase was dried over anhydrous sodium sulphate. Product **3b** was recovered in quantitative yield after evaporation of the solvent. **^{1}H-NMR** (250 MHz, $CDCl_3$, 25°C) δ (ppm): 0.77 (t, J = 8.1 Hz, 2H, $NCH_2CH_2CH_3$), 1.41 (m, 2H, $NCH_2CH_2CH_3$), 2.81-2.89 (m 8H, $NCH_2CH_2CH_3$ e $N(CH_3)_2$), 4.62 (brad, 1H, $NHCH_2CH_2CH_3$), 7.19 (d, J = 7.4 Hz, 1H, CH_{DNS}), 7.49-7.60 (m, 2H, CH_{DNS}), 8.23-8.31 (m, 2H, CH_{DNS}), 8.52 (d, J = 8.3 Hz, 1H, CH_{DNS}). **^{13}C-NMR** (62.9 MHz, $CDCl_3$, 25 °C) δ (ppm): 14.0 ($NCH_2CH_2CH_3$), 22.8 ($NCH_2CH_2CH_3$), 50.5 ($NCH_2CH_2CH_3$), 115.1 ($N(CH_3)_2$), 118.7, 123.2, 125.3, 128.2, 129.0, 129.5, 129.9, 130.3, 134.9, 152.0 (C_{DNS}). **ESI-MS** (MeOH/TFA 1%) m/z: 293 (100%, M+H^+), 607 (12%,2M+Na^+).

(7-Nitro-benzo[1,2,5]oxadiazol-4-yl)-(3-triethoxysilyl-propyl)-amine (4a): A 10 mL toluene solution of APTES (0.47 mL, 2.0 mmol) was slowly added to a stirred 10 mL solution of 4-Chloro-7-nitro-benzo[1,2,5]oxadiazole (NBD-Cl, 400 mg, 2.0 mmol) and triethylamine (0.36 mL, 2.6 mmol) in the same solvent. The reaction was monitored by TLC (petroleum ether : ethyl acetate 1/1). The crude product obtained by solvent evaporation was purified by flash chromatography (silica gel, petroleum ether : ethyl acetate 1/1) to afford 395 mg of the title product **4a** (51%), as a red-brown solid. **^{1}H-NMR** (250 MHz, $CDCl_3$, 25°C) δ: 0.768 (t, J^3 = 7.25 Hz, 2H, $NCH_2CH_2CH_2$-Si), 1.24 (t, J^3 = 7.25 Hz, 9H, $NCH_2CH_2CH_2$-Si-(OCH_2CH_3)$_3$), 1.95 (m, J^3 = 7.25 Hz, 2H, $NCH_2CH_2CH_2$-Si), 3.53 (m, J^3 = 7.25 Hz, 2H, $NCH_2CH_2CH_2$-Si), 3.86 (q, J^3 = 7.25 Hz, 6H, $NCH_2CH_2CH_2$-Si-(OCH_2CH_3)$_3$), 6.18 (d, J^3 = 8.6 Hz, 1H), 6.88 (t broad, 1H, (NBD)-$NHCH_2CH_2CH_2$), 8.48 (d, J^3 = 8.6 Hz, 1H). **^{13}C-NMR** (69.9MHz, $CDCl_3$, 25°C) δ: 8.12 ($NCH_2CH_2CH_2$-Si), 18.59 ($NCH_2CH_2CH_2$-Si-(OCH_2CH_3)$_3$), 22.08 ($NCH_2CH_2CH_2$-Si), 46.43 ($NCH_2CH_2CH_2$-Si), 58.99 ($NCH_2CH_2CH_2$-Si-(OCH_2CH_3)$_3$), 98.92,

123.33, 137.18, 144.27, 144.58, 144.80 (C_{arom}). **ESI-MS** (MeOH) m/z: 439 (100%, M+MeOH+Na^+). **Elemental analysis** for $C_{15}H_{24}N_4O_6Si$ (384.47 g/mol): calculated: C 46.86; H 6.29; N 14.57; found: C 47.16; H 6.17; N 14.09.

