Supporting Information

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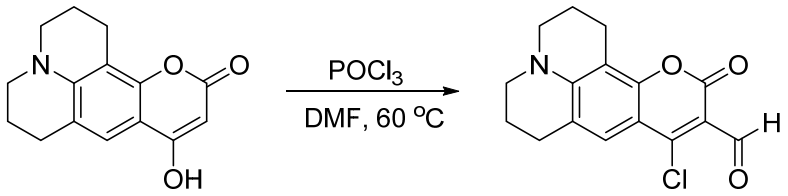
Contents:

1. General: All the chemicals and solvents were purchased from following suppliers and used without further purifications: Gentamicin (Fluka), Paromomycin (Fluka), Apramycin (Fluka), Kanamycin A (Sigma-Aldrich), Kanamycin B (Fluka), Neomycin (Applichem GmbH), tryptamine (Applichem GmbH), tyramine, (Acros), Fmoc-protected amino acids and Fmoc-rink amide AM resin (0.31 mmol/g resin) were purchased from GL Biotech (Shanghai, China). O-Benzotriazole-N,N,N',N'-tetramethyl-uronium-hexafluoro-phosphate (HBTU, GL Biotech), Hydroxybenzotriazole (HOBt, GL Biotech), N,N-Diisopropylethylamine (DIPEA, Iris Biotech GmbH, Marktredwitz, Germany), Trifluoroacetic acid (TFA, Sigma-Aldrich Chemie GmbH, Steinheim, Germany), 1,2-Ethanedithiol (EDT, Fluka Chemie GmbH, Buchs, Switzerland), Thioanisole (Fluka), Piperidine (Fluka) and Phenol (Acros Organics, Geel, Belgium). 8-hydroxyjulolidine (AlfaAesar), Sodium dodecyl sulfate (SDS), 4 (2-hydroxyethyl)piperazine-1-ethanesulfonic acid (HEPES), pentachlorophenol, (Sigma-Aldrich), malonic acid, phosphoryl chloride, (Fluka), (5-leucine)encephalin (Bachem AG), (5-methionine)encephalin (Bachem AG), Bradykinin (Fluka). HEPES buffer(100 mM, pH 7.4) was prepared with bidistilled water and used for all experiments. Absorption spectra were measured on a Cary 50 bio spectrometer (Varian) in 10 mm path polymethylmethacrylate cuvettes (Semadeni). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Advance DPX 400. Multiplicities of the ^{1}H NMR signals are assigned as following: s (singlet), d (doublet), t (triplet), m (multiplet). Chemical shifts (δ) are reported in parts per million (ppm) relative to the residual peak of the solvent. The LC-MS analyses were performed with an Autoprep system from Waters equipped with pumps 2525 binary gradient module, column fluidics organizer, sample manager 2767, PDA 2996 detector, ZQ4000 ESI-MS, and a reversed-phase C18 column from Vydac (218TP54). The mobile phase was composed of eluents A (H_2O 99.89%, HCOOH 0.1%, TFA 0.01%) and B (CH_3CN 90%, H_2O 9.89%, HCOOH 0.1%, TFA 0.01%). Gradient: from 2 to 100% B over 22 min at a flow rate of 1 mL/min. Electrospray was used for the MS analysis with both positive and negative mode. The MS experiment parameters were set as following; cone voltage: 25 volts, source temperature: 120 °C, mass range: *m/z* 100-1000 in 1 sec. The UV detection was programmed in the range of 190 to 600nm with a sampling rate of 5 spectra/sec.

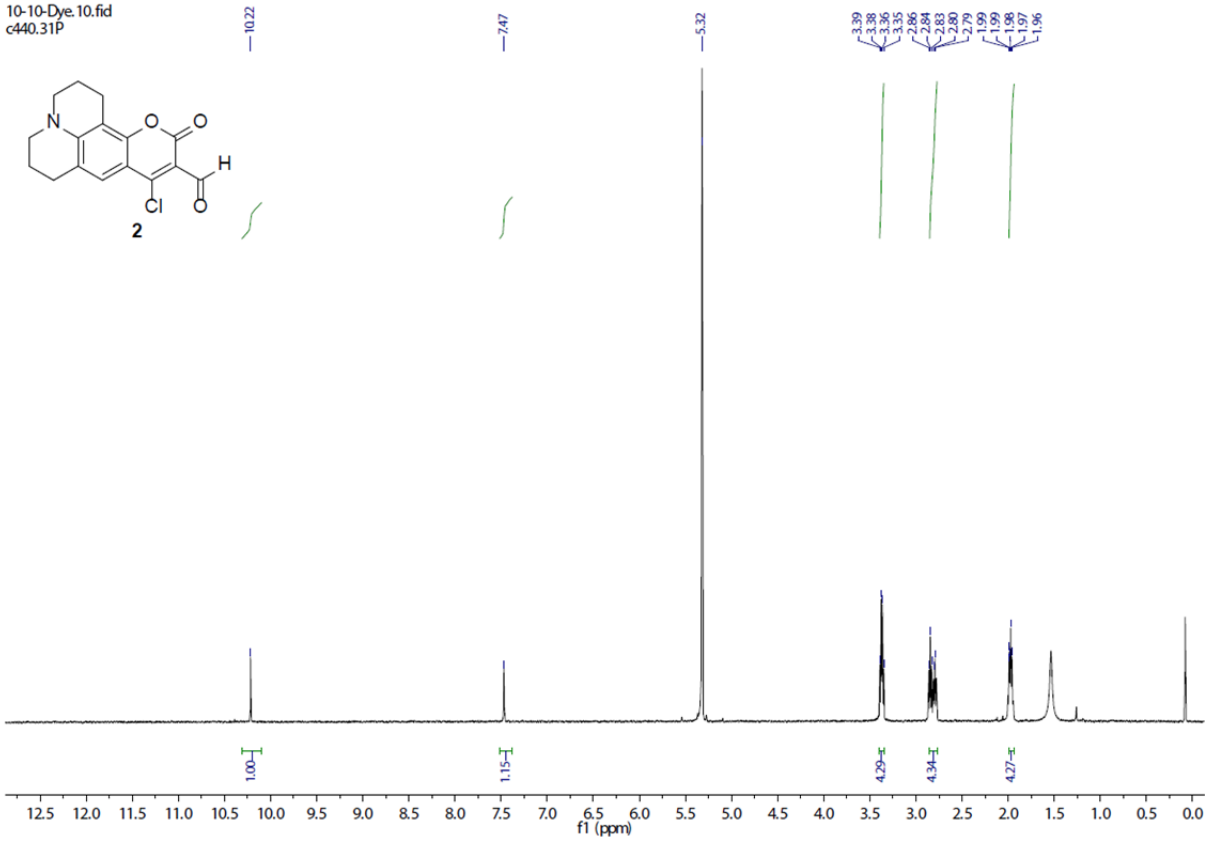
2. Synthesis of probe 2:

