Michał Chmielewski, PhD

From simple building blocks to receptors, sensors and transporters for anions and anion templated self-organization

Summary of professional accomplishments submitted for the habilitation procedure

Warsaw 2019

1. Name and surname:

Michał Jan Chmielewski

2. Diplomas and academic degrees:

PhD in chemical sciences (with honours), Institute of Organic Chemistry of the Polish Academy of Sciences, Warsaw, 2003.
Thesis title: "Synthesis and structure of macrocyclic polylactams and their anionic complexes".
Supervisor: professor Janusz Jurczak

MSc (Summa Cum Laude), Faculty of Chemistry, University of Warsaw, Warsaw, 1999.
Thesis title: "Optimization of the synthesis of azacoronands".
Supervisor: professor Janusz Jurczak

3. Information on previous employment in scientific institutions:

02.2010 – now	**Assistant Professor** („adiunkt") at the Faculty of Chemistry, University of Warsaw
09.2007 – 09.2009	**Postdoctoral research assistant** in the group of Professor J.-M. Lehn at the *Institut de Science et d'Ingénierie Supramoléculaires*, *Université Louis Pasteur*, Strasbourg
01.2006 – 06.2007	**Postdoctoral research assistant** in the group of Professor P. D. Beer at the Chemistry Department, University of Oxford
09.2005 – 12.2005	**Research fellow** in the group of Professor L. Latos-Grażyński at the Faculty of Chemistry, Wrocław University
11.2003 – 12.2005	**Assistant** at the Institute of Organic Chemistry, Polish Academy of Sciences

4. Indication of the achievement resulting from art. 16 sec. 2 of the Act of 14 March 2003 on academic degrees and academic title, and on degrees and title in the field of art (Journal of Laws of 2016, item 882, as amended in Journal of Laws of 2016, item 1311):

a) title of scientific achievement:

"From simple building blocks to receptors, sensors and transporters for anions and anion templated self-organization"

b) a list of scientific publications on which scientific achievement is based:[1]

		IF_{2017}	MS&HE points[1]	Number of citations[2]
H1	**M. J. Chmielewski**, M. Charon, J. Jurczak* „1,8-Diamino-3,6-dichlorocarbazole – a promising building block for anion receptors" *Org. Lett.* **2004**, *6*, 3501-3504.	6.492	45	145/135
H2	**M. J. Chmielewski**, J. J. Davis*, P. D. Beer* „Interlocked host rotaxane and catenane structures for sensing charged guest species via optical and electrochemical methodologies" (review) *Org. Biomol. Chem.* **2009**, *7*, 415-424.	3.423	35	81/81
H3	**M. J. Chmielewski**, L. Zhao, A. Brown, D. Curiel, M. R. Sambrook, A. L. Thompson, S. M. Santos, V. Felix, J. J. Davis*, P. D. Beer* „Sulfate anion templation of a neutral pseudorotaxane assembly using an indolocarbazole threading component" *Chem. Commun.* **2008**, 3154–3156.	6.290	40	72/67
H4	K. M. Bąk, **M. J. Chmielewski*** „Sulfate templated assembly of neutral receptors in aqueous DMSO – orthogonal versus biplane structures" *Chem. Commun.* **2014**, *50*, 1305-1308.	6.290	40	9/5
H5	K. M. Bąk, **M. J. Chmielewski*** „Sulfate Anion as a pH-Switchable Template: Three-State Switchable Systems Based on Diamidocarbazoles" *Eur. J. Org. Chem.* **2015**, 4077-4080.	2.882	35	3/1
H6	**M. J. Chmielewski*** „A short, multigram synthesis of 1,8-diaminocarbazole" *Synthesis*, **2010**, 3067-3069.	2.722	30	9/7

[1] Here, the most up to date Impact Factors (for 2017) and MS&HE points (i.e. points assigned to scientific journals by Polish Ministry of Science and Higher Education in 2016) are provided. IF values from the year of publication are given at the end of this document and also in the Annex no. 4.

[2] The number of citations and the number of citations excluding self-citations were taken from the Web of Science database on 20 February 2019.

H7	K. M. Bąk, K. Chabuda, H. Montes, R. Quesada, **M. J. Chmielewski*** „1,8-Diamidocarbazoles: an easily tuneable family of fluorescent anion sensors and transporters" *Org. Biomol. Chem.* **2018**, *16*, 5188–5196.	3.423	35	2/1
H8	P. Piotrowski, R. Pomorski, B. Pałys, J. Bukowska, **M. J. Chmielewski*** „Sulfate Sensing in Self-Assembled Monolayers by Surface Infrared and Raman Spectroscopy Techniques" *Sensors and Actuators B: Chemical* **2019**, *283*, 172-181.	5.667	40	0/0
	H1 – H8 together:	**37.189**	**300**	**321/297**

c) discussion of the scientific purpose of the above papers and results achieved, including discussion of their possible use

Since its inception over half a century ago, supramolecular chemistry has developed into one of the most important branches of modern chemistry. Its spectacular development was largely due to the fact that molecules reveal many interesting features, properties and functions only upon non-covalent interactions with other molecules or ions. They can, for example, change their shape, colour, fluorescence, acidity, basicity, redox potential, magnetic moment and many other properties. They can also dissolve or precipitate, get extracted or permeate through lipophilic membranes, catalyse reactions or self-organize into complex architectures with non-trivial structure, topology and functionalities. They can also create multimolecular aggregates, such as membranes, monolayers and films, mesophases, crystals and many other materials whose properties depend heavily on how their molecular building blocks interact with each other. For the above reasons, supramolecular chemistry finds more and more applications and exerts a growing influence on other branches of chemistry, such as analytical, medicinal and material chemistry, catalysis and even neighbouring disciplines - physics and biology.

Recently, for example, supramolecular chemistry plays an increasingly important role in the quest for new materials, especially materials which are dynamic, adaptable, stimuli-responsive, capable of self-repair and friendly to environment and living organisms. Supramolecular chemistry is also one of the key pillars of nanotechnology. Self-assembly of molecules by means of non-covalent interactions is an extremely important method of producing well-defined structures of nanometric dimensions. Further, supramolecular assistance to organic synthesis enabled efficient production of mechanically interlocked structures, such as catenanes, rotaxanes and knots, which allowed the development of topological chemistry and the construction of increasingly complex molecular machines.

Last but not least, many life processes are based on non-covalent intermolecular interactions and therefore their in-depth understanding is not possible without the tools,

concepts and methods of supramolecular chemistry. This understanding, in turn, allows to rationally interfere with these processes, e.g. for therapeutic purposes. Also, the fascinating new field of research, which aims to uncover the origins of life and to create artificial life, has its roots buried deep in supramolecular chemistry.

Effective design and self-organization of functional supramolecular architectures requires that the molecular recognition between their components is highly specific, i.e. that the information contained in the structure of molecules should be read as faithfully as possible by their mutual interaction. A spectacular example of how much can be achieved with building blocks that connect to each other in a strictly defined way are the so-called 'DNA origami'. It relies on designing DNA sequences in such a way that they spontaneously fold into two- or three-dimensional structures of almost any chosen shape. It has recently been shown that it is possible in this way to program self-organization of even tens of thousands of different building blocks into the one, strictly predefined structure (Figure 1).[3]

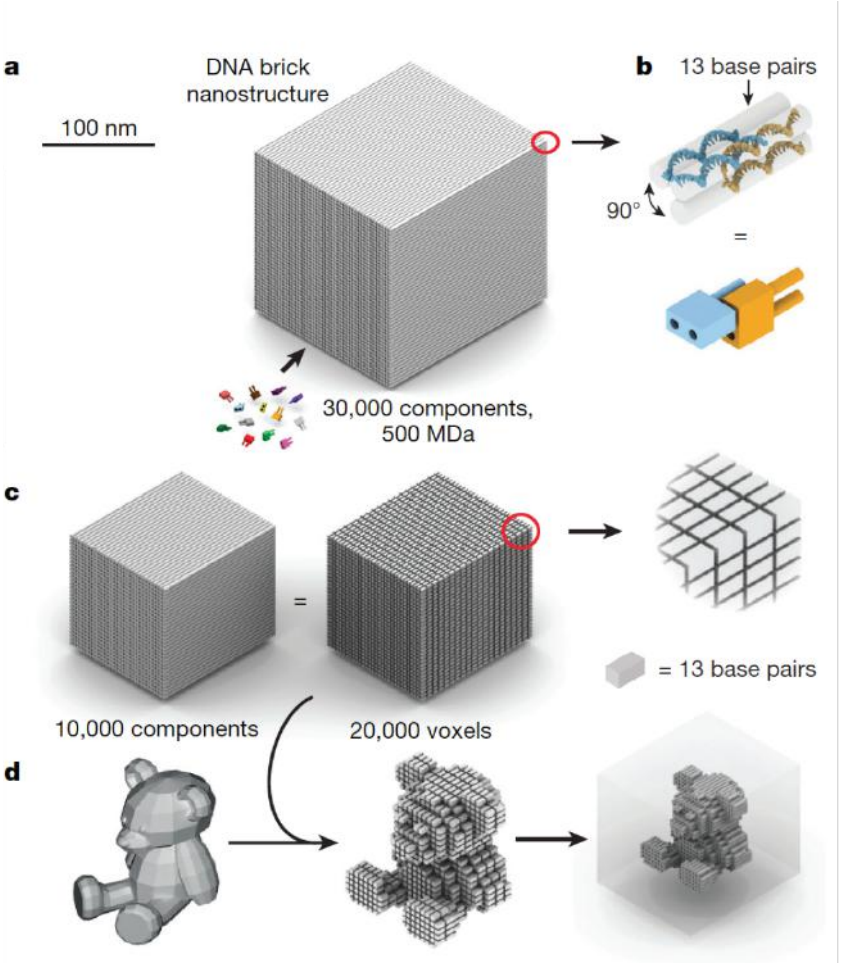


Figure 1. Three-dimensional nanostructures self-assembled from appropriately designed DNA fragments. These structures reach masses up to 500 MDa and consist of up to 30 000 components ("bricks").[3]

[3] L. L. Ong, N. Hanikel, O. K. Yaghi, C. Grun, M. T. Strauss, P. Bron, J. Lai-Kee-Him, F. Schueder, B. Wang, P. Wang, J. Y. Kishi, C. Myhrvold, A. Zhu, R. Jungmann, G. Bellot, Y. Ke, P. Yin, *Nature* **2017**, *552*, 72-77.

Drawing inspiration and encouragement from Nature, chemists have been developing new building blocks and specific interaction patterns not occurring in nature. Initially, they were based primarily on the coordination chemistry of metal cations with their well-known coordination preferences and a plethora of interesting electrochemical, spectroscopic, catalytic and magnetic properties. Presumably due to these properties, in the pioneering period of supramolecular chemistry most researchers focused on self-organization of metallosupramolecular structures, while non-covalent interactions with anions have long remained on the sidelines of the mainstream research.

Nevertheless, chemical entities bearing negative charge play important roles in many biological, chemical and technological processes as well as in medicine and environmental protection. Anions can be poisons (e.g., cyanides, nitrites, arsenates, chromates) and drugs (e.g. various types of carboxylates and phosphates), dangerous environmental pollutants and valuable fertilizers (e.g. phosphates and nitrates), radioactive waste products from the nuclear industry (pertechnetate, iodide) and highly desirable raw materials (e.g. complex anions of precious metals). It is estimated that ca. 70% of all cofactors and substrates of enzymatic reactions are anionic in character. Also, anions carry genetic information (DNA and RNA) and are responsible for energy transfer in cells (ATP). Special proteins are responsible for the maintenance of appropriate concentrations of anions in the cells by transporting them through biological membranes, often against their concentration gradient. Dysfunctions of these proteins may cause serious diseases, including the most common genetic disease of the Caucasians - cystic fibrosis. Accordingly, the role of anion sensing in medical diagnostics is constantly growing.

Thus, receptors able to strongly and selectively bind anions are becoming more and more desirable because they enable their detection, removal and transport, and may also catalyse reactions proceeding through anionic transition states. Particularly attractive in view of potential applications, but also extremely difficult to design, are receptors operating in aqueous environment.[4] Advances in supramolecular chemistry of anions allow their use in many applications where the coordination of cations has previously dominated, for example in the template-assisted synthesis and self-organization of complex supramolecular structures.

Unfortunately, anion binding is much more difficult than complexation of metal cations, from which supramolecular chemistry emerged. Firstly, anions generally have lower charge densities and therefore interact less strongly with receptors. Secondly, they are strongly solvated, which means that the receptors suffer strong competition from solvent molecules. In addition, many anions occur only in a fairly narrow range of pH values, which prevents the use of certain types of receptors (e.g. protonated polyamines). Finally, even relatively simple, inorganic anions display a wide variety of shapes, which makes the design of receptors with complementary geometry extremely challenging.

[4] M. J. Langton, C. J. Serpell, P. D. Beer, *Angew. Chem. Int. Ed.* **2016**, *55*, 1974-1987.

