Hybrid inorganic-organic molecular scavengers – synthesis, properties and applications

Grzegorz SCHROEDER*, Joanna KURCZEWSKA – Faculty of Chemistry, Adam Mickiewicz University in Poznań, Poland

Please cite as: CHEMIK 2016, **70**, 2, 81–88

Introduction

Hybrid inorganic-organic materials are produced by combining inorganic and organic compounds [1 – 4]. Such systems represent a growing proportion of usable materials due to their properties and a low cost of preparation. The properties of these materials at a molecular level are well-defined and different from those of their individual components. These interesting properties of hybrid materials are a combination of the properties of their components and the effect of specific structure responsible for a new quality of a material. The properties of hybrid materials can be defined before the synthesis procedure. Depending on the type of bonding between organic and inorganic, carbon or polymer components, there are two classes of hybrid systems [2, 5, 6]. The first class is made of the systems held through the hydrogen, ionic, coordinate bond or van der Waals forces, while the second class includes the covalently bound systems.

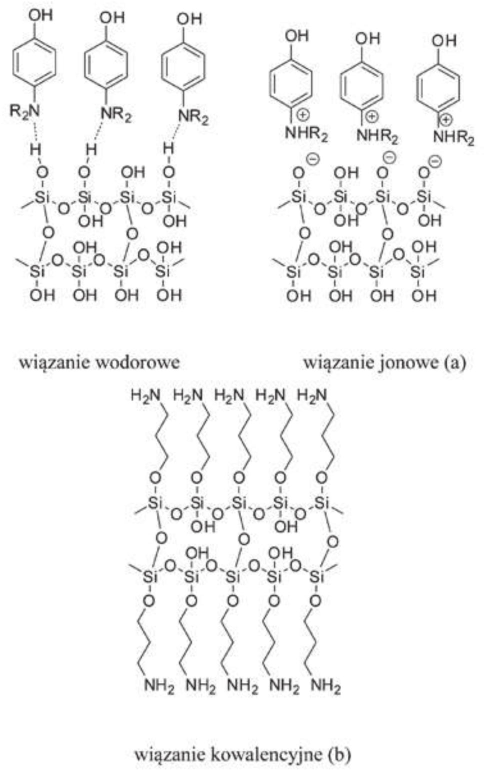


Fig. 1. Examples of hybrid materials with weak bonds (a) and covalent bonds (b).

Hybrid systems composed of insoluble inorganic or polymer carrier, on which functional reactive groups, capable of binding to analyte, are deposited through a linker act as molecular scavengers if they meet two conditions [7 – 9]. The analyte in the solution should be effectively bound (above 90 %) in no longer than 1 minute by the functional groups of a hybrid material. In addition, the effectiveness of analyte trapping cannot depend on the analyte form (ion, ion pair, complex, associated molecules) in a solution.

Corresponding author:
Grzegorz SCHROEDER – Ph.D., D.Sc., Eng., e-mail: schroede@amu.edu.pl

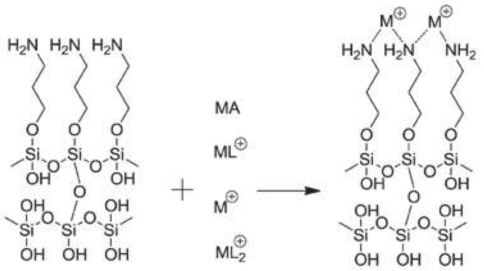


Fig. 2. The scheme of molecular scavenger functioning

A particular group of hybrid materials is made of the systems that contain ferromagnetic particles (iron oxide, nano – iron, cobalt or nickel) in a structure of inorganic, carbon or polymer carrier [10–14]. Such systems, described as magnetic hybrid materials (magnetic molecular scavengers), are usually composed of a magnetic core (diameter 8-100 nm) with silica shell. The synthesis of systems made of a magnetic core and a silica shell is very attractive from the point of view of further functionalization of the system because the number of functional groups that can be attached on the silica surface is much greater than that possible to attach on the magnetic core. Additionally, a magnetic core with a silica layer does not interact with a solution, which makes it chemically and biologically inert.