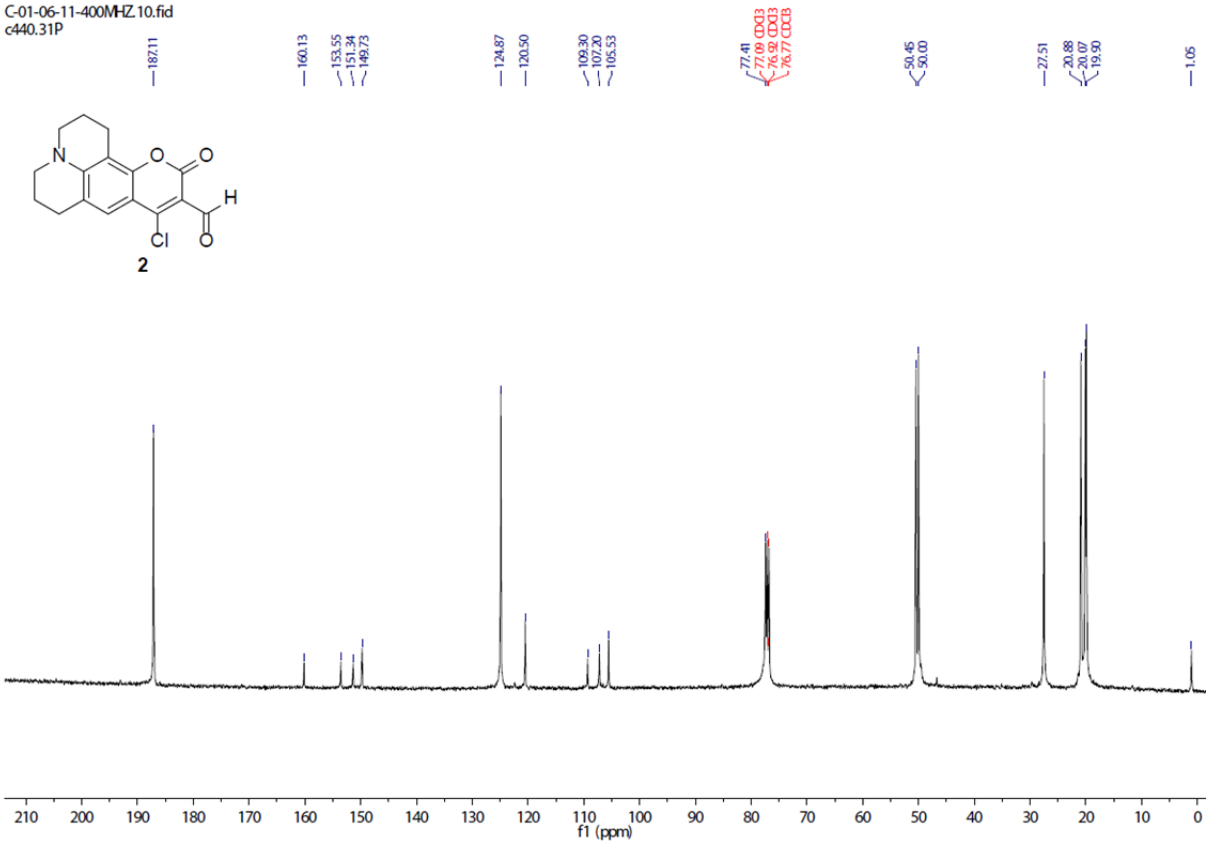


I **2**

Probe 2 has been prepared in analogy to a reported procedure.[1] $POCl_3$ (1.6 mL) and dry DMF (1.6 mL) were mixed in a 50 mL Schlenk flask and heated at 50 ˚C for 30 min. The julolidine-based 4-hydroxycoumarin precursor **I**[2] (1.4 g, 5.6 mmol) dissolved in dry DMF (8 mL) was then added to yield a scarlet suspension. The mixture was stirred at 60 ˚C for 24 h. The solution was allowed to cool to RT and ice water (100 mL) was added to quench the reaction. Neutralization with NaOH (20%, 150 mL) resulted in the formation of a precipitate, which was isolated by filtrations, washed with water (3 x 30 mL), and dried under vacuum. Crystallization from absolute ethanol gave coumarin **2** in 88% yield (1.5 g). m.p. 162 – 165 ˚C (dec); ^{1}H-NMR (400 MHz, CD_2Cl_2) δ 22 (s, 1H, CHO), 7.47 (s, 1H, CH_{arom}), 3.39 (m, 4H, CH_2), 2.86 (m, 2H, CH_2), 2.80 (m, 2H, CH_2), 1.99 (m, 4H, CH_2). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 187.11, 160.13, 153.55, 151.4, 149.3, 124.7, 120.50, 109.30, 107.20, 105., 50.45, 50.00, 27. 51, 20.88, 20.07, 19.90. Elemental analysis calc. for ($C_{16}H_{14}ClNO_3$): C (63.27), H (4.65); N (4.61) and found: C (63.33), H (4.14), N (4.37). m/z (high resol. TOF-MS-ES+) 304.0733 (cal. For $C_{16}H_{14}ClNO_3$ x H+ 304.0782).

[1] Kirpichenok, M. A.; Bakulev, V. M.; Karandashova, L. A.; Grandberg. I. I. *Khimiya Geterotsiklicheskikh Soedinenii* **1991**, 1480-1487.
[2] Cumarin **I** was prepared as described in: Coleman, R. S.; Berg, M. A.; Murphy, C. J. *Tetrahedron* ***2007***, *63*, 3450.


10-10-Dye.10.fid
c440.31P
10.22
7.47
5.32
3.39
3.38
3.36
3.35
2.86
2.84
2.83
2.80
2.79
1.99
1.99
1.98
1.97
1.96
N
O
O
H
Cl
O
2
1.00
1.15
4.29
4.34
4.27
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


C-01-06-11-400MHZ.10.fid
c440.31P
187.11
160.13
153.55
151.34
149.73
124.87
120.50
109.30
107.20
105.53
77.41
77.09 CDCl3
76.92 CDCl3
76.77 CDCl3
50.45
50.00
27.51
20.88
20.07
19.90
1.05
N
O
O
H
Cl
O
2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3. Reactions with tryptamine and tyramine: To examine the reactivity of probe **2**, we have performed test reactions with the simple biogenic amines tryptamine and tyramine. The reactions were carried out under typical sensing conditions (HEPES buffer, 50 mM, pH 7.4, [**2**] = 20 μM, [SDS] = 6.0 mM, [amine] = 500 μM). The reaction mixtures were analysed by HPLC using an instrument with coupled diode array and MS detectors (for details see part 1. of the SI). Adducts of type **A**, **B** and **C** (or their tautomeric forms) could be identified, (Figure S1). The adducts **A** and **C** were dominating in reactions with tryptamine, whereas **B** and **C** were dominating in reactions with tyramine. *Attempts to perform similar HPLC analyses for reactions with peptides or aminoglycosides were not successful due to interference of the surfactant.*

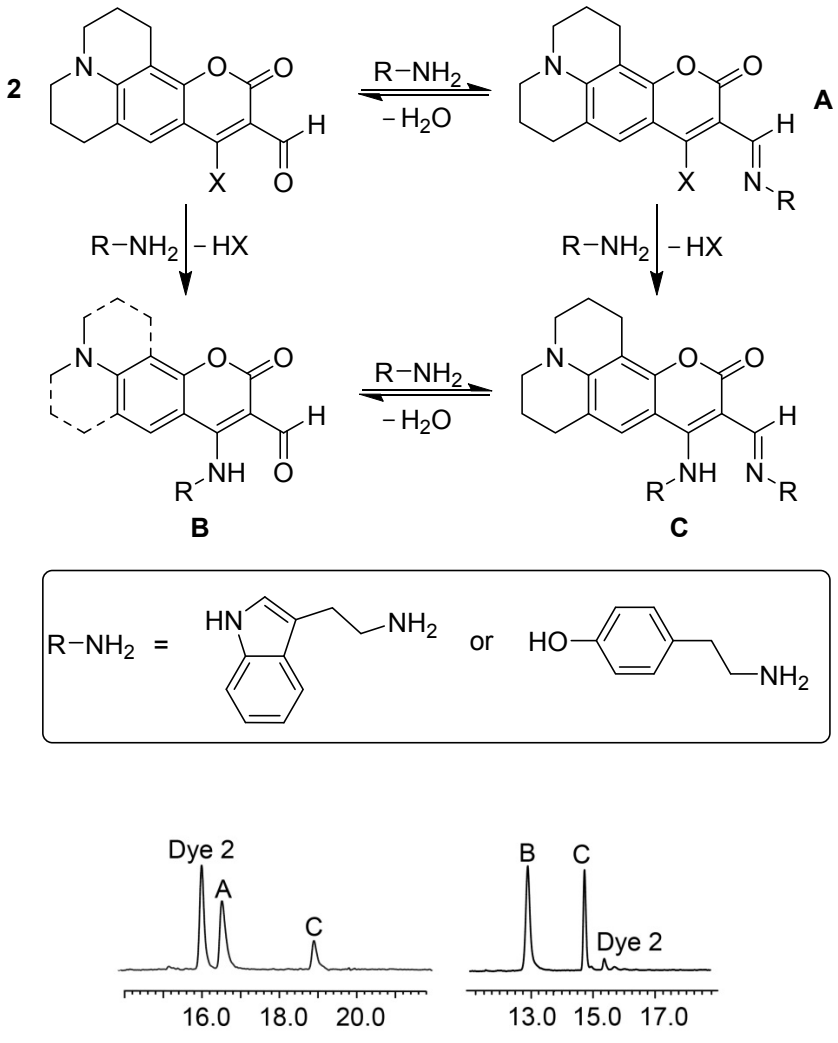
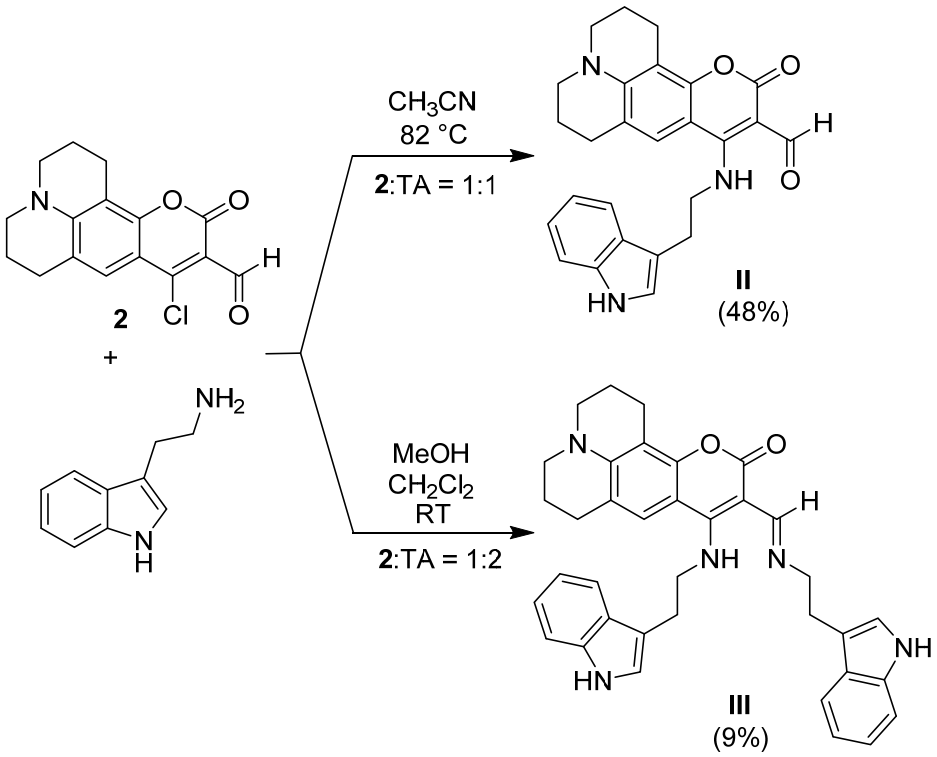


Figure S1. Part of the HPLC traces of solutions containing **2** (20 μM), SDS (6.0 mM), HEPES buffer (50 mM. pH 7.4), and tryptamine (left) or tyramine (right) (0.5 mM). The measurements were performed 8 h after addition of the amine. Detection was set to 453 nm.

