Supporting information

Conformational selection in anion recognition: cGMP-selective binding by a naphthalimide-functionalized amido-amine macrocycle

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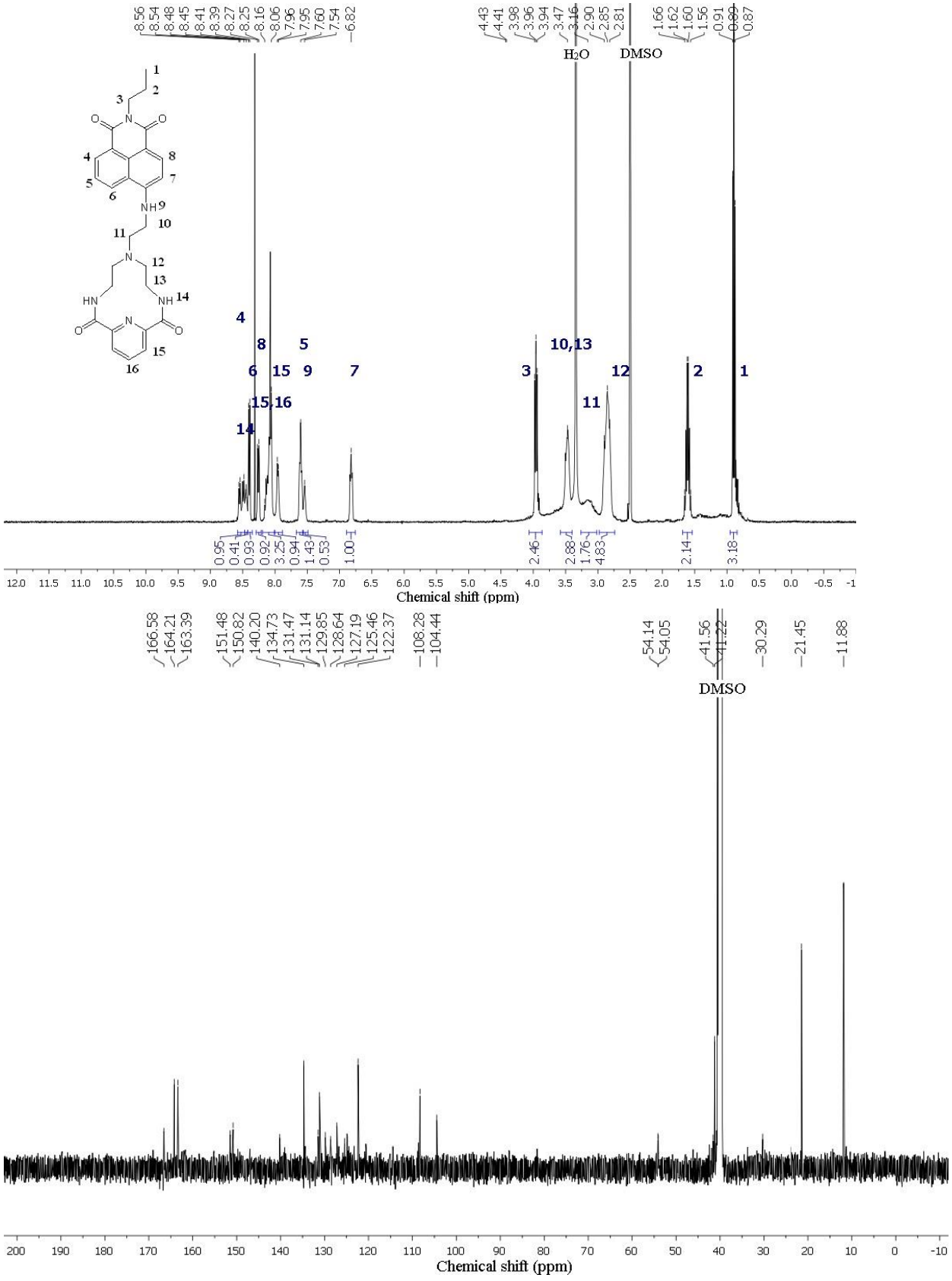
[c]*National Research Center "Kurchatov Institute", Moscow, Russia*