(7-Nitro-benzo[1,2,5]oxadiazol-4-yl)-propyl-amine (4b), Propylamine (0.20 mL, 2.5mmol) was added to 12 mL of a CH_3CN solution of 4-chloro-7-nitrobenzofurazan (4-chloro-7-nitro-1,2,3-benzoxadiazole) (0.10 g, 0.5 mmol). The reaction mixture was stirred for 12 h, diluted with 100 mL of CH_2Cl_2 and exctracted with a Na_2CO_3(10%): brine 1/1 solution. The organic phase was dried over anhydrous sodium sulphate. 0.10 g (89%) of product **4b** were recovered after evaporation of the solvent. **^{1}H-NMR** (250 MHz, $CDCl_3$, 25°C) δ: 1.11 (t, J^3 = 7.25 Hz, 3H, $NCH_2CH_2CH_3$), 1.86 (m, J^3 = 7.25 Hz, 2H, $NCH_2CH_2CH_3$), 3.47 (m, J^3 = 7.25 Hz, 2H, $NCH_2CH_2CH_3$), 6.18 (d, J^3 = 8.5 Hz, 1H), 8.50 (d, J^3 = 8.5 Hz, 1H). **ESI-MS** (MeOH/H_20/TFA 66:33:1) m/z: 223 (100%, M+H^+), 245 (35%, M+Na^+). **Elemental Analysis** for $C_9H_{10}N_4O_3$ (222.20 g/mol): calculated: C 48.65; H 4.54; N 25.21; found: C 48.52; H 4.88; N 24.89.

2-Oxo-2H-chromene-3-carboxylic acid (3-triethoxysilyl-propyl)-amide (5a): Thionyl chloride (0.57 mL, 7.8 mmol), was added to a 100 mL of a CH_2Cl_2 solution of coumarin 3-carboxylic acid (1.30 g, 6.8 mmol) and triethylamine (2.98 mL, 21.4 mmol) at about 0°C. The reaction mixture was allowed to warm at room temperature for about 40 minutes, and then cooled again to 0° C before APTES (2.50 mL, 10.7 mmol) was added with a syringe. The reaction was monitored by TLC (toluene : ethyl acetate 1/1). Solvent was evaporate and the crude product was purified by flash chromatography (silica gel, toluene : ethyl acetate 7/3) to give 1.96 g of **5a** (73%) as a yellow-brown solid. **^{1}H-NMR** (300 MHz, $CDCl_3$, 25°C) δ: 0.70 (t broad, J^3 = 8.9 Hz, 2H, $NCH_2CH_2CH_2$-Si), 1.23 (t, J^3 = 10.5 Hz, 9H, $NCH_2CH_2CH_2$-Si-$(OCH_2CH_3)_3$), 1.75 (m, 2H, $NCH_2CH_2CH_2$-Si), 3.47 (q, J^3 = 10.7 Hz, 2H, $NCH_2CH_2CH_2$-Si), 3.83 (q, J^3 = 10.5 Hz, 6H, $NCH_2CH_2CH_2$-Si-$(OCH_2CH_3)_3$), 7.52 (m, $4H_{arom}$), 8.88 (t broad, 1H, $(CO)NHCH_2$), 8.91 (s, 1H, H_{arom}). **^{13}C-NMR** (69.9MHz, $CDCl_3$, 25°C) δ: 7.73 ($NCH_2CH_2CH_2$-Si), 18.13 ($NCH_2CH_2CH_2$-Si-$(OCH_2CH_3)_3$), 22.82 ($NCH_2CH_2CH_2$-Si), 42.32 ($NCH_2CH_2CH_2$-Si), 58.89 ($NCH_2CH_2CH_2$-Si-$(OCH_2CH_3)_3$), 116.9, 120.1, 124.0, 126.7, 131.2, 133.1, 145.6, 150.9 (C_{arom}), 162.0, 167.9 (C=O). **ESI-MS** (MeOH) m/z: 416 (100%, M+Na^+). **Elemental Analysis** for $C_{19}H_{27}N_2O_6Si$ (393.51 g/mol): calculated: C 57.99; H 6.92; N 3.56; found: C 58.32; H 7.19; N 3.63.