Nevertheless, significant progress has been achieved in the supramolecular chemistry of anions, as evidenced, among other things, by the increasing emphasis put recently on practical applications.[5]

In my opinion, this progress is mainly due to the discovery of ever-better building blocks, able to bind anions more and more strongly. Two publications by Crabtree and co-workers, from 1997 and 1999, were particularly significant milestones on that way; they showed that even very simple, electrically neutral binding units, such as diamides of isophthalic and 2,6-pyridinedicarboxylic acids (Figure 2, structures **1** and **2**) are able to extremely strongly bind inorganic anions in dichloromethane with binding constants up to 61 000 M^{-1} for chloride.[6]

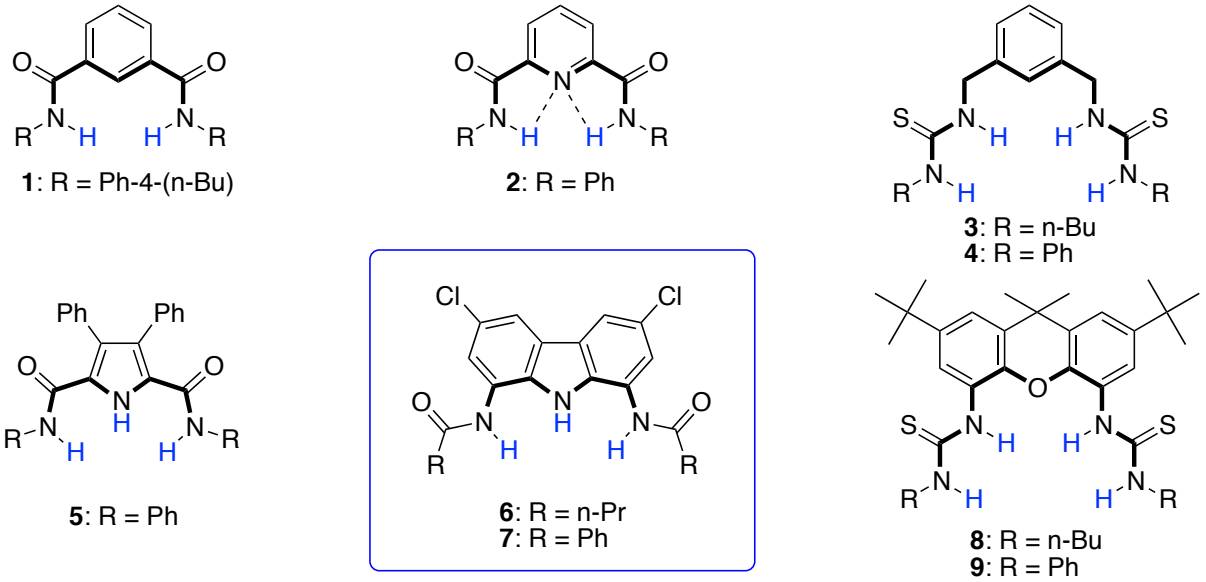


Figure 2. Examples of binding motifs (building blocks) used for the construction of anion receptors.

Although dichloromethane is one of the least-competing solvents used in these investigations, and the appropriate binding constants measured, for example, in DMSO would certainly be a few orders of magnitude lower, these amides quickly became one of the most commonly used structural motifs in anion binding studies. What is more, their success encouraged a significant number of scientists to study simple, model receptors and look for rules governing anion complexation. For example, in 2001 Gale and co-workers published a building block containing three, instead of two, strong hydrogen bond donors: a diamide derived from pyrrole-2,5-dicarboxylic acid (Figure 2, structure **5**).[7] Amides of this type were able to bind anions in a much more competitive solvent, dimethylsulfoxide containing 0.5% of water, although the resulting binding constants were not impressive:

[5] N. Busschaert, C. Caltagirone, W. Van Rossom, P. A. Gale, *Chem. Rev.*, **2015**, *115*, 8038-8155.

[6] a) K. Kavallieratos, S. R. de Gala, D. J. Austin, R. H. Crabtree, *J. Am. Chem. Soc.*, **1997**, *119*, 2325-2326; b) K. Kavallieratos, C. M. Bertao, R. H. Crabtree, *J. Org. Chem.* **1999**, *64*, 1675-1683.

[7] P. A. Gale, S. Camiolo, G. J. Tizzard, Ch. P. Chapman, M. E. Light, S. J. Coles, M. B. Hursthouse, *J. Org. Chem.* **2001**, *66*, 7849-7853.

11 M^{-1} for chloride and 560 M^{-1} for benzoate. Despite that this structural motif was successfully used to construct a whole range of anion receptors, sensors and transporters in the following years.[8]

The third example, which is worth mentioning in this introduction, are dithioureas of Umezawa and co-workers (Figure 2, structures **8** and **9**).[9] These compounds have two thiourea groups attached to a rigid, tricyclic central platform and are therefore potential donors of up to four strong hydrogen bonds. Although the central oxygen atom in the xanthene system can repulse anions, it also has a positive role - it preorganizes the side arms for anion binding by means of intramolecular hydrogen bonds. The binding constants of these receptors with dihydrogenphosphate anion reached impressive values of 55 000 M^{-1} for **8** and 195 000 M^{-1} for **9**, in the highly competitive solvent DMSO. For comparison, the respective binding constants for dithioureas **3** and **4** are 820 M^{-1} and 4600 M^{-1} respectively. This example shows how important is the role of molecular platform in the appropriate organization of hydrogen bonds donors.

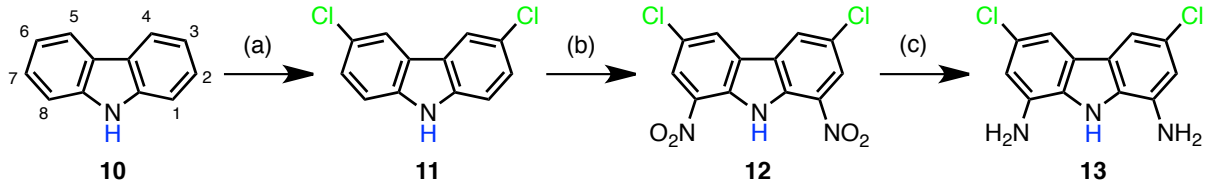
Own studies. [H1].

Inspired by the results of Gale's group on one hand, and Umezawa's on the other, I proposed a new building block for the construction of anion receptors - 1,8-diaminocarbazole (**H1**, Figure 2, structures **6** and **7**). It has a very similar geometry of binding sites to the Gale's diamidopyrroles, and a tricyclic central unit like the Umezawa's receptors. It also has a number of advantages in comparison with the designs of my predecessors. First, carbazole is a much better hydrogen bond donor than pyrrole, as evidenced for example by the comparison of Abraham parameters α_2^H for pyrrole (0.41),[10] indole (0.44)[11] and carbazole (0.47)[11]. In this respect, the 1,8-diaminocarbazole has a particular advantage over the Umezawa's design, where there is an acceptor instead of donor in the middle of the binding cleft. In addition, carbazole is an excellent fluorophore, which opens the door to the construction of fluorescent anion sensors. It is worth highlighting that unlike in many competing designs, this fluorophore is directly involved in anion binding and hence is very likely to be strongly perturbed by its presence. Finally, from synthetic point of view, the 1,8-diaminocarbazole seems to be a more useful synthon than dicarboxylic acids, because it can be easily converted into a whole range of potential receptors, such as amides, thioamides, ureas, thioureas, sulfonamides, carbamates, guanidines and others.

1,8-Diaminocarbazole was already described in the literature, but it was obtained in a very impractical, multi-step synthesis involving the construction of carbazole skeleton with the use of, *inter alia*, sulfur nitride.[12] Much more attractive seemed to be the synthesis of

[8] P. A. Gale, *Chem. Commun*., **2005**, 3761-3772.
[9] P. Bülmann, S. Nishizawa, K. P. Xiao, Y. Umezawa, *Tetrahedron* **1997**, *53*, 1647-1654.
[10] M. H. Abraham, *Chem. Soc. Rev.* **1993**, *22*, 73-83.
[11] P. Guardado, M. Balon, C. Carmona, M. A. Muñoz, C. Domene, *J. Pharm. Sci.* **1997**, *86*, 106-109.
[12] K. Takahashi, H. Eguchi, S. Shiwaku, T. Hatta, E. Kyoya, T. Yonemitsu, S. Mataka, M. Tashiro, *J. Chem. Soc., Perkin Trans. 1* **1988**, 1869-1873.

1,8-diamino-3,6-dichlorocarbazole described by Mužik and colleagues in 1958.[13] It consisted in blocking the most reactive positions 3 and 6 of the carbazole system with chlorine atoms, followed by nitration of the thus obtained 3,6-dichlorocarbazole at positions 1 and 8 and catalytic reduction of nitro groups with hydrogen (Scheme 1).



Scheme 1. The synthesis of 1,8-diamino-3,6-dichlorocarbazole 13 described in the paper H1. (a) SO_2Cl_2, CH_2Cl_2, rt, 3h, 60%; (b) HNO_3 (100%), Ac_2O, AcOH, 73%; (c) H_2, Pd/C, CH_3CN, 89%.

Because the chlorine substituents at positions 3 and 6 of the carbazole are on the opposite side of the carbazole platform with respect to the anion binding site and can therefore affect the anion binding only indirectly, and also because in the particular case of the electron-withdrawing substituents this effect should be beneficial, I decided to first examine the anion binding properties of model bisamides **6** and **7**, derived from 1,8-diamino-3,6-dichlorocarbazole.

Unfortunately, in practice, the synthesis described by Mužik and co-workers turned out to be very difficult to reproduce. Aiming at industrial applications, these authors optimized carbazole chlorination on a 500 g scale, using gaseous chlorine as a chlorinating agent. The progress of the reaction was monitored by weighing the reactor and measuring, at regular intervals, the melting point of the reaction mixture. All attempts to repeat this synthesis on a smaller scale in the scientific laboratory ended in failure: each time I obtained a mixture of many different chlorinated carbazoles containing from 1 to 6 chlorine atoms in the molecule. What makes it even worse, these compounds are so poorly soluble, that their chromatographic separation is possible only on a very small scale (on the order of several dozen milligrams).

Literature survey revealed that selective chlorination of carbazole is not easy to accomplish.[14] After testing several literature methods, none of which gave the expected product in satisfactory purity, I decided to test the method from the late nineteenth century, described by Mazzarra and Lamberti-Zanardi.[15] It involved the chlorination of carbazole with sulfuryl chloride in chloroform. Although the authors did not give the yield and the product was isolated by multiple crystallizations, it was this method that we successfully developed to obtain the desired product with a yield of about 60% on a multigram scale, and without the need for chromatographic purification.

[13] F. Mužik, Z. Allan, J. Poskočil, *Collect. Czech. Chem. Commun.* **1958**, *23*, 770-772.
[14] J. Kyzioł, J. Pielichowski, "Halogenopochodne karbazolu", *Zesz. Nauk. Politech. Kr. Chemia*, **1978**, *10*, 3-132.
[15] G. Mazzara, M. Lamberti-Zanardi, *Gazz. Chim. Ital.* **1896**, *26*, 236-242.

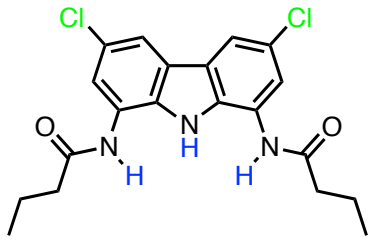
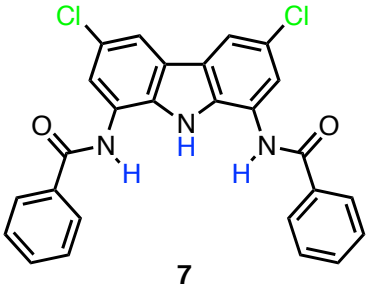
The next step, nitration, went exactly according to the procedure by Mužik and co-workers, which this time proved to be reproducible and scalable. This reaction uses 100% nitric acid in a mixture of acetic acid and acetic anhydride to give pure product in 73% yield.

The last step of the synthesis, the reduction of nitro groups, also had to be developed from scratch, since Mužik and co-workers hydrogenated 3,6-dichloro-1,8-dinitrocarbazole in an autoclave using 50 atm. of H_2 at 100°C, using Raney nickel as catalyst. Although typical conditions for the reduction of nitro groups (H_2, Pd/C, MeOH) gave the desired product, it was contaminated with significant amounts of dechlorination products: 1,8-diamino-3-chlorocarbazole and 1,8-diaminocarbazole. These products are not easy to separate from the desired 1,8-diamino-3,6-dichlorocarbazole **13**, since all three amines have very similar physicochemical properties and are also very poorly soluble in typical organic solvents. The use of contaminated amine **13** as a substrate for the synthesis of receptors was not an option too, because the amide derivatives of 1,8-diaminocarbazoles are even less soluble and even more difficult to separate than the starting amines. Therefore we performed tedious optimization of the reduction conditions (duration, solvent, catalyst), which finally resulted in a convenient method for the synthesis of pure 1,8-diamino-3,6-dichlorocarbazole **13** in 89% yield.

The product was then transformed into two model amide derivatives, with the side arms respectively: aliphatic (**6**) and aromatic (**7**).

Preliminary results of anion binding studies with these compounds proved very promising. Titration of receptors **6** and **7** with tetrabutylammonium chloride, benzoate and dihydrogenphosphate in DMSO + 0.5% H_2O leads to large downfield shifts of NH signals (up to 3.75 ppm for carbazole proton and 2.09 ppm for amides), indicating the formation of three strong hydrogen bonds with each anion, the strongest of which seems to be with carbazole NH. Quantitative analysis of anion binding constants confirmed that both model receptors strongly bind oxoanions in this strongly competing solvent, while chlorides are significantly less strongly bound (Table 1).

Table 1. Association constants [M^{-1}] of 1:1 complexes of receptors 6 and 7 with model anions in DMSO-d_6 + 0.5% H_2O, determined by ^{1}H NMR titrations.