Content

1. NMR spectra

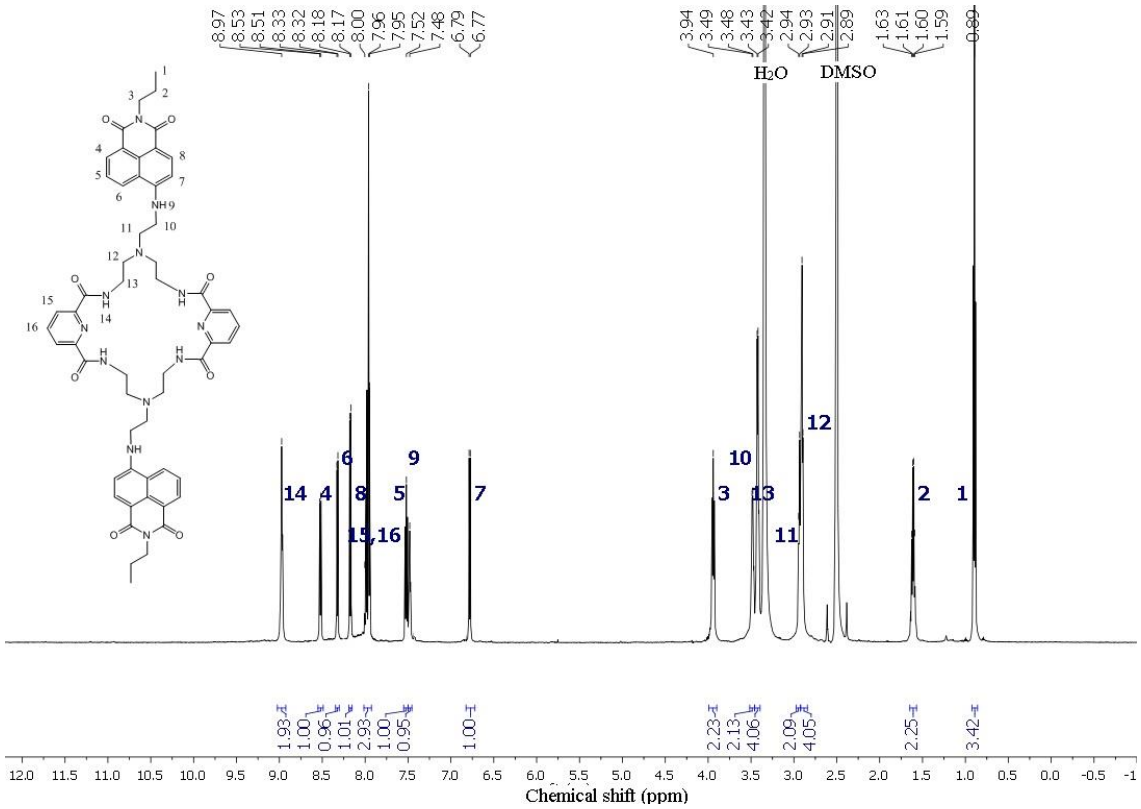
Compound **5**

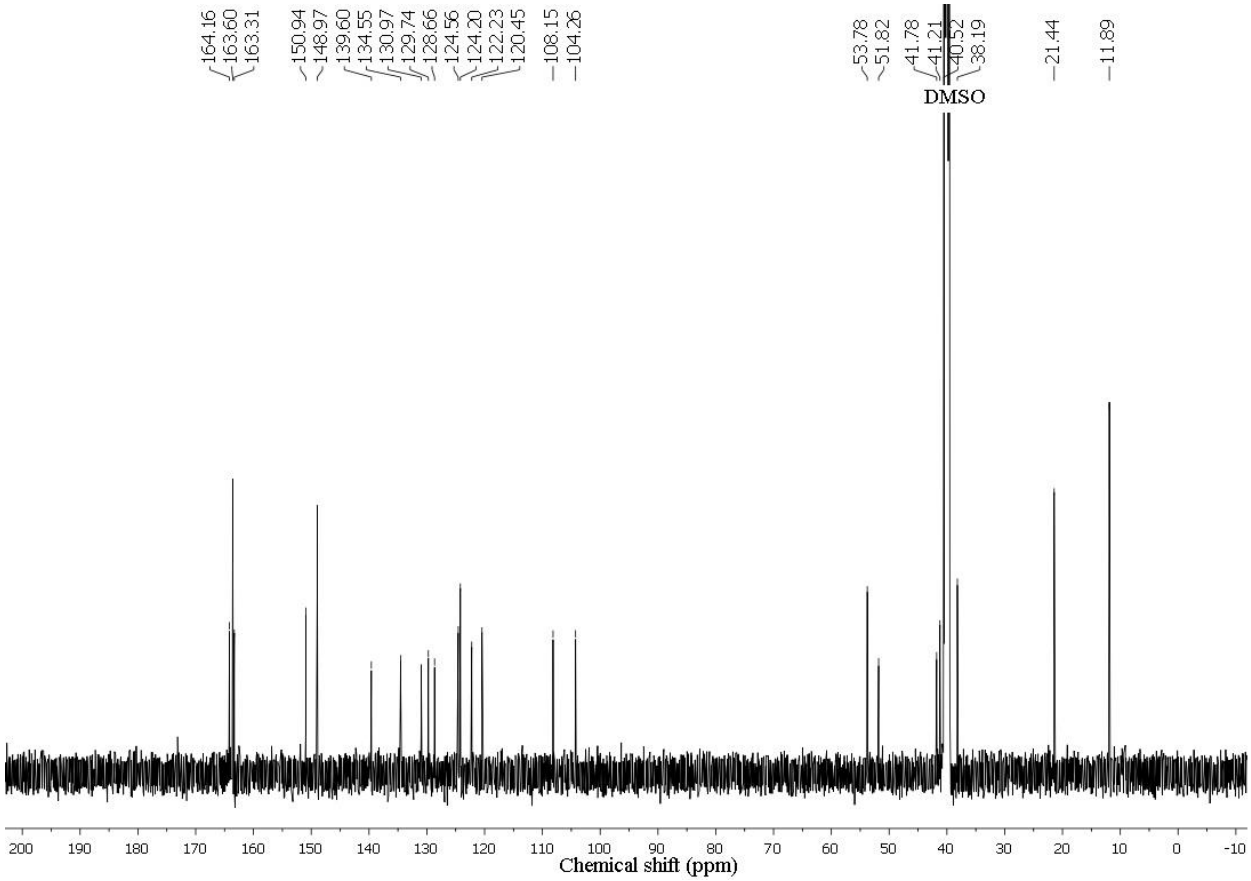
^{1}H, ^{13}C NMR, DMSO-*d6*



Compound **3**

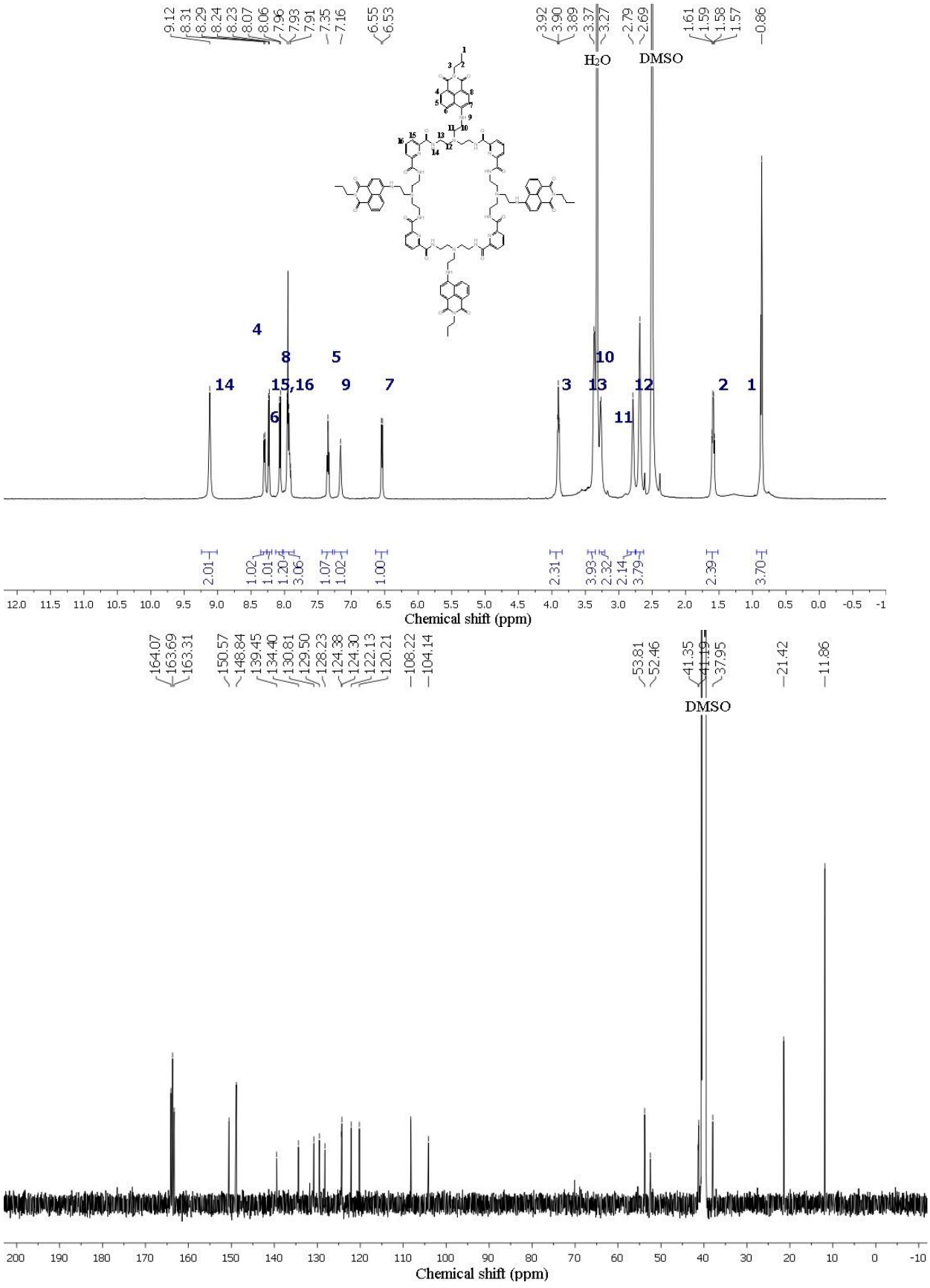
^{1}H, ^{13}C NMR, DMSO-*d6*





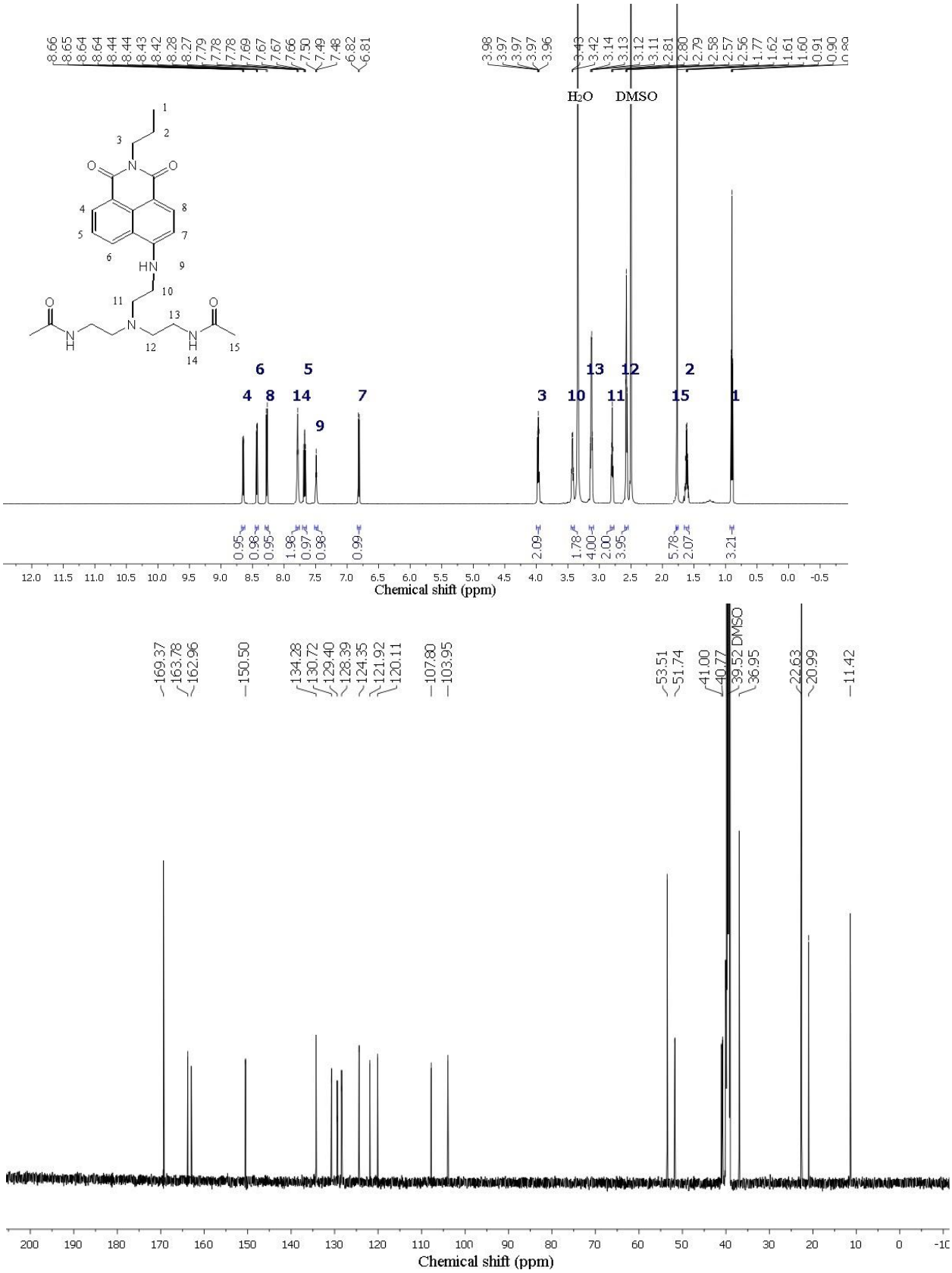
Compound **4**

^{1}H, ^{13}C NMR, DMSO-*d6*



Compound **4**

^{1}H, ^{13}C NMR, DMSO-*d6*



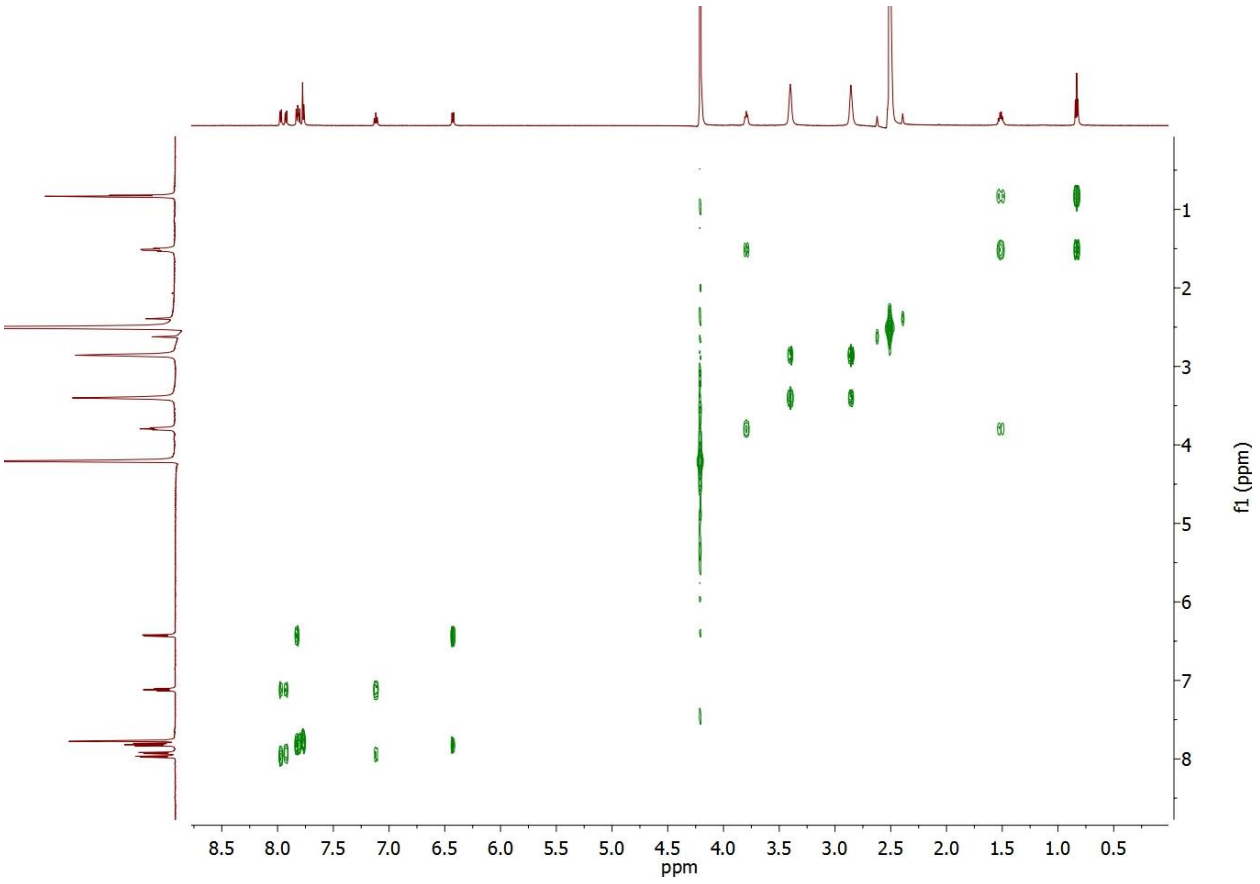


Figure S1. ^{1}H-^{1}H COSY and ROESY of **3** measured in 7:3 DMSO-d_6–D_2O.

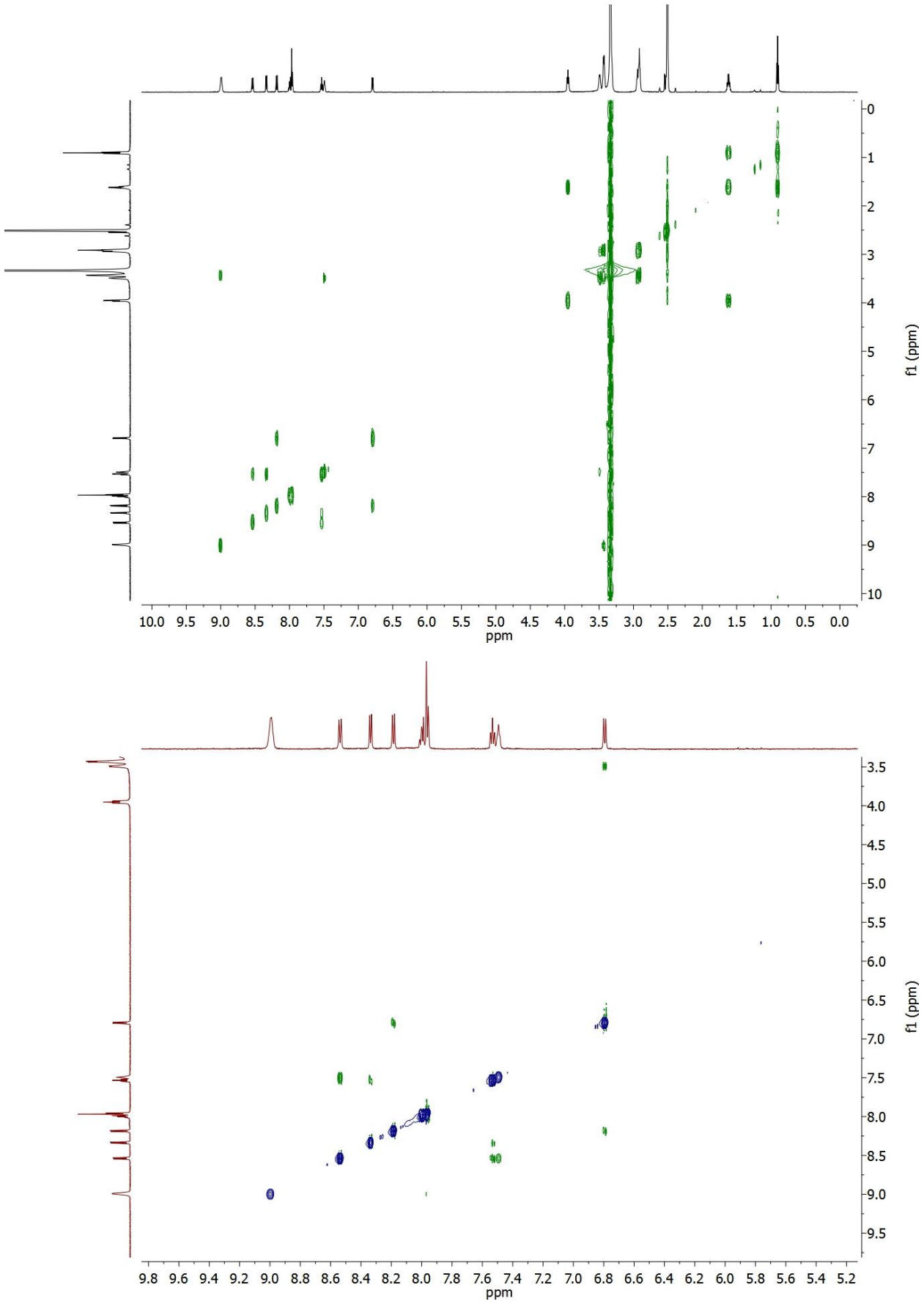


Figure S2. ^{1}H-^{1}H COSY and ROESY of **3** measured in DMSO-d_6.

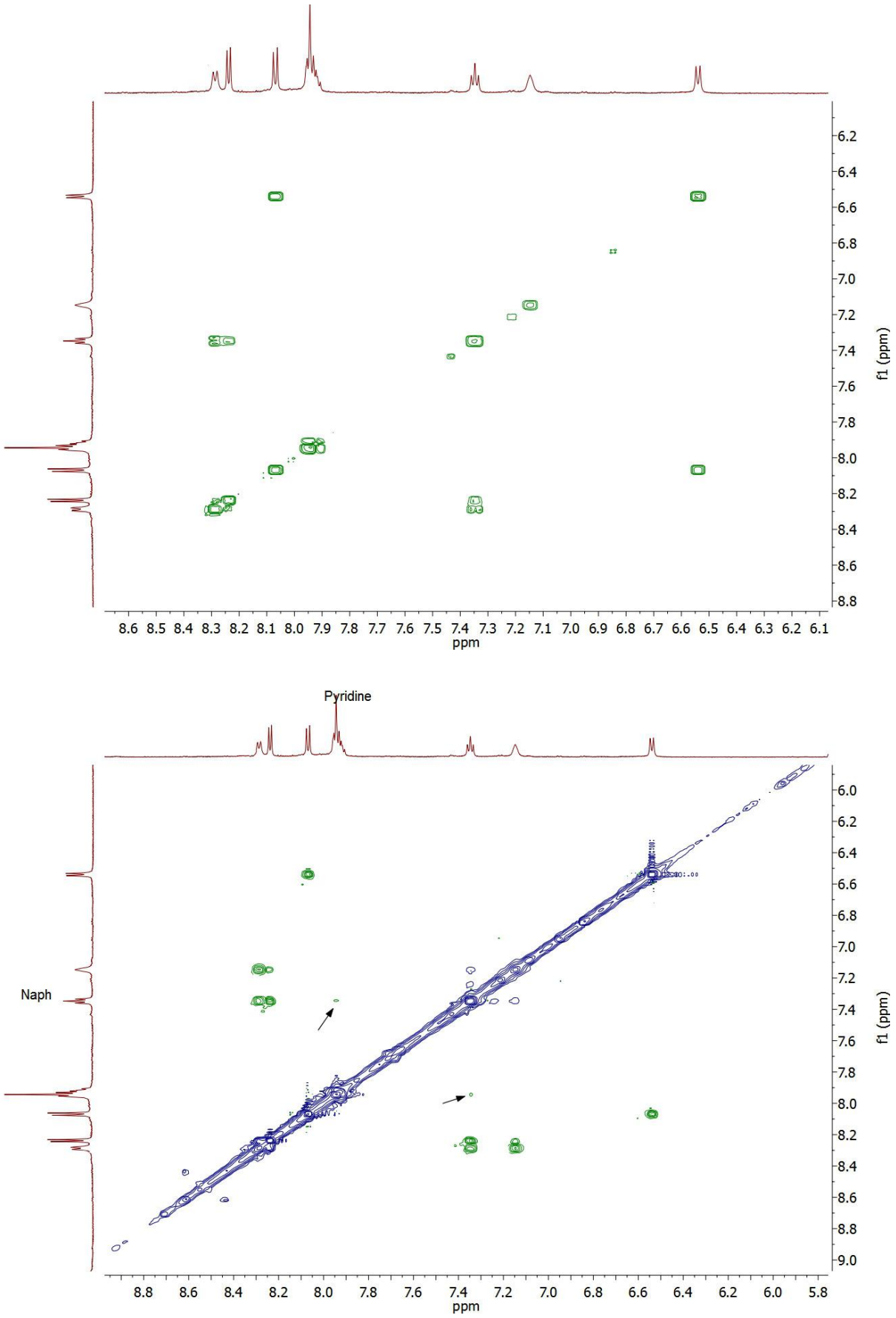


Figure S3. ^{1}H-^{1}H COSY and ROESY of **4** measured in DMSO-d_6.