Coumarin 3-carboxylic acid propylamide (2-Oxo-4a,8a-dihydro-2H-chromene-7-carboxylic acid propylamide, 5b): Thionyl chloride (0.71 mL, 9.7 mmol) was slowly added by syringe to 100 mL of a CH_2Cl_2 solution of coumarin 8-carboxylic acid (1.50 g, 7.89 mmol) and triethylamine (3.44 mL, 24.7 mmol) at 0°C. The stirred reaction mixture was left at 0°C for 10 minutes and then allowed to warm at room temperature for about 40 minutes. After this time, the light brown suspension was cooled again to about 0°C and 20 mL of a CH_2Cl_2 solution of propylamine (1.01 mL, 12.3 mmol) wewe added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 3 hours (TLC, toluene / ethyl acetate 1:1). The reaction mixture was extracted with a Na_2CO_3(5%): brine 1/1 solution and then with brine and the organic phase was dried over anhydrous Na_2SO_4. The solvent was evaporated to provide 1.56 g of **5b** (85%). **^{1}H-NMR** (250 MHz, $CDCl_3$, 25°C) δ: 1.00 (t, J^3 = 7.5 Hz, 3H, $NCH_2CH_2CH_3$), 1.66 (m, 2H, $NCH_2CH_2CH_3$), 3.44 (q, J^3 = 5.8 Hz, 2H, $NCH_2CH_2CH_3$), 7.35-7.43 (m, 4H_{arom}), 7.63-7.72 (m, 4H_{arom}), 8.82 (s, broad, 1H, (CO)N*H*CH_2), 8.92 (s, 1H, H_{arom}). **ESI-MS** (MeOH/TFA 1%) m/z: 232 (100%, $M+H^+$), 254 (9%, $M+Na^+$). **Elemental Analysis** for $C_{13}H_{13}NO_3$ (231.25 g/mol): calculated: C 67.52; H 5.95; N 6.10; found: C 67.52; H 5.95; N 6.10.

2-Allyl-benzo[de]isoquinoline-1,3-dione (10): 1,8-Naphtalic anhydride (3.00 g, 15.1 mmol) was dissolved in 100 mL of anhydrous dimethylacetamide. To this solution was added allylamine (2.36 mL, 31.3 mmol), and the reaction mixture was stirred at 100°C for 2 h. The solvent was evaporated under vacuum, and the crude product was purified by flash chromatography (silica gel, eluente) to give 2.27 g of **20** (76%). **^{1}H-NMR** (250 MHz, $CDCl_3$, 25°C) δ: 4.64 (d, J^3 = 5.5 Hz, 2H, NC*H*$_2$(allylic)), 5.13 (d, J^3 = 10.25 Hz, 1H), 5.25 (d, J^3 = 17.25 Hz, 1H), 5.91 (m, 1H),), 7.51 (dd, J^3 = 7.5 Hz, J^3 = 7.25 Hz, 2H), 7.96 (dd, J^3 = 7.25 Hz, J^4 = 0.75 Hz), 8.31 (dd, J^3 = 7.5 Hz, J^4 = 0.75 Hz,). **^{13}C-NMR** (69.9 MHz, $CDCl_3$, 25°C) δ: 42.48 (N*C*H_2(allylic)), 117.89, 122.40, 126.91, 127.90, 131.13, 131.42, 132.42, 133.91(C_{arom} + $C_{vinylic}$), 163.65 (*C*O).

2-(3-triethoxysilyl-propyl)-benzo[de]isoquinoline-1,3-dione (6a): A solution of **10** (1.56 g, 6.6 mmol) and triethoxysilane (12.11 mL, 66.0 mmol) was stirred under N_2 atmosphere at room temperature. To this solution were added few drops of a solution of H_2PtCl_6*H_2O in 2-propanol (0.17 mg/mL). The reaction mixture was stirred for 18 h and after this time the triethoxysilane excess was removed by distillation under reduced pressure. The crude product was purified by flash chromatography (silica gel, eluente) to afford 1.47 g of coumpound **6a** (56%), as a light