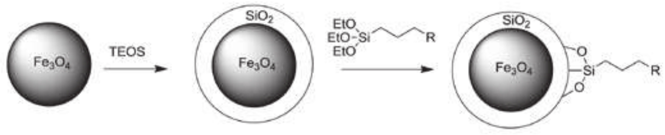


Fig. 3. Magnetic molecular scavengers with a silica layer bearing functional groups

Magnetic hybrid materials are susceptible to a magnetic field, which enables their transport, mixing, extracting form a solution using permanent magnets or electromagnets. Due to these properties, these systems have been used in a chemical synthesis for removal of selected products, for concentration of products obtained in low yields, as well as in chemical analysis and medicine for a transport of bioactive compounds controlled by external magnetic field.

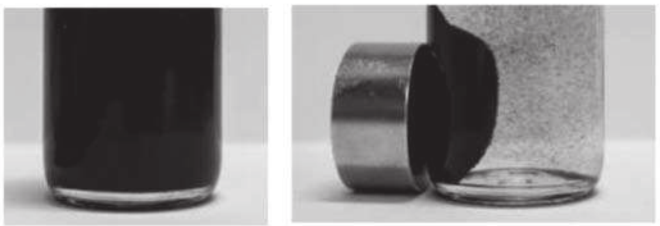
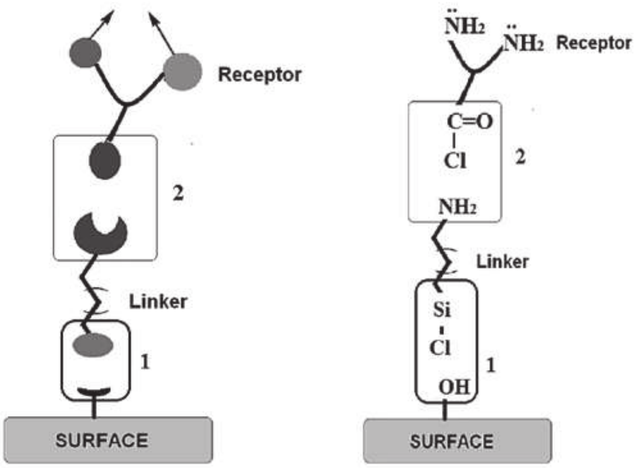


Fig. 4. The influence of a magnetic field on magnetic hybrid materials in aqueous solution

Synthesis methods

The synthesis of hybrid materials is based on two essential stages [1 – 3, 15 – 19]. The first one consists of a development of a synthesis method leading to a formation of reactive functional groups at a carrier (inorganic, carbon, polymer) surface with terminal linker substituents ($X–CH_2–CH_2–CH_2$-). These reactive substituents are capable of forming further molecules or biomolecules (proteins, sugars, enzymes) with high efficiency by classical organic reactions. The process in terms of covering of a carrier surface by organic monolayer is sterically controlled. The sizes of deposited organic molecules determine the percentage of monolayer filling. The second synthesis step, involving terminal functional groups of monolayer, is the synthesis of another organic layer and it enables the preparation of functionalized hybrid materials. This process is carried out for a predefined application of a hybrid material. A selection of molecular receptor with reactive substituents allows obtaining "intelligent" material with specific properties. Similarly to the first step, steric effects determine the amount of receptors deposited at a material surface.



A general synthesis method of hybrid materials involving bifunctional linkers capable of reacting with inorganic surface [1] and molecular receptor [2].

Properties

The properties of hybrid materials (scavengers) depend on the molecular size, structure and shape (balls, needles, blocks, spirals) of inorganic, carbon or polymer carrier, as well as on the properties of organic component and the degree of surface filling. The ability of easy modification of material characteristics, make it multifunctional and capable of a wide range of applications.