In order to obtain additional information about the covalent adducts formed between dye **2** and tryptamine, we have performed reactions in organic solvents on a preparative scale. Heating a solution of dye **2** and tryptamine (1:1) under reflux for 5 h resulted in the formation of enamine **II**, which was isolated in 48% yield. The double condensation product **III**, on the other hand, was isolated in low yield (9%) when the reaction was performed in a mixture of methanol and dichloromethane (7:3). The formation of mono- and di-condensation products such as **I** and **II** is in line with what has been reported previously for reactions of probe **2** with primary amines.[3]

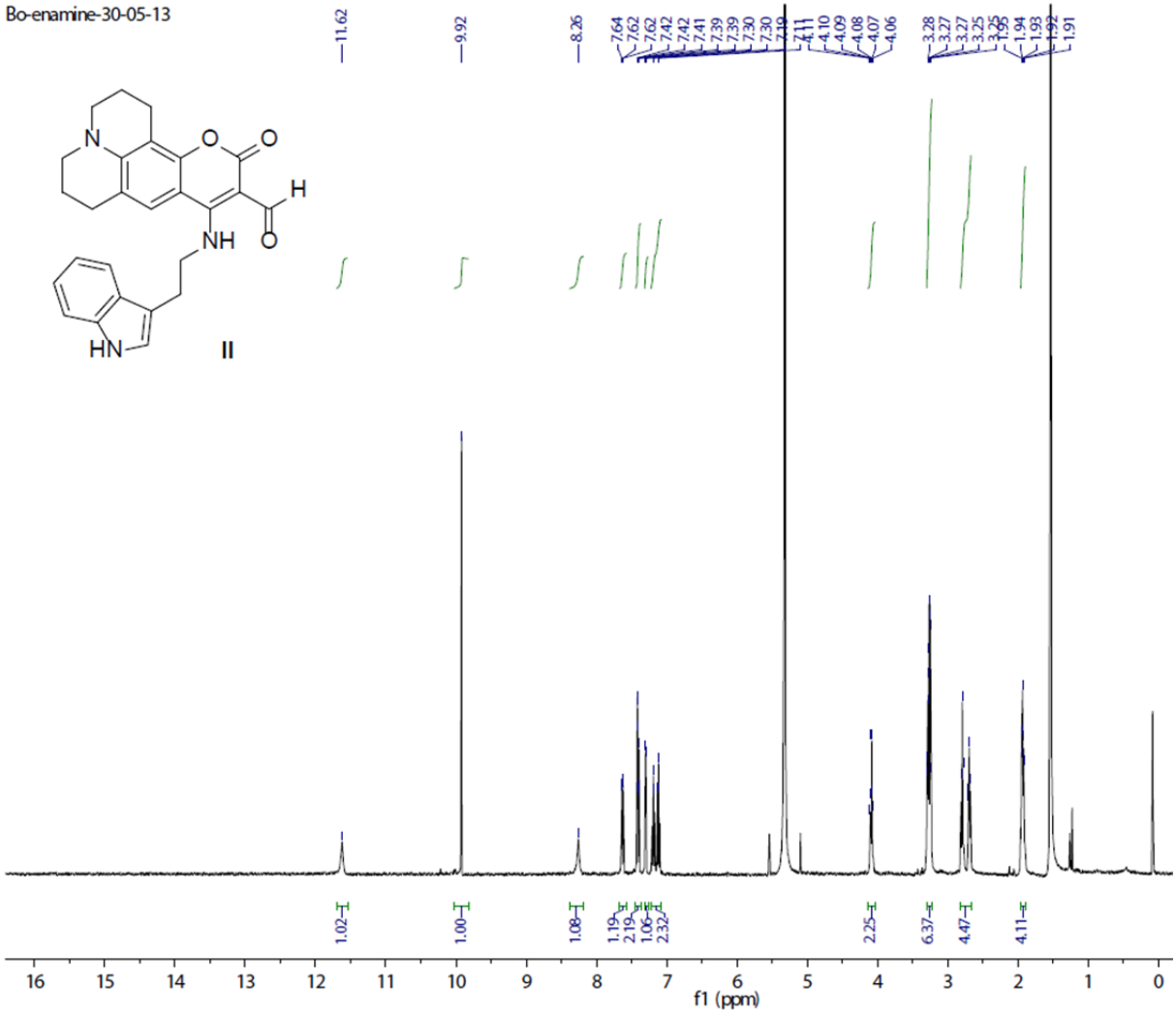
The adducts **II** and **III** were characterized by NMR spectroscopy, high-resolution mass spectrometry and single crystal X-ray diffraction (Figure S2). As expected, one can observe an intramolecular hydrogen bond between the NH group of the enamine and the adjacent aldehyde group (4; N···O = 2.6647(15) Å) or the imine group (5; N···N = 2.685(3) Å).

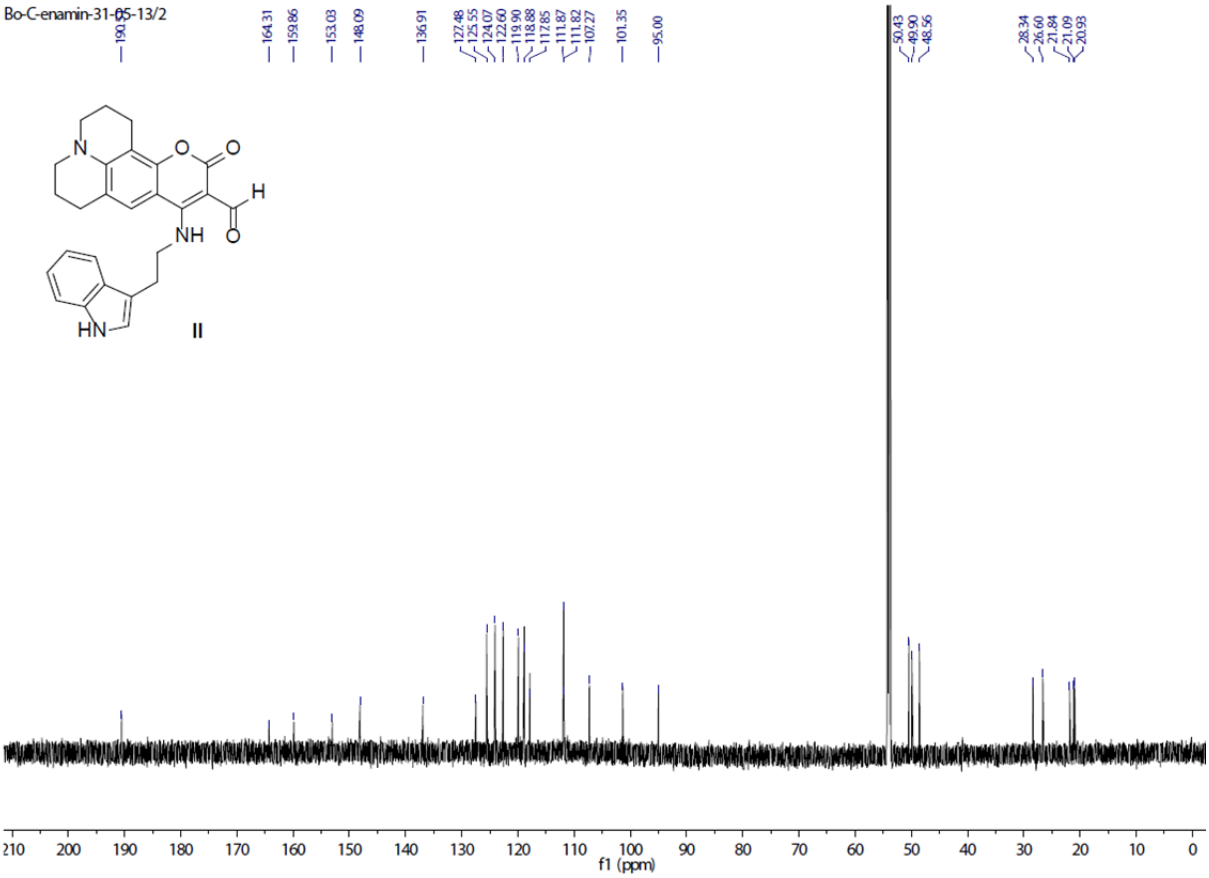


Synthesis of II: Dye **2** (110 mg, 0.36 mmol) was combined with tryptamine (54.8 mg, 0.34 mmol) in CH_3CN (40 mL). The mixture was heated under reflux for 5 h under an atmosphere of N_2. The solution was allowed to cool to RT and the precipitate was filtered off. The filtrate was concentrated and purified by column chromatography over silica gel using CH_3OH and

