Cooperative binding and extraction of sodium nitrite by a ditopic receptor incorporated into a polymeric resin
by
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GENERAL INFORMATION

Unless specifically indicated, all other chemicals and reagents used in this study were purchased from commercial sources and used as received. Purification of products was performed using column chromatography on silica gel (Merck Kieselgel 60, 230-400 mesh) with mixtures of chloroform/methanol. Thin-layer chromatography (TLC) was performed on silica gel plates (Merck Kieselgel 60 F254).

\(^1\)H and \(^13\)C NMR spectra used in the characterization of products were recorded on Bruker 300 spectrometer using a residual protonated solvent as internal standard.

High resolution mass spectra (HRMS) were measured on a Quattro LC Micromass unit using ESI technique.

UV-vis analyses were performed using Thermo Spectronic Unicam UV500 Spectrophotometer.

The X-ray measurement of receptor 2 was performed at 100(2) K on a Bruker D8 Venture Photon100 diffractometer equipped with a TRIUMPH monochromator and a MoK\(\alpha\) fine focus sealed tube (\(\lambda = 0.71073\) Å).
Scheme 1. Synthesis of receptors 1, 2 and resin 3.

Preparation of compound 4.

To a solution of 3-nitrobenzoyl chloride (1 g, 5.39 mmol) and 0.9 ml of triethylamine in 50 ml of dry dichloromethane, 1-aza-18-crown-6 (1.42 g, 5.40 mmol) at 0 °C (ice bath) was added. The reaction mixture was stirred for 30 min and then left at room temperature overnight. The organic phase was then washed twice with distilled water, 1M HCl, sat. NaHCO₃ and dried over MgSO₄. After evaporation of dichloromethane the residue was purified by silica gel column chromatography (5% methanol in chloroform) to give the title product as a colorless oil (2.15 g, 97% yield).


¹H NMR (300 MHz, DMSO-d₆) δ 3.40-3-80 (m, 24H), 7.71-7.77 (m, 1H), 7.80-7.89 (m, 1H), 8.20-8.35 (m, 2H).

¹³C NMR (75 MHz, DMSO-d₆) δ 45.66, 50.08, 68.71, 70.19, 70.40, 70.64, 122.25, 124.27, 130.60, 133.77, 138.92, 147.97, 169.15.
IR (KBr): 3240, 3102, 3054, 2877, 2746, 2607, 2447, 1962, 1828, 1625, 1597, 1522, 1468, 1429, 1350, 1287, 1249, 1118, 1028, 945, 870, 848, 704 cm$^{-1}$.

**Preparation of compound 5.**

![Chemical Structure](image)

To a degassed solution of 4 (2 g, 4.85 mmol) in 150 ml of THF/MeOH (1:4) catalytic amounts of 10% Pd/C was added. The reaction mixture was kept under H$_2$ atmosphere (balloon pressure) at room temperature overnight. The catalyst was removed by filtration through a pad of Celite and washed with MeOH. The filtrate was concentrated under reduced pressure to give the crude product in quantitative yield (1.85 g). The amine was used in next step without further purification.


$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.12–7.20 (m, 1H), 6.84–6.61 (m, 3H), 3.50–3.85 (m, 24H).

$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 172.37, 146.61, 137.87, 129.35, 116.50, 115.73, 113.24, 70.77, 70.69, 69.61, 50.00, 46.18.

**Preparation of receptor 1.**

![Chemical Structure](image)
To the solution of amine 5 (400 mg, 1.05 mmol) in 30 ml of dry THF, 4-nitrophenyl isothiocyanate (198 mg, 1.1 mmol) and triethylamine (0.153 ml, 1.1 mmol) were added. After stirring overnight at room temperature, the reaction mixture was concentrated and purified by silica gel column chromatography (2% methanol in chloroform) to give receptor 1 as a yellow solid (424.8 mg, 72% yield). Receptor 1 was recrystallized from acetonitrile.