Anion	 **6**	 **7**
Cl^-	115	13
$PhCOO^-$	8340	1230
$H_2PO_4^-$	> 10 000	1910

The X-ray crystal structure analysis of the chloride complex of **7** confirmed the assumed binding model, but also showed that the binding site of the receptor is a bit too large for the relatively small chloride anion, which explains the clear preference of both receptors for oxyanions (Figure 3). The shortest hydrogen bond with the anion is formed by the carbazole NH, which confirms the key role of this bond in the stabilization of the complex.

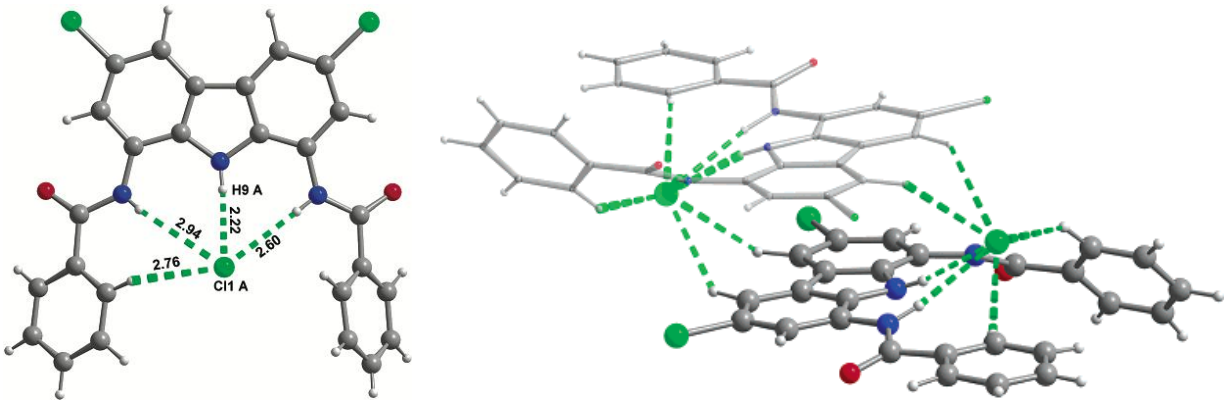


Figure 3. The X-ray crystal structure of the complex of the receptor 7 with tetrabutylammonium chloride: $(7)_2\times(TBACl)_2\times(C_2H_5)_2O$. On the left: top view of one of the two symmetrically independent chloride complexes found in this structure along with the key contacts given in Å. On the right: side view of the second chloride complex present in the same crystal with its (symmetrically equivalent) neighbour (shown in light grey).

In conclusion, we have developed a convenient method for the synthesis of 1,8-diamino-3,6-dichlorocarbazole **13** - an attractive building block for the construction of various potential anion receptors and fluorescent sensors: amides, thioamides, sulfonamides, ureas, thioureas, guanidines and others. Preliminary studies of the complex forming properties of simple amide derivatives of **13** have been very promising: these compounds have a high affinity for benzoate and dihydrogenphosphate, primarily due to the strong hydrogen bonds formed by their carbazole NH.

The new building block **13** was the first in which the carbazole ring was used to construct anion receptors. To the best of my knowledge, this was also the first example of the use of any benzopyrrole for the construction of anion receptors. The receptors **6** and **7** thus became the precursors of the entire family of benzopyrrole anion receptors, encompassing indoles, carbazoles, biindoles, indolocarbazoles, indolomethanes and others (Figure 4).[16] Since its publication, **H1** has already been cited more than 140 times and at least 12 papers have been published in which the same binding motif was included in the receptor structure (excluding the publications of my team). More in-depth studies of the properties of the 1,8-diamidocarbazoles family are presented in the publication **H7** of this cycle.

[16] a) J. Jurczak, M. J. Chmielewski, P. Dydio, D. Lichosyt, F. Ulatowski, T. Zieliński, *Pure Appl. Chem.* **2011**, *83*, 1543-1554;
b) P. A. Gale *Chem. Commun.*, **2008**, 4525-4540;
c) P. Dydio, D. Lichosyt, J. Jurczak, *Chem. Soc. Rev.*, **2011**, *40*, 2971-2985.

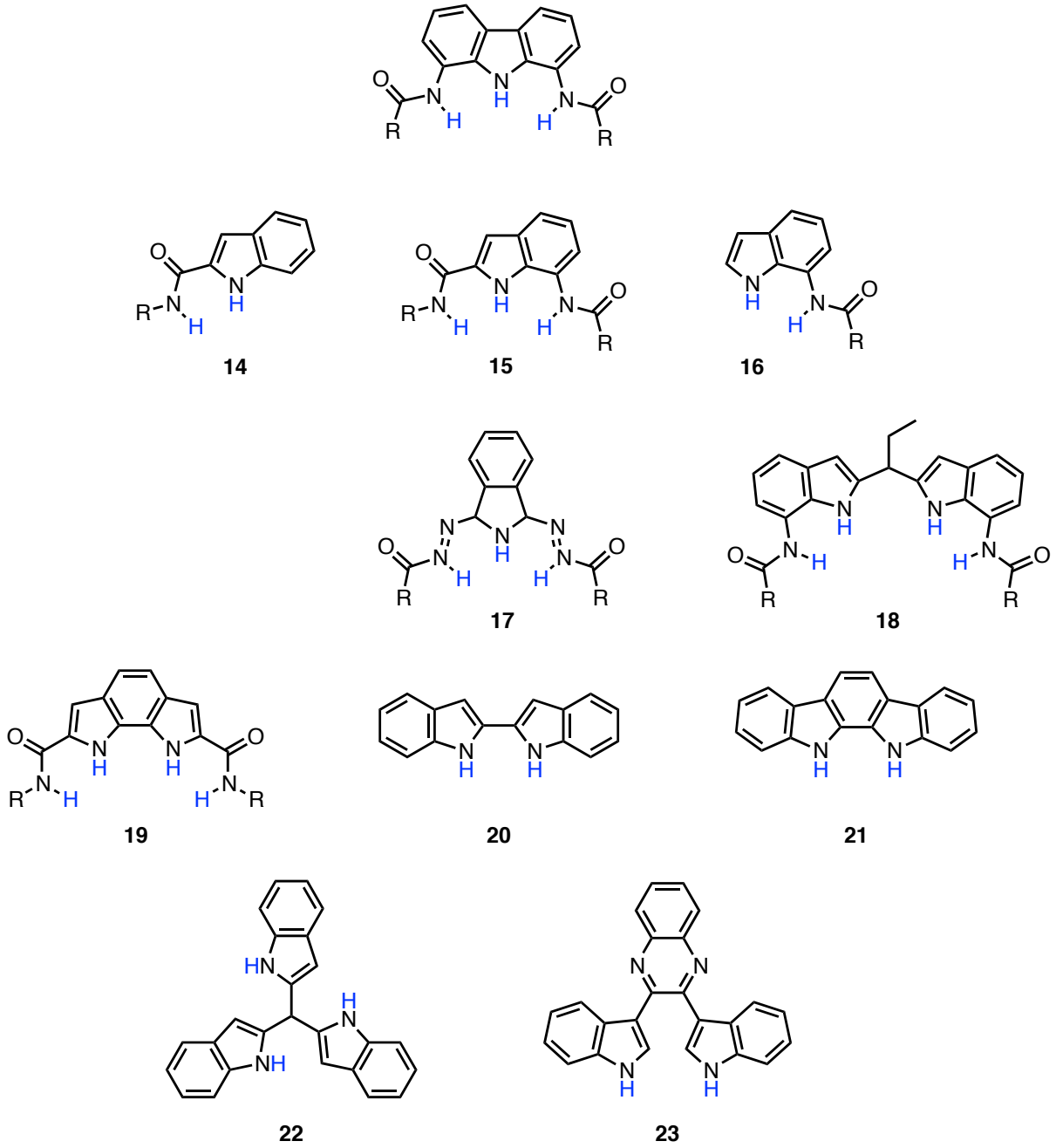
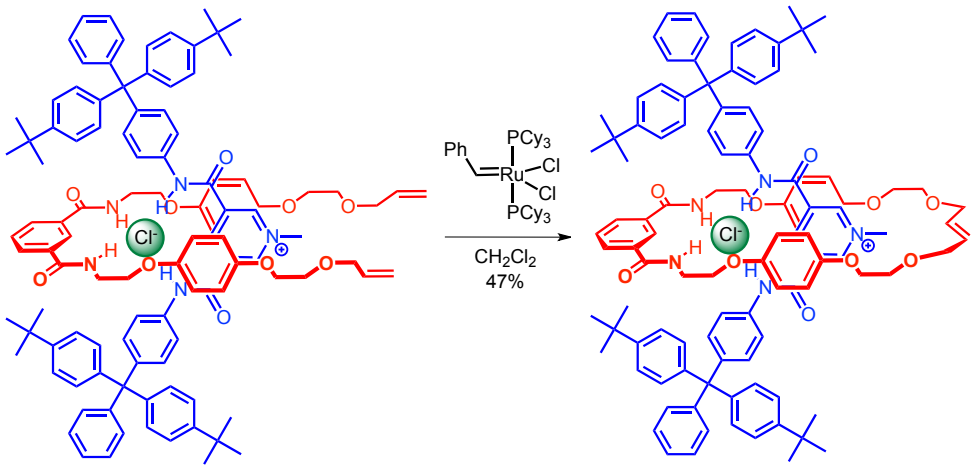


Figure 4. Examples of anion-binding motifs based on various benzopyrrole skeletons.

[H2]

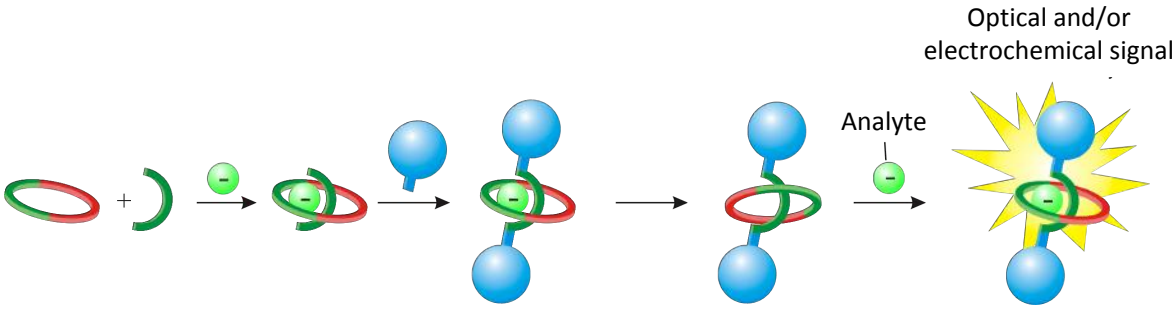
The discovery of binding motifs having high affinity for anions opened up a number of new possibilities in the supramolecular chemistry of anions. In 2001, Beer and co-workers showed that halide anions can be used to template the synthesis of mechanically interlocked architectures, such as pseudorotaxanes, rotaxanes and catenanes. The methodology developed by this team consists in combining, using an anionic template, of two components containing in their structure anion-binding sites into a stable, orthogonal

complex, which then undergoes irreversible reaction giving a mechanically interlocked structure (Scheme 2).[17]



Scheme 2. An example of template-based synthesis of rotaxane developed by Beer and co-workers. In this method, the macrocycle precursor binds chloride anion which is strongly associated with the positively charged axis.

In order for an anion to be an effective template, both ligands have to bind it strongly, but at the same time none of them should saturate its coordination sphere. These two conditions are difficult to reconcile and therefore for quite a long time this strategy was limited to the complexation of ion pairs, in which halide anions are strongly associated with positively charged "axis" by means of Coulombic interactions. Despite these limitations, it has been shown that anion templation is a very promising way to obtain topologically non-trivial structures such as pseudorotaxanes, rotaxanes and catenanes that would not be possible to synthesize using other methods. What is more, these compounds, after removing the template, have in their structures three-dimensional binding cavities, in which they strongly and selectively bind anions (Scheme 3).



Scheme 3. Anion templated synthesis of mechanically interlocked molecular sensors developed by the Beer group.

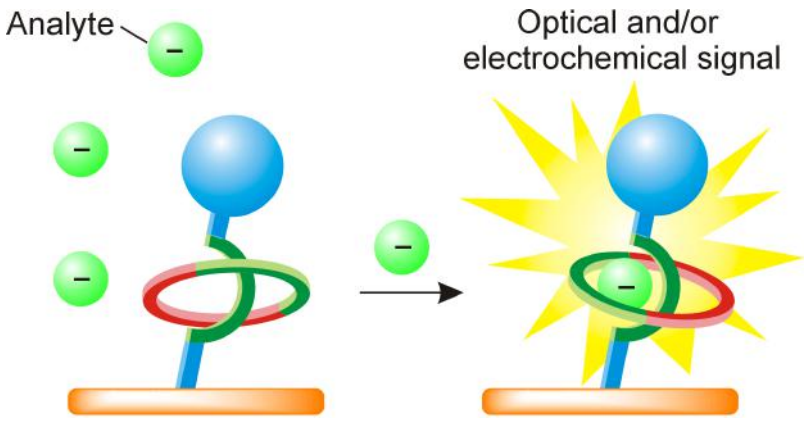
It is worth noting that these cavities are equipped with binding groups belonging to both components (for instance to the axis and the macrocycle) and therefore should bind anions more strongly than each of these components separately. On the other hand, topological

[17] M. J. Chmielewski, P. D. Beer, "Strategic anion templation for the assembly of interlocked structures", Review article in "Organic Nanostructures", eds.: J. L. Atwood and J. W. Steed, Wiley-VCH, 2008.

and geometrical constraints mean that some anions are bound less strongly, for example because they are unable to fit inside the cavity. For this reason, catenanes and rotaxanes are often more selective than their building blocks and have a particularly high affinity for the anion that best templated their formation.