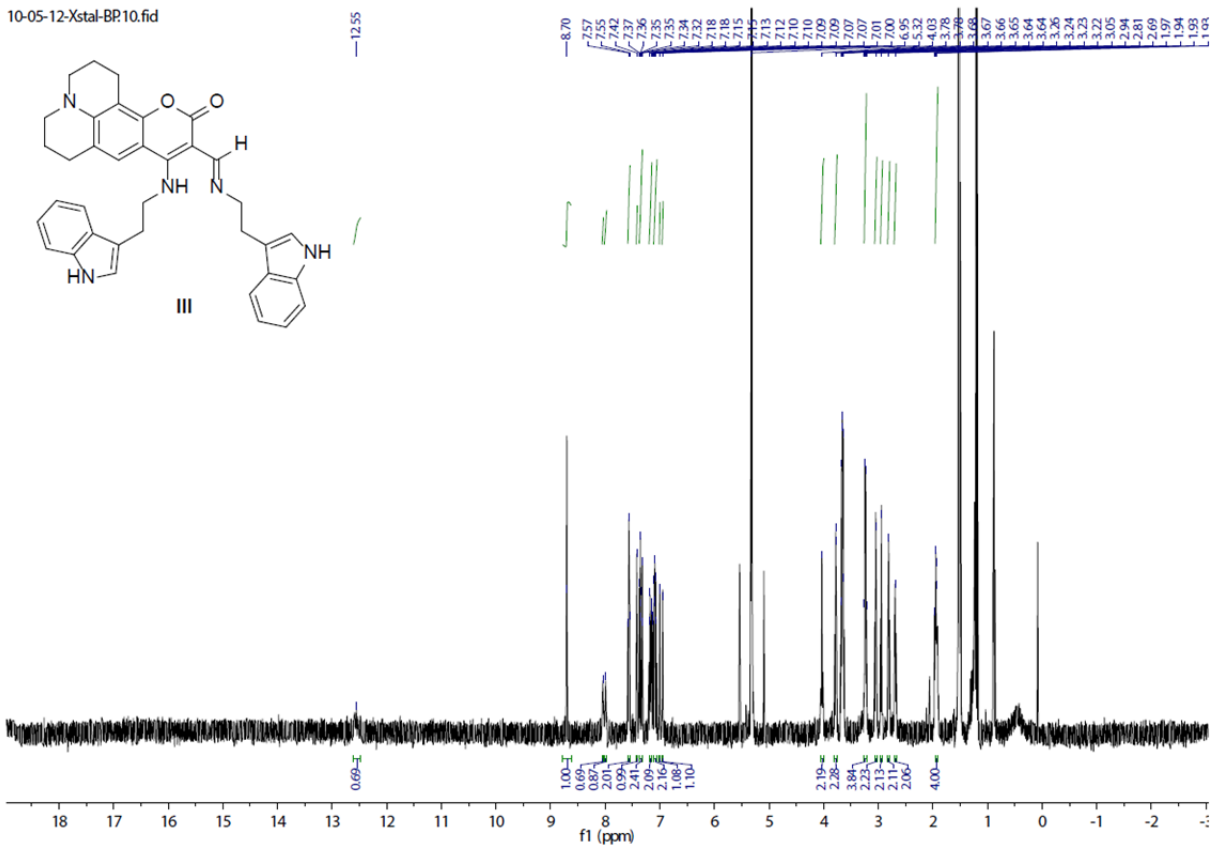
[3] Bakulev, V. M.; Gridunova, G. V.; Kirpichenok, M. A.; Karandashova, L. A.; Struchkov, Y. T.; Grandberg. I. I. *Khimiya Geterotsiklicheskikh Soedinenii* **1993**, 338-348.

CH_2Cl_2 (3:7) as eluent to give **II** in 48% yield (74.5mg). ^{1}H-NMR (400 MHz, CD_2Cl_2) δ 11.62 (s, br, 1H, NH), 9.92 (s, 1H, CHO), 8.26 (s, 1H, NH_{indole}), 7.64-7.62 (d, J = 3.7 Hz, 1H, CH_{arom}), 7.42-7.39 (m, 2H, CH_{arom}), 7.30 (d, J = 4 Hz 1H, CH_{arom}), 7.19-11m24.11-4.06 (m, 2H, CH_2), 3.20-3.23 (m, 6H, CH_2), 2.81-2.68 (m, 4H, CH_2), 1.95-1.91 (m, 4H, CH_2).^{13}C-NMR (200 MHz, CD_2Cl_2) δ 190.51, 164.31, 159.86, 153.03, 148.09, 136.91, 127.48, 125.55, 124.07, 122.60, 119.90, 118.88, 117.85, 111.87, 111.82, 107.27, 101.35, 95.00, 50.43, 49.90, 48.56, 28.34, 26.60, 21.84, 21.09, 20.93. *m/z* (high resol. TOF-MS-ES$^+$) 428.1974 (cal. For $C_{26}H_{25}N_3O_3$ x H^+ 428.1976).





Synthesis of III: Dye **2** (110 mg, 0.36 mmol) was combined with tryptamine (104.1 mg, 0.65 mmol) in a mixture of CH_3OH and CH_2Cl_2 (7:3, 40 mL). The solution was stirred for 2 h at RT and the solvents were removed under vacuum. The crude product was then purified twice by column chromatography over silica gel using a) CH_3OH and CH_2Cl_2 (3:7), and b) the same eluent with 1 % of CH_3OH. Compound **III** was obtained in 9% yield (18.6 mg). ^{1}H-NMR (400 MHz, CD_2Cl_2) δ 12.55 (s, br, 1H, NH), 8.70 (s, 1H, N=H), 8.04 (s, 1H, NH_{indole}), 7.99 (s, 1H, NH_{indole}), 7.59−7.55 (m, 2H, CH_{arom}), 7.42 (s, 1H, CH_{arom}), 7.37-7.32 (m, 2H CH_{arom}), 7.18−7.13 (m, 2H CH_{arom}), 7.10−7.07 (m, 2H CH_{arom}), 7.00-6.95 (m, 2H CH_{arom}), 4.03 (t, J = 6.9 Hz, 2H, CH_2), 3.78 (t, J = 7 Hz, 2H, CH_2), 3.26 (m, 4H, CH_2), 3.05-2.69 (m, 12H, CH_2). Due to low yield of the isolated product, a ^{13}C NMR spectrum was not recorded. *m/z* (high resol. TOF-MS-ES$^+$) 570.2880 (cal. For $C_{36}H_{35}N5O_2$ x H^+ 570.2871).



Crystallographic analyses: Single crystals of **II** and **III** were obtained from CH_3CN and ethanol, respectively. The diffraction data of **II** were measured at low temperature [100(2) K] using MoK_α radiation on a Bruker APEX II CCD diffractometer equipped with a kappa geometry goniometer. The dataset was reduced by EvalCCD [4] and then corrected for absorption.[5] The data collection of compound **III** was performed at room temperature using CuK_α radiation on an Agilent Technologies SuperNova dual system in combination with an Atlas CCD detector. The data reduction was carried out by Crysalis PRO.[6] The solutions and refinements were performed by SHELX.[7] The crystal structures were refined using full-matrix least-squares based on F^2 with all non hydrogen atoms anisotropically defined. Hydrogen atoms were placed in calculated positions by means of the "riding" model. Additional electron density found in the difference Fourier map of compound **3** was treated by the SQUEEZE algorithm of PLATON.[8] Disorder was found in the backbone of compound **4** and treated by geometrical restraints (SADI card).

[4] Duisenberg, A. J. M.; Kroon-Batenburg, L. M. J.; Schreurs, A. M. M. *J. Appl. Crystallogr*. **2003**, *36*, 220.
[5] Blessing, R. H. *Acta Crystallogr*. *Sect*. *A*, **1995**, *51*, 33.
[6] *Crysalis PRO*, Agilent Technologies, release 1.171.35.21, **2012**.
[7] *SHELX*, Sheldrick, G. M. *Acta Crystallogr*., *Sect*. *A* **2008**, *64*, 112.
[8] *PLATON*, Spek, A. L. *Acta Crystallogr*., *Sect*. *D* **2009**, *65*, 148.