Mp. 139-142 °C

HRMS (ESI): calcd for C_{26}H_{34}N_{4}O_{8}SNa [M+ Na]^+: 585.1995, found: 585.1988

$^1$H NMR (300 MHz, DMSO) δ 10.47 (s, 1H), 10.34 (s, 1H), 8.31 – 8.15 (m, 2H), 7.91 – 7.75 (m, 2H), 7.60 – 7.36 (m, 3H), 7.16 (d, $J$ = 7.4 Hz, 1H), 3.40 – 3.70 (m, 24H).

$^{13}$C NMR (75 MHz, DMSO) δ 179.98, 170.76, 146.59, 142.87, 139.39, 137.65, 129.28, 124.89, 124.63, 123.60, 122.27, 122.14, 70.46, 70.37, 70.23, 69.23, 68.75, 49.69, 45.77.

IR (KBr): 3268, 3013, 2948, 2873, 2583, 2436, 1932, 1585, 1496, 1471, 1416, 1330, 1296, 1253, 1206, 1177, 1108, 853, 713 cm$^{-1}$.

**Preparation of receptor 2.**

Receptor 2 was synthesized analogously to receptor 1 with exception that amine 4-nitrophenyl isocyanate was used. Receptor 2 was purified by silica gel column chromatography (5% methanol in chloroform) to give a yellow oil (70% yield).

HRMS (ESI): calcd for C_{26}H_{34}N_{4}O_{9}Na [M+ Na]^+: 569.2224, found: 569.2202
$^1$H NMR (300 MHz, CDCl$_3$) \( \delta \) 9.17 (s, 1H), 8.65 (s, 1H), 8.13 – 8.18 (m, 2H), 7.73 – 7.60 (m, 2H), 7.51 (d, \( J = 8.0 \text{ Hz} \), 1H), 7.35 (s, 1H), 7.23 (t, \( J = 7.3 \text{ Hz} \), 1H), 6.96 (d, \( J = 6.3 \text{ Hz} \), 1H), 3.40 – 4.00 (m, 24H).

$^{13}$C NMR (75 MHz, CDCl$_3$) \( \delta \) 172.83, 152.35, 145.96, 141.87, 139.42, 136.61, 129.34, 125.07, 120.39, 120.25, 117.64, 116.87, 70.28.

IR (KBr): 3485, 3348, 3313, 3152, 3087, 2868, 2599, 2442, 2224, 1923, 1720, 1615, 1594, 1551, 1505, 1470, 1428, 1332, 1300, 1271, 1971, 1231, 1197, 1175, 1111, 851, 751 cm$^{-1}$.

**Preparation of compound 6.**

![SCN](image)

To a solution of compound 5 (750 mg, 1.96 mmol) in dichloromethane (40 ml) 1,1’-thiocarbonyldi-2(1H)-pyridone (683 mg, 2.94 mmol) was added. After 30 min. the reaction was completed (as monitored by TLC). The reaction mixture was concentrated under reduced pressure and the residue was purified by silica gel column chromatography (5% methanol in chloroform) to give the title product as a colorless oil (515 mg, 62% yield).

HRMS (ESI): calcd for C$_{20}$H$_{28}$N$_2$O$_6$SNa [M+ Na]$^+$: 447.1566, found: 447.1560

$^1$H NMR (300 MHz, DMSO) \( \delta \) 7.51, 7.49, 7.49, 7.48, 7.47, 7.46, 7.46, 7.38, 7.38, 7.38, 7.37, 7.36, 7.35, 3.64, 3.56, 3.54, 3.45.

$^{13}$C NMR (75 MHz, DMSO) \( \delta \) 169.65, 154.71, 139.12, 134.72, 130.56, 126.79, 126.53, 124.72, 79.63, 70.43, 70.18, 68.90, 68.65, 49.97, 45.64.

IR (KBr): 3226, 3071, 2942, 2895, 2853, 2737, 2690, 2582, 2493, 2445, 2202, 2124, 1620, 1573, 1488, 1462, 1417, 1349, 1301, 1276, 1249, 1128, 1008, 940, 813, 737 cm$^{-1}$.
Preparation of resin 3.

To a suspension of TentaGel™ resin (500 mg) in dichloromethane (5 ml) compound 6 (143.1 mg, 0.34 mmol) was added and the reaction was stirred overnight. Then the resin was separated and washed several times with dichloromethane and methanol. Finally it was washed with deionized water until disappearance of sodium cations in filtrate (monitored by ASA). After drying 450 mg of resin 3 was obtained. The receptor loading was calculated based on sulfur content (combustion analysis) and was found to be 0.45 mmol/g.