Although catenanes and rotaxanes have been extensively studied, among others, as models of molecular machines and due to their potential applications in nanotechnology, the aforementioned aspect of their chemistry remained almost unnoticed for a long time. In the review article **H2**, we collected all previously known examples of topologically non-trivial receptors and highlighted the potential of these structures as molecular sensors, with particular emphasis on anion detection. This potential is due, on the one hand, to the strong and more selective binding of anions in the molecular cavities remaining after the removal of the template, and on the other hand, to the numerous signal transduction mechanisms offered by the mutual mechanical motions of their subunits. In order to realize this potential, it is necessary to equip catenanes and rotaxanes with chromophores, fluorophores or electrochemically active groups in such a way, that they change some easily measurable properties upon binding of a specific anion (scheme 3).

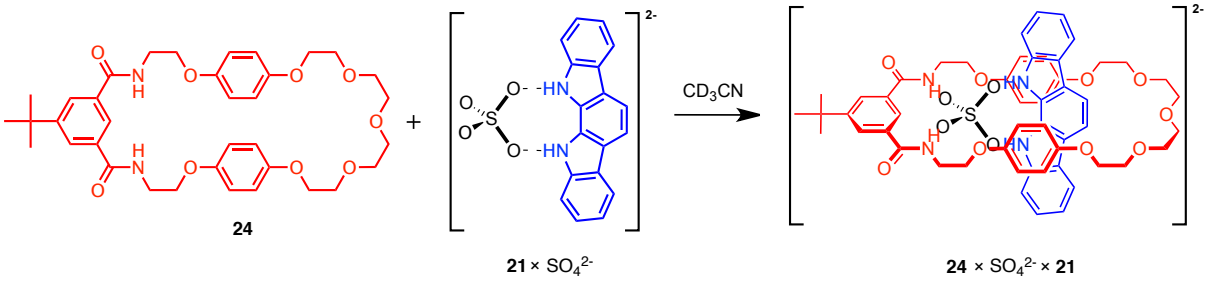
The publication **H2** outlines also the three-staged research program aimed at developing highly selective sensors for anion detection. The first step involves the development of a general anion templation methodology for the construction of a variety of interpenetrated and interlocked molecular structures. As has been shown, such structures strongly and selectively bind anions. At the second stage, the incorporation of redox- and photo-active groups into these interlocked frameworks converts them into electrochemical/optical molecular sensors. In the final third stage, the confinement of interlocked anion receptors at surfaces results in the fabrication of devices exhibiting highly selective binding and electrochemical and/or optical sensing behaviour (Scheme 4).



Scheme 4. Schematic representation of a rotaxane based sensor permanently anchored to the surface (for example, the surface of gold).

[H3]

During my post-doctoral stay in the team of Professor Paul D. Beer, I joined the research program outlined above. My main task was to synthesize fluorescent pseudorotaxanes, rotaxanes and catenanes based on electrically uncharged fluorophore - indolocarbazole (scheme 5). However, as mentioned above, this required extending the applicability of the anion templation strategy to uncharged building blocks. Attempts to thread indolocarbazole **21** through the centre of macrocycle **24** using chloride template, made by my predecessors, were unsuccessful. Also, the use of fluoride as anion with a much higher charge density and the ability to form strong hydrogen bonds, did not give the desired results due to its too high basicity - fluoride anions deprotonate indolocarbazole.



Scheme 5. Sulfate anion templated self-assembly of a pseudorotaxane from two electrically neutral building blocks.

I managed to overcome this impasse by using a new template, the sulfate anion, which has never been used in the synthesis of pseudorotaxanes, rotaxanes or catenanes. This anion has a very strong affinity for both pseudorotaxane components, but is less basic than fluoride and does not cause receptor deprotonation. I have demonstrated that both macrocycle **24** and axis **21** form very strong 2:1 and 1:1 complexes with sulfate in acetonitrile. Most importantly, however, it turned out that in the solution containing all three components in a ratio of 1:1:1, the desired heterodimer with the pseudorotaxane structure, **24** × SO_4^{2-} × **21**, dominates. Thus, for the first time, we managed to obtain a pseudorotaxane from electrically uncharged components.

Encouraged by these results, we attempted to deposit pseudorotaxes as self-assembled monolayer on gold. To this end, I developed the synthesis of unsymmetrically substituted indolocarbazoles with an easy-to-functionalise hydroxyl group that was used to attach a disulphide anchor. The axis thus obtained can be chemisorbed on the gold surface, and in the presence of sulfate anions and the macrocycle **24** forms a molecular monolayer of pseudorotaxanes. This process can be followed by measuring changes in the surface refractive index by SPR technique. This was the first example of anion-templated self-organisation of mechanically bonded structures on surfaces. In subsequent papers we showed that pseudorotaxanes and rotaxanes can be obtained in a similar way on metal

surfaces [**P11**, **P14**][18], silica [**P15**][18] and polymer [**P15**].[18] These accomplishments paved the way to the construction of macroscopic anion sensors.

The sulfate template that I proposed was used in a series of subsequent works by the Beer group, abolishing significant limitations of the anion templation strategy. It was used, for example, in the anion-templated synthesis of a catenane by double macrocyclization method, the synthesis which gave [2]catenane with an impressive yield of 80%.[19] The same cyclisation performed in the presence of the best template used so far, the chloride anion, does not give catenane at all. More examples of the use of sulfate anion in the templated synthesis of macrocycles, molecular capsules and mechanically related systems can be found in the review by Mullen and Beer from 2009.[20]

[H4]

Although we showed in publication **H3** how to solve the problem of pulling neutral axes through the annulus of uncharged macrocycles, serious difficulties related to the synthesis of appropriately functionalized indolocarbazoles hampered the synthesis of fluorescent rotaxanes and catenanes. Therefore, after returning to Poland I decided to use for the construction of rotaxanes and catenanes the previously proposed 1,8-diamino-3,6-dichlorocarbazole, building block which is also strongly fluorescent and has high affinity for anions, but is much easier to functionalise than the indolocarbazole.

The prerequisite for success was, of course, to find anions that would be able to combine two diamidocarbazole receptors in a stable 2:1 complex with orthogonal geometry. Since the preliminary studies described in **H1** showed that diamidocarbazoles do not form 2:1 complexes with chloride, benzoate or dihydrogenphosphate, I decided to use for this purpose the doubly charged sulfate anion SO_4^{2-}. Each of the two perpendicular O-S-O triangles of the sulfate resembles the carboxylate anions O-C-O, to which diamidocarbazoles have a particularly strong affinity; I expected therefore that the sulfate would bind two such receptors and set them orthogonally to each other. Indeed, X-ray structural analysis of the first sulfate complex with a diamidocarbazole receptor has largely confirmed these expectations. Although one of the ligands was seen to create hydrogen bonds with three, instead of two, oxygen atoms of the sulfate anion, and the angle between the carbazole planes is only 62.6, instead of 90 degrees, this structure bodes well for the attempts to synthesize catenanes, rotaxanes and other topologically non-trivial structures from diamidocarbazoles (Figure 5).

An additional encouragement came from the solution studies which showed that these complexes are very stable. Although the sulfate anion has extremely high hydration energy (-1080 kJ/mol), the association constants of sulfate with **25** remain surprisingly high even in the presence of 10% of water in DMSO: $\log K_{11} = 3.74$ and $\log K_{2:1} = 3.21$ (in DMSO alone the

[18] The list of my publications (denoted by **P**), which were not included in the present scientific achievement, is provided at the end of this document.
[19] B. Huang, S. M. Santos, V. Felix, P. D. Beer, *Chem. Commun.*, **2008**, 4610–4612.
[20] K. M. Mullen, P. D. Beer, *Chem. Soc. Rev.* **2009**, *38*, 1701−1713.

respective binding constants are too high to be measured using UV-Vis titrations). This suggests that diamidocarbazoles may be excellent building blocks for the construction of fluorescent sulfate anion sensors. (Recently, we were able to confirm this hypothesis by showing that indeed linking two such carbazole units with a flexible linker gives a receptor with extremely strong affinity to sulfate anions, capable of their selective binding and fluorescent detection even in the presence of 25% water; see **P22** for details).

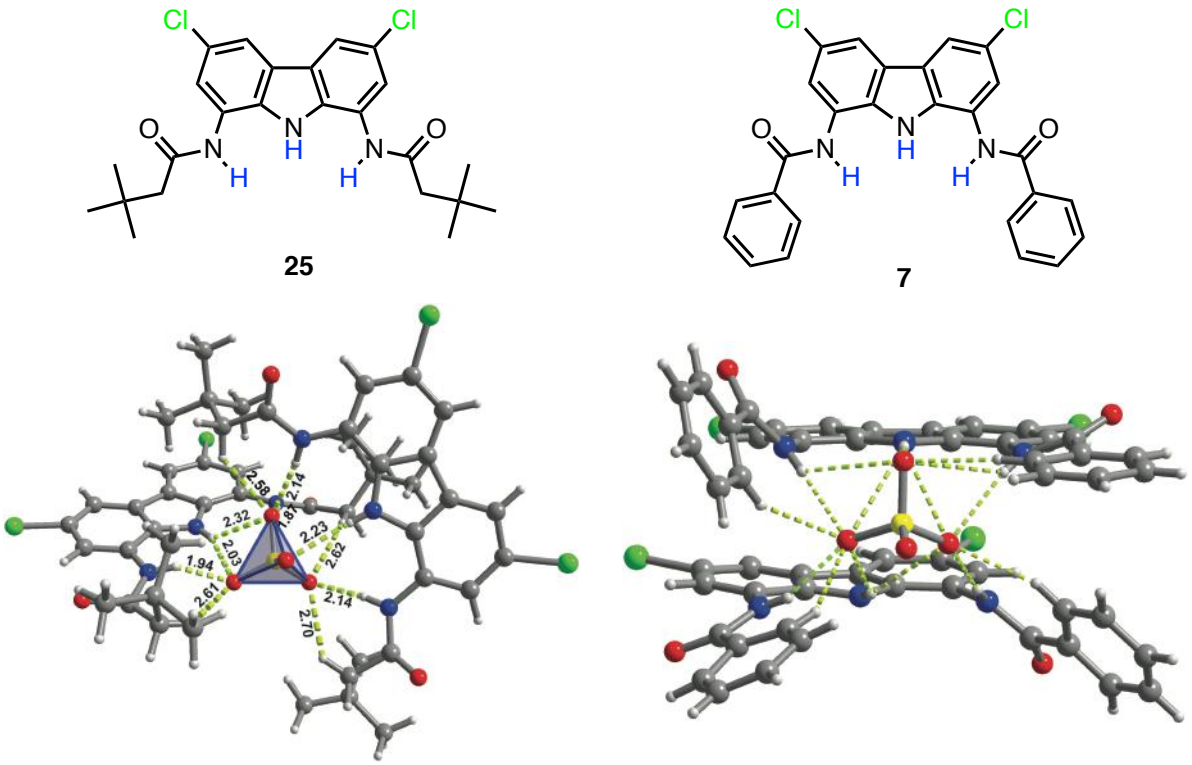


Figure 5. X-ray crystal structures of a) orthogonal complex and b) biplanar complex of receptors 25 and 7, respectively, with tetrabutylammonium sulfate.

Surprisingly, however, the crystalline structure of the second sulfate complex described in the work **H4** undermined the optimistic conclusions outlined above. It showed a completely different binding model that did not have a close precedent in the literature: two receptors arranged parallel one above the other and joined by π-stacking interactions, binding one sulfate anion from the same side (Figure 5). Such a complex is not suitable for the synthesis of mechanically interlocked structures.

An in-depth analysis of chemical shifts changes in the ^{1}H NMR spectra of receptors **25** and **7** induced by sulfate binding showed that the structures observed in the solid state dominate also in solution. Importantly, the spectral changes are so characteristic that they allow to easily determine whether a given ligand prefers orthogonal or parallel binding mode. What is more, the comparison of the preferences of the four model receptors tested in this work suggests that they can be easily influenced by the appropriate selection of substituents in the amide arms. Most probably the biplanar structure dominates when the substituents create steric hindrance and destabilize the orthogonal complex.