yellow oil. **^{1}H-NMR** (250 MHz, $CDCl_3$, 25°C) δ: 0.71 (t, J^3 = 6.5 Hz, 2H, $NCH_2CH_2CH_2$-Si), 1.16 (t, J^3 = 7.0 Hz, 9H, $NCH_2CH_2CH_2$-Si-$(OCH_2CH_3)_3$), 1.80 (m, 2H, $NCH_2CH_2CH_2$-Si), 3.77 (q, J^3 = 7.0 Hz, 6H, $NCH_2CH_2CH_2$-Si-$(OCH_2CH_3)_3$), 4.08 (t, J^3 = 7.6 Hz, 2H, $NCH_2CH_2CH_2$-Si), 7.61 (dd, J^3 = 8.25 Hz, J^3 = 7.5 Hz, 2H), 8.06 (dd, J^3 = 8.25 Hz, J^4 = 1.25 Hz), 8.42 (dd, J^3 = 7.5 Hz, J^4 = 1.25 Hz). **^{13}C-NMR** (69.9 MHz, $CDCl_3$, 25°C) δ: 8.07 ($NCH_2CH_2CH_2$-Si), 18.42 ($NCH_2CH_2CH_2$-Si-$(OCH_2CH_3)_3$), 21.58 ($NCH_2CH_2CH_2$-Si), 42.861 ($NCH_2CH_2CH_2$-Si), 58.42 ($NCH_2CH_2CH_2$-Si-$(OCH_2CH_3)_3$), 122.58, 126.81, 127.93, 130.98, 131.43, 133.71 (C_{arom}), 163.93 (*C*O). **ESI-MS** (MeOH) m/z: 356 (100%, M-EtO$^-$), 424 (100%, M+Na$^+$).

2-(3-propyl)-benzo[de]isoquinoline-1,3-dione (6b): 1,8-Naphtalic anhydride (1.50 g, 7.55 mmol) was dissolved in 5 mL of anhydrous dimethylacetamide. To this solution was added propylamine (1.24 mL, 15.1 mmol), and the reaction mixture was stirred at 100°C for 2 h. The solvent was evaporated under vacuum, the crude product was dissolved in 50 ml CH_2CH_2 and extracted with a 0.5 M citric acid solution (3 × 50 ml). The organic phase was dried over anhydrous Na_2SO_4 and the solvent was evaporated to provide 1.47 g of **2b** (81.4 %). **^{1}H-NMR** (250 MHz, $CDCl_3$, 25°C) δ: 1.02 (t, J^3 = 7.5 Hz, 3H, $NCH_2CH_2CH_3$), 1.76 (m, J^3 = 7.7 Hz, J^3 = 7.5 Hz, 2H, $NCH_2CH_2CH_3$), 4.15 (t, J^3 = 7.6 Hz, 3H, $NCH_2CH_2CH_3$), 7.75 (dd, J^3 = 7.5 Hz, J^3 = 7.25 Hz, 2H), 8.20 (dd, J^3 = 8.3 Hz, J^4 = 0.75 Hz, 2H), 8.59 (dd, J^3 = 6.2 Hz, J^4 = 1.1 Hz, 2H).

6-Methoxy-naphthalene-2-carboxylic acid (3-triethoxysilyl-propyl)-amide (7a): 6-Methoxy-2-naphthoic acid (0.10 g, 0.49 mmol), ethyl-diisopropyl-amine (0.33 mL, 1.9 mmol) and DMF (0.15 mL), were dissolved in 25 mL of anhydrous toluene, and this solution was cooled at 0°C. Thionyl chloride (0.060 ml, 0.82 mmol) was then added by a syringe, and the reaction mixture was warmed to room temperature and stirred for 2 h. After this time APTES (0.23 mL, 0.98 mmol) was added and the reaction mixture was stirred for 12 h. The solvent was evaporated under reduced pressure and the crude product was purified by flash chromatography (silica gel, ethyl acetate / petroleum ether 1:2) to give 0.13 g of **7a** (66%). **^{1}H-NMR** (250 MHz, $CDCl_3$, 25°C) δ: 0.74 (t, J^3 = 6.5 Hz, 2H, $NCH_2CH_2CH_2$-Si), 1.23 (t, J^3 = 7.0 Hz, 9H, $NCH_2CH_2CH_2$-Si-$(OCH_2CH_3)_3$), 1.81 (m, 2H, $NCH_2CH_2CH_2$-Si), 3.50 (q, J^3 = 7.6 Hz, 2H, $NCH_2CH_2CH_2$-Si), 3.80-3.97 (m, 9H, $NCH_2CH_2CH_2$-Si-$(OCH_2CH_3)_3$; -OCH_3), 6.93 (t broad, 1H, (CO)N*H*CH_2)), 7.12 (m, 1H), 7.71-7.82 (m, 3H), 8.21-8.30 (m, 1H). **^{13}C-NMR** (69.9 MHz, $CDCl_3$, 25°C) δ: 7.73 ($NCH_2CH_2CH_2$-Si), 18.14 ($NCH_2CH_2CH_2$-Si-$(OCH_2CH_3)_3$), 22.82 ($NCH_2CH_2CH_2$-Si), 42.24 ($NCH_2CH_2CH_2$-Si), 55.15 (-OCH_3)58.32 ($NCH_2CH_2CH_2$-Si-$(OCH_2CH_3)_3$), 105.41, 119.38, 124.19, 126.79, 126.98, 127.86, 129.79, 130.20,135.95 ($C_{aromatic}$), 158.73, 167.48 (*C*O).