Preparation of reference receptor 7.

To the solution of 3-amino-N,N-diethylbenzamide (1 mmol, 192 mg) in 30 ml of dry THF, 4-nitrophenyl isothiocyanate (1 mmol, 180 mg) and triethylamine (1 mmol, 139.4 µl) were added. After stirring overnight at room temperature, the reaction mixture was concentrated and purified by silica gel column chromatography (2% methanol in chloroform) to give receptor 7 as a light yellow solid (279 mg, 75% yield).

Mp. 170-172 °C

**Preparation of reference receptor 8.**

![Chemical Structure](image)

To the solution of aniline (1 mmol, 93 mg) in 30 ml of dry THF, 4-nitrophenyl isothiocyanate (1 mmol, 180 mg) and triethylamine (1 mmol, 139.4 µl) were added. After stirring overnight at room temperature, the reaction mixture was concentrated and purified by silica gel column chromatography (2% methanol in chloroform) to give receptor 8 as a yellow solid (246 mg, 90% yield).

HRMS (ESI): calcd for C_{13}H_{10}N_{3}O_{2}S [M-H]: 272.0494, found: 272.0487.

$^1$H NMR (300 MHz, DMSO) δ 10.39 (s, 1H), 10.27 (s, 1H), 8.26 – 8.14 (m, 2H), 7.95 – 7.78 (m, 2H), 7.54 – 7.44 (m, 2H), 7.41 – 7.31 (m, 2H), 7.24 – 7.14 (m, 1H).

$^{13}$C NMR (75 MHz, DMSO) δ 179.79, 146.75, 142.75, 139.41, 129.09, 125.50, 124.21, 122.02.
Preparation of receptor 9.

To a solution of isothiocyanate 6 (130 mg, 0.3 mmol) in 20 ml of tetrahydrofuran, 2-methoxyethylamine (23 mg, 0.3 mmol) was added. The reaction mixture was stirred overnight. After evaporation of THF the residue was purified by silica gel column chromatography (5% methanol in chloroform) to give the title product as a colorless oil (115 mg, 77% yield).

HRMS (ESI): calcd for C_{23}H_{37}N_{3}O_{7}SNa [M+ Na]^+: 522.2250, found: 522.2252.

\(^1\)H NMR (300 MHz, DMSO) \(\delta\) 9.67 (s, 1H), 7.86 (s, 1H), 7.56 (s, 1H), 7.45 (d, \(J = 8.9\) Hz, 1H), 7.36 (t, \(J = 7.8\) Hz, 1H), 7.07 (d, \(J = 7.5\) Hz, 1H), 3.77 – 3.38 (m, 28H), 3.30 (s, 3H).

\(^13\)C NMR (75 MHz, DMSO) \(\delta\) 181.12, 170.92, 139.95, 137.55, 129.08, 123.52, 122.44, 121.08, 70.50, 70.39, 69.29, 68.81, 58.44, 49.66, 45.75, 43.87.

IR (film CH\(_2\)Cl\(_2\)): 3464, 3268, 3068, 2873, 2251, 2124, 1624, 1543, 1467, 1351, 1310, 1354, 1193, 1115, 1026, 944, 758, 713 cm\(^{-1}\).
UV-VIS EXPERIMENTS

Fig. S1: Job plot (Host: Receptor 1, guest: Cl⁻)

Fig. S2: Job plot (Host: Receptor 2, guest: Cl⁻)
**General procedure for UV-Vis titration:** The UV-Vis titration was performed using Thermo Spectronic Unicam UV500 Spectrophotometer at 298K in acetonitrile. NaClO₄ were dried under high vacuum at 30–45 °C prior to use. In this case, a 2500 μL of freshly prepared 4.13×10⁻⁵ M solution of receptor 1 was added to a cuvette. Small aliquots of TBAX, containing 1 at constant concentration, were added and a spectrum was acquired after each addition. In the case of ion pair titration, receptor 1 was firstly pretreated with one equivalent of appropriate salt (NaClO₄, KPF₆ or NH₄PF₆). Titration isotherms for NH protons were fitted to a 1:1 binding model using HypSpec program.
Fig. S4. UV-Vis titration binding isotherms of receptor 1 with TBACl and TBACl in the presence of 1 equivalent of NaClO₄, KPF₆ or NH₄PF₆.