In conclusion, simple and easily available diamidocarbazole receptors form very stable 2:1 complexes with sulfate anion even in the presence of a large excess of water. Appropriate selection of side arms directs their self-organization towards the formation of either orthogonal or biplanar structures, both in the solid state and in the solution. These findings are of key importance for the design of catenanes and rotaxanes based on the 1,8-diaminocarbazole unit. Thanks to them, we have recently been able to obtain the first fluorescent catenanes of this type and show their potential as sensors of sulfate anions.[21]

[H5]

The extremely strong affinity of diamidocarbazoles to the sulfate anion has prompted us to study the interaction of this family of receptors with the hydrogen sulfate anion, HSO_4^-. It turned out that, despite all similarities to SO_4^{2-}, hydrogen sulfate has almost no affinity to diamidocarbazoles. In contrast to the doubly charged sulfate, whose binding constants in DMSO exceed 10^5 M^{-1}, the stability constants of the complexes with hydrogen sulfate are too small to be reliably measured (lower than 10 M^{-1}). This behaviour is typical for HSO_4^- and hydrogen binding receptors. This means that the strong complexing and templating properties of sulfate can be "switched off" by protonation. It is worth noting that in non-aqueous solutions, e.g. in DMSO, it is very simple: while sulfate is a weak base in water and requires strongly acidic environment to be completely protonated, in DMSO it is more basic than benzoate, acetate or DBU, i.e. it can be "turned off" by using a relatively weak acid, that is under mild conditions. SO_4^{2-} is therefore a switchable anionic template; a fully functional analogue of switchable cationic templates, such as Cu^{2+}/Cu^+ pair, which drastically change their coordination preferences upon oxidation/reduction.[22]

To demonstrate the potential usefulness of such a switchable template, we used orthogonal and biplanar complexes described in the publication **H4**. We have shown that system consisting of the diamidocarbazole receptor **25** and the sulfate anion can be reversibly switched between three states, in which, respectively, the free ligand, orthogonal complex with 2:1 stoichiometry or the 1:1 complex predominate (Figure 6). We also carried out an analogous experiment with the receptor **7**; in this case, however, the 2:1 complex has a biplanar structure and a different colour (yellow) than the other forms (colourless). These two examples show the possibility of controlling supramolecular systems by protonation/deprotonation of the sulfate template.

[21] Krzysztof M. Bąk, PhD thesis. Faculty of Chemistry, University of Warsaw, Warszawa 2018.

[22] Reversible oxidation/reduction of the Cu^{2+}/Cu^+ pair has been applied, inter alia, for the interconversion of double helicate and grid. A.-M. Stadler, C. Burg, J. Ramirez, J.-M. Lehn, *Chem. Commun.* **2013**, *49*, 5733–5735.

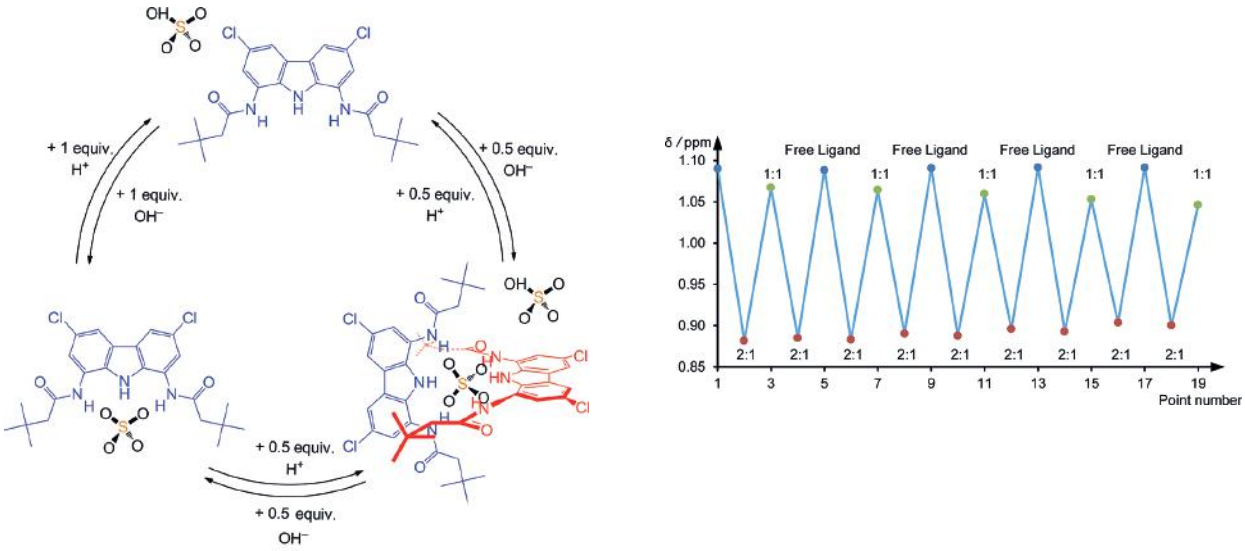


Figure 6. On the left: the three states of the system composed of the receptor 25 and the sulfate anion and a scheme showing the switching between them. Right: changes in the chemical shift of the proton *t*-Bu of the receptor 25 during the switching.

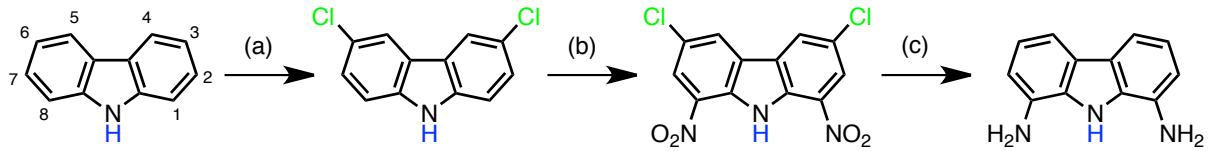
During these studies we discovered also that the complexation of sulfate by diamidocarbazole receptors reduces its basicity by more than 5 orders of magnitude: while hydrogen sulfate ($pKa(HSO_4^-)$ = 14.5) is not noticeably deprotonated by triethylamine ($pKa(Et_3NH^+)$ = 9.0) in DMSO, it can be deprotonated completely in the presence of 2 equivalents of the receptor. Thus, just like the protonation of sulfate drastically reduces its affinity for receptors, so does complexation lower its basicity. The SO_4^{2-} and HSO_4^- anions can thus be considered to be a switchable (by complexation) base and acid, respectively. This also means that the HSO_4^-/Et_3N mixture can be considered a "hidden" or "virtual" template that reveals its power only in the presence of an appropriate receptor. Looking from yet another point of view, this is the first example of selecting a virtual template from (extremely simplified) dynamic combinatorial library, composed of just three interconverting elements: SO_4^{2-}, HSO_4^- and H_2SO_4.

[H6]

Because the previously discussed papers clearly indicate the high potential of diaminocarbazoles as building blocks for the construction of anion receptors and fluorescent sensors, as well as in the anion templated synthesis, I decided to develop the synthesis of 1,8-diaminocarbazole which lacks any substituents in positions 3 and 6. Such a reference compound would allow to estimate the effect of Cl substitutes on the strength of anion complexation and on the fluorescent response of the receptors. There are known literature reports on reduced quantum yield of fluorescence in chlorinated aromatic compounds, suggesting that dechlorinated receptors should exhibit more intense fluorescence.

Hydrodechloration of 3,6-dichloro-1,8-dinitrocarbazole was already observed in the publication **H1** as a side reaction accompanying the reduction of nitro groups with hydrogen catalysed by palladium on carbon. However, the product of double dechlorination appeared

in this reaction only in trace amounts. So, I tested a number of other literature methods for hydrodechlorination and obtained the best results using triethylamine formate and palladium catalyst, according to the procedure of Cortese and Heck.[23] However, unlike in the original publication of these authors, in the case of our substrate, the reduction of nitro groups proceeded faster than dechlorination, and therefore it was impossible to obtain 1,8-dinitrocarbazole by this route. Nevertheless, if the reaction is carried out long enough, the transiently formed 1,8-diamino-3,6-dichlorocarbazole is finally converted to 1,8-diaminocarbazole **26** in good yield. The final product can be obtained on a 5 mmol scale in 70% yield (after column chromatography) or on a 50 mmol scale in 51% yield (after crystallization).



10 **11** **12** **26**

Scheme 6. The synthesis of 1,8-diaminocarbazole described in the publication H6. (a) SO_2Cl_2, CH_2Cl_2, rt, 3h, 60%; (b) HNO_3 (100%), Ac_2O, AcOH, 73%; (c) HCOOH+Et_3N, $Pd(AcO)_2$/Ph_3P, reflux, 48 h, 70%.

A short, three-step reaction sequence leading from very cheap industrial product, carbazole, to the 1,8-diaminocarbazole **26**, on a multigram scale and without the need for chromatographic separations, allowed me not only to obtain a new series of model receptors described in **H7**, but also to investigate the electropolymerization of this compound in cooperation with the team of prof. Magdalena Skompska from the Faculty of Chemistry, University of Warsaw. These studies resulted in the discovery of a new conductive polymer with very attractive properties, which became the subject of further comprehensive research, described *inter alia* in four joint publications: **P9**, **P12**, **P13**, **P21**.

[H7]

The results presented so far convincingly demonstrate that 1,8-diaminocarbazole and its derivatives are very promising building blocks for the construction of anion receptors, including receptors operating in an aqueous media, and for the anion templated synthesis of fluorescent catenanes, rotaxanes and other mechanically bonded structures. However, the ability of diamidocarbazoles to transport anions through biological membranes (lipid bilayers) has never been investigated before, and their potential in fluorescent anion sensing have so far been limited only to the 3,6-dichlorosubstituted derivatives. It was also unclear to what extent these receptors owe their extremely strong affinity for anions to their unique geometry, and to what extent to the influence of electron withdrawing substituents. The problem of very limited solubility of these compounds in most common solvents also remained to be solved. I decided therefore to examine the relationship between the structure and properties of this class of receptors more thoroughly.

[23] N. A. Cortese, R. F. Heck, *J. Org. Chem.* **1977**, *42*, 3491-3494.

With this in mind, we designed and synthesized a family of fourteen amide derivatives of 1,8-diaminocarbazole (Figure 7) that differ in substituents at the positions 3 and 6 (hydrogen or chlorine) and side arms (aromatic or aliphatic, linear or branched, etc.). During these studies we refined the methodology of their synthesis and then examined their solid state structures, binding constants with selected anions, fluorescence response to the addition of various anions and the ability to transport anions through lipid bilayers.

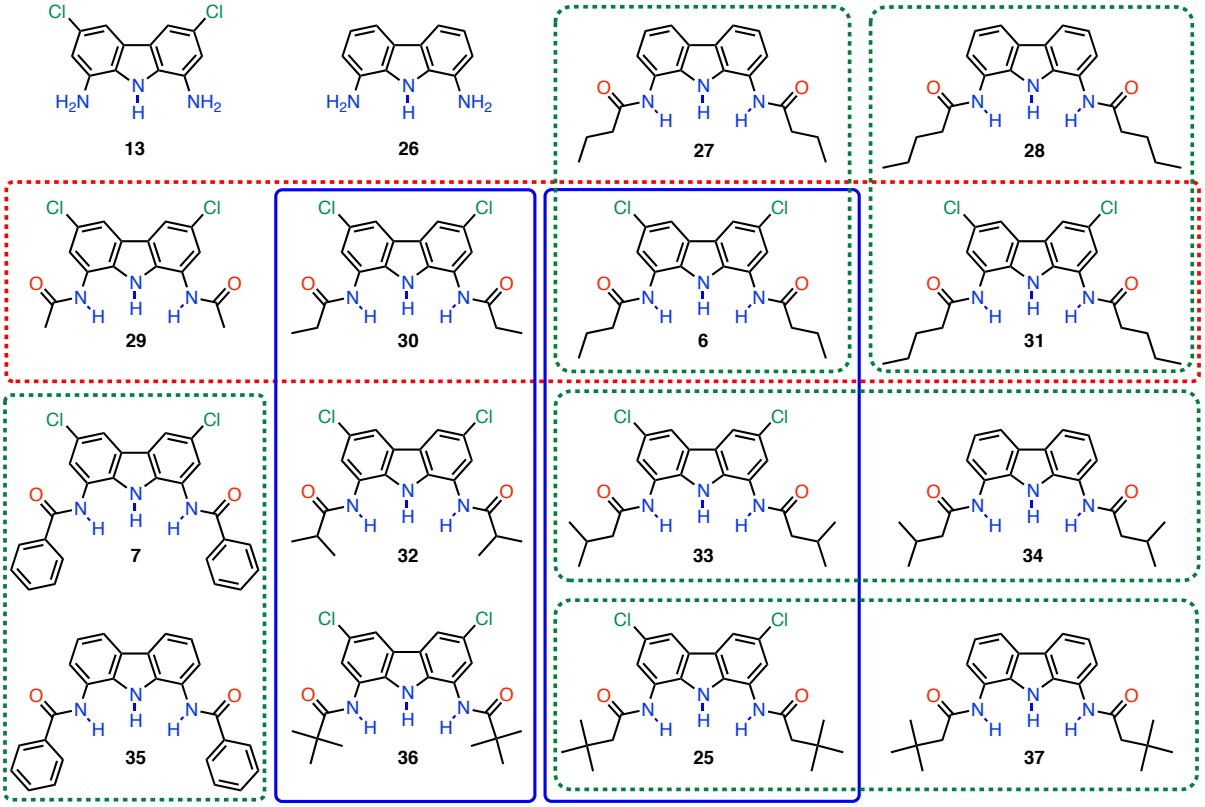


Figure 7. Structural relationships within diamidocarbazole family discussed in paper H7: pairs of chlorinated and non-chlorinated receptors are encircled by a green dotted line, receptors differing in the length of their alkyl chains are marked by a red dotted line and the receptors differing with the degree of branching – by a blue solid line.

The crystal structures of receptors with aliphatic (**28**) and aromatic (**35**) substituents are shown in Figure 8.