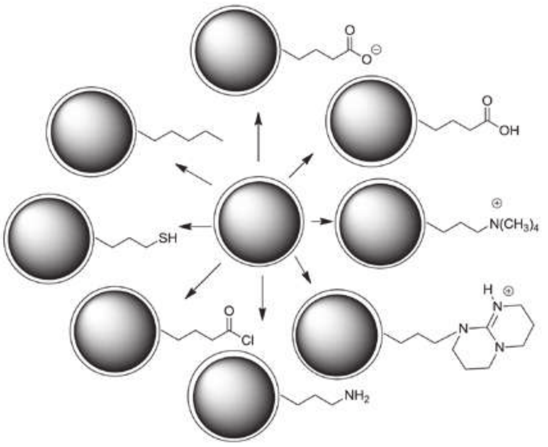


Fig. 6. Examples of functionalization of inorganic carrier in order to obtain different properties of a hybrid material

The methods for the synthesis of different molecular scavengers based on different inorganic carriers have been thoroughly described in scientific literature and industrial patents [1 – 4]. Many hybrid materials are commercially available and produced at a relatively low cost. Therefore their synthesis does not constitute the technological threshold limiting their application. Moreover, each year many new hybrid materials are described in the literature, which greatly extends the existing variety of these systems. Consumers of chemical products are not so much interested in a synthesis of new compounds as chemists. Their interest concentrates not on the structure, but on the characteristics, the influence on environment and human health as well as the price of a new material. Thanks to the possibility of a very good prediction of their properties, hybrid inorganic-organic molecular scavengers find application in many fields of science, medicine, environmental protection and industry.

At a molecular level, the properties of hybrid scavengers are determined by properties of terminal groups. They not only affect the binding of analytes, but also their potential release in changing environmental conditions (pH, ionic strength, enzyme presence, competitive ligand, temperature). Therefore, the binding of analytes by hybrid materials is used for storage and transport of bioactive molecules, as well their controlled release in specified conditions [20–24]. The scheme of formation of analyte-scavenger complex and the process of analyte release in presented in Figure 7.

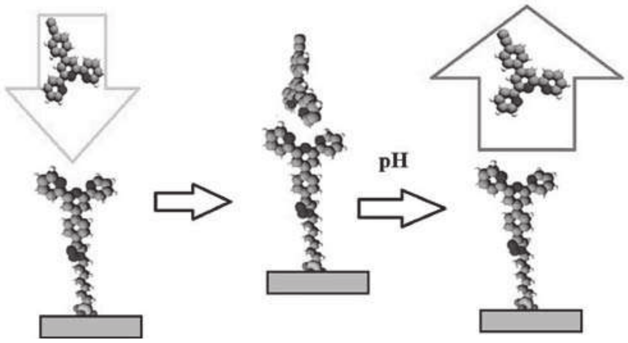


Fig. 7. The formation of analyte-scavenger complex and the process of analyte release

Figure 8 presents different methods of antibiotic binding at the surface of modified silica, permitting a controlled release of the drug in different conditions.

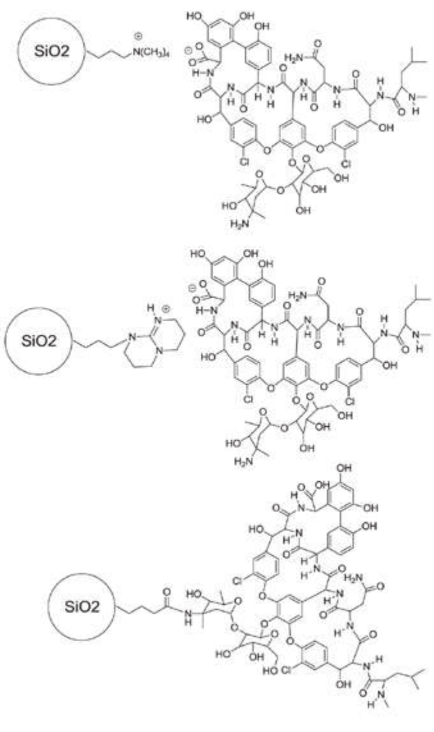


Fig. 8. Vancomycin attached to the modified silica surface through ionic and covalent bond

One of the major problems in analytical chemistry is direct determination of trace components of a mixture, whose concentration is below a detection limit of analytical methods. The application of selective molecular scavengers for concentration, storage and transport has solved this problem to a significant degree. The methodology for determination of amines and carboxylic acids in liquid and gaseous phase and a universal procedure for determination of organic compounds, previously concentrated by molecular scavengers (Fig. 9), using mass spectrometry with DBD ionization (dielectric barrier discharge ionization) are presented in [25].