Elemental Analysis for $C_{21}H_{31}NO_5Si$ (405.56 g/mol): calculated: C 62.19; H 7.70; N 3.45; found: C 61.45; H 7.13; N 3.83.

6-Methoxy-naphthalene-2-carboxylic acid propylamide (7b): 6-Methoxy-2-naphthoic acid (0.097 g, 0.48 mmol), ethyl-diisopropyl-amine (0.33 mL, 1.9 mmol) and DMF (0.15 mL), were dissolved in 15 mL of anhydrous toluene, and this solution was cooled at 0°C. Thionyl chloride (0.060 ml, 0.82 mmol) was then added by a syringe, and the reaction mixture was warmed to room temperature and stirred for 2 h. After this time propylamine (0.060 mL, 0.73 mmol) was added and the reaction mixture was stirred for 12 h. The solvent was evaporated under reduced pressure and the crude product was dissolved in CH_2Cl_2 and extracted with a 0.5 M citric acid solution, saturated Na_2CO_3 and water to give 0.089 g of **7b** (76%). **^{1}H-NMR** (250 MHz, $CDCl_3$, 25°C) δ: 1.01 (t, J^3 = 7.0 Hz, 3H, $NCH_2CH_2C\mathit{H_3}$), 1.71 (t, J^3 = 7.0 Hz, 2H, $NCH_2C\mathit{H_2}CH_3$), 3.47 (q broad, 2H, $NC\mathit{H_2}CH_2CH_3$), 3.93 (s, 3H, -$OC\mathit{H_3}$), 6.25 (s broad, 1H, (CO)N$\mathit{H}CH_2$)), 7.16 (m, 1H), 7.74-7.82 (m, 3H), 8.20 (m, 1H).

7-Methoxy-4-[(3-triethoxysilyl-propylamino)-methyl]-chromen-2-one (8a): A 5 mL CH_3CN solution of APTES (0.52 mL, 2.2 mmol) and ethyl-diisopropyl-amine (0.20 mL, 2.6 mmol) was added to a 25 mL stirred solution of 4-bromomethyl-7-methoxy coumarin (0.30 g, 1.1 mmol) in the same solvent. The reaction mixture was warmed at 60°C for 6 h (TLC, CH_2Cl_2: EtOH 5:2) and then stirred at room temperature for 24 h. The solvent was removed by rotary evaporation and the crude product was purified by flash chromatography (silica gel, CH_2Cl_2: EtOH 5:2) to effort 0.40 g (88%) of **8a** as a light brown solid.
^{1}H-NMR (250 MHz, $CDCl_3$, 25°C) δ: 1.11 (t, J^3 = 7.25 Hz, 2H, $NCH_2CH_2C\mathit{H_2}$-Si), 1.65 (t, J^3 = 7.25 Hz, 9H, $NCH_2CH_2CH_2$-Si-($OCH_2C\mathit{H_3}$)$_3$), 2.15 (m, J^3 = 7.25 Hz, 2H, $NCH_2C\mathit{H_2}CH_2$-Si), 3.22 (m, J^3 = 7.25 Hz, 2H, $NC\mathit{H_2}CH_2CH_2$-Si), 4.18-4.30 (m, 8H, $NCH_2CH_2CH_2$-Si-($OC\mathit{H_2}CH_3$)$_3$; -$NHC\mathit{H_2}$-arom), 4.42 (s, 3H; -$OC\mathit{H_3}$), 6.86 (s, 1H), 7.21-7.29 (m, 2H, H_{arom}), 8.01 (d, J^3 = 8.6 Hz, 1H). **^{13}C-NMR** (69.9MHz, $CDCl_3$, 25°C) δ: 7.61 ($NCH_2CH_2\mathit{C}H_2$-Si), 18.04 ($NCH_2CH_2CH_2$-Si-($OCH_2\mathit{C}H_3$)$_3$), 22.59 ($NCH_2\mathit{C}H_2CH_2$-Si), 48.76 ($N\mathit{C}H_2CH_2CH_2$-Si), 51.92 (-$NH\mathit{C}H_2$-arom)55.50 ($O\mathit{C}H_3$), 58.16 ($NCH_2CH_2CH_2$-Si-($O\mathit{C}H_2CH_3$)$_3$),100.72, 110.25, 111.67, 112.10, 124.83, 152.80, 155.16, 161.18 (C_{arom}), 162.34 (C=O).