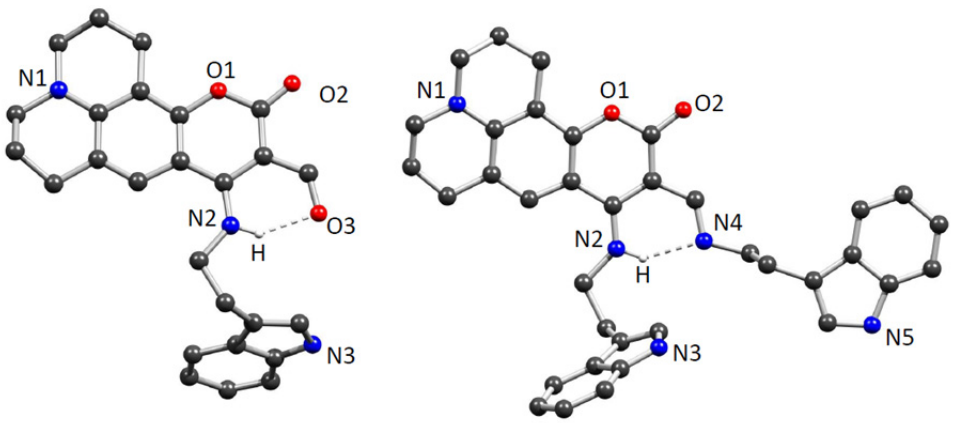


Figure S2. Molecular structures of **II** (left) and **III** (right) in the solid state. Hydrogen atoms not involved in hydrogen bonding are omitted for clarity.

4. Reactions with tryptamine and tryptophan:

Reactions with tryptamine and the more polar tryptophan give rise to very different UV-sis spectra (Figure S3).

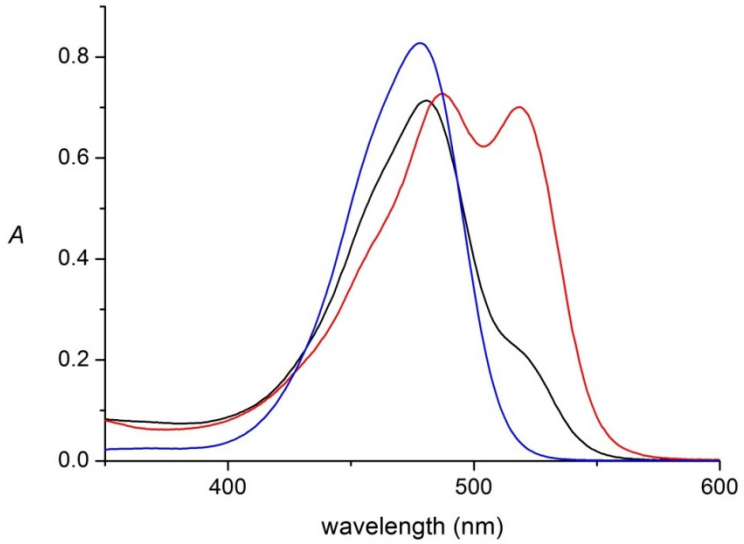


Figure S3. Absorption spectra of a buffered aqueous solution (HEPES, 50 mM, pH 7.4) containing **2** (20 µM), SDS (6.0 mM) and tryptamine (red line), tryptophan (black line) or no amine at all (blue line) ([amine] = 0.5 mM). The measurements were performed after an incubation time of 4 h.

5. Pattern-based analysis of aminoglycosides

Analysis of six different aminoglycosides: Buffered aqueous solutions (HEPES buffer, 50 mM, pH 7.4) containing probe **2** (20 μM), SDS (6.0 mM) and the respective aminoglycoside (50 μM) were prepared. After an incubation time of 2 h, UV/Vis spectra of the solutions were recorded. Eight independent measurements were performed for each analyte. The absorption values in the region between 350 and 560 nm with incremental steps of 5 nm (350, 355, 360, 365, etc) were used as input for a stepwise variable selection algorithm as implemented in SYSTAT 11. Four wavelengths were selected: 530 nm, 515 nm, 465 nm, and 455 nm. The absorption values at these wavelengths provide a characteristic pattern for each aminoglycoside (Figure S4). The resulting data set was then used to perform a principal component analysis (a score plot is shown in the main text).

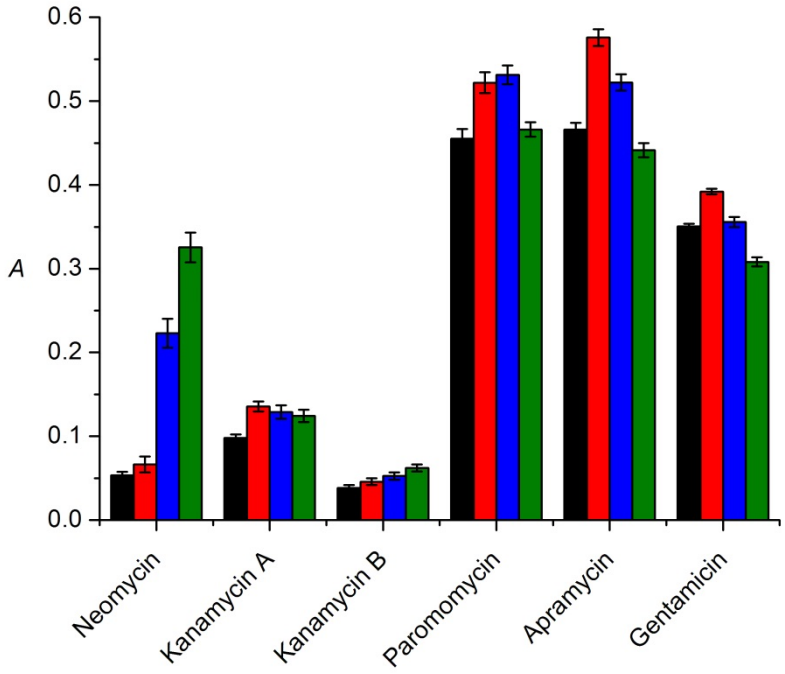


Figure S4. Absorbance at 530 (black), 515 (red), 465 (blue) and 455 (green) of buffered aqueous solutions containing **2** (20 μM), SDS (6.0 mM), HEPES buffer (50 mM. pH 7.4), and six different aminoglycosides (50 μM). The data represent averaged values from eight independent measurements.

Analysis of mixtures of aminoglycosides: Buffered aqueous solutions (HEPES buffer, 50 mM, pH 7.4) containing probe **2** (20 μM), SDS (6.0 mM) and Kanamycin B (K), Neomycin (N), Apramycin (A), or mixtures of the aminoglycosides were prepared ($[\text{aminoglycosides}]_{\text{total}}$ = 50 μM). After an incubation time of 2 h, UV/Vis spectra of the solutions were recorded. Eight independent measurements were performed for each sample. The absorption values in the region between 350 and 560 nm with incremental steps of 5 nm (350, 355, 360, 365, etc) were used as input for a stepwise variable selection algorithm as implemented in SYSTAT 11. Four wavelengths were selected: 530 nm, 485 nm, 445 nm, and 395 nm. The absorption values at these wavelengths provide a characteristic pattern for each sample (Figure S5). The resulting data set was then used to perform a principal component analysis (Figure S6).

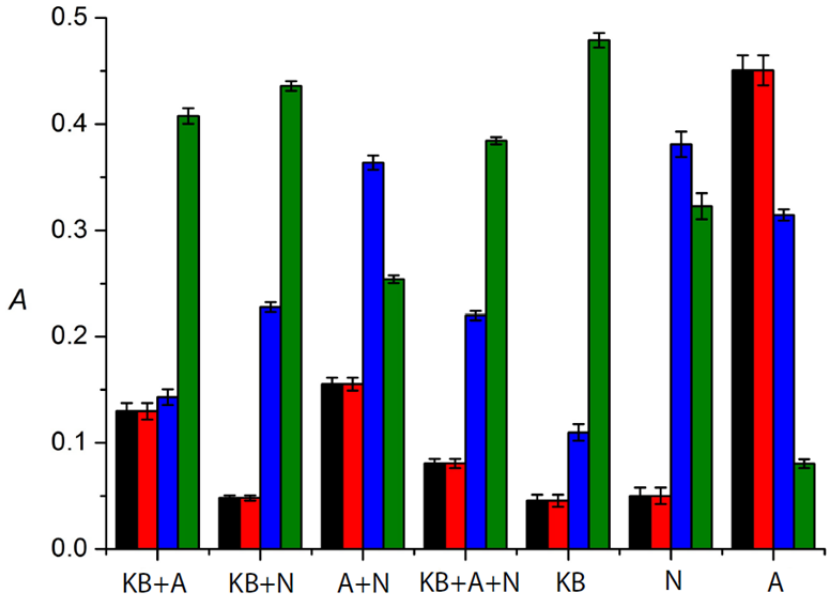


Figure S5. Absorbance at 530 (black), 485 (red), 445 (blue) and 395 (green) of buffered aqueous solutions containing **2** (20 μM), SDS (6.0 mM), HEPES buffer (50 mM. pH 7.4), and Apramycin (A), Kanamycin B (KB), Neomycin (N), or equimolar mixtures of A+N, KB+N, KB+A and KB+A+N (50 μM). The data represent averaged values from eight independent measurements.