Fig. S5. UV-Vis titration binding isotherms of receptor 1 with TBABr and TBABr in the presence of 1 equivalent of NaClO₄.
Fig. S6. UV-Vis titration binding isotherms of receptor 1 with TBANO$_3$ and TBANO$_3$ in the presence of 1 equivalent of NaClO$_4$.

![Graph of Fig. S6](image)

Fig. S7. UV-Vis titration binding isotherms of receptor 2 with TBANO$_2$ and TBANO$_2$ in the presence of 1 equivalent of NaClO$_4$.

![Graph of Fig. S7](image)
NMR TITRATION

The $^1$H NMR titration was performed on a Bruker 300 spectrometer, at 298K in CD$_3$CN. NaClO$_4$ were dried under high vacuum at 30−45 °C prior to use. In this case, a 500 μL of freshly prepared 3.20 mM solution of receptor 9 was added to a 5mm NMR tube. Small aliquots of 25.7 mM solution of NaClO$_4$ or 33.5 mM solution of TBANO$_2$, containing 1 at 3.20 mM concentration, were added and a spectrum was acquired after each addition. Titration isotherms for NH protons were fitted to a 1:1 binding model using the HypNMR 2008 program.

![Chemical Structure](image)

**Fig. S8.** NMR titration binding isotherm of receptor 9 with TBANO$_2$ and TBANO$_2$ in the presence of 1 equivalent of NaClO$_4$. 

![Graph](image)
Fig. S9. NMR titration binding isotherm of receptor 9 with NaClO₄

Fig. S10. Variation of the $^1$HNMR spectrum of receptor 9 in CD₃CN upon addition of increasing amounts of TBANO₂
Fig. S11. Variation of the $^1$HNMR spectrum of receptor 9 in CD$_3$CN upon addition of increasing amounts of TBANO$_2$ in the presence of 1 equivalent of sodium perchlorate

COMPARISON OF RECEPTORS 1 AND 2 BEHAVIOR UPON INTERACTION WITH NITRITE ANIONS

Fig. S12. UV-Vis titration spectra of receptor 1 (upon gradual addition of tetrabutylammonium nitrite)
Fig. S13. UV-Vis titration spectra of receptor 2 (upon gradual addition of tetrabutylammonium nitrite)

Fig. S14. $^1$H NMR spectra of receptor 1 (upon gradual addition of tetrabutylammonium nitrite)
EXTRACTION EXPERIMENTS

A certain amount of the adsorbing material were added to the bottles, that contain 10 ml saturated solution of NaNO₂ or NaClO₄ (Cₙa⁺ = 6 mg/L) in acetonitrile, and the mixture was gently shaken for 2 h at room temperature. The supernatant was then decanted and the concentration of Na⁺ remaining in the solution, that correspond to concentration of the salt, was determined by AAS.

A saturated solution NaNO₂ was obtaining by adding excess of salt crystal to acetonitrile. Then solution was ultrasonicated about 0.5 h and after next 12 h a solution was decanted. The concentration of Na⁺ was determined by atomic absorption spectrometry (AAS) and was ~ 6 mg/L.
In the same manner comparative experiment between TBANO₂ and NaNO₂ was conducted. However, concentration of NO₂⁻ remaining in the solution, that correspond to concentration of the salt, was determined by UV-Vis spectroscopy. Calibration curve was generated using a standard solution of TBANO₂ in acetonitrile and is presented below. Absorbance was taken for wavelength 214 nm, which corresponds to the maximum.

**Regeneration of the resin 3.**
After extraction experiments the resin was washed several times with deionized water until complete disappearance of sodium cations in the solution (monitored by AAS).