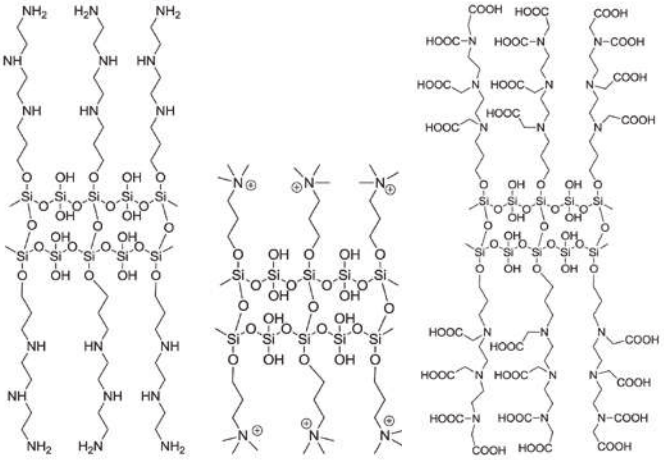


Fig. 9. Molecular scavengers applied for concentration of amines and carboxylic acids

The main sources of soil contamination with toxic elements is connected with human industrial activity (mining and processing of non-ferrous ores, energy, chemical industry). The presence of increased concentration of toxic elements in soil causes their leaching to surface waters and ground waters, fito – and eco – toxicity, and a dust pollution as a result of wind erosion. The threat for humans is associated with inclusion of toxic elements into the food chain through their uptake by plants and animals, and consequently their increased content in food. It has been established that hybrid functionalized silicas (Fig. 10) are capable of permanent binding of copper, lead, zinc, cadmium and arsenic regardless of their form in the soil. Taking into regard their effectiveness and low cost of production, it seems that the use of hybrid materials as scavengers of toxic elements is highly promising [26 – 27].

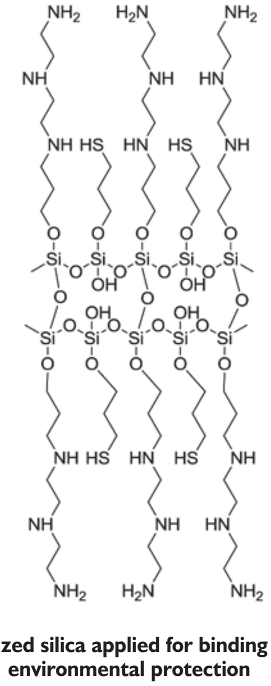


Fig. 10. Functionalized silica applied for binding of toxic metals in environmental protection

Conclusions

Functional materials combine common nanoscale inorganic and organic active components. In order to obtain a functional material, it is necessary to modify its structure by molecular receptors that are capable of interacting with specific chemical compounds or groups of compounds. This new class of materials with defined properties, obtained in chemical reactions with high yield, opens up new possibilities for the use of chemicals in optics, electronics, energy storage and conversion, as well as active membranes, active surfaces, catalysts and sensors.

Acknowledgements.

The authors would like to thank The National Science Center of Poland (Grant No. 2011/03/B/ST5/01573) for financial support.