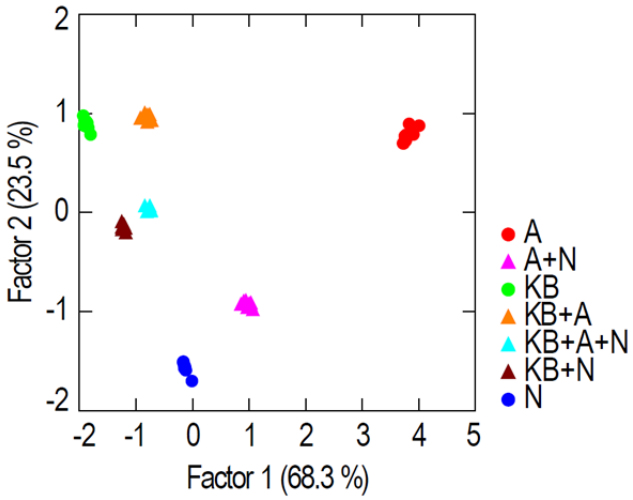


Figure S6. Two-dimensional PCA score plot for the analysis of Apramycin (A), Kanamycin B (KB), Neomycin (N), and equimolar mixtures of these aminoglycosides. UV-Vis spectra (eight independent measurements) of buffered aqueous solutions (HEPES, 50 mM, pH 7.4) containing probe **2** (20 µM), SDS (6.0 mM), and the respective analyte (50 µM) were used as input for the statistical analysis. The spectra were recorded after incubation for 2 h.

6. Pattern-based analysis of peptides

Analysis of eleven different peptides: Buffered aqueous solutions (HEPES buffer, 50 mM, pH 7.4) containing probe **2** (20 µM), SDS (6.0 mM) and the respective peptide (500 µM) were prepared. After an incubation time of 4 h, UV/Vis spectra of the solutions were recorded. Eight independent measurements were performed for each analyte. The absorption values in the region between 350 and 560 nm with incremental steps of 5 nm (350, 355, 360, 365, etc) were used as input for a stepwise variable selection algorithm as implemented in SYSTAT 11. Six wavelengths were selected: 530 nm, 445 nm, 425 nm, 410 nm, 400 nm, and 285 nm. The absorption values at these wavelengths provide a characteristic pattern for each aminoglycoside (Figure S7). The resulting data set was then used to perform a principal component analysis (a score plot is shown in the main text).

WAGGDASGE-NH_2 (**3**)
RPPGFSPFR (**4**)
YGGFM (**5**)
TGGFL (**6**)
KWDNQ-NH_2 (**7**)
VNFSTGW-NH_2 (**8**)
FLWGPRALV-NH_2 (**9**)
FSWGAEGQR-NH_2 (**10**)
WFSGAEGQR-NH_2 (**11**)
FSGAEGQRW-NH_2 (**12**)
WGPNDPRR-NH_2 (**13**)

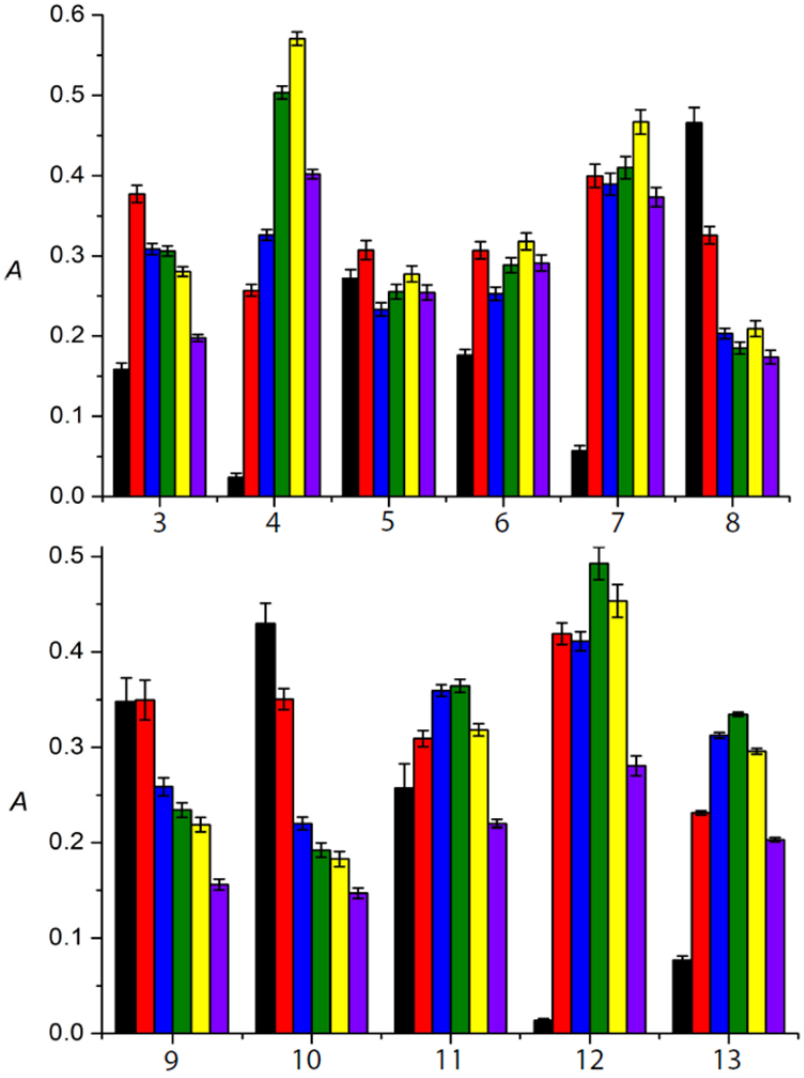


Figure S7. Absorbance at 530 (black), 445 (red), 425 (blue), 410 (green), 400 (yellow) and 385 (purple) of buffered aqueous solutions containing 2 (20 μM), SDS (6.0 mM), HEPES buffer (50 mM. pH 7.4), and the respective peptide (500 μM). The data represent averaged values from eight independent measurements.

Classification of peptides with a linear discriminant analysis (LDA): The data shown in Figure S7 was also used as input for an LDA. The corresponding score plot is shown in Figure S8. A jack-knife validation procedure was performed, in which 50% of the data was randomly omitted, and the remaining data were used as a training set for the LDA. The omitted observations were then classified resulting in a correct classification in all cases (100%).

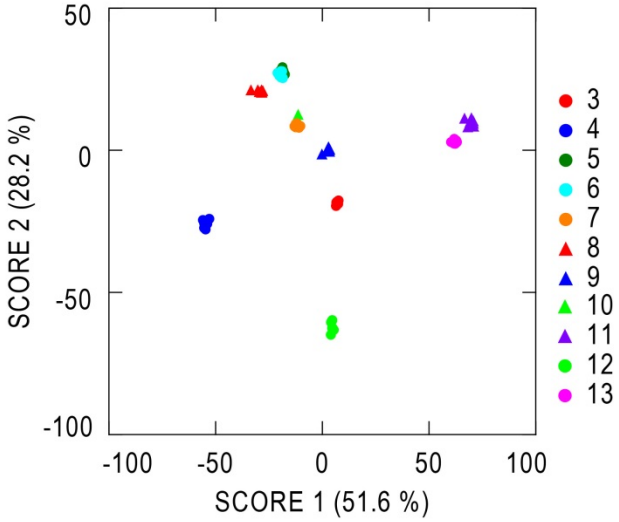


Figure S8. Two-dimensional LDA score plot for the analysis of eleven different peptides. UV-Vis spectra (eight independent measurements) of buffered aqueous solutions (HEPES, 50 mM, pH 7.4) containing probe **2** (20 μM), SDS (6.0 mM), and the respective peptide (500 μM) were used as input for the statistical analysis. The spectra were recorded after incubation for 4 h.

Analysis of three peptides at four different concentrations: Buffered aqueous solutions (HEPES buffer, 50 mM, pH 7.4) containing probe **2** (20 μM), SDS (6.0 mM) and the peptides **10**, **11** or **12** at four different concentrations (100, 300, 500, or 700 μM) were prepared. After an incubation time of 4 h, UV/Vis spectra of the solutions were recorded. Eight independent measurements were performed for each analyte. The absorption values in the region between 350 and 560 nm with incremental steps of 5 nm (350, 355, 360, 365, etc) were used as input for a stepwise variable selection algorithm as implemented in SYSTAT 11. Four wavelengths were selected: 550 nm, 520 nm, 410 nm, and 400 nm. The absorption values at these wavelengths provide a characteristic pattern for each aminoglycoside (Figure S9). The resulting data set was then used to perform a principal component analysis (Figure S10).