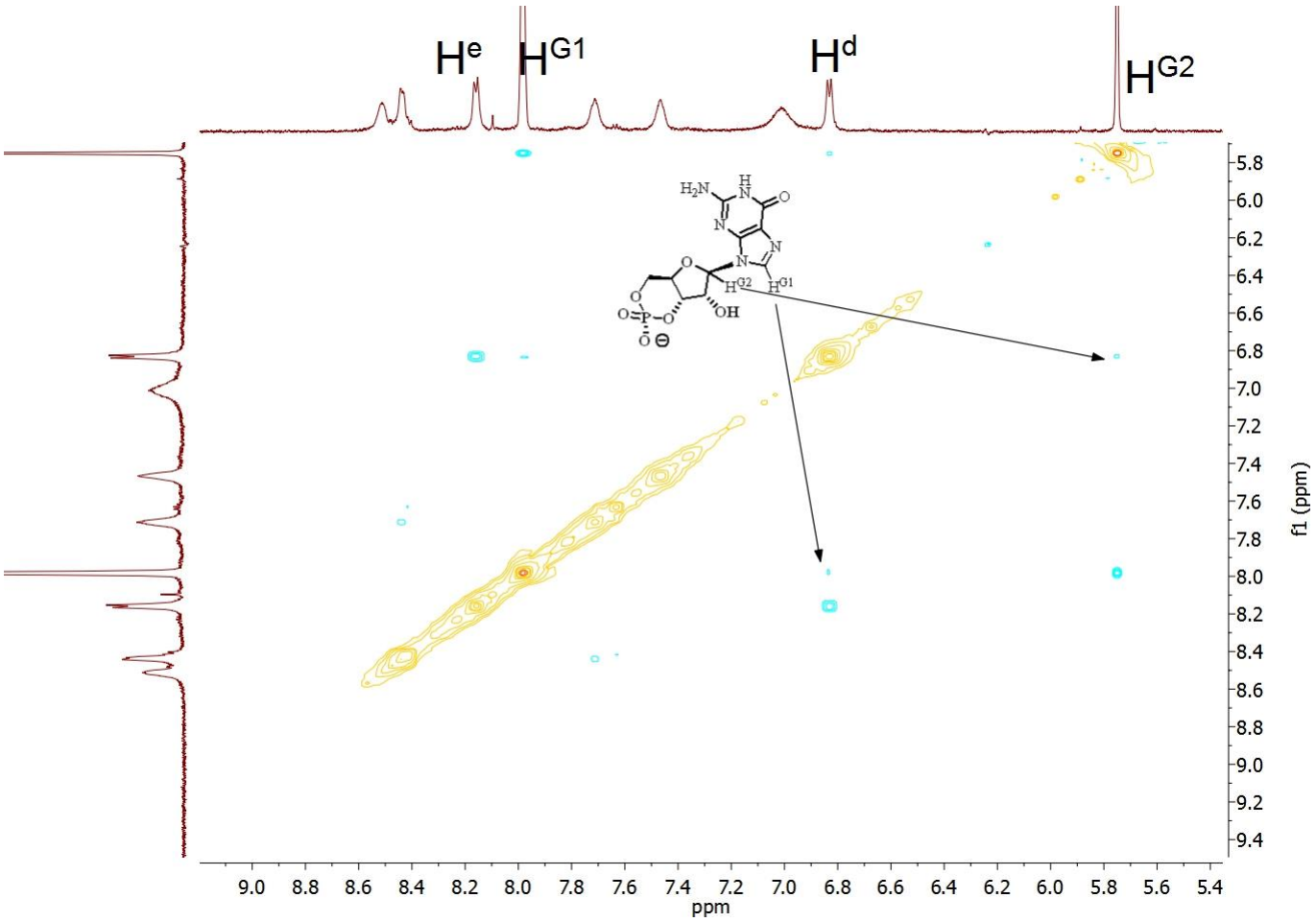


Figure S4. ^{1}H-^{1}H ROESY NMR of **3** with 5 equiv. cGMP and 5 equiv. HClO4 measured in DMSO-d_6-D_2O (7:3) mixture.

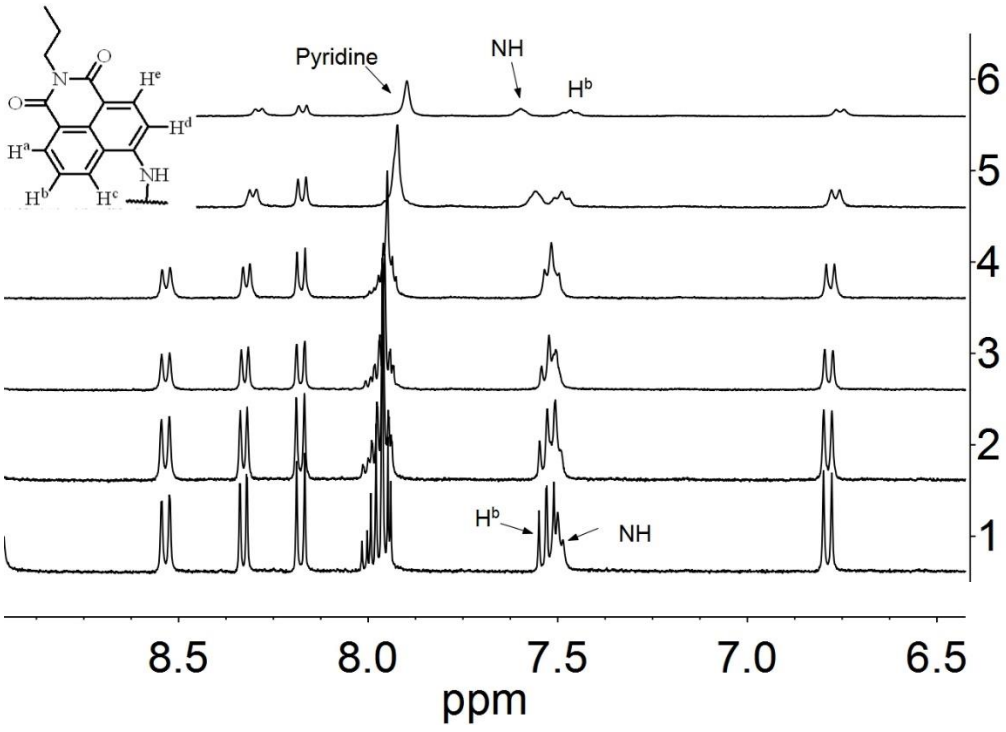


Figure S5. ^{1}H NMR of receptor **3** in the presence of $TBAHSO_4$ in DMSO-*d6*–D_2O mixture. Additions 1 to 5 are 0.25, 0.5, 1, 4 and 10 equiv of $TBAHSO_4$.

2. Atomic Force Microscopy (AFM) measurements

For AFM imaging, we prepared samples on polished Si wafers covered with a 100 nm thick oxide layer by spin-casting (1000 rpm, 60 s) an aqueous solution (pH 3.6, 50 mM acetate buffered with 2% DMSO addition) of **3** in the presence of 5 equiv of Na_2SO_4 or ATP. AFM measurements were performed at ambient conditions in the amplitude modulation mode (also known as tapping mode) using a NanoWizard ll AFM (JPK Instruments AG, Berlin, Germany) and silicon cantilevers (Pointprobe NCH, NanoWorld AG, Neuchâtel, Switzerland) with a resonance frequency of typical 350 kHz and a tip radius of 8 nm as given by the manufacturer. The free amplitude A_0 was ≈ 60 nm and the amplitude setpoint $A/A_0 \approx 0.8$.

3. DFT calculations

Molecular modeling calculations were performed first using program "ORCA". A BP86 functional which includes electron density gradient was used. def2-SVP basis set-atomic basis sets of grouped Gaussian functions were used to solve the Kohn—Sham equations. The criterion for convergence was a difference below 0.01 kcal/mol/Angstrom in the energy between two sequential structures. The host-guest model structures were generated by combining a preoptimized structure of the receptor with the anion, followed by simultaneous optimization of the proposed structures. Searches for the relevant global minima were performed by calculating different anion-to-receptor coordination modes. In order to get more accurate energies, we performed single-point calculations for the received geometries, using the BP86 functional and def2-TZVP basis set.

Coordinates of complex **3**H_2^{2+}•cGMP$^-$:

O	-2.451873	6.143204	-1.441870
O	-6.478353	0.320873	-0.872045
O	-1.582951	-1.552375	2.366985
O	3.560320	2.817927	0.254097
O	5.092587	-1.141433	0.923536
O	4.327749	-3.750351	4.621533
O	-3.219701	1.421762	3.142008
O	0.091243	1.358320	6.327163
N	-2.210429	4.237957	-2.706734
H	-2.532207	3.263138	-2.825868
N	-4.212873	3.033522	-1.430970
N	-4.714933	0.536901	-2.325198
H	-3.930687	1.144242	-2.615807
N	-3.649843	-2.056936	-1.073262
H	-2.841008	-1.561591	-1.594277
N	-1.638274	-0.212746	0.502555
H	-1.056300	0.479480	0.016301
N	0.875376	0.590399	0.899427
N	2.173166	1.739286	-1.225589
H	1.529669	0.945042	-1.331081

N	0.884348	3.756010	-2.943983
H	0.438882	3.275181	-2.130280
N	-0.796517	-3.137465	-0.619254
H	-0.969026	-2.425655	-1.346783
N	4.716075	-2.468379	2.757461
N	1.308291	4.786666	0.014714
H	2.302227	4.790579	0.255749
N	-1.572542	1.409927	4.747423
C	-2.792421	4.987924	-1.719118
C	-3.869705	4.246891	-0.964947
C	-4.468599	4.829666	0.166366
H	-4.130938	5.821169	0.497025
C	-5.473593	4.108405	0.828993
H	-5.958549	4.521788	1.725312
C	-5.851350	2.851225	0.333594
H	-6.636115	2.239929	0.800568
C	-5.187785	2.354256	-0.804206
C	-5.547298	0.986178	-1.341732
C	-4.863199	-0.765237	-2.941807
H	-4.064075	-0.864787	-3.700379
H	-5.834699	-0.829406	-3.481333
C	-4.851962	-1.973238	-1.993401
H	-5.758224	-1.970173	-1.361230
H	-4.857757	-2.887011	-2.618565
C	-3.869663	-1.364937	0.259499
H	-3.583598	-2.058063	1.069372
H	-4.948437	-1.137643	0.348325
C	-3.081689	-0.072676	0.414694
H	-3.276531	0.596928	-0.436782
H	-3.462548	0.420032	1.339344
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C	0.357581	-0.220616	1.840736
C	1.029122	-0.534353	3.034451
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C	2.274427	0.065472	3.275255
H	2.821206	-0.139655	4.206426
C	2.813069	0.922825	2.308741
H	3.786285	1.414079	2.428522
C	2.078358	1.138390	1.126499
C	2.675761	1.982041	0.038115
C	2.869709	2.273431	-2.377287
H	3.481818	1.497137	-2.885824
H	3.565785	3.042334	-1.984756
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H	2.509695	3.338919	-4.243595
H	1.398030	1.960939	-3.924165
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H	0.390212	4.326873	-4.912436
H	-0.519557	2.909429	-4.262846
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H	-1.048360	5.831307	-3.339521
H	-1.877386	4.980738	-4.658071

C	-3.216599	-3.498910	-0.932723
H	-3.030776	-3.861469	-1.963841
H	-4.074616	-4.062685	-0.516313
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H	-2.148206	-3.431326	0.982943
H	-1.889646	-4.864577	-0.056436
C	0.432221	-2.973602	-0.029417
C	1.273047	-2.017311	-0.648661
H	0.841730	-1.455380	-1.483546
C	2.539823	-1.711743	-0.164831
H	3.180674	-0.972010	-0.664603
C	3.008868	-2.296193	1.016265
C	4.327188	-1.918363	1.528391
C	3.933399	-3.369064	3.522140
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C	1.914247	-4.791899	3.577495
H	2.310442	-5.198363	4.518768
C	0.701535	-5.243602	3.023735
H	0.133742	-6.043210	3.520659
C	0.214968	-4.683414	1.845501
H	-0.722150	-5.076878	1.446104
C	0.913449	-3.652055	1.157697
C	2.192177	-3.247687	1.692078
C	5.990748	-2.023944	3.338774
H	6.697073	-1.861233	2.502751
H	6.356879	-2.849570	3.977251
C	5.847493	-0.739279	4.163127
H	5.128224	-0.929205	4.988757
H	5.408270	0.047408	3.513270
C	7.187420	-0.267066	4.731592
H	7.645491	-1.039966	5.383669
H	7.065803	0.651343	5.340086
H	7.911312	-0.038729	3.921541
C	1.471494	5.068691	-2.455761
H	1.315963	5.814472	-3.259424
H	2.561254	4.911057	-2.347819
C	0.902611	5.575383	-1.125008
H	1.279251	6.618619	-1.019349
H	-0.203104	5.675362	-1.150387
C	0.481944	4.081758	0.864813
C	-0.787318	3.632612	0.459686
H	-1.125775	3.812650	-0.566329
C	-1.623853	2.919905	1.332229
H	-2.626944	2.613747	1.008181
C	-1.197297	2.564979	2.613813
C	-2.082943	1.768412	3.487844
C	-0.292559	1.754149	5.228758
C	0.544814	2.615638	4.351885
C	1.785645	3.049752	4.818698
H	2.096598	2.742901	5.827713
C	2.601620	3.864579	4.004998
H	3.570219	4.222232	4.382488

C	2.184227	4.223268	2.725143
H	2.842959	4.859334	2.117667
C	0.938483	3.776880	2.205700
C	0.091449	2.981950	3.053492
C	-2.417170	0.591381	5.634685
H	-3.460678	0.753370	5.306476
H	-2.286597	0.985333	6.661545
C	-2.060334	-0.898868	5.586561
H	-2.108481	-1.244885	4.534123
H	-1.008220	-1.018051	5.921691
C	-2.988005	-1.733288	6.471558
H	-2.710737	-2.806197	6.440224
H	-4.045888	-1.650425	6.142857
H	-2.943226	-1.408392	7.532479
C	2.467781	-1.101626	-3.985876
C	-0.952163	-1.580258	-5.429419
C	0.549813	-1.330691	-5.336260
C	2.515494	-2.448545	-4.775407
C	0.959121	-1.015892	-3.895531
C	2.825220	-4.693644	-1.947931
C	1.384988	-4.406557	-3.517497
C	3.387732	-3.730711	-2.809265
C	3.537446	-5.020650	-0.726649
C	5.179648	-3.277475	-1.542015
H	-1.301450	-1.719478	-6.469202
H	3.918698	-0.170989	-4.894166
H	-1.248167	-2.460850	-4.819617
H	2.981552	-1.203360	-3.008230
H	0.641747	-1.881823	-3.275743
H	0.518276	-4.478197	-4.184742
N	6.331613	-2.598224	-1.229649
N	2.458778	-3.557576	-3.823938
N	1.587719	-5.100105	-2.413932
O	3.255160	-5.780507	0.188728
N	4.516695	-2.993850	-2.660554
N	4.766670	-4.258221	-0.671505
O	2.969754	-0.004531	-4.735504
O	1.370175	-2.470476	-5.630230
O	-1.594352	-0.376912	-4.931943
O	0.380175	0.174180	-3.356479
O	-1.874848	1.407826	-3.079011
O	-1.646291	-1.180645	-2.490275
P	-1.298467	0.038996	-3.361077
H	3.440334	-2.537418	-5.384090
H	6.335983	-2.207768	-0.273088
H	6.521335	-1.865151	-1.917774
H	5.336751	-4.463418	0.155102
H	0.816523	-0.477383	-5.999655

FINAL SINGLE POINT ENERGY -4962.027996893603

4. Absorption and fluorescence titrations

The stock solutions of compounds **3**, **4** (10^{-5} M) in pH 3.6: 50 mM acetate buffer (2% DMSO vol.) were prepared in 50 ml volumetric flasks. The solutions of sodium salts (0.001 – 0.01 M) were prepared in the solution of compounds to keep the concentration of the compound constant throughout the titrations. The receptor solution in a 10mm cuvette (2.0 ml) was then titrated with the salt solution and each time the spectrum was recorded. Following setup parameters for fluorescent titration were used λ_{ex}: 440 nm, slit 2/2, λ_{em}: 480-680 nm. (For absorption titrations λ_{abs}=320-550 nm). The resulting data was imported in HypSpec program and the data was fitted to obtain stability constants with anions.