**Fig. S16. Calibration curve generated using a standard solution of sodium hexafluorophosphate in acetonitrile (AAS).**

\[
y = 0.2330x - 0.0152 \\
R = 0.9998
\]

**Fig. S17. Calibration curve was generated using a standard solution of TBANO₂ in acetonitrile**

\[
y = 5.2602x + 0.0287 \\
R = 0.9988
\]
Crystal data

The crystal structures were deposited at the Cambridge Crystallographic Data Centre. The data have been assigned to the following deposition numbers: CCDC 1474520 for 2*NaNO$_2$ and CCDC 1474521 for 2*NaNCS.

Crystallization procedures

Crystallization of 2*NaNO$_2$: To a solution of 2.5 mg of receptor 2 (5 μmol) in 100 μl of MeCN was added a solution of 0.85 mg of NaPF$_6$ (1 equiv., 5 μmol) in 150 μl of MeCN and was stirred for 30 min. Then a solution of 1.4 mg of TBANO$_2$ (1 equiv., 5 μmol) in 100 μl of MeCN was added, the mixture was stirred for 30 minutes and then centrifuged to obtain a clear solution. The above was subjected to slow Et$_2$O vapor/vapor diffusion at 4°C to produce crystals of 2*NaNO$_2$.

Crystallization of 2*NaNCS: To a solution of 5.5 mg of receptor 2 (10 μmol) in 500 μl of MeOH was added a solution of 1.6 mg of NaSCN (2 equiv., 20 μmol), the mixture was centrifuged to obtain a clear solution. The above was subjected to slow Et$_2$O vapor/vapor diffusion at RT to produce crystals of 2*NaNCS.

Data collection, structure refinement and final crystal data

The X-ray measurement of 2*NaNO$_2$ was performed at 100(2) K on a Bruker D8 Venture Photon100 diffractometer equipped with a TRIUMPH monochromator and a MoKα fine focus sealed tube (λ = 0.71073 Å). A total of 1160 frames were collected with Bruker APEX2 program [S1]. The frames were integrated with the Bruker SAINT software package [S2] using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 34193 reflections to a maximum θ angle of 25.05° (0.84 Å resolution), of which 5710 were independent (average redundancy 5.988, completeness = 99.8%, R$_{int}$ = 4.08%, R$_{sig}$ = 3.43%) and 4276 (74.89%) were greater than 2σ(F$^2$). The final cell constants of a = 10.2165(7) Å, b = 27.9980(19) Å, c = 11.4145(7) Å, β = 98.9264(17)°, volume = 3225.5(4) Å$^3$, are based upon the refinement of the XYZ-centroids of 9970 reflections above 20σ(I) with 5.945° < 2θ < 50.77°. Data were corrected for absorption effects using the multi-scan method (SADABS) [S3]. The ratio of minimum to maximum apparent transmission was 0.946. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9540 and 0.9900. The structure was solved and refined using SHELXTL Software Package [S4] using the space group P 1 21/c 1, with Z = 4 for the formula unit.
C_{28}H_{39}N_6NaO_{12}. The final anisotropic full-matrix least-squares refinement on F^2 with 448 variables converged at R1 = 4.24%, for the observed data and wR2 = 9.94% for all data. The goodness-of-fit was 1.059. The largest peak in the final difference electron density synthesis was 0.263 e/Å³ and the largest hole was -0.288 e/Å³ with an RMS deviation of 0.044 e/Å³. On the basis of the final model, the calculated density was 1.389 g/cm³ and F(000), 1424 e⁻.

The atomic scattering factors were taken from the International Tables [S5].

In the structure the NO₂⁻ anion is disordered over two sites and one O atom common with the occupancy ratio yielding 0.75:0.25. O and N atoms with 25% occupancy, except the common site atoms, were refined with isotropic thermal parameters. All other non-H atoms were refined anisotropically. Most of hydrogen atoms were placed in calculated positions and refined within the riding model. The temperature factors of these hydrogen atoms were not refined and were set to be equal to either 1.2 or 1.5 times larger than U_{eq} of the corresponding heavy atom. Positions of two hydrogen atoms engaged in hydrogen bonds, except H(1S) and H(2S) atoms, were refined together with their isotropic temperature factors. Geometry of water molecule coordinating Na atom was modelled using O-H and H...H distances constrains.