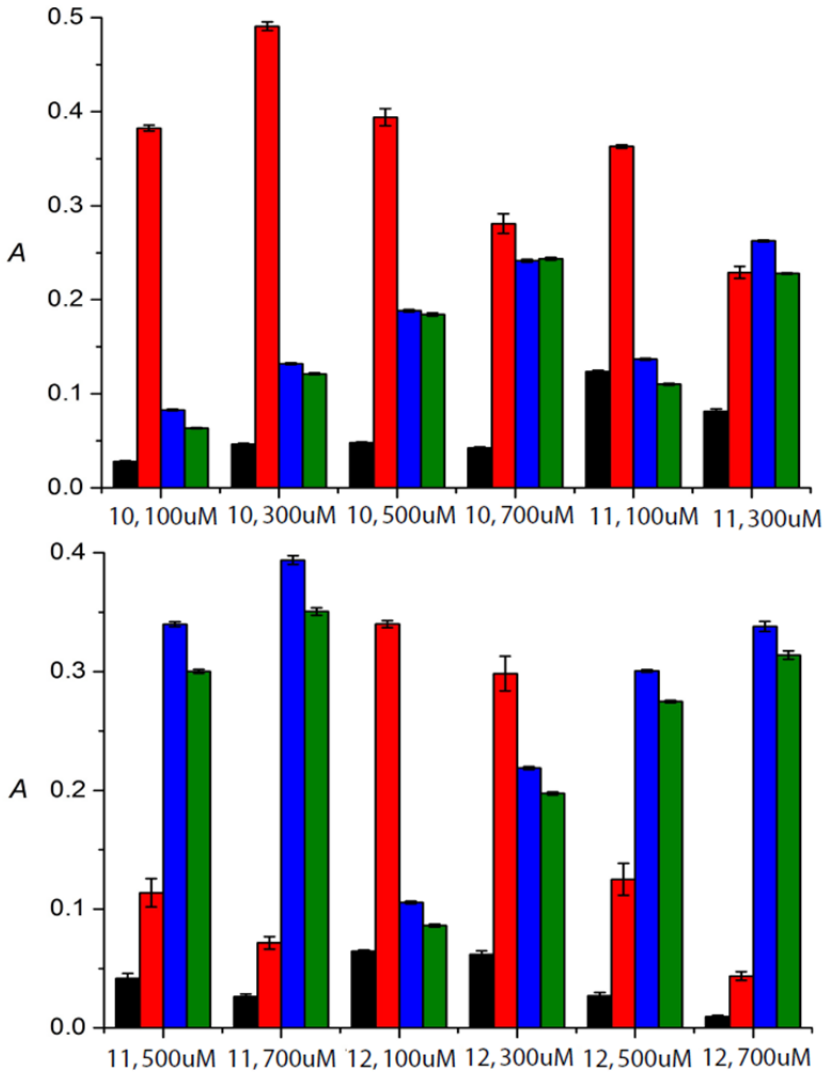


Figure S9. Absorbance at 550 (black), 520 (red), 410 (blue) and 400 (green) of buffered aqueous solutions containing **2** (20 μM), SDS (6.0 mM), HEPES buffer (50 mM. pH 7.4), and peptides **10**, **11**, or **12** at four different concentrations (100, 300, 500, or 700μM). The data represent averaged values from eight independent measurements.

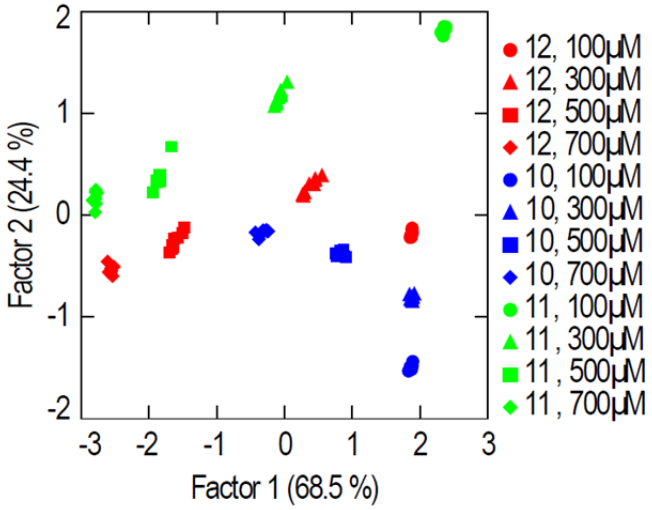
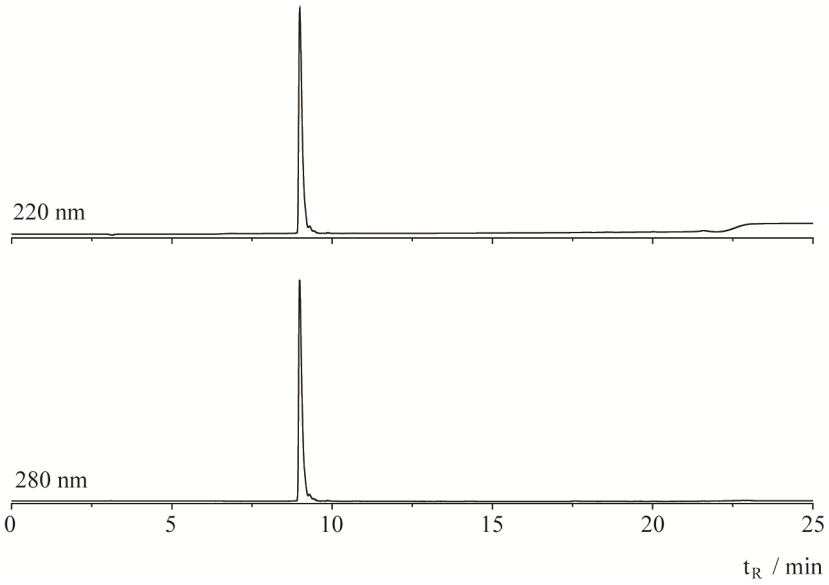


Figure S10. Two-dimensional PCA score plot for the discrimination of buffered aqueous solutions containing **2** (20 μM), SDS (6.0 mM), HEPES buffer (50 mM. pH 7.4), and the peptides **10** (blue), **11** (green), and **12** (red) at four different concentrations (100 μM = ●, 300 μM = ▲, 500 μM = ■, 700 μM = ♦.).

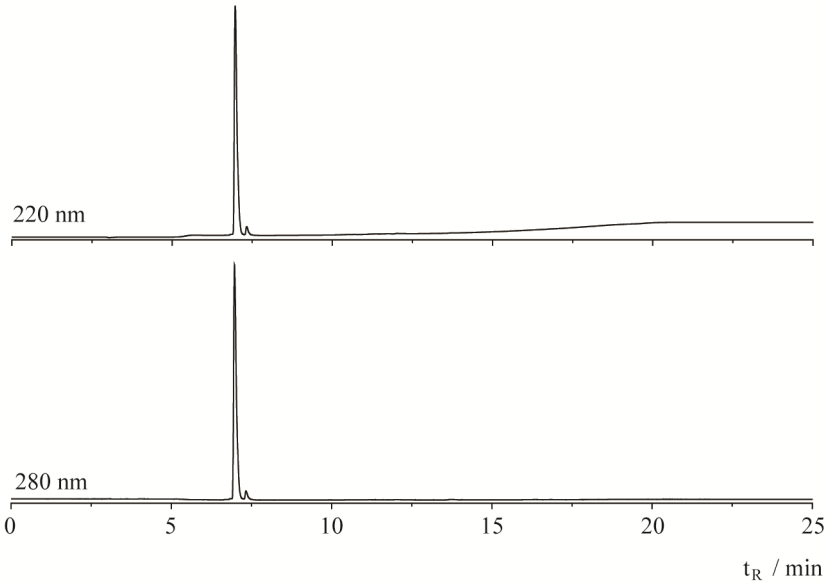
7. Synthesis and characterization of the peptide analytes: The peptides were synthesized on an Advanced ChemTech 348Ω peptide synthesizer (Aapptec, Louisville, USA) by standard Fmoc (9-fluorenylmethyloxycarbonyl) solid-phase chemistry on a Rink Amide AM resin (0.03 mmol scale). Coupling steps were carried out twice. For each coupling, amino acid (4 eq, 0.2 M solution in DMF), HBTU (4 eq, 0.45 M solution in DMF), HOBt (4 eq, 0.45 M solution in DMF) and DIPEA (6 eq, 0.5 M solution in DMF) were used. Fmoc groups were removed using a 20% (v/v) solution of piperidine in DMF (2.5 mL × 2). The peptides were deprotected (side-chain protected groups) and cleaved from the resin by adding a solution of TFA/thioanisole/H_2O/phenol/EDT (90/2.5/2.5/2.5/2.5 v/v, 4 mL) and shaking for 3 h at room temperature. The resin was removed by filtration and the peptides were precipitated with cold diethyl ether (40 mL). The precipitated peptides were re-suspended and washed twice with diethyl ether (20 mL each time). Deprotected peptides were purified by preparative reversed-phase HPLC (RP-HPLC) using a Vydac C18 (218TP) column (22 × 250 mm) (Grace & Vydac, Hesperia, USA). A linear gradient with a mobile phase composed of eluent A (99.9 % v/v H_2O, 0.1% v/v TFA) and eluent B (94.9% v/v acetonitrile, 5% v/v H_2O and 0.1% v/v TFA) from 5% to 50% over 30 minutes at a flow rate of 20 mL/min, was applied. The masses of peptides in different fractions were determined by MALDI-TOF mass spectrometry. The fractions with desired product were lyophilized. The purity of the peptides was assessed by

analytical RP-HPLC on an Agilent 1260 system, using a C18 column and the same buffer system as for preparative RP-HPLC.