7-Methoxy-4-propylaminomethyl-4a,8a-dihydro-chromen-2-one (8b): Propylamine (0.092 mL, 1.1 mmol) and EDA (0.10 ml, 2.6mmol) were added to 25 mL of a CH_3CN stirred suspension of 4-bromomethyl-7-methoxy coumarin (0.150 g, 0.56 mmol). The reaction mixture

was warmed at 60°C for 3 h (TLC, CH_2Cl_2: EtOH 5:2) and then stirred at room temperature for 48 h. The solvent was removed by rotary evaporation and the crude product was purified by flash chromatography (silica gel, CH_2Cl_2: EtOH 5:2) to effort 0.12 g (85%) of **8b** as a light brown solid. **^{1}H-NMR** (250 MHz, d_6-DMSO, 25°C) δ: 0.95 (t, J^3 = 7.5 Hz, 3H, $NCH_2CH_2CH_3$), 1.26 (m, J^3 = 5 Hz, J^3 = 6 Hz, 2H, $NCH_2CH_2CH_3$1.69 (m, J^3 = 7.5 Hz, 2H, $NCH_2CH_2CH_3$), 3.32 (s, 2H, -$NHCH_2$-arom), 3.90 (s; 3H, -OCH_3), 4.43 (s, 1H, -CH_2NHCH_2-), 6.49 (s, 1H, H_{arom}), 7.08-7.00 (m, 2H, H_{arom}), 7.75 (d, J^3 = 8.8 Hz, 1H).

2. Potentiometric titrations

Table 1 Deprotonation and Cu(II) complexation constants for ligands **1b-2b** determined from potentiometric titrations.

	H_nL^{n+}		$[L_nCu]^{2-n}$		
Ligand	pK^1	pK^2	log K_{11}	log K_{12}	log K_{13}
1b	1.93	-	-	-8.6	-17.6
2b	8.18	3.96	3.3	-	-

[a] 0.1 M NaCl, 25° C. [b] $K_{1n} = [ML_n^{2-n}]\cdot[H^+]^n/[LH]^n\cdot[M^{2+}]$

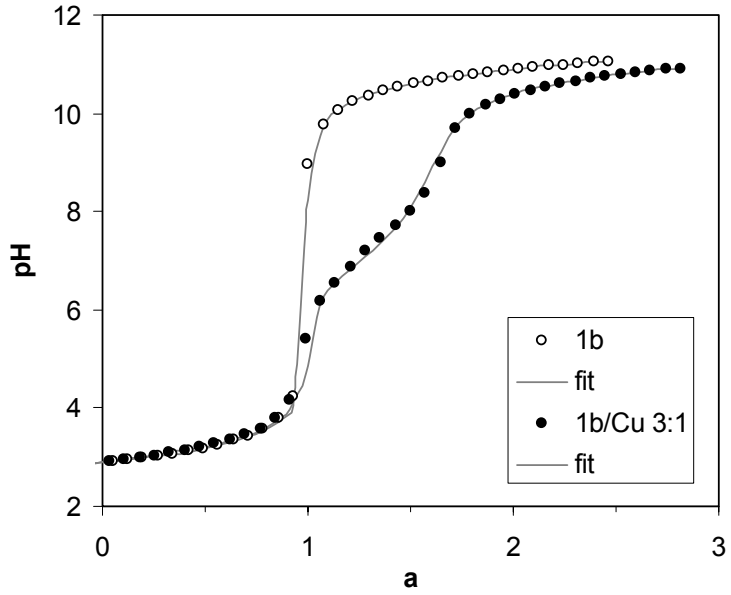

Figure S1. Potentiometric titrations of **1b**·HCl (○) and **1b**·HCl in the presence of 0.33 equivalents of $Cu(NO_3)_2$ at 25° C. [**1b**] = 1.34 mM, $[Cu(NO_3)_2]$ = 0.46 mM, [NaCl] = 0.1 M. a = number of added equivalents of NaOH, the lines report the calculated curves.