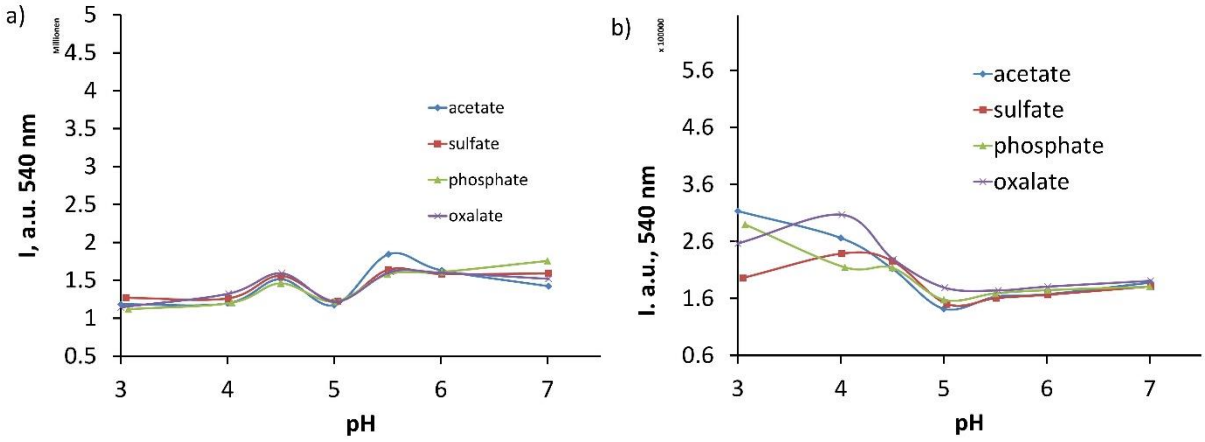


Figure S6. Fluorescence intensity of receptor a) **5** and b) **4** at 540 nm in the presence of an excess of different anions depending on the pH of the solution. Content of the solution with different pH values: 0.01 mM receptor in 50 mM NaOH/acetic acid mixtures containing 2% DMSO and 1 mM anions as sodium salts.

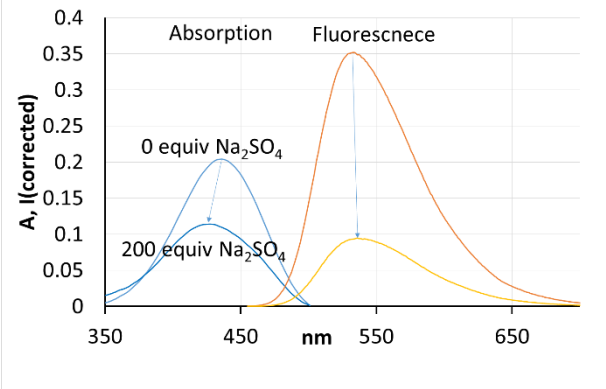


Figure S7. Corrected absorption and fluorescence spectra before and after addition of 200 equiv of Na_2SO_4 to **3**.

4.1 Binding constants with anions and nucleotides

Table S1. Binding constants, $\log\beta_{11}$ and $\log\beta_{12}$ of macrocycles **3** and **4** with anions determined by UV-Vis and fluorescence titrations (in parenthesis) in a 50 mM acetate buffer containing 2% (vol.) DMSO, pH 3.6, 23°C.

Anion/Receptor	**3**	**4**
Na_2SO_4	4.41 ± 0.02 (4.20 ± 0.03)	3.96 ± 0.05 $\log\beta_{12}$ = 7.00 ± 0.05

NaH_2PO_4	4.23 ± 0.02 (4.10 ± 0.03)	4.79 ± 0.02 $\log\beta_{12}$ = 7.46 ± 0.05
$Na_2C_2O_4$	4.25 ± 0.03 $\log\beta_{12}$ = 8.00 ± 0.03	5.49 ± 0.02 $\log\beta_{12}$ = 8.50 ± 0.06
$NaClO_4$	3.03 ± 0.01	4.00 ± 0.03
$NaNO_3$	2.83± 0.01	4.55 ± 0.03
NaCl	3.02± 0.01 (2.88 ± 0.01)	3.84 ± 0.04
NaBr	2.82± 0.01 (2.55 ± 0.01)	4.00 ± 0.03
NaI	2.54± 0.01 (2.24 ± 0.01)	3.58 ± 0.04

Table S2. Binding constants, logK_{11} of macrocycles **3** and **4** with nucleotides determined by UV-Vis and fluorescence titrations (in parenthesis). Conditions: 50 mM acetate buffer (2% DMSO, pH 3.6, 23°C); ex. 450 nm.

Nucleotide	receptor **3**	receptor **4**
AMP	4.40 ± 0.02 (4.10 ± 0.04)	3.29 ± 0.02 (2.97 ± 0.04)
cAMP	4.60 ± 0.01 (4.80± 0.01)	3.90 ± 0.02 (3.33 ± 0.02)
GMP	4.31 ± 0.01; (4.25 ± 0.01)	4.00 ± 0.03 (3.60 ± 0.02)
cGMP	4.91 ± 0.01 (4.80 ± 0.01)	4.20 ± 0.03 (3.55 ± 0.02)
CMP	4.35 ± 0.02	4.15 ± 0.02
TMP	4.32 ± 0.02	4.20 ± 0.02
UMP	4.38 ± 0.03	4.25 ± 0.02

4.2. Photophysical properties of the compounds

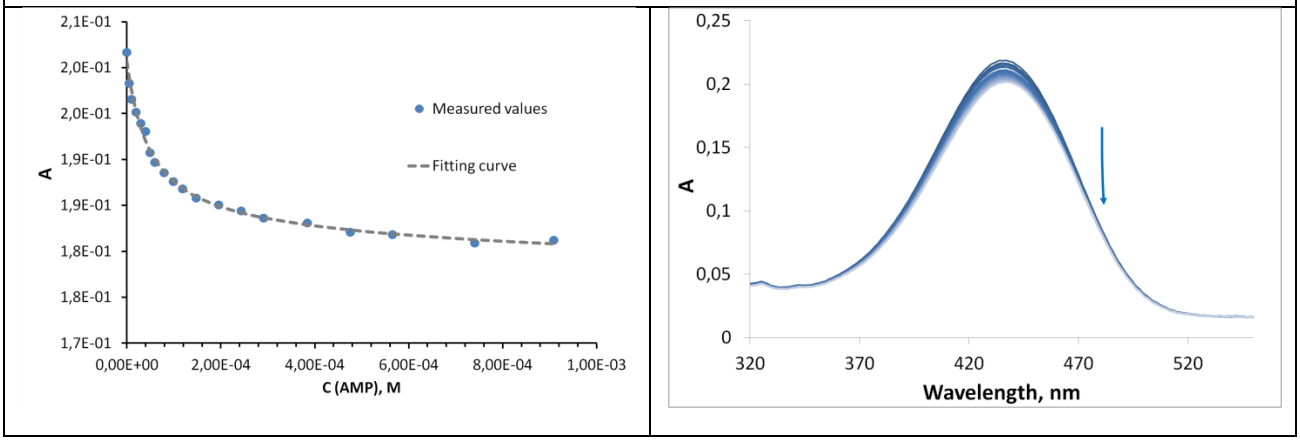
Table S3. Photophysical properties of the compounds determined in a 50 mM acetate buffer pH 3.6, at full-protonated state.

Compound	ε(max)[$Lmol^{-1}cm^{-1}$]	Absorption	Emission

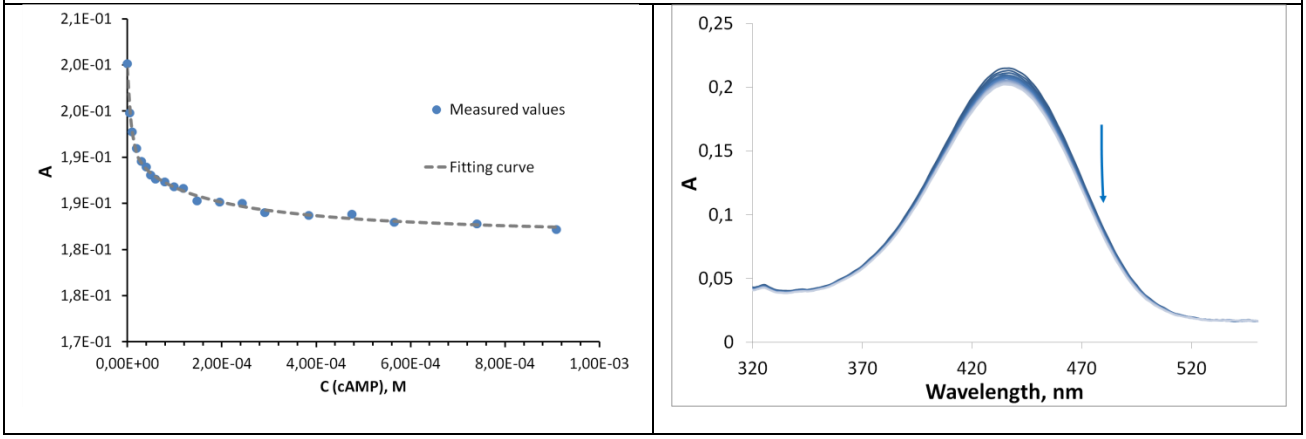
		λ_{max},nm	λ_{max}, nm
6	17010	430	528
3	20290	436	529
4	39690	441	534