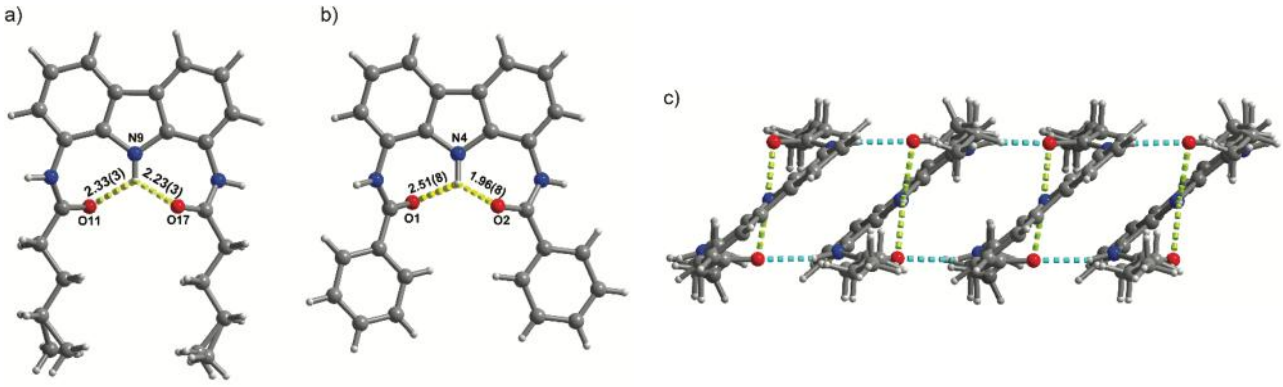


Figure 8. a) X-ray crystal structures of (a) 28, (b) 35 and (c) crystal packing of 28.

Both compounds adopt a very similar conformation in the solid state, with NH bonds directed outside the binding cleft. This conformation is stabilized by two strong intramolecular hydrogen bonds between the C=O amide groups and the carbazole NH proton. Of course, both of these bonds have to be broken so that the receptor can bind an anion with its all three NH groups, and this requires substantial amount of energy.

The X-ray structural analysis of the benzoate complexes of the same receptors **28** and **35** shows the two molecules in a convergent, binding conformation, in which the amide NH bonds are facing towards the centre of the binding cleft and form hydrogen bonds with the guest (Figure 9).

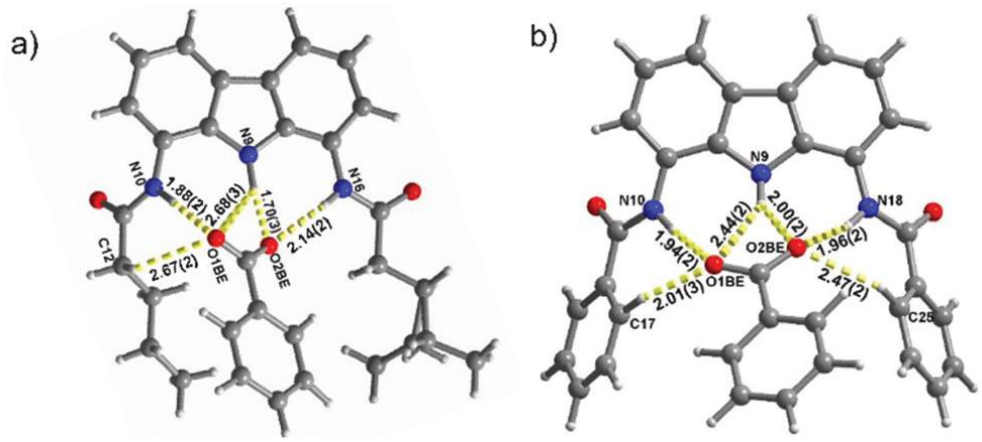


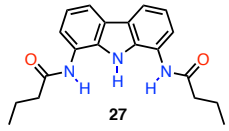
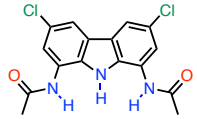
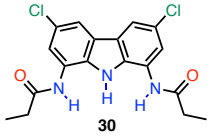
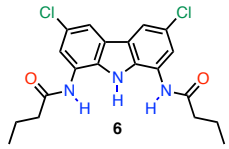
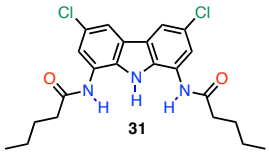
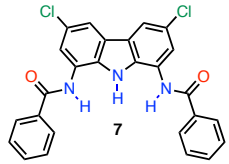
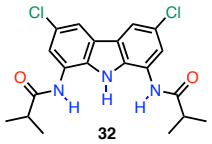
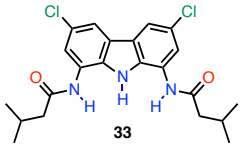
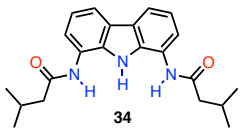
Figure 9. X-ray crystal structures of (a) 28 × $PhCOO^-$ and (b) 35 × $PhCOO^-$.

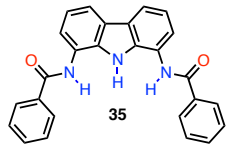
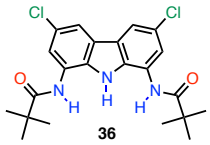
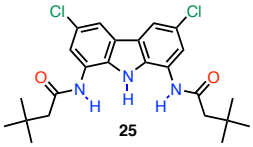
Importantly, in both complexes the central NH atom of the carbazole molecule forms two strong hydrogen bonds with the benzoate anion. This indicates the key role of this donor in stabilizing anionic complexes. These structures also seem to suggest that the receptors' cavities are somewhat too small for the carboxylate anion: in both cases the anion is well above the carbazole plane, and the amide arms are twisted toward the guest to form an angle from 18 to as many as 58 degrees with the carbazole plane.

In spite of the inadequate preorganization and imperfect geometric fit, diamidocarbazoles bind strongly to benzoate, dihydrogenphosphate and sulfate anions in DMSO containing 0.5% of water. The binding constants of these anions with the majority of the receptors studied were found to be too high to be reliably measured by ^{1}H NMR titrations, and were therefore determined by UV-Vis titrations (Table 2).

In all cases, the complexation constants with dihydrogenphosphate anions were found to be higher than with benzoate, and these in turn were significantly higher than with chlorides, what is generally consistent with the well-known hydrogen bond accepting abilities of these anions. In the best cases, the selectivity factors for $H_2PO_4^-$ over Cl^- exceeded 1600, and for $PhCOO^-$ over Cl^- – 180. The selected model receptor **25** was additionally titrated with acetate, bromide, iodide and nitrate. Acetate ions are better hydrogen bonds acceptors than benzoate and indeed the stability constant with acetate is, in this case, equal to that of dihydrogenphosphate. The logarithms of binding constants with the three remaining anions were found to be very low: 1.10, <1 and <1.

Table 2. Association constants K_a [M^{-1}] and logarithms of association constants (in brackets) of carbazole receptors with various anions in DMSO + 0.5% H_2O (w/w), determined by ^1H NMR and UV-Vis titrations.

Receptor	$H_2PO_4^-$ [a]	$PhCOO^-$ [a]	Cl^- [b]
 27	1.41×10^4 (4.15)	3.00×10^3 (3.48)	42 (1.62)
 29	1.21×10^5 (5.08)	7.55×10^3 (3.88)	75 (1.88)
 30	9.86×10^4 (4.99)	1.08×10^4 (4.03)	104 (2.02)
 6	9.62×10^4 (4.98)	1.60×10^4 (4.20)	109 (2.04)
 31	9.40×10^4 (4.97)	1.34×10^4 (4.13)	111 (2.05)
 7	6.98×10^3 (3.84)	1.79×10^3 (3.25)	14 (1.15)
 32	1.21×10^5 (5.08)	1.31×10^4 (4.12)	131 (2.12)
 33	9.68×10^4 (4.99)	2.18×10^4 (4.34)	123 (2.09)
 34	1.10×10^4 (4.04)	4.43×10^3 (3.65)	42 (1.62)

 35	1.66×10^3 (3.22)	5.73×10^2 (2.76)	< 10 (< 1)
 36	4.71×10^3 (3.67)	2.01×10^3 (3.30)	56 (1.75)
 25	8.32×10^4 (4.92)	2.90×10^4 (4.46)	159 (2.20)
 37	1.02×10^4 (4.01)	4.65×10^3 (3.67)	48 (1.68)

[a] Determined by UV-Vis titrations. [b] Determined by ^{1}H NMR titrations.

The receptor **25** gives the highest binding constant with benzoate among all 13 receptors tested by us; it is therefore worth comparing its affinity with other similar receptors from literature. The Leito team determined the complexation constants of 38 different model ureas, thioureas, indoles, carbazoles and indolocarbazoles with benzoate and acetate in the same solvent that we used (DMSO + 0.5% H_2O). None of them bound these anions more strongly than **25**, even though some of them had 4 or even 6 strong hydrogen bond donors.[24] In another contribution from the same team,[25] the complexes of 22 receptors, of which 7 new, were compared and only in one case the binding constant with acetate turned out to be higher than for **25**: logK = 4.98 compared to 4.96 (taking into account the uncertainty of measurement these constants must be considered equal). However, this value was obtained for the receptor, which was also based on the 1,8-diaminocarbazole backbone, although equipped with as many as eight NH bonds. This comparison shows, on the one hand, that despite its simplicity, **25** binds carboxylates extremely strongly, and on the other, that improving this result by expanding the receptor structure is not simple.

As expected, chlorinated receptors display much higher affinities for anions than non-chlorinated ones: about 7-9 times higher for dihydrogenphosphate, 5-6 times for benzoate and 2-3 times for chloride. However, the introduction of electron withdrawing substituents into the receptor structure may increase the acidity of the receptors to the extent that instead of binding the anions they will be deprotonated. Fortunately, UV-Vis spectra show that none of the chlorinated receptors is deprotonated under the conditions of our

[24] S. A. Kadam, K. Martin, K. Haav, L. Toom, C. Mayeux, A. Pung, P. A. Gale, J. R. Hiscock, S. J. Brooks, I. L. Kirby, N. Busschaert and I. Leito, *Chem. Eur. J.*, **2015**, *21*, 5145-5160.

[25] K. Martin, J. Nõges, K. Haav, S. A. Kadam, A. Pung, I. Leito, *Eur. J. Org. Chem.* **2017**, 5231-5237.

measurements, unlike, for example, the chlorinated diamidopyrrolic receptors by Gale and co-workers.[26]

As already indicated in the publication **H1**, amides with aromatic substituents bind anions much less strongly than those with aliphatic ones, which seems to contradict the generally better hydrogen bond donating properties of aromatic amides and the results of X-ray structural analysis, which suggests additional stabilization of the complex by aromatic substituents through CH---O interactions. This might be rationalised by assuming that the receptors with aromatic arms create stronger intramolecular hydrogen bonds; the bonds that compete with anion binding. However, this hypothesis awaits verification.

Attempts to improve solubility by expanding the aliphatic substituents in the amide arms ended with only a slight improvement: only **36**, the receptor with *t*-Bu group directly connected to the amide bonds, is clearly more soluble. Unfortunately, this receptor binds anions significantly less strongly than the others, presumably due to steric hindrance. Interestingly, in other receptors additional substituents on the carbon α to the carbonyl group do not interfere with anion binding, at least as long as there is at least one hydrogen attached to this carbon atom. It should therefore be possible to introduce chirality into these positions without significant deterioration of the anion binding properties.

Interesting results were obtained by studying the fluorescence response of two model receptors **25** and **37** to the presence of various anions. The most strongly bonded $H_2PO_4^-$ and AcO^- anions induce about twofold increase of the fluorescence of the chlorinated receptor **25** and up to 15-fold of the non-chlorinated **37**. The distinction of these two anions is also possible, because the first one produces new bands in the spectrum of **25**, most likely as a result of proton transfer in the excited state.[27] In contrast to $H_2PO_4^-$ and AcO^-, the benzoate anion, which also binds to these receptors very strongly, suppresses fluorescence of **25** and causes only slight changes in the emission of **37**. The fluorescent response of diamidocarbazoles is therefore much more selective than their binding.

Of course, it should not be expected that such simple receptors will highly specifically bind and sense anions, but from the point of view of practical applications, this is not necessarily indispensable; on the contrary - using libraries of poorly selective receptors, one can build "chemical noses" and "tongues" that allow recognition and sensing of many different analytes.[28] From this point of view, the easy availability of diamidocarbazoles is an asset. From a practical point of view, it is also very attractive that the fluorescence of diamidocarbazoles increases upon anion binding; it is less common and at the same time more desirable response than quenching. What is more, these receptors emit light in the visible range. The 3,6-unsubstituted derivatives are particularly attractive as sensors, because their fluorescence is stronger and grows much more than their chlorinated counterparts.

[26] S. Camiolo, P. A. Gale, M. B. Hursthouse, M. E. Light, A. J. Shi, *Chem. Commun*. **2002**, 758-759.
[27] There is no sign of deprotonation in the ground state as judged by UV-Vis spectra.
[28] A. P. Umali, E. V. Anslyn, *Curr. Opin. Chem. Biol.* **2010**, *14*, 685-692.