The X-ray measurement of 2*NaNCS was performed at 100(2) K on a Bruker D8 Venture Photon100 diffractometer equipped with a TRIUMPH monochromator and a MoKα fine focus sealed tube (λ = 0.71073 Å). A total of 1932 frames were collected with Bruker APEX2 program [S1]. The frames were integrated with the Bruker SAINT software package [S2] using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 33274 reflections to a maximum θ angle of 25.05° (0.84 Å resolution), of which 5567 were independent (average redundancy 5.977, completeness = 99.9%, R_{int} = 3.05%, R_{sig} = 2.52%) and 4420 (79.40%) were greater than 2σ(F²). The final cell constants of a = 10.2359(5) Å, b = 27.7408(15) Å, c = 11.1772(6) Å, β = 97.5158(14)°, volume = 3146.5(3) Å³, are based upon the refinement of the XYZ-centroids of 9995 reflections above 2θ = 4.705° with 4.705° < 2θ < 52.67°. Data were corrected for absorption effects using the multi-scan method (SADABS) [S3]. The ratio of minimum to maximum apparent transmission was 0.937. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9490 and 0.9840. The structure was solved and refined using SHELXTL Software Package [S4] using the space group P 1 21/c 1, with Z = 4 for the formula unit, C_{28}H_{38}N_3NaO_{10}S. The final anisotropic full-matrix least-squares refinement on F^2 with 436 variables converged at R1 = 4.47%, for the observed data and wR2 = 11.36% for all data. The
goodness-of-fit was 1.063. The largest peak in the final difference electron density synthesis was 0.351 e/Å³ and the largest hole was -0.235 e/Å³ with an RMS deviation of 0.051 e/Å³. On the basis of the final model, the calculated density was 1.393 g/cm³ and F(000), 1392 e⁻.

Structure contains disordered methanol solvent molecule. The molecule occupies two alternative positions with occupancy ratio 0.81:0.19. This disorder is associated with alternative coordination of Na⁺ (trapped by crown ether fragment) ether by N or S terminate atoms of NCS⁻ ion. NCS⁻ ion coordinating Na⁺ one via S atom has occupancy 81%. To model geometry of less occupy fragments of methanol and SCN⁻ anion similarity restraints were used (SAME instruction). The occupancy ratio of disordered fragments of methanol and SCN⁻ ion were refined and converged to c.a. 0.8:0.2, and at the final stages of refinement it was fixed at 0.81:0.19.

The non-hydrogen atoms were refined anisotropically except atoms of low occupancy in disordered molecules. Isotropic temperature factor of C atom in SCN⁻ ion was fixed at 0.2 value. Most of hydrogen atoms were placed in calculated positions and refined within the riding model. Positions of two hydrogen atoms of urea fragment engaged in hydrogen bonds were refined. The temperature factors of hydrogen atoms were not refined and were set to be equal to either 1.2 or 1.5 times larger than Ueq of the corresponding heavy atom. The atomic scattering factors were taken from the International Tables [S5].

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The X-ray structures were determined in the Advanced Crystal Engineering Laboratory (aceLAB) at the Faculty of Chemistry of the University of Warsaw by dr Łukasz Dobrzycki.
ORTEP plots and packing diagrams for complex $2\text{NaNO}_2$

Fig. S18. ORTEP ($P=50\%$) of $2\text{NaNO}_2$.

Fig. S19. Supramolecular ribbon packing motif in the crystal structure of $2\text{NaNO}_2$. 
Fig. S20. Packing in crystal of 2*NaNO₂. Perspective projections along: a) x, b) y, and c) z crystallographic axes.
ORTEP plots and packing diagrams for complex $2^*\text{NaNCS}$

Fig. S21. ORTEP ($P=50\%$) of $2^*\text{NaNCS}$.

Fig. S22. Supramolecular ribbon packing motif in the crystal structure of $2^*\text{NaNO}_2$. 
Fig. S23. Packing in crystal of 2*NaNCS. Perspective projections along: a) $x$, b) $y$, and c) $z$ crystallographic axes.
Fig. S24. MS spectra of 1 and its complexes with selected cations and anions.
NMR SPECTRA
References.