4.3.Absorption titration of 3 with nucleotides

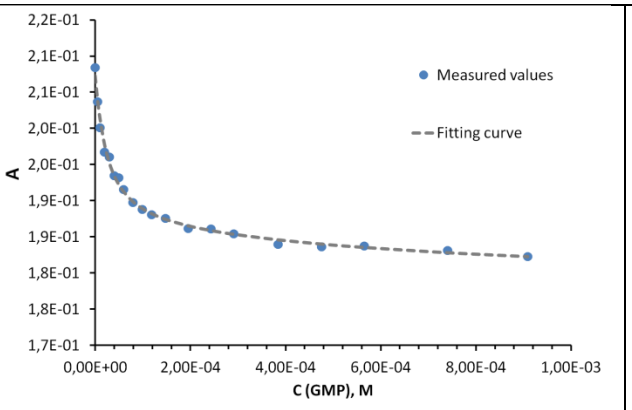
AMP

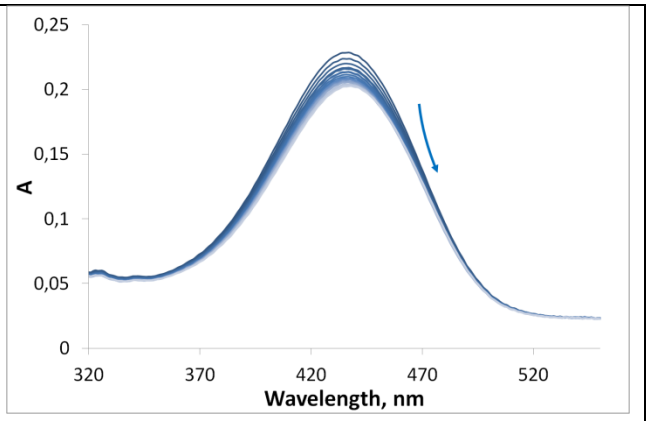


cAMP

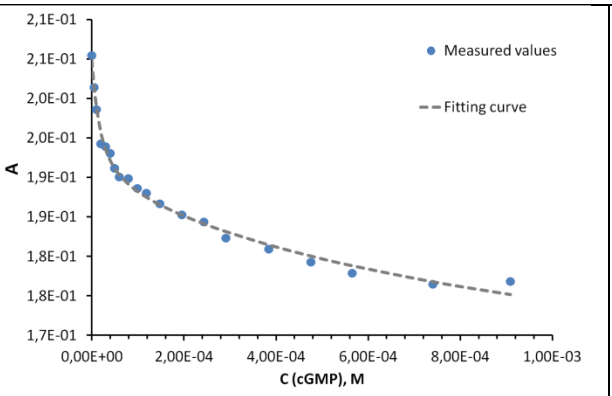


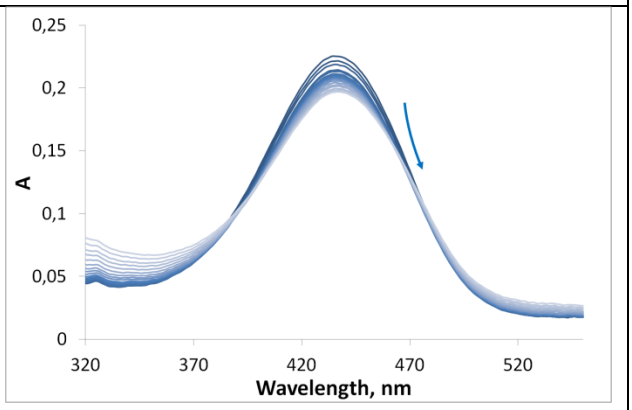
GMP


Measured values
Fitting curve
A
C (GMP), M

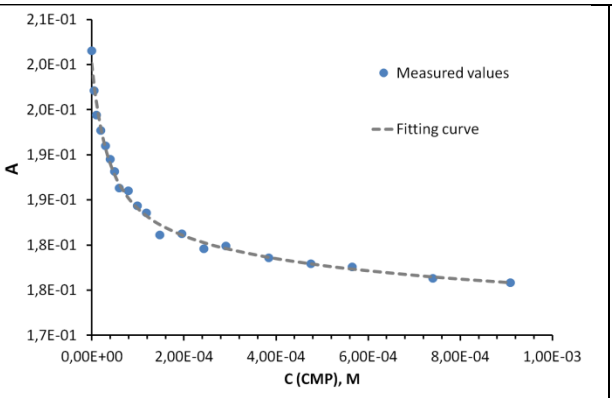

A
Wavelength, nm

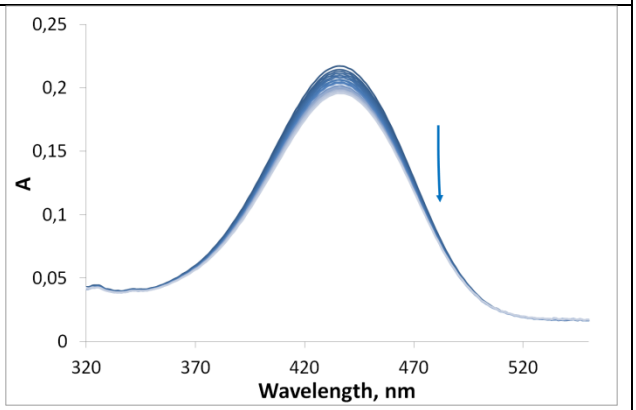
cGMP


Measured values
Fitting curve
A
C (cGMP), M

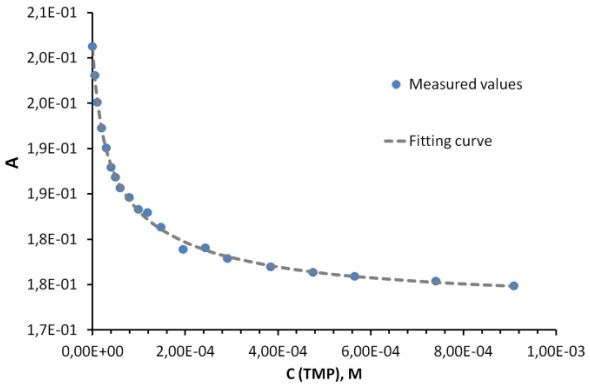

A
Wavelength, nm

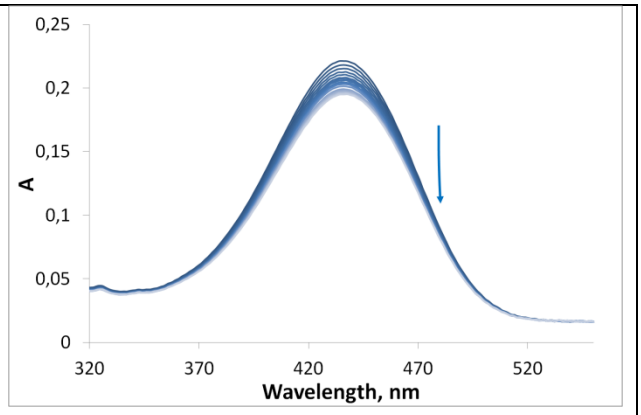
CMP


Measured values
Fitting curve
A
C (CMP), M

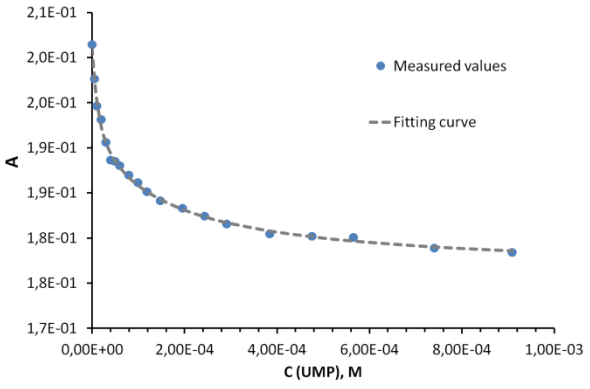

A
Wavelength, nm

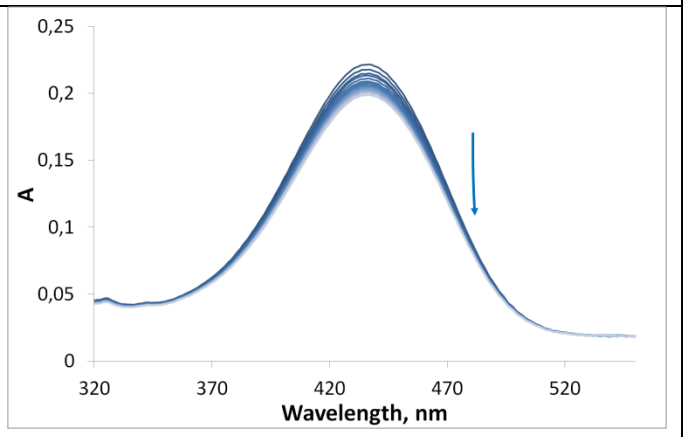
TMP





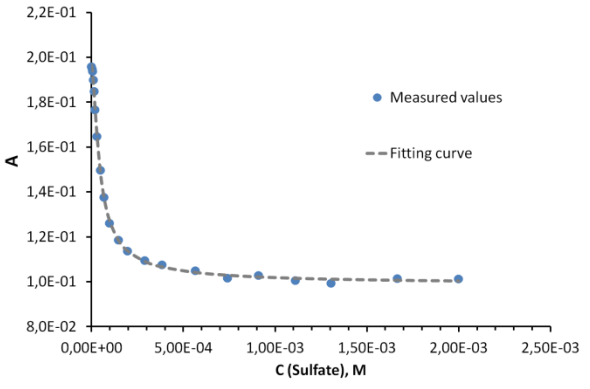
UMP

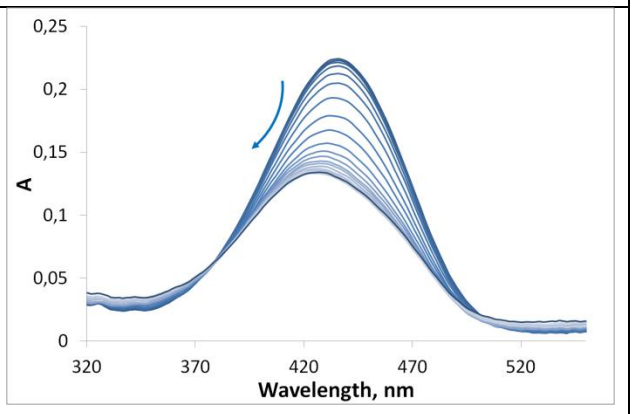




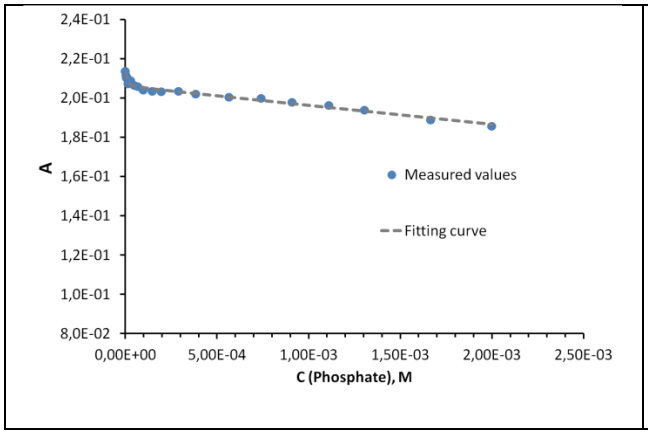
4.4. Absorption titration of 3 with anions

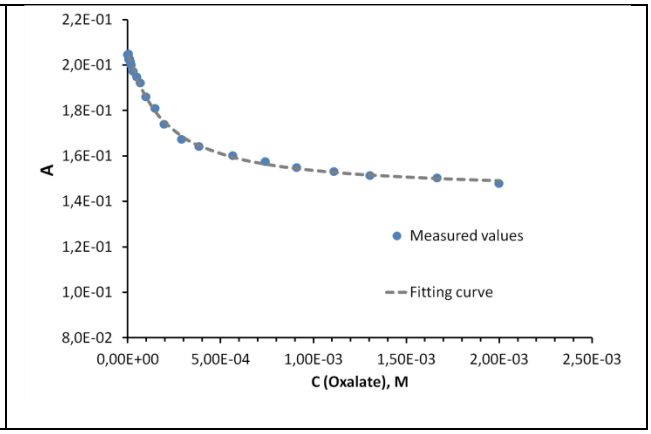
Na_2SO_4

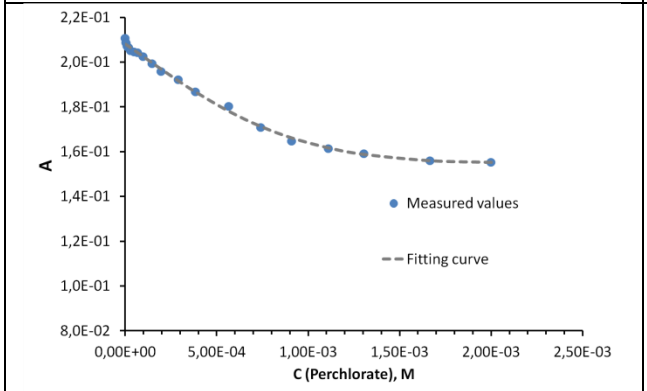
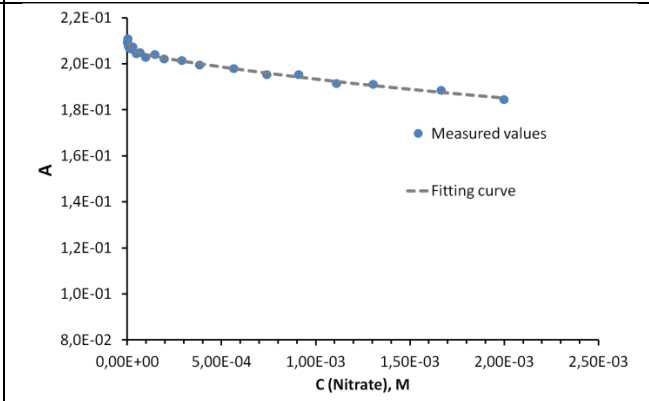


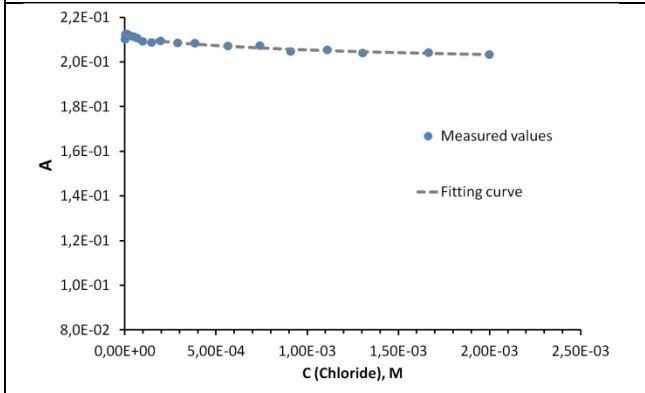
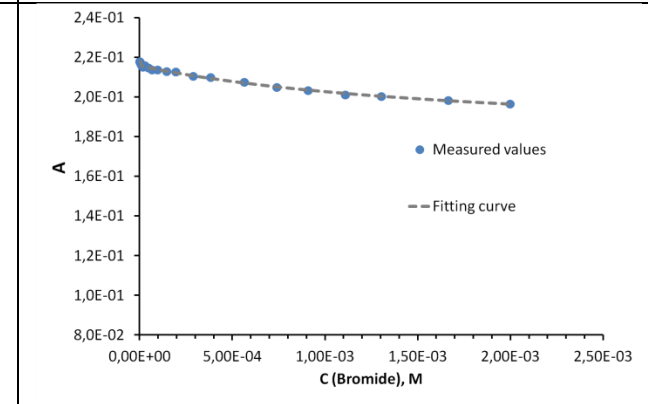


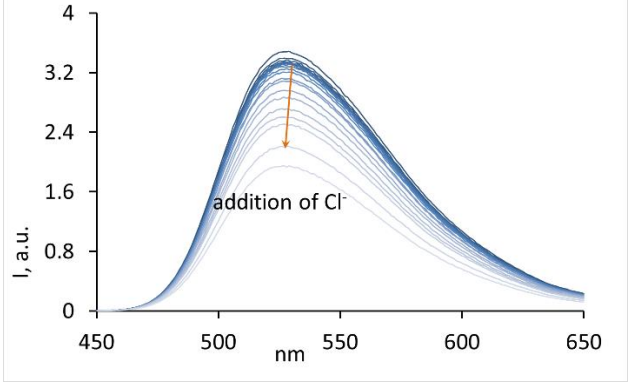
NaH_2PO_4	$Na_2C_2O_4$

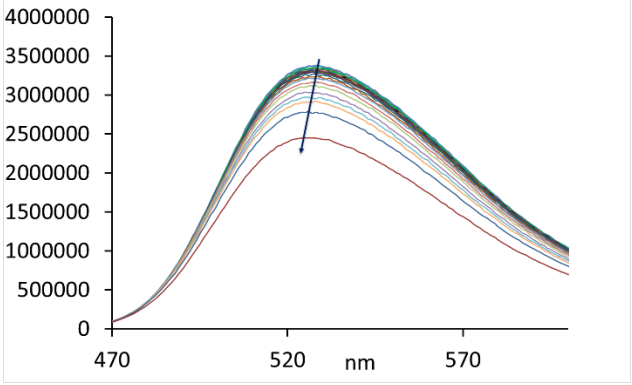




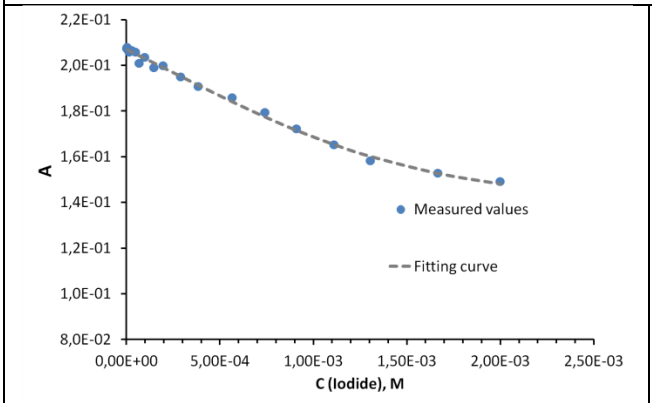
$NaClO_4$	$NaNO_3$
	

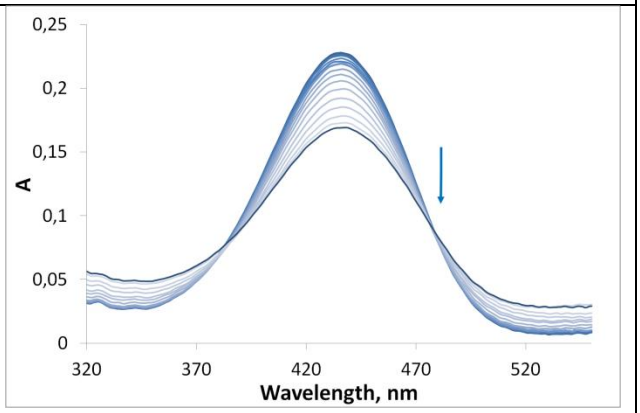
NaCl	NaBr
	





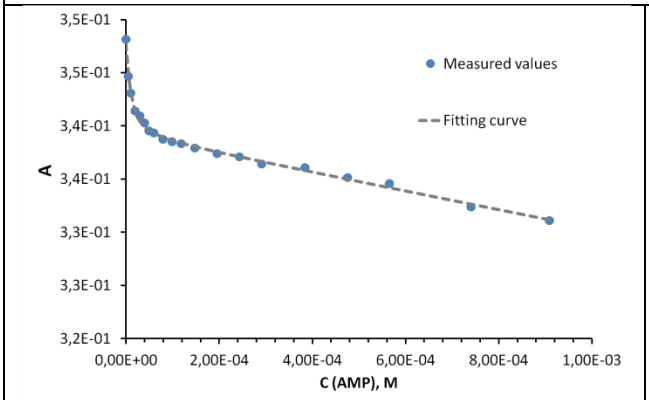
NaI

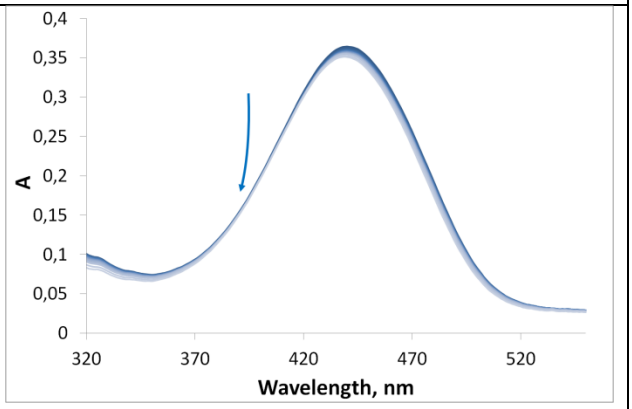




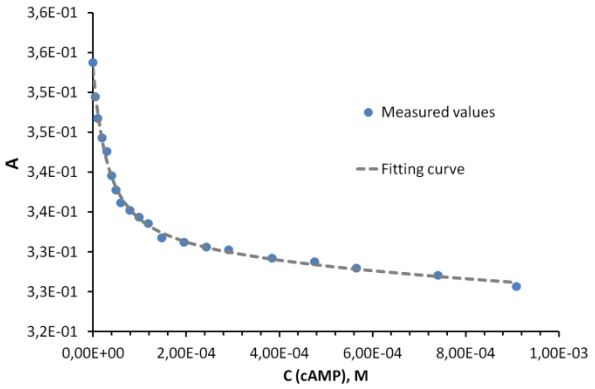
4.5. Absorption titration of 4 with nucleotides