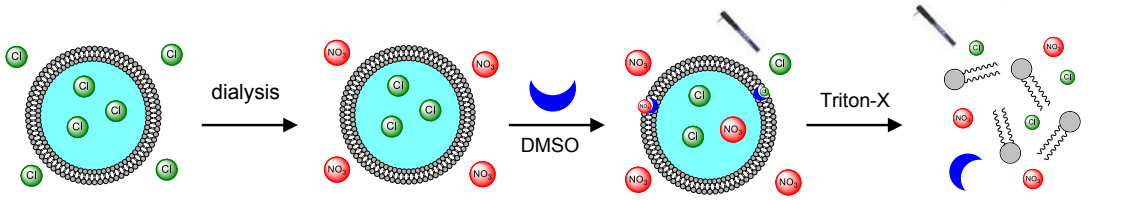
Receptors capable of facilitating anion transport through lipid bilayers (the so-called anionophores) are currently being intensively studied due to their potential biological activity.[29] In living organisms, it is necessary to maintain specific concentrations of various anions on opposite sides of biological membranes and compounds that significantly interfere with ion homeostasis can not be indifferent to cells. Some of these substances can induce apoptosis and have anti-cancer properties, others limit the growth of antibiotic-resistant bacteria, and still others can replace natural anion transporters that have lost their functionality due to genetic defects. Particular attention has been paid in these studies to chloride transporters, what is usually motivated by the prospect of their future use in the therapy of cystic fibrosis, a genetic disorder caused by chloride channel malfunction. However, no 1,8-diaminocarbazole derivatives have ever been studied for their anion transport properties.

Therefore I started cooperation with professor Roberto Quesada from the University of Burgos, a well-known expert in the field of anion transport, who agreed to investigate the anionophoric properties of our diamidocarbazoles. These studies consisted in the preparation of a suspension of large unilamellar vesicles (LUVs) filled with concentrated NaCl solution and suspended in an isotonic $NaNO_3$ solution. An ion-selective electrode placed in such a suspension does not indicate the presence of chlorides because they are not able to escape out of the liposomes. On the other hand, the addition of a very small amount of receptor solution to this suspension causes the receptor to build into the liposome membrane and begin to transport the chlorides according to the their concentration gradient, i.e. outside. The kinetics of chloride escape into the external solution is measured by means of an electrode and then compared between individual receptors (Scheme 7).

It turned out that several diamidocarbazoles showed significant activity in such a test. Analysis of the relationship between the activity and structure of these compounds led to the following observations:

1. Receptors with chlorine atoms in positions 3 and 6 are more active transporters than their unsubstituted analogues.
2. Benzamide derivatives are almost completely inactive under these conditions.
3. The activity of amides derived from aliphatic acids strongly depends on minor structural variations in the side chains. For example, the introduction of methyl groups in the positions β to the carbonyl groups results in a large increase in activity on transition from **6** to **33**, followed by a sharp decline from **33** to **25**. Similarly, the addition of one methyl group in the position α to the CONH groups turns very poorly active **32** into the most active **36**.

[29] N. Busschaert, P. A. Gale, *Angew. Chem. Int. Ed.* **2013**, *52*, 1374-1382.



Scheme 7. Schematic representation of a method of investigation of anion transport kinetics through lipid bilayers of large unilamellar vesicles (LUVs).

These relationships result from the overlap of many factors, such as the affinity of the receptors to chloride anion, membrane solubility, lipophilicity, diffusion rate, and others; so it is difficult to predict them *a priori*. Therefore, finding anionophores with desirable properties requires the synthesis and testing of many derivatives, in which the ease of synthesis of 1,8-diaminocarbazole derivatives is very helpful.

To shed some light on the transport mechanism, the above experiment was modified by replacing the $NaNO_3$ solution outside the liposomes with an isotonic sodium sulfate solution. Under these conditions, chloride transport is not observed, because the outflux of negative charges (in the form of chloride anions) from the interior of the liposomes is not balanced by the influx of nitrate anions. Apparently, the diffusion of the doubly charged and extremely hydrophilic sulfate anion through the lipid membrane is not fast enough even in the presence of anionophores. However, it is enough to add bicarbonate anions to the external sulfate solution to observe the chloride transport again. This suggests firstly that our receptors transport chloride anions according to the antiport mechanism and, secondly, that they promote not only the most easy Cl^-/NO_3^- antiport, but also much more difficult Cl^-/HCO_3^- antiport.

It is worth noting that compounds **33** and **36** are active chloride transporters despite their relatively low affinity for these anions (and even lower for NO_3^-). It is a well-known fact that both too weak and too strong binding of anions slows down the transport due to, respectively, ineffective extraction of anions from water into the bilayer or too slow release of anions into the aqueous solution on the other side. Although there is no simple relationship between the anion binding strength and the ability of a receptor to transport them through lipid bilayers, the strong affinity of diamidocarbazoles for the phosphate and carboxylate anions suggests that these receptors could also be capable of transporting these biologically important oxoanions. Testing this hypothesis, however, was not easy, among other factors due the lack of commercially available ion-selective electrodes for phosphates and carboxylates, and required the development of new methods for measuring transport kinetics. It is only recently that we managed to overcome these difficulties and show that at least some 1,8-diamidocarbazoles are able to transport many different oxoanions of biological importance, including drugs, metabolites, toxins, anions of amino acids and model

organic phosphates.[30] So I hope that in not too distant future the carbazole transporters discovered by us will serve many other research groups as leading structures in the development of new, selective anionophores.

Summing up, the work **H7** laid the foundations for further investigations on the use of diamidocarbazole receptors for the strong and selective binding of anions, their fluorescent detection and transport through lipid bilayers. We showed that these receptors can be easily obtained and modified and that they bind anions very strongly even in a highly competitive solvent - DMSO + 0.5% H_2O. We examined the properties of the 3,6-unsubstituted receptors for the first time and showed that although their affinity for anions is several times weaker than the 3,6-dichlorosubstituted receptors, they are excellent fluorescent sensors whose emission increases upon anion binding up to several times. We also found that some diamidocarbazoles are active anion transporters through lipid bilayers in model liposomes, facilitating their transport according to the antiport mechanism.

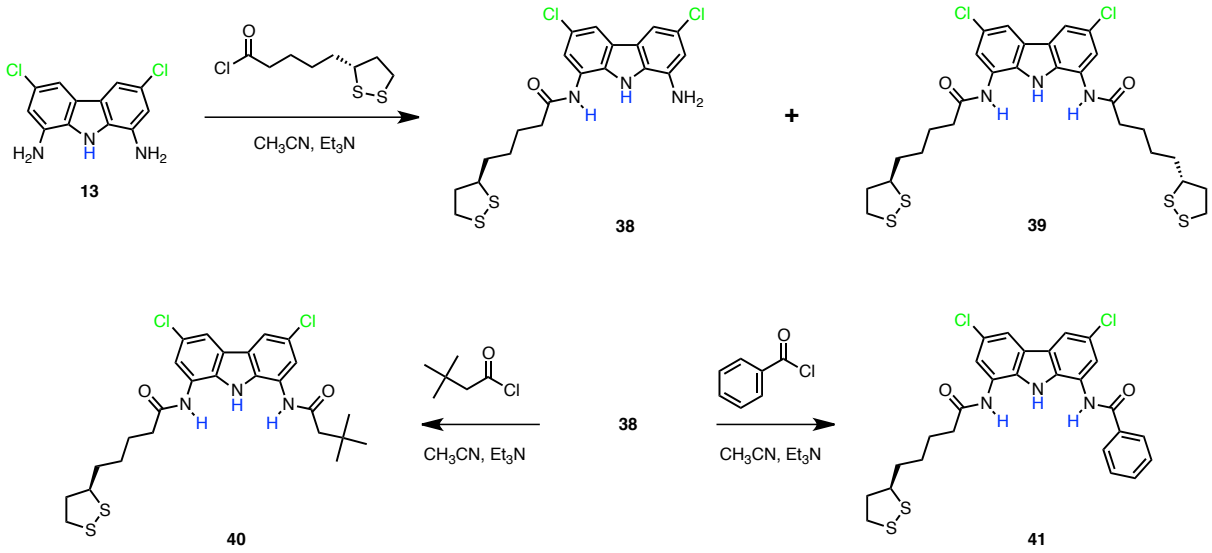
[H8]

Although anion sensing is becoming increasingly important in various fields of science and technology, such as medical diagnostics, food control, environmental protection, biochemistry and various industries, the vast majority of the anion-sensitive molecular sensors described in the literature have only been studied in solution. However, an important step towards practical applications of molecular receptors is their immobilization on a solid support, e.g. in the form of self-assembled monolayers (SAMs). This is a prerequisite for the construction of reusable sensors operating in various environments (also those in which the receptors are not soluble) and in real time. The particular advantages of molecular monolayers are the short response times and the possibility of patterning surfaces with different receptors, which can be used to construct "chemical noses".

Although only a small fraction of all anion receptors have so far been deposited on surfaces, there are a number of examples of self-assembled monolayers whose response to the anions was tested using various techniques: cyclic voltammetry (**P11**), spectrofluorimetry (**P15**), surface plasmon resonance (**H3**) or electrochemical impedance spectroscopy. The results obtained with these techniques are very encouraging; they suggested, among others, that anion binding by receptors immobilized on two-dimensional surfaces is much stronger than in solution.[31] However, these methods give little insight into the receptor-anion interaction at the molecular level and the real causes of the observed changes in signal are often questionable. Therefore, we decided to investigate, in cooperation with prof. Jolanta Bukowska and prof. Barbara Pałys from the Faculty of Chemistry of the University of Warsaw, the detection of anions by diamidocarbazole monolayers by means of surface infrared spectroscopy.

[30] K. M. Bąk, PhD thesis. Faculty of Chemistry, University of Warsaw, Warszawa 2018.
[31] N. H. Evans, H. Rahman, J. J. Davis, P. D. Beer, *Anal. Bioanal. Chem.* **2012**, *402*, 1739-1748.

For this purpose we have synthesized three model carbazole receptors equipped with disulfide anchors for immobilization on gold and silver surfaces. Two of them were asymmetric: in addition to the lipoic acid residue they also had an amide arm with an aliphatic (**40**) or aromatic substituent (**41**), while the third one had two lipoic acid anchors (**39**). The synthesis of receptors **39**-**41** consisted of the reaction of 1 equivalent of lipoic acid chloride with diaminocarbazole **13**, resulting in the formation of a mixture of monosubstituted **38** and disubstituted **39** products (scheme 8).



Scheme 8. The synthesis of receptors 39-41.

The lipoic acid residues gave these compounds solubility good enough for purification by column chromatography. In this way, we obtained the disubstituted receptor **39** in 13% yield as well as monosubstituted intermediate **38** in 40% yield. The latter was reacted with *t*-butylacetic or benzoic acid chloride, resulting in the desired receptors **40** and **41**, respectively.

Monolayers of **39**-**41** on gold have been obtained by simply immersing gold substrates in ethanolic solutions of each receptor for 2 days. Studies with PM-IRRAS (polarization modulation infrared reflection absorption spectroscopy) have shown that all three receptors form ordered monolayers on the surface of gold. In the case of the receptor with the *t*-BuCH_2 substituent – the analysis of orientation-related signal suppression in the PM-IRRAS spectra suggests that the carbazole skeleton is approximately parallel to the gold surface, while the amide groups - roughly perpendicular. On the other hand, in case of receptors **39** and **41**, both the carbazole platform and amide groups are inclined to the surface.

As a model anion for our studies we chose sulfate SO_4^{2-}; primarily due to its particularly high affinity for diamidocarbazoles, and also due to the growing role of this anion in medical diagnostics (sulfate is the fourth anion in the human bloodstream and has many important roles in physiological processes) and environmental protection. Analysis of changes in PM-IRRAS spectra after immersion of monolayers in solutions of tetrabutylammonium sulfate in acetonitrile showed that:

- sulfate anions bind to the carbazole receptors immobilized on the surface in such a way that their main axis of symmetry is parallel to the gold surface
- interaction with the anion introduces disorder in monolayers of single-anchor receptors, but not in the monolayer of receptor with two disulfide anchors;
- all three monolayers capture sulfate anions from dilute solutions in acetonitrile, which can be directly observed in the PM-IRRAS spectra by measuring signals derived from SO_4^{2-};
- sulfate anions bind to carbazole receptors immobilized on the surface in such a way that their main axis of symmetry is parallel to the gold surface;
- in a certain concentration range the ratio of the intensity of the sulfate band to the amide band correlates linearly with the logarithm of the sulfate concentration in the solution; however, the slope of such a line is smaller in the concentration range of 10^{-6} to 10^{-3} M than in the range of 10^{-3} to 10^{-1} M. This indicates a different absorption mechanism under these conditions. Presumably, initially anions bind to receptors on the surface with hydrogen bonds, as intended. However, already at a concentration of 10^{-3} M all binding sites on the surface become saturated and the surface becomes negatively charged. It attracts counterions from the solution, which form a new, positively charged adlayer. At high concentrations of SO_4^{2-} this positively charged, external cation layer attracts more sulfate anions;
- comparison of the inclination angles of the above-mentioned straight lines allows to estimate the relative binding strength of anions by receptors **39** - **41**. In accordance with the trends observed for the model receptors in the publication **H7**, the highest affinity for sulfates is exhibited by the monolayer of receptor **40** with two *t*-BuCH_2 substituents, slightly weaker – by that of receptor **39** with two lipoic anchors and the weakest – by receptor **41** with an aromatic substituent.

Unfortunately, none of the obtained monolayers was able to bind sulfate anions in water. This is not surprising if one considers that sulfate is one of the most hydrophilic anions. We have found, however, that dilute aqueous solutions of sulfate cause the hydrolysis of the amide bond connecting carbazole with the lipoic anchor. Unexpectedly, this hydrolysis progresses much faster for the receptor **39** with two lipoic anchors. It is worth noting that this process can easily go unnoticed if studies are carried out by other techniques, such as SPR.

The SERS spectra confirmed the binding of sulfate anions through carbazole receptors immobilized on the silver surface, which opens the way to further research on the construction of sulfate sensitive nanosensors.