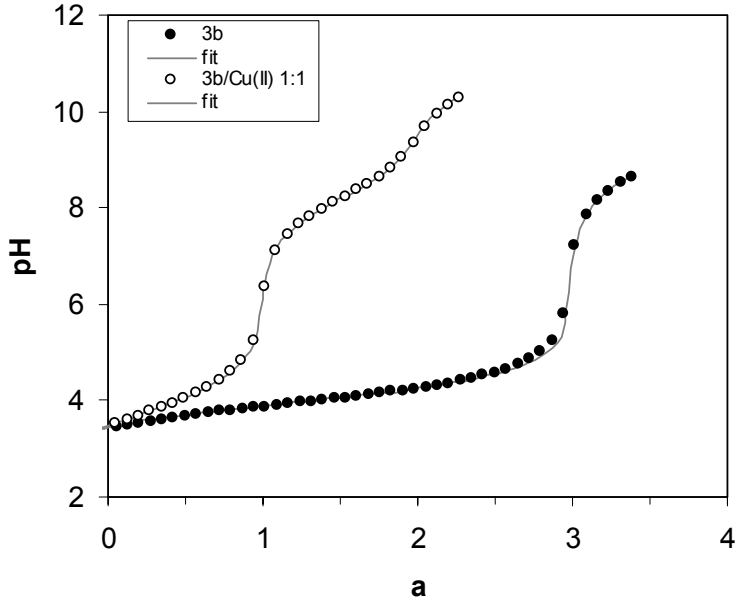

Figure S2. Potentiometric titrations of **2b**·2HCl (○) and **2b**·2HCl in the presence of one equivalent of $Cu(NO_3)_2$ at 25° C. [**1b**] = 1.34 mM, [$Cu(NO_3)_2$] = 0.46 mM, [NaCl] = 0.1 M. a = number of added equivalents of NaOH, the lines report the calculated curves.

3. Fluorescence quenching with 2a/3a CSNs

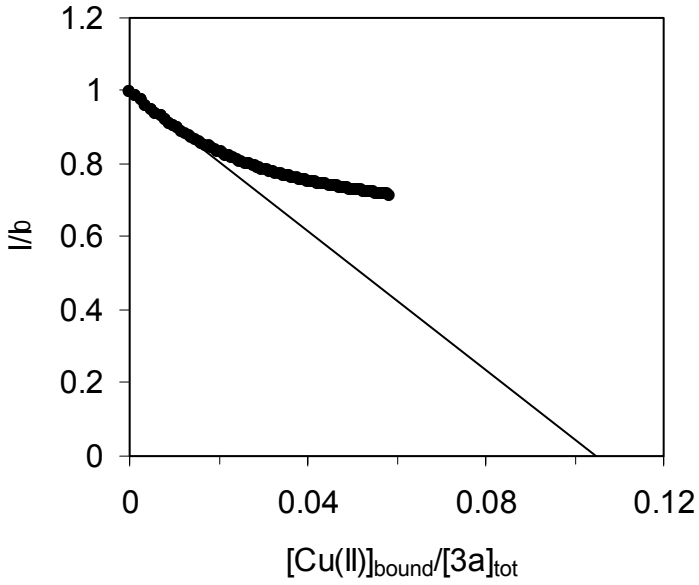

Figure S3. Relative fluorescence emission versus bound Cu(II) to dye ratio for χ = 0.02 **2a**/**3a** CSNs. (0.003 mg/mL, $[\mathbf{2a}]_{tot} = 8.9 \cdot 10^{-8}$ M, $[\mathbf{3a}]_{tot} = 4.4 \cdot 10^{-6}$ M) Bound Cu(II) has been calculated on the basis of the binding constants determined by the fitting of titration curves. The line represents the linear fit of the first points: about 10 dansyl units are quenched by a single metal ion. Conditions 10% water - DMSO, HEPES buffer 0.01 M pH 7, 25 °C, λ_{exc} = 340 nm, λ_{em} = 520 nm.