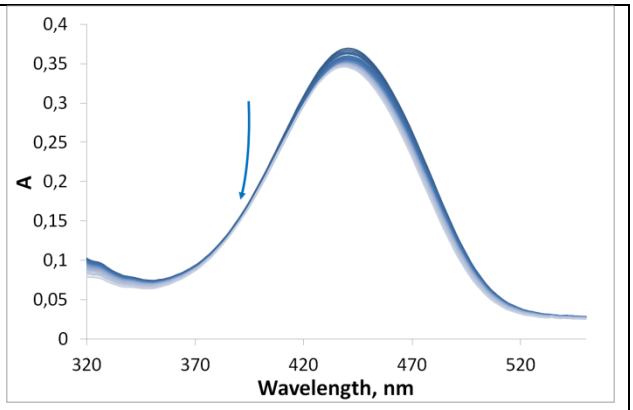
AMP



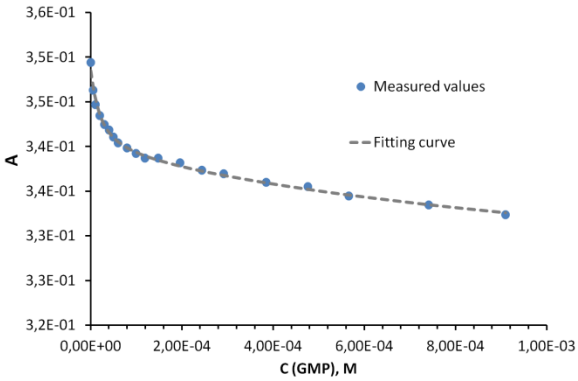


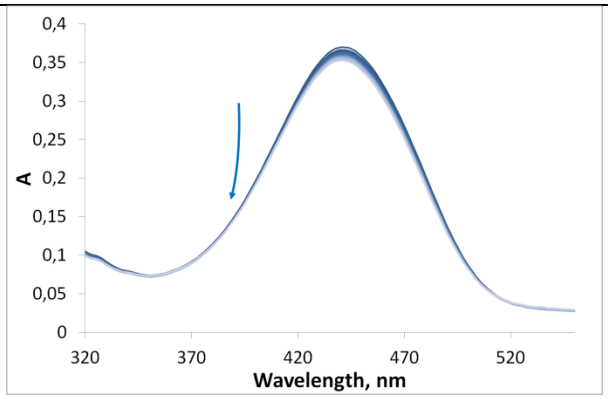
cAMP


3,6E-01
3,6E-01
3,5E-01
3,5E-01
3,4E-01
3,4E-01
3,3E-01
3,3E-01
3,2E-01
A
Measured values
Fitting curve
0,00E+00
2,00E-04
4,00E-04
6,00E-04
8,00E-04
1,00E-03
C (cAMP), M

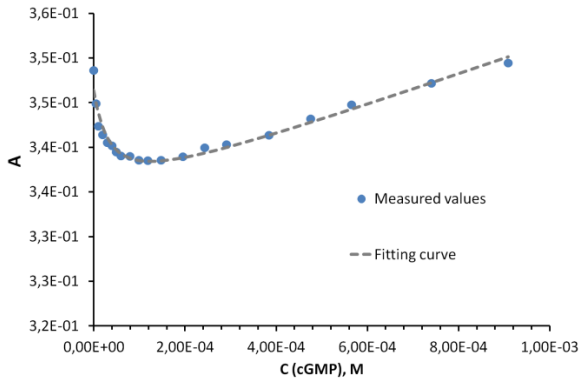

0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
A
320
370
420
470
520
Wavelength, nm

GMP


3,6E-01
3,5E-01
3,5E-01
3,4E-01
3,4E-01
3,3E-01
3,3E-01
3,2E-01
A
Measured values
Fitting curve
0,00E+00
2,00E-04
4,00E-04
6,00E-04
8,00E-04
1,00E-03
C (GMP), M


0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
A
320
370
420
470
520
Wavelength, nm

cGMP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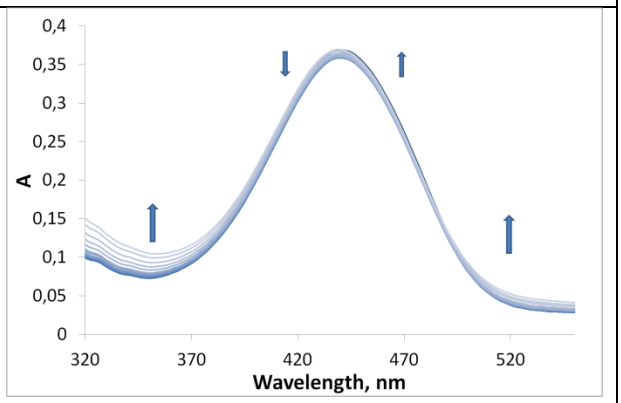
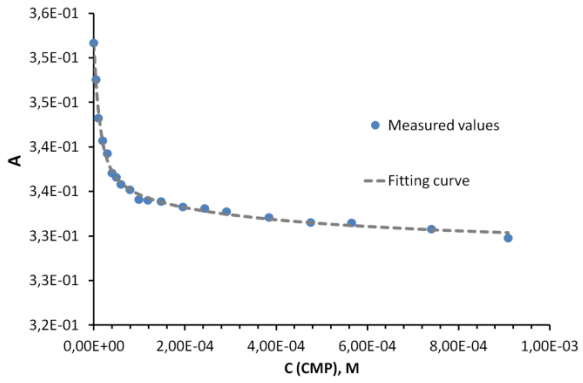
3,5E-01
3,5E-01
3,4E-01
3,4E-01
3,3E-01
3,3E-01
3,2E-01
A
Measured values
Fitting curve
0,00E+00
2,00E-04
4,00E-04
6,00E-04
8,00E-04
1,00E-03
C (cGMP), M


0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
A
320
370
420
470
520
Wavelength, nm

CMP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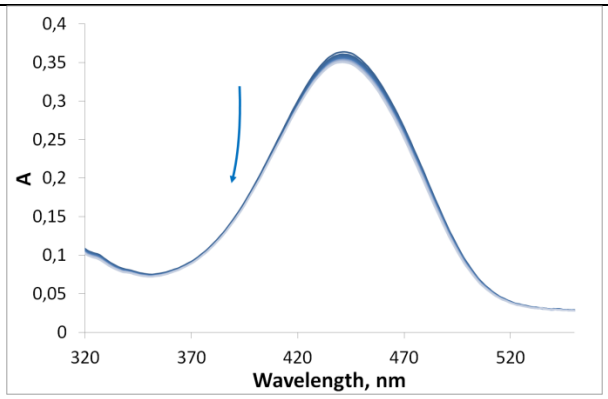
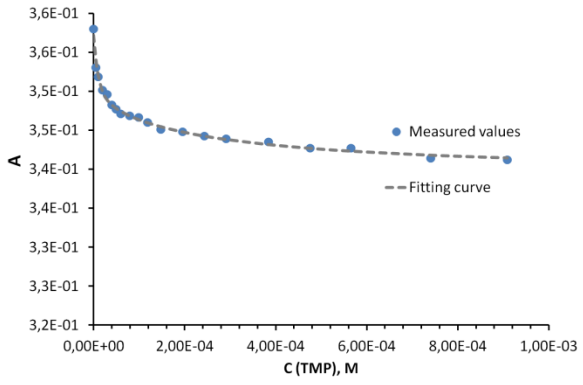
3,5E-01
3,5E-01
3,4E-01
3,4E-01
3,3E-01
3,3E-01
3,2E-01
A
Measured values
Fitting curve
0,00E+00
2,00E-04
4,00E-04
6,00E-04
8,00E-04
1,00E-03
C (CMP), M


0,4
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
A
320
370
420
470
520
Wavelength, nm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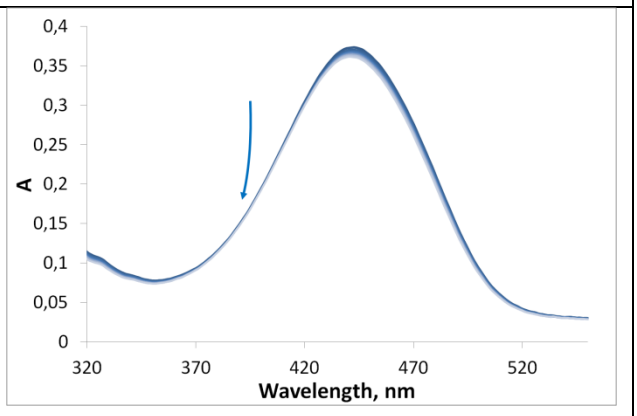
3,6E-01
3,5E-01
3,5E-01
3,4E-01
3,4E-01
3,3E-01
3,3E-01
3,2E-01
A
Measured values
Fitting curve
0,00E+00
2,00E-04
4,00E-04
6,00E-04
8,00E-04
1,00E-03
C (TMP), M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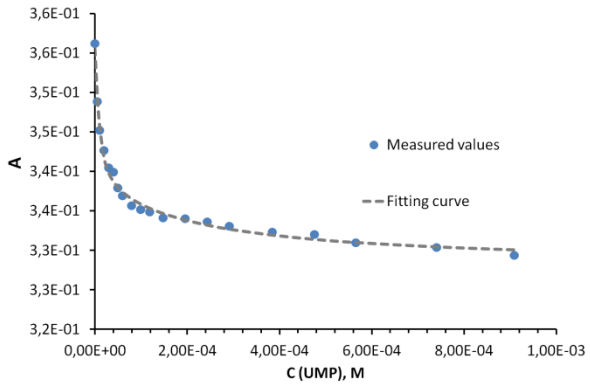
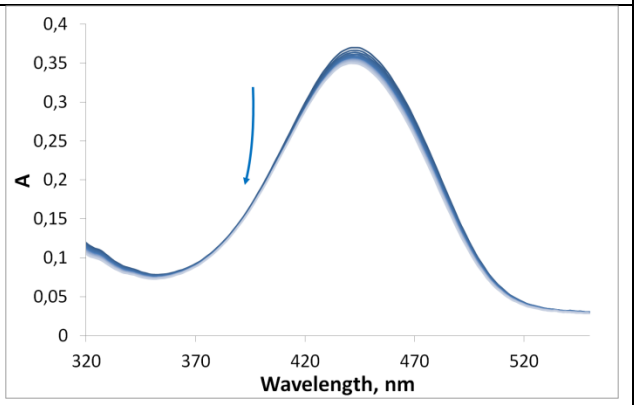
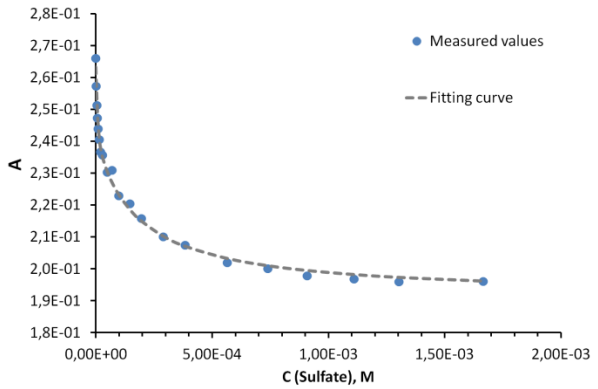
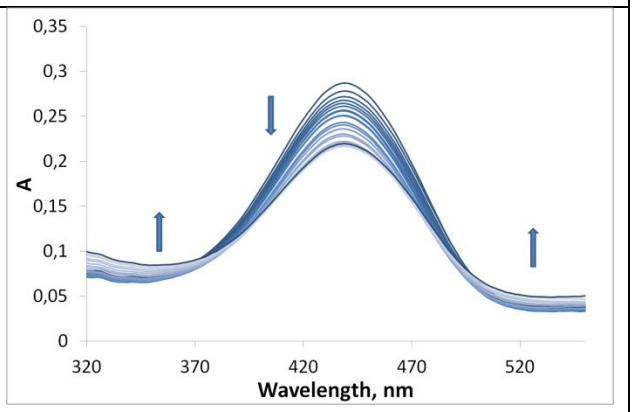
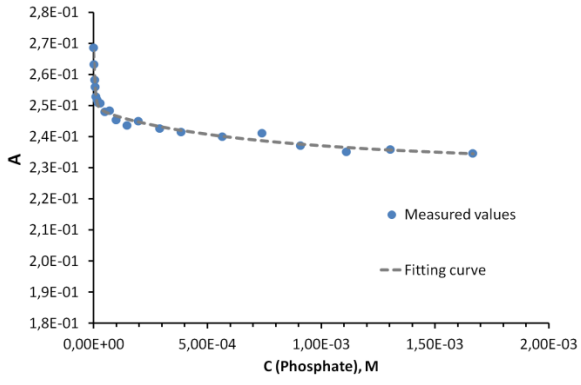
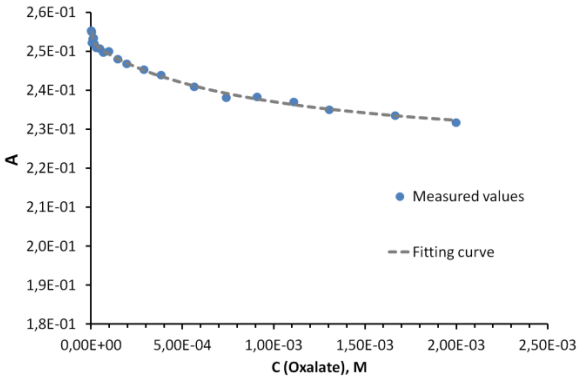
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
A
320
370
420
470
520
Wavelength, nm