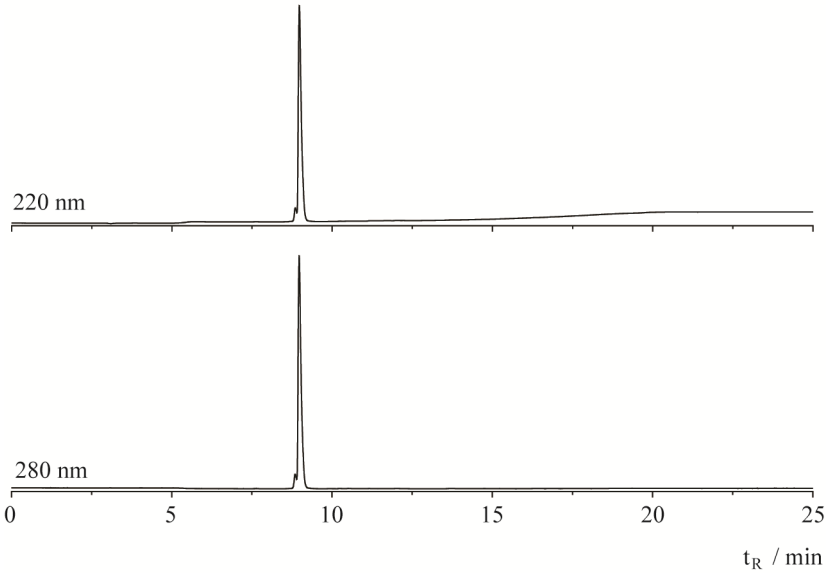
a) Peptide **3** (WAGGDASGE-NH_2): (*m/z* (ESI^+) 424.25 (cal. for $C_{35}H_{50}N_{11}O_{14}$ x $2H^+$ 424.93).



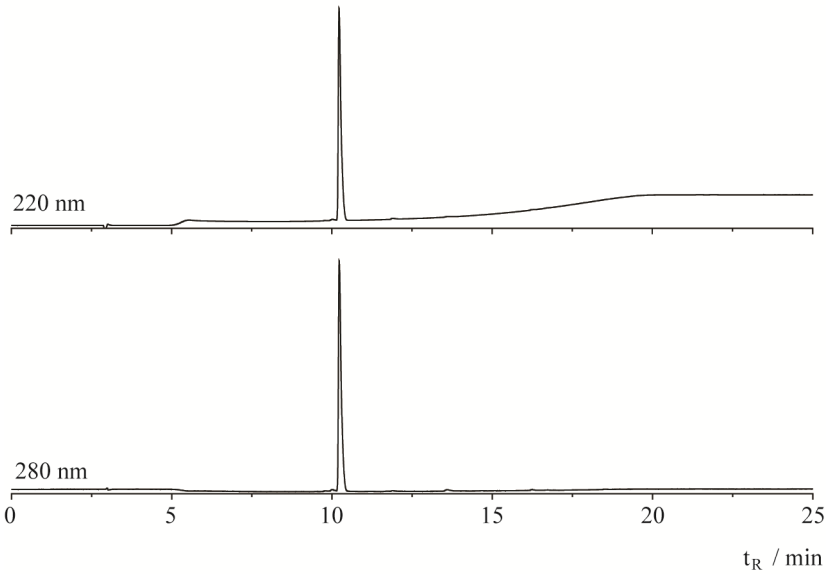
b) Peptide **7** (KWDNQ-NH_2): (*m/z* (ESI^+) 689.58 (cal. for $C_{30}H_{45}N_{10}O_9$ x H^+ 689.74).



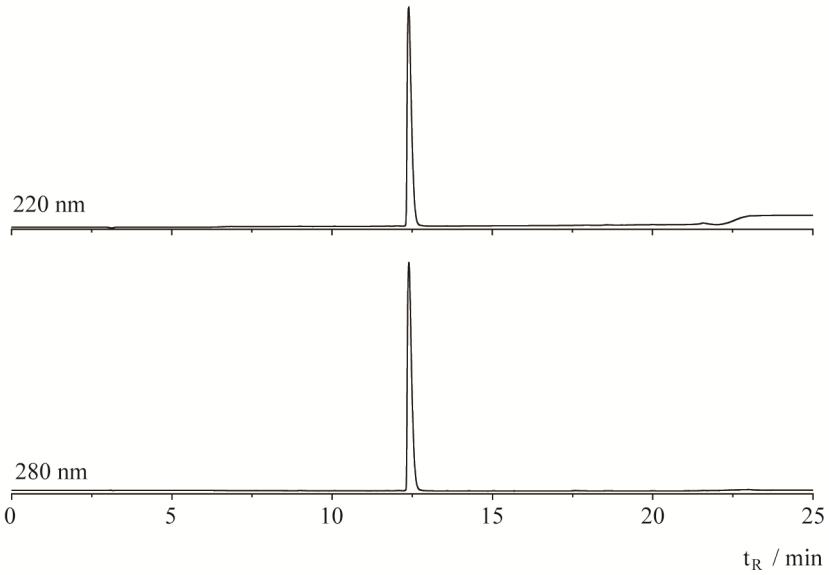
c) Peptide **8** (VNFSTGW-NH_2): (*m/z* (ESI^+) 809.67 (cal. for $C_{38}H_{53}N_{10}O_{10}$ x H^+ 809.90).



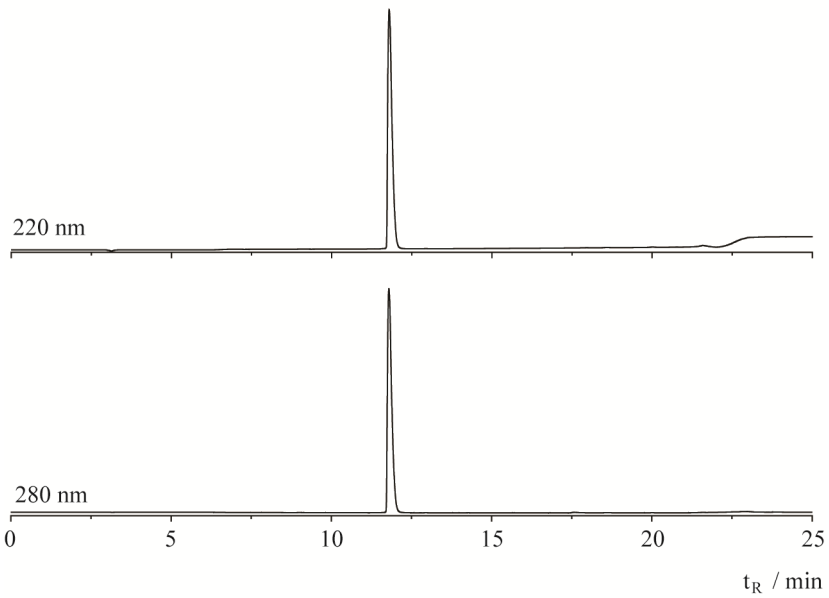
d) Peptide **9** (FLWGPRALV-NH_2): (*m/z* (ESI^+) 529.67 (cal. for $C_{53}H_{81}N_{14}O_9$ x $2H^+$ 529.66).



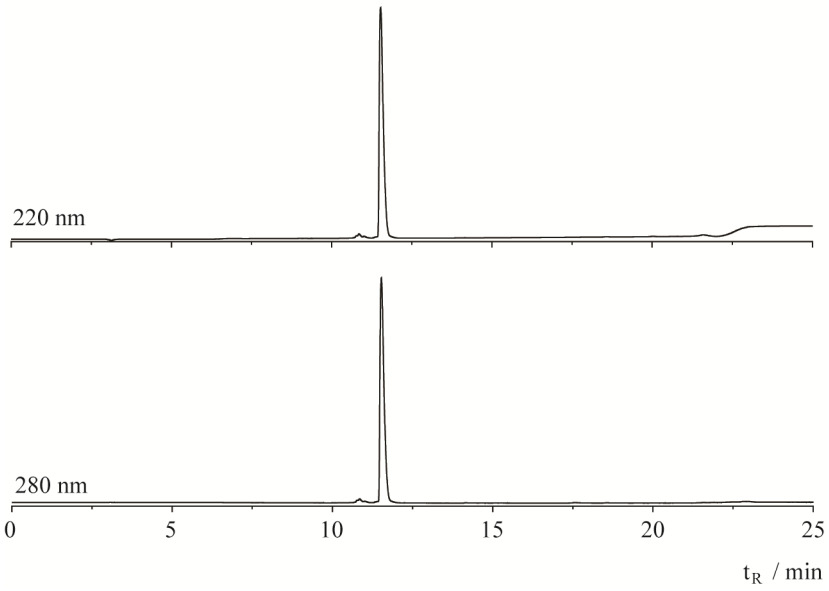
e) Peptide **10** (FSWGAEGQR-NH_2): (*m/z* (ESI^+) 519.17 (cal. for $C_{46}H_{66}N_{15}O_{13}$ x $2H^+$ 519.07).



f) Peptide **11** (WFSGAEGQR-NH_2): (*m/z* (ESI^+) 519.08 (cal. for $C_{46}H_{66}N_{15}O_{13}$ x $2H^+$ 519.07).



g) Peptide **12** (FSGAEGQRW-NH_2): (*m/z* (ESI^+) 519.08 (cal. for $C_{46}H_{66}N_{15}O_{13}$ x $2H^+$ 519.07).



h) Peptide **13** (WGPNDPRR-NH_2): (*m/z* (ESI^+) 499.08 (cal. for $C_{43}H_{66}N_{17}O_{11}$ x $2H^+$ 499.06).