In summary, surface infrared spectroscopy techniques provide much better insight into the structure and binding of anions through molecular monolayers of receptors than the most popular methods used up to now. However, on the way to the practical applications of carbazole receptors in the detection of anions there remains the problem of their permanent immobilization on surfaces and elaboration of their structure in such a way that they become capable of binding sulfates in water.

Summary of the results of the scientific achievement outlined above

I consider that the most important achievements of my habilitation are:

- The discovery of 1,8-diaminocarbazoles, a new family of building blocks for the construction of anion receptors, whose outstanding affinity for Y-shaped oxygen anions opened up a whole range of possibilities, such as anion templated synthesis, anion recognition in aqueous media, fluorescent detection of anions and fabrication of anion-sensitive molecular monolayers, as well as anion transport through lipid bilayers; opportunities which I explored in the subsequent works.
- Introduction of a new, extremely effective anionic template for the synthesis of rotaxanes and catenanes – the sulfate anion SO_4^{2-}. This template significantly expanded the scope of anion templated synthesis, what we have demonstrated by making the first electrically neutral pseudorotaxanes and rotaxanes, including the first such structures deposited on the surface.
- Demonstration that diamidocarbazoles form two fundamentally different types of complexes with sulfate anion, orthogonal and biplanar, and that this self-assembly process can be easily directed in any direction by the appropriate selection of substituents. The first of the aforementioned complexes is particularly attractive, because it can be used for the synthesis of catenanes, rotaxanes, helicates and other topologically non-trivial supramolecular structures
- Demonstration that the sulfate anion is not only a powerful template but also a switchable template, because it can be easily "switched" off and on by protonation/deprotonation. This is the first example of a switchable template in supramolecular chemistry of anions. Such templates can be used, among other applications, for the construction of molecular switches, as demonstrated here using 1:1 and 2:1 complexes of model diamidocarbazoles.
- Development of a convenient method for the synthesis of unsubstituted 1,8-diaminocarbazole, interesting building block for the synthesis of fluorescent anion receptors and monomer for the synthesis of conductive polymers with very attractive properties.
- Demonstration, in cooperation with professor R. Quesada, that some diamidocarbazoles are able to transport chlorides through lipid bilayers. This discovery opens up a wide field for further exploration and rises hopes for finding receptors with interesting biological activity.
- Supporting the first model diamidocarbazole receptors on metal surfaces and demonstration of the usefulness of infrared spectroscopy in studying their interaction with anions. This is important step towards practical applications of diamidocarbazoles in the construction of anion sensors.

5. Description of other scientific and research achievements

I gathered my first research experience in the team of professor M. Mąkosza at the Institute of Organic Chemistry of the Polish Academy of Sciences, where, during summer holidays after the first year of my studies, I was involved in attempts to develop halomethylation of nitroarenes by vicarious nucleophilic substitution of hydrogen (VNSH). During the next holiday internship in the same team I tried to develop the synthesis of aromatic thiols using the VNSH method. The results of these studies have not been published.

My first publishable results were obtained during the preparation of my master's thesis under the supervision of prof. Jurczak at the Faculty of Chemistry, University of Warsaw. This work concerned 1) the influence of various protic solvents on macrocyclization by aminolysis of esters and 2) optimization of the reduction of macrocyclic oligoamides thus obtained to amines with azacoronand structure. The results obtained in this work were included in publication **P7**.

In my doctorate, also prepared under supervision of prof. Jurczak, I investigated three families of macrocyclic, electrically uncharged amide receptors for anions. These works revealed the relationship between their structure and anion binding properties and allowed to formulate a number of guidelines for the design of new receptors with improved properties. The results were published in seven publications (**P1** - **P6** and **P10**), some of which belong to the canon of supramolecular chemistry of anions and are cited extensively in all monographs of this subject and even in academic textbooks for students.

After PhD I worked as an assistant at the Institute of Organic Chemistry of Polish Academy of Sciences studying simple, acyclic anion receptors based on the carbazole backbone. I described the results of these studies in the publication **H1** and in this self-report.

I spent my first post-doctoral internship (3 months) in the team of professor Latos-Grażyński at the University of Wrocław, working on the synthesis and studying properties of carbaporphyrinoids with thiophene ring and their cadmium and zinc complexes. This internship resulted in publication **P8**.

During my second postdoctoral internship (15 months) I was working in the team of prof. P. D. Beer at the University of Oxford, where I joined pioneering research on the synthesis of fluorescent pseudorotaxanes, rotaxanes and catenanes for anion sensing applications. My most important achievement from this period was to propose sulfate anion as a convenient and exceptionally effective anionic template for the synthesis of such structures (**H2** and **H3**). In addition, I developed the synthesis of various symmetric and asymmetric indolocarbazoles with easily to functionalise substituents, which enabled the generation of a series of fluorescent pseudorotaxanes and rotaxanes (**P14**, **P15** and **P16**). I managed also to accomplish a twenty-three-step synthesis of electrochemically active rotaxane, which made it possible to complete and publish the results of my predecessors (**P11**).

Then I worked for two years as a Marie Curie postdoctoral fellow in the laboratory of a Nobel Prize winner, prof. J.-M. Lehn at the *Université Louis Pasteur* in Strasbourg (now *Université de Strasbourg*). During this time I was involved, among others, in studying component selection in self-organization of multi-nuclear grid-type complexes and in the synthesis of sugar decorated grids as multivalent ligands for lectins (**P18**).

After returning to Poland, I received a Powroty/Homing grant from the Foundation for Polish Science, which allowed me to start research on photoswitchable acylhydrazone receptors and efforts to establish independent laboratory. Unfortunately, this project could not be fully realized in the modest laboratory conditions I had at the time, and therefore I returned to it a few years later, in much better equipped laboratories at the Biological and Chemical Research Centre of the University of Warsaw. As a result of these studies we have developed the first photoswitchable ion pair receptor (published in the prestigious *Journal of the American Chemical Society*, **P25**).

In 2011, I received an OPUS grant from the National Science Centre, Poland, for the study of fluorescent anion sensors and anion transporters based on 1,8-diaminocarbazole. This grant covered most of the studies described in this report.

After developing convenient synthesis of the unsubstituted 1,8-diaminocarbazole (**H6**), I initiated cooperation with prof. Skompska from the Faculty of Chemistry, University of Warsaw, which resulted in the discovery of a new conductive polymer with interesting properties (**P9**, **P12**, **P13**, **P21**).

In parallel, I became interested in a the chemistry of Metal-Organic Frameworks (MOFs), that is crystalline, ultraporous coordination polymers made of metal clusters connected with organic ligands. Within a few years I established a fully professional, well-equipped laboratory dedicated to MOF research and secured funding for the implementation of the first major project in this field, devoted to catalytic MOFs (IDEAS PLUS grant from the Ministry of Science and Higher Education). I am particularly proud that my very first publication in this new subject appeared in the renowned *Chemical Communications* (**P19**), and the following papers in journals with an even higher impact factor (IF). As part of this project, we achieved a whole range of important results, among which I would like to mention in the first place:

- development of the first post-synthetic method of protecting and deprotecting amino groups in MOFs and performing the first post-synthetic sequence protection - functionalization - deprotection in MOFs (publication in *Chem. Commun.*, **P19**);
- development of a new, remarkably easy and effective method of immobilization of catalysts in MOFs, consisting of a simple physical adsorption of (polar) catalysts from the solution. Using this approach we developed (in cooperation with the team of professor K. Grela from our Faculty) the first MOF catalysts for olefin metathesis reaction (publication in *ACS Catalysis*, **P20**, and patent application);
- covalent immobilization of stable organic radicals TEMPO in MOFs, in-depth studies of structure and catalytic activity in the aerobic oxidation of alcohols to aldehydes of the

MOFs obtained this way (first publication in *ACS Appl. Mater Interfaces*, **P24**, second in preparation);

- development of the first post-synthetic method of removing amino groups from MOFs and its application for the synthesis, for the first time, the missing parent material of an important family of MOFs - (Al)MIL-101 (published in *Chem. Commun*., **P23**);
- development of new methods of non-covalent immobilization of catalysts in MOFs: by acid-base reaction, ion exchange and covalent post-synthetic pore gateing (publications in preparation);
- demonstration of the first enantioselective hydrogenation on a MOF-supported catalyst and demonstration that at least in some cases this catalyst gives higher enantiomeric excess than the homogeneous catalyst (publications in preparation).

Currently, we are launching a new research project in the field of MOF chemistry, which aims to create an entirely new class of "smart" porous materials, combining the robustness of MOFs with the ability to respond to stimuli and adaptability to the external environment which are characteristic for supramolecular materials (OPUS 14 grant from the National Science Centre).

List of my publications which are not included in my habilitation:

P1. **M. J. Chmielewski**, J. Jurczak*
"Size complementarity in anion recognition by neutral macrocyclic tetraamides"
Tetrahedron Lett. **2004**, *45*, 6007-6010.
IF_{2004} = 2.484 Number of citations: 57 (52)

P2. **M. J. Chmielewski**, A. Szumna, J. Jurczak*
"Anion induced conformational switch of a macrocyclic amide receptor"
Tetrahedron Lett. **2004**, *45*, 8699-8703.
IF_{2004} = 2.484 Number of citations: 30 (26)

P3. **M. J. Chmielewski**, J. Jurczak*
"A hybrid macrocycle containing benzene and pyridine subunits is a better anion receptor than both its homoaromatic congeners"
Tetrahedron Lett. **2005**, *46*, 3085-3088.
IF_{2005} = 2.477 Number of citations: 34 (32)

P4. **M. J. Chmielewski**, Ł. Dobrzycki, J. Jurczak*, K. Woźniak*
"Unusual anion-anion self assembly inside a macrocycle-defined channel in the crystal lattice"
Cryst. Growth Des. **2005**, *5*, 1339-1341.
IF_{2005} = 3.551 Number of citations: 4 (3)

P5. **M. J. Chmielewski**, J. Jurczak*
"Anion Recognition by Neutral Macrocyclic Amides"
Chem. Eur. J. **2005**, *11*, 6080-6094.
IF_{2005} = 4.907 Number of citations: 138 (135)

P6. **M. J. Chmielewski**, J. Jurczak*
"Anion Binding versus Intramolecular Hydrogen Bonding in Neutral Macrocyclic Amides"
Chem. Eur. J. **2006**, *12*, 7652-7667
IF_{2006} = 5.015 Number of citations: 53 (51)

P7. E. Paśniczek, **M. J. Chmielewski**, P. Grzegorzewski, A. Kulesza, J. Jurczak*
"An Improved Method for the Synthesis of Macrocyclic Benzodiamides and Dibenzotetraamides"
Polish J. Chem., **2006**, *80*, 899-906
IF_{2006} = 0.491 Number of citations: 0 (0)

P8. **M. J. Chmielewski**, M. Pawlicki, N. Sprutta, L. Szterenberg, L. Latos-Grażyński*
"Cadmium(II) and Zinc(II) Complexes of S-Confused Thiaporphyrin"
Inorg. Chem., **2006**, *45*, 8664-8671
IF_{2006} = 3.911 Number of citations: 20 (20)

P9. M. Skompska*, **M. J. Chmielewski**, A. Tarajko,
"Poly(1,8-diaminocarbazole)-a Novel Conducting Polymer for Sensor Application"

Electrochem. Commun., **2007**, *9*, 540-544
IF_{2007} = 4.396 Number of citations: 15 (13)

P10. **M. J. Chmielewski**, T. Zieliński, J. Jurczak*
"Synthesis, structure, and complexing properties of macrocyclic receptors for anions",
Pure Appl. Chem. **2007**, *79*, 1087–1096.
IF_{2007} = 2.232 Number of citations: 24 (24)

P11. S. R. Bayly, T. M. Gray, **M. J. Chmielewski**, J. J. Davis*, P. D. Beer*
"Anion templated surface assembly of a redox-active sensory rotaxane",
Chem. Commun. **2007**, 2234–2236
IF_{2007} = 5.141 Number of citations: 57 (53)

P12. A. Tarajko, H. Cybulski, **M. J. Chmielewski**, J. Bukowska, M. Skompska*
"Electrochemical and spectroscopic characterization of poly(1,8-diaminocarbazole). Part I. Electropolymerization and determination of the polymer structure"
Electrochimica Acta **2009**, *54*, 4743-4750
IF_{2009} = 3.325 Number of citations: 10 (8)

P13. A. Tarajko, A. Michota, **M. J. Chmielewski**, J. Bukowska, M. Skompska*
"Electrochemical and spectroscopic characterization of poly(1,8-diaminocarbazole). Part II. Electrochemical, in-situ Vis/NIR and Raman studies of redox reaction of PDACz in protic and aprotic media"
Electrochimica Acta **2009**, *54*, 4751-4759
IF_{2009} = 3.325 Number of citations: 8 (6)

P14. L. Zhao, J. J. Davis*, K. M. Mullen, **M. J. Chmielewski**, R. M. J. Jacobs, A. Brown, P. D. Beer*
"Anion Templated Formation of Pseudorotaxane and Rotaxane Monolayers on Gold from Neutral Components",
Langmuir **2009**, *25*, 2935-2940.
IF_{2009} = 3.898 Number of citations: 38 (37)

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All publications together (H+P):	**34**
Total impact factor according to the Journal Citation Reports (JCR) list, according to the year of publication:	**156,55**
Total number of citations according to the Web of Science database (WoS):	**954/895**
Hirsch index:	**16**

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