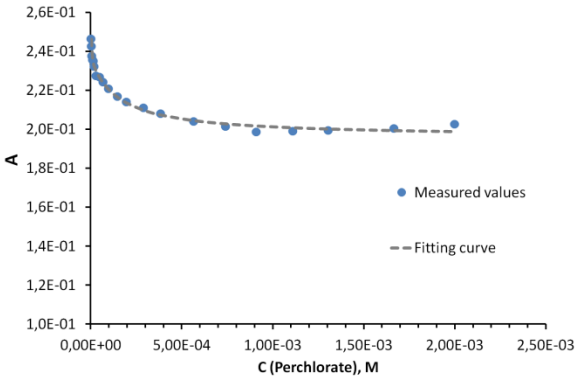
UMP	
	

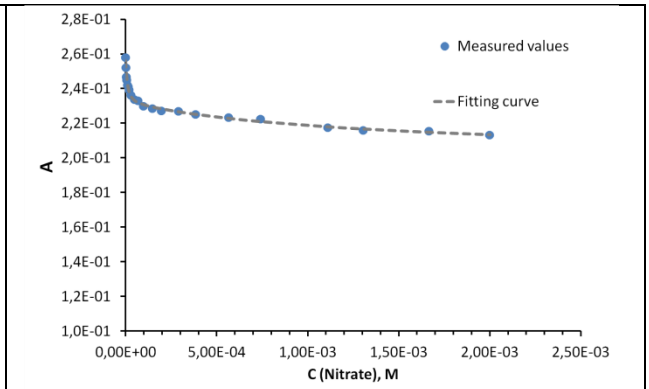
4.6. Absorption titration of 4 with anions

Na_2SO_4	
	

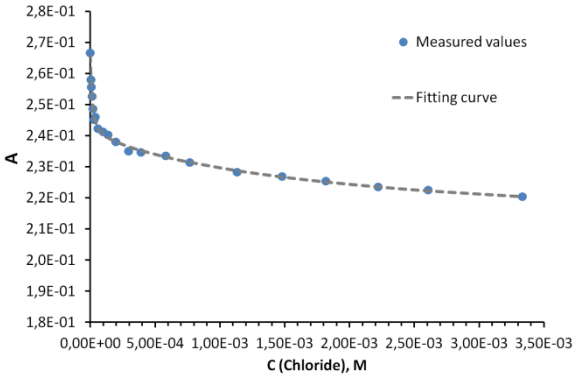
NaH_2PO_4	$Na_2C_2O_4$
	

$NaClO_4$	$NaNO_3$

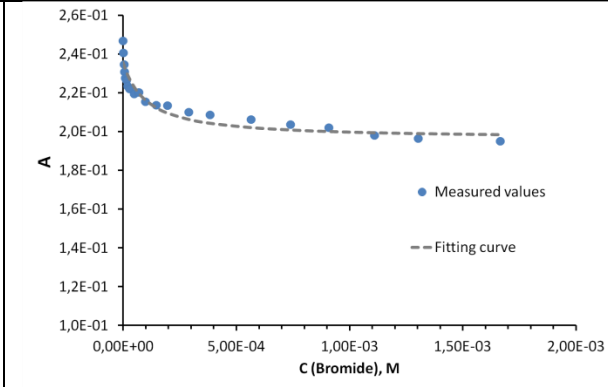




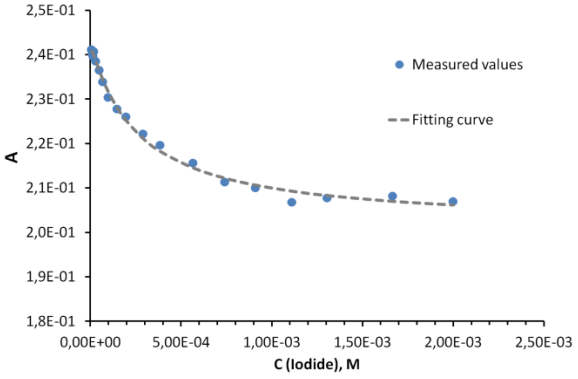
NaCl

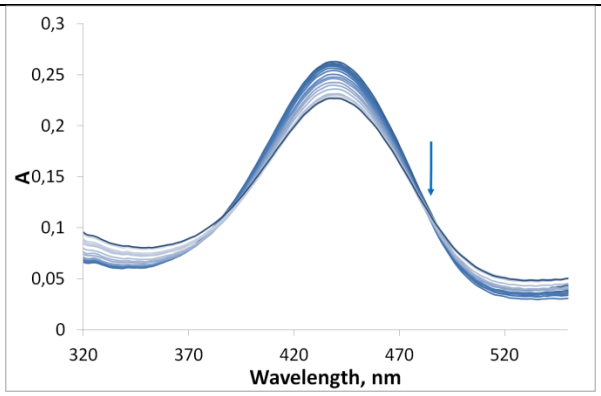


NaBr

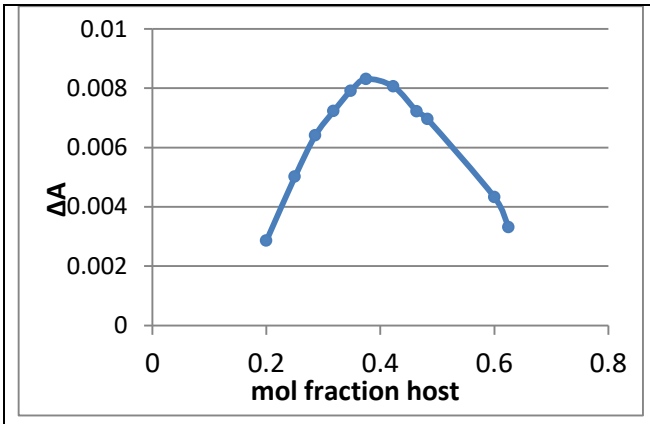


NaI

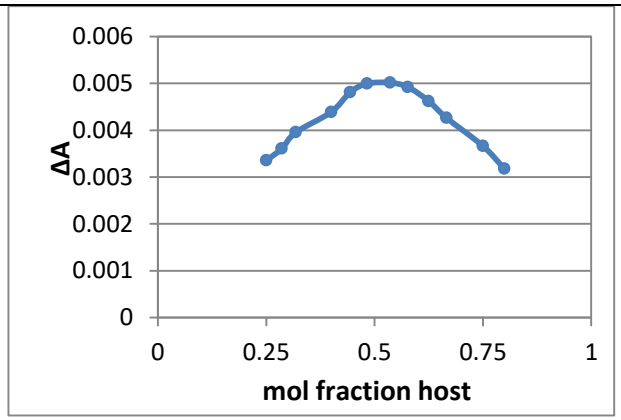




Job plots for the titrations experiments were constructed according to the classical method described by Cooper.[1] The second method to determine the stoichiometry is based on the best fit of the experimental data and described earlier by Jurczak.[2] The stock solution of compounds and anions with identical concentration (10^{-5}M) were mixed together producing different mol fractions of guest. Assuming that in this concentration range there is a linear relationship between absorbance intensity and concentration, one can predict the intensity of the receptor at each concentration as follows: $k = I_0/c_0$, where k is a coefficient; the predicted intensity I_c at concentration c will be $I_c = c*k$. The difference between the expected value and measured $D = I_{obs} - I_c$ is plotted versus mol fraction of the guest to find the maximum.



Compound **3** and Na_2C2O_4.



Compound **3** and cGMP

Figure S8. Selected Job plots.

4.7 Fluorescence titration of 4 with tetranucleotides

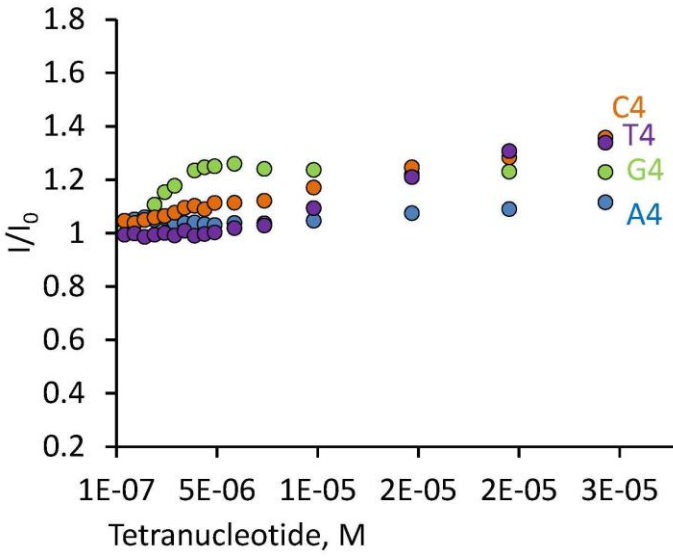


Figure S9. Changes in fluorescence intensity of **4** at 600 nm observed during the addition of tetranucleotides. Conditions: 50 mM acetate buffer (2% DMSO, pH 3.6, ex. 450 nm).

5. X-ray structure analysis.

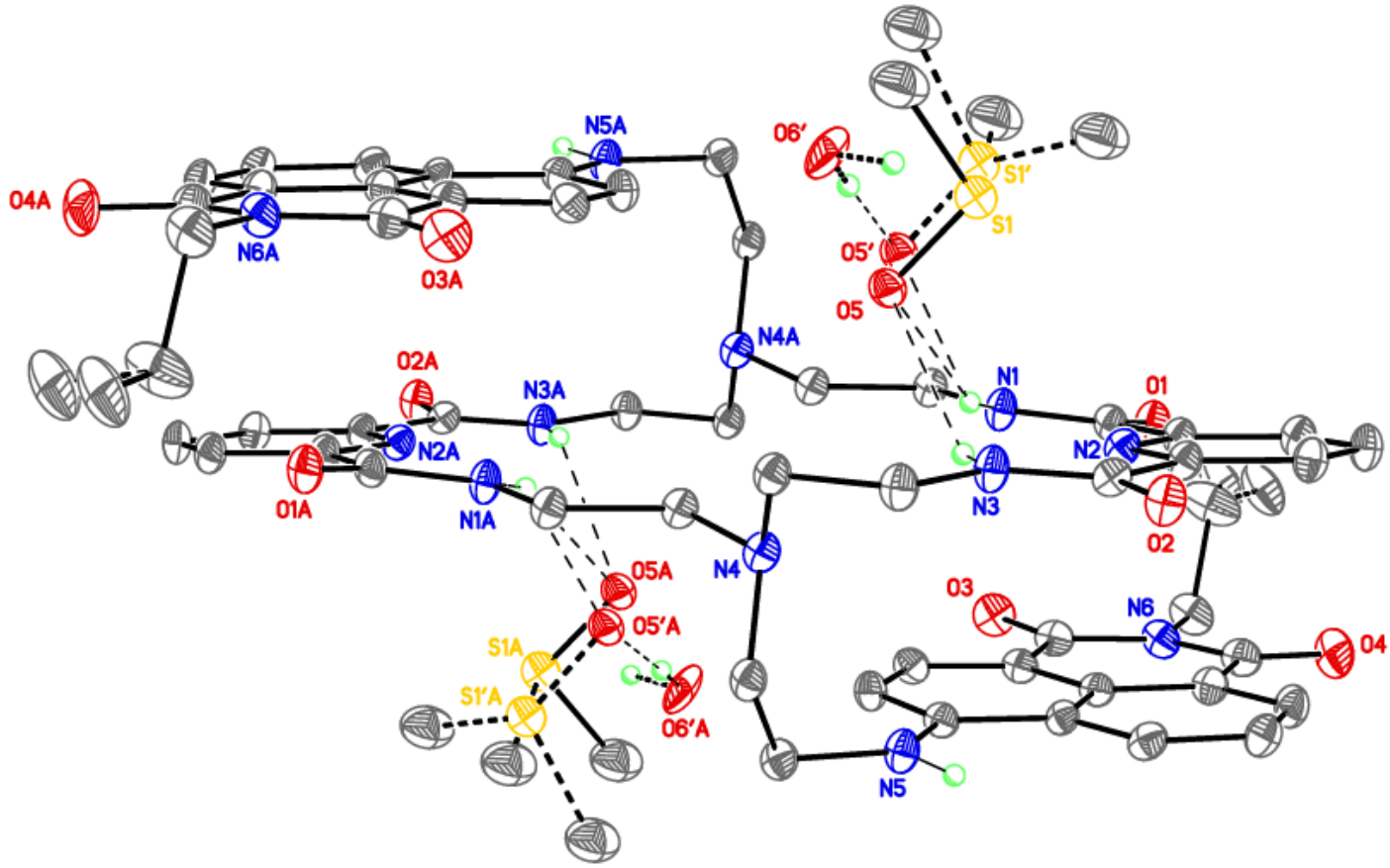
The single-crystal X-ray diffraction data for compounds **3**, $[\mathbf{3}H_2]^{2+}[SO_4]^{2-}$, and **4** (from different solvents) were collected on the 'Belok' beamline of the National Research Center 'Kurchatov Institute' (Moscow, Russian Federation)

using a Rayonix SX165 CCD detector.[3] In total, 720 frames were collected with an oscillation range of 1.0° in the φ scanning mode using two different orientations for each crystal. The semi-empirical correction for absorption was applied using the Scala program.[4] The data were indexed and integrated using the utility iMOSFLM from the CCP4 software suite.[3,5] For details, see Table 1. The structures were solved by intrinsic phasing modification of direct methods and refined by a full-matrix least-squares technique on F^2 with anisotropic displacement parameters for all non-hydrogen atoms. All investigated crystals contained solvate molecules of the corresponding solvents. The hydrogen atoms of the NH-groups as well as the solvate water and methanol molecules were localized in the difference-Fourier maps and included into the refinement within the riding model with fixed isotropic displacement parameters [U_{iso}(H) = 1.5U_{eq}(C), 1.2U_{eq}(N), and 1.5U_{eq}(O)]. The other hydrogen atoms in all compounds were placed in calculated positions and refined within the riding model with fixed isotropic displacement parameters [U_{iso}(H) = 1.5U_{eq}(C) for the methyl groups and 1.2U_{eq}(C) for the other groups]. All calculations were carried out using the SHELXTL program suite.[6]

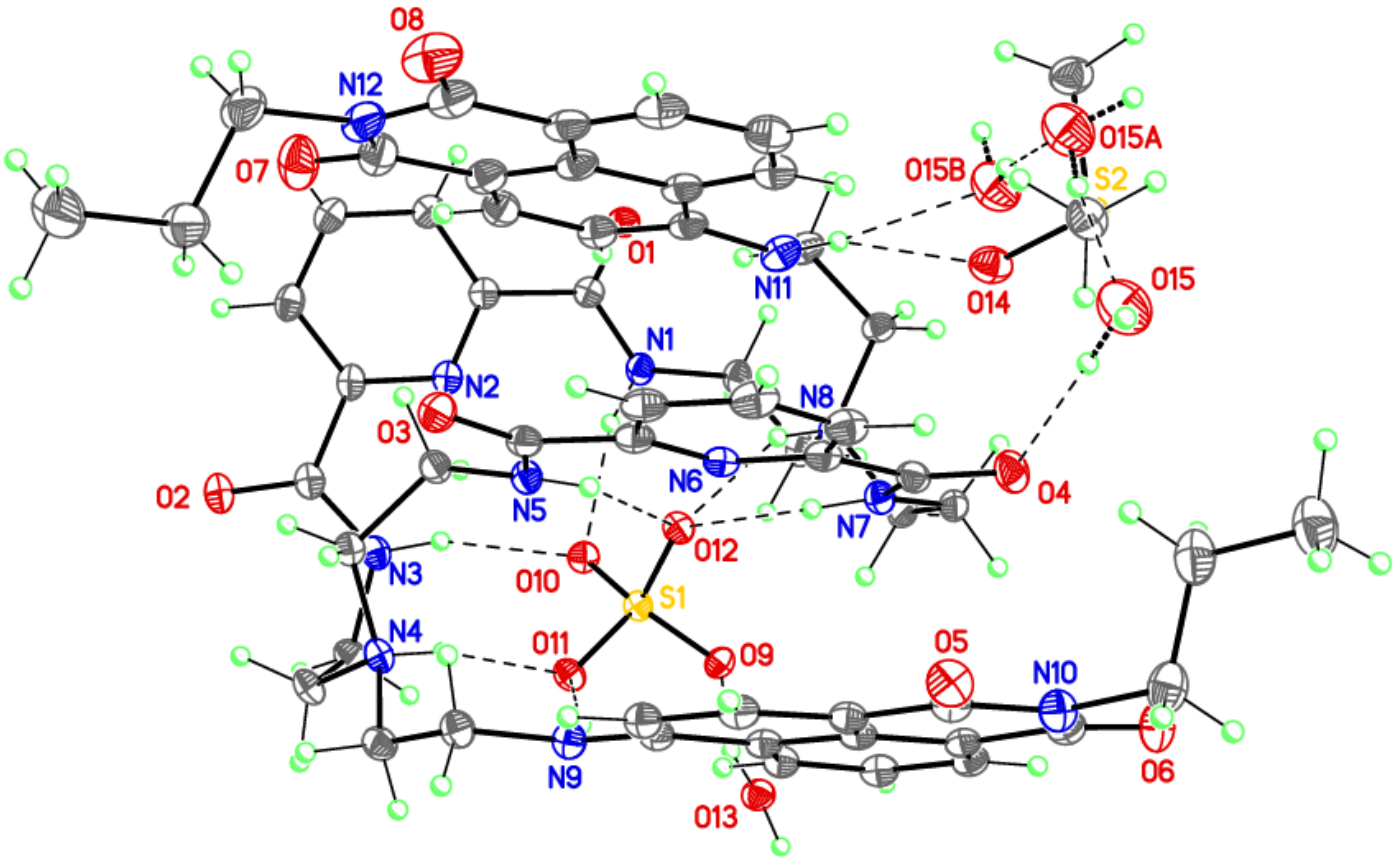
Table S2. Crystal data and structure refinement.

Compound	**3** • *2DMSO* • *0.3H_2O*	[**3**H_2]$^{2+}$[SO_4]$^{2-}$ • *¾DMSO* • *¼H_2O*	**4** • *3⅕DMSO* • *2⅕$CHCl_3$*	**4** • *7¾CH_3OH* • *1¼H_2O*
Empirical formula	$C_{60}H_{72.6}N_{12}O_{10.3}S_2$	$C_{57,5}H_{70}N_{12}O_{14,5}S_{1,75}$	$C_{121.8}H_{145}N_{24}O_{19.8}S_{3.8}Cl_{6.6}$	$C_{119.75}H_{153.5}N_{24}O_{25}$
Formula weight	1190.82	1217.36	2617.82	2329.16
Temperature, K	100(2)	100(2)	100(2)	100(2)
λ, Å	0.96990	0.80246	0.96990	0.96990
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	$P\ \bar{1}$	$C2/c$	$P\ \bar{1}$	$P\ \bar{1}$
a, Å	11.232(2)	48.205(10)	13.580(3)	14.357(3)
b, Å	11.984(2)	10.714(2)	15.990(3)	15.749(3)
c, Å	12.359(3)	23.955(5)	16.320(3)	30.441(6)
α, deg.	93.83(3)	90	75.75(3)	84.29(3)
β, deg.	115.42(3)	117.53(3)	83.99(3)	77.01(3)
γ, deg.	94.22(3)	90	65.84(3)	63.61(3)
V, Å^3	1489.5(7)	10971(5)	3133.9(14)	6008(3)
Z	1	8	1	2
D_{calc}, g·cm^{-3}	1.328	1.474	1.387	1.287
Absorption coefficient, μ	0.358	0.230	0.677	0.193
F(000)	631	5144	1375.2	2480
Crystal size, mm	0.03×0.10×0.20	0.05×0.05×0.10	0.10×0.15×0.20	0.03×0.15×0.20
θ range for data collection	2.34 – 38.49	3.16 – 30.89	1.76 – 38.42	3.17 – 38.59
Index ranges	-13 < h < 14 -15 < k < 14 -15 < l < 11	-61 < h < 61 -13 < k < 13 -30 < l < 30	-17 < h < 16 -20 < k < 18 -20 < l < 19	-18 < h < 18 -19 < k < 19 -38 < l < 38

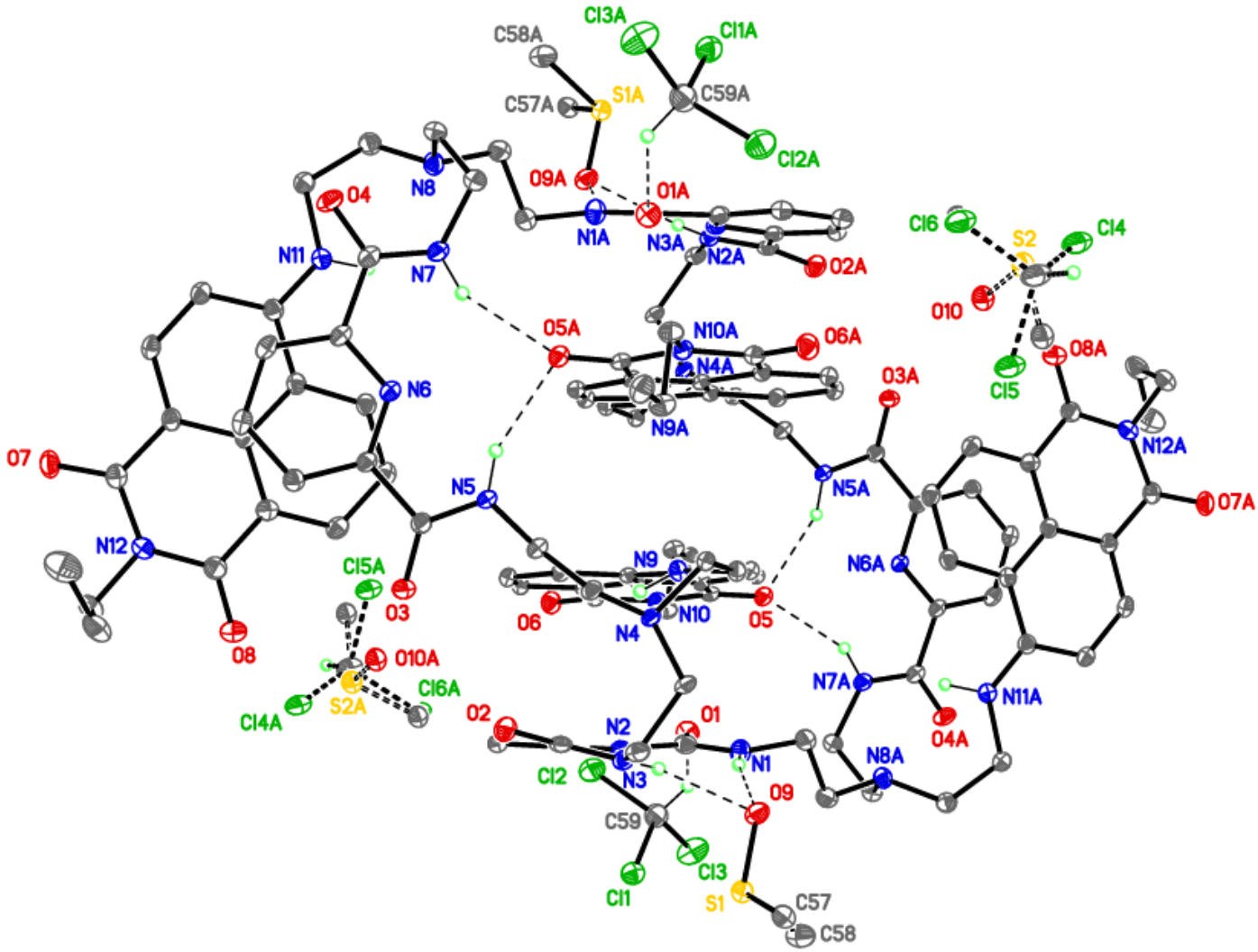
Reflections collected	15837	61869	45525	78233
Independent reflections, R_{int}	6030, 0.107	12004, 0.085	13089, 0.112	24936, 0.095
Reflections with $I > 2\sigma(I)$	3561	9231	9305	13670
Data / restraints / parameters	6030 / 12 / 404	12004 / 0 / 795	13089 / 12 / 800	24936 / 6 / 1559
R_1 [$I > 2\sigma(I)$]	0.065	0.070	0.073	0.091
wR_2 [all data]	0.172	0.180	0.189	0.204
Goodness-of-fit on F^2	1.003	1.045	1.032	1.023
Extinction coefficient	0.017(3)	0.00251(15)	0.0016(3)	0.00306(14)
T_{min} / T_{max}	0.920 / 0.980	0.970 / 0.980	0.860 / 0.930	0.950 / 0.980
$\Delta\rho_{max}$ / $\Delta\rho_{min}$, e·Å^{-3}	0.377 / -0.437	0.765 / -0.551	0.653 / -0.983	0.461 / -0.530
Crystallization conditions	crystallized from DMSO concentrated solution over 5 days	crystalized from DMSO-water solution 1:5 in the presence of 3 equiv. of sulfuric acid	crystallized from DMSO concentrated solution over 5 days	crystallized from MeOH concentrated solution over 5 days



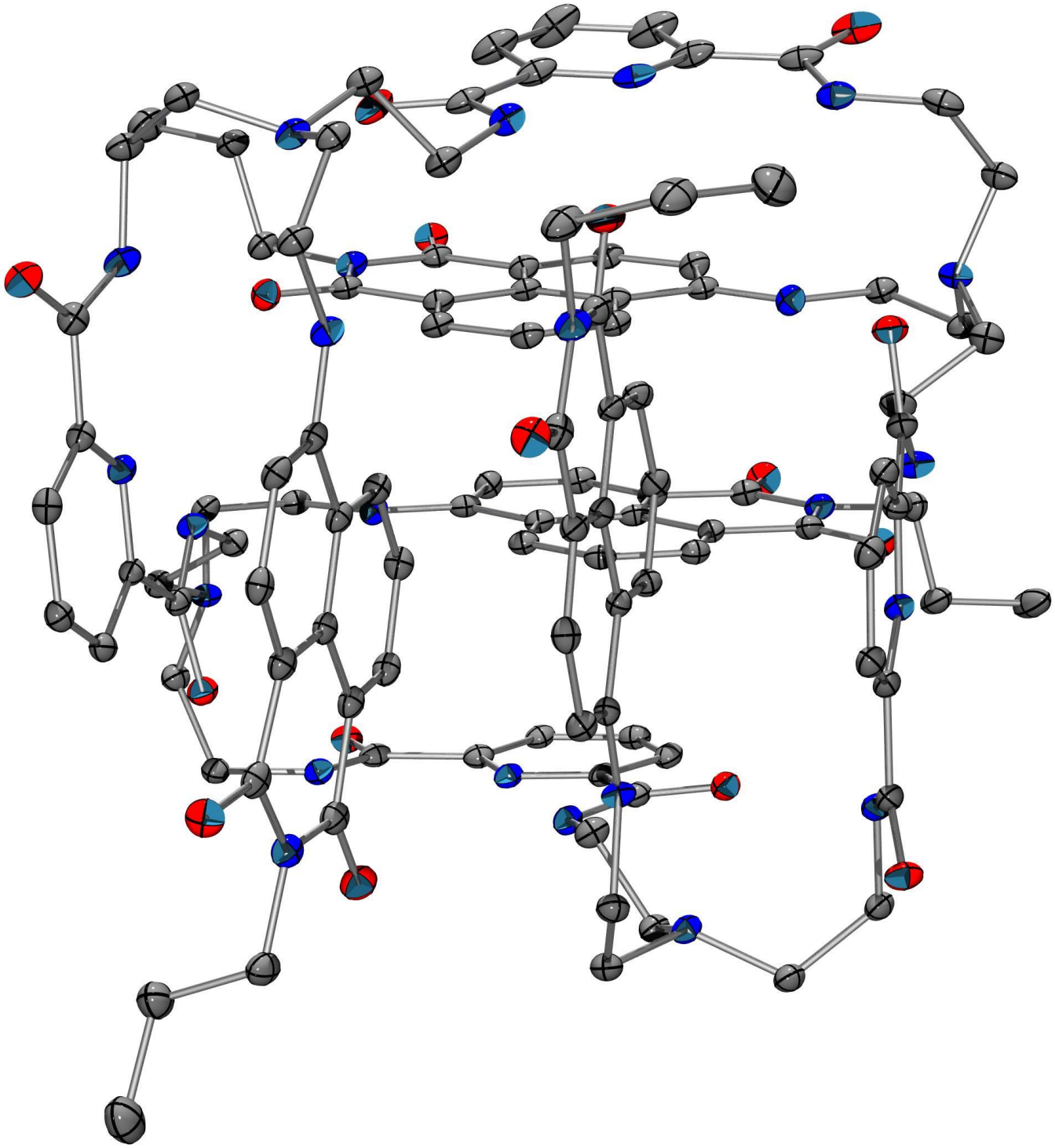
Thermal ellipsoid plot (ORTEP) diagrams for compound **3**. Most hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.



Thermal ellipsoid plot (ORTEP) diagrams for compound **3***H_2SO_4. Thermal ellipsoids are shown at the 50% probability level.



Thermal ellipsoid plot (ORTEP) diagrams for compound **4** crystalized from DMSO. Most hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.



Thermal ellipsoid plot (ORTEP) diagrams for compound **4** crystalized from MeOH. Most hydrogen atoms and solvent molecules are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

6. References

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