Literature

1. Sanchez C., Belleville P., Popall M., Nicole L.: *Applications of advanced hybrid organic–inorganic nanomaterials: from laboratory to market*. Chem. Soc. Rev. 2011, **40**, 696–753.
2. *Functional Hybrid Materials*. Ed. Gómez-Romero P., Sanchez C., WILEY-VCH Verlag GmbH & Co. KGaA, 2004.
3. *Hybrid Materials, Synthesis, Characterization, and Applications*. Ed. Kickelbick G., WILEY-VCH Verlag GmbH & Co. KGaA, 2007.
4. *The Supramolecular Chemistry of Organic–Inorganic Hybrid Materials*. Ed. Rurack K., Martinez-Manez R., John Wiley & Sons, 2010.
5. Amosa M. K., Mohammed I. A., Yaro S. A.: *Sulphide Scavengers in Oil and Gas Industry – A Review*. Nafta 2010, **61**, 85-92.
6. Kainz Q. M., Reiser O.: *Polymer- and Dendrimer-Coated Magnetic Nanoparticles as Versatile Supports for Catalysts, Scavengers, and Reagents, Accounts of Chemical Research*. 2014, **47**, 667-677.
7. Hodges J. C.: *Covalent Scavengers for Primary and Secondary Amines*. Synlett, 1999, **1**, 152-158.
8. Sharma R., Dhingra S.: *Functionalized Silica Gel as Metal Scavenger, Sensor, and Catalyst*. LAP Lambert Acad. Publ. 2011.
9. Schroeder G.: Wymiatacze molekularne, w Receptory Supramolekularne, Red. Schroeder G. Betagraf, Poznań, 2007, 89-101.
10. Govan J., Gun'ko Y. K.: *Recent Advances in the Application of Magnetic Nanoparticles as a Support for Homogeneous*. Catal. Nanomat. 2014, **4**, 222-241.
11. Kainz Q. M., Schätz A., Zöpfl A., Stark W. J., Reiser O.: *Combined Covalent and Noncovalent Functionalization of Nanomagnetic Carbon-Surfaces with Dendrimers and Bodipy Fluorescent Dye*. Chem. Mater. 2011, **23**, 3606-3613.
12. Wei S., Wang Q., Zhu J., Sun L., Lin H., Guo Z.: *Multifunctional composite core – shell nanoparticles*. Nanoscale 2011, 3, 4474-4502.
13. Rostami A., Atashkar B., Moradi D.: *Synthesis, characterization and catalytic properties of magnetic nanoparticle supported guanidine in base catalyzed synthesis of α-hydroxyphosphonates and α-acetoxyphosphonates*. Appl. Cat. A 2013, **467**, 7-16.
14. Li Y., Zhang X., Deng C.: *Functionalized magnetic nanoparticles for sample preparation in proteomics and peptidomics analysis*. Chem. Soc. Rev. 2013, 42, 8517-8539.
15. Lewandowski D., Bajerlein D., Schroeder G.: *Adsorption of hydrogen peroxide on functionalized mesoporous silica surfaces*. Struct. Chem. 2014, **25**, 1505-1512.
16. Kurczewska J., Schroeder G., Narkiewicz U.: Copper removal by carbon nanomaterials bearing cyclam-functionalized silica. Central Eur. J. Chem. 2010, **8**, 341-346.
17. Kurczewska J., Schroeder G.: Silica surface modified by aliphatic amines as effective copper complexing agents. Inter. J. Mater. Res. 2010, **101**, 1037-1041.
18. Gierczyk B., Schroeder G., Cegłowski M.: *New polymeric metal ion scavengers with polyamine podand moieties*. React. Funct. Polym. 2011, **71**, 463-479.
19. Kurczewska J., Schroeder G.: *The bifunctionality of silica gel modified with Congo red*. Central Eur. J. Chem. 2011, **9**, 41-46.
20. Kurczewska J., Lewandowski D., Olejnik A., Schroeder G., Nowak I.: *Double barrier as an effective method for slower delivery rate of ibuprofen*. Inter. J. Pharm. 2014, **472**, 248-250.

21. Krzyminiewski R., Kubiak T., Dobosz B., Schroeder, G., Kurczewska J.: *EPR spectroscopy and imaging of TEMPO-labeled magnetite nanoparticles*. Curr. Appl. Phys. 2014, **14**, 798-804.
22. Song S. W., Hidajat K., Kawi S.: *Functionalized SBA-15 materials as carriers for controleed drug delivery: Influence of surface properties on matrix-drug interactions*. Langmuir 2005, **21**, 9568-9575.
23. Vallet-Regí M., Rámila A., del Real R. P., Pérez-Pariente J.: *A new property of MCM-41: Drug delivery system*. Chem. Mater. 2001, **13**. 308-311.
24. Kell, A. J., Stewart, G., Ryan, S., Peytavi, R., Boissinot, M., Huletsky, A., Bergeron, M. G., Simard, B.: *Vancomycin-modified nanoparticles for efficient targeting and preconcentration of gram-positive and gram-negative bacteria*. Acs Nano 2008, **2**, 1777–1788.
25. Smoluch M., Cegłowski M., Kurczewska J., Babij M., Gotszalk T., Silberring J., Schroeder G.: *Molecular Scavengers as Carriers of Analytes for Mass Spectrometry Identification*. Anal. Chem. 2014, **86**, 11226-11229.
26. Grzesiak P., Łukaszyk J., Hłyń T., Gabała E., Kurczewska J., Schroeder G.: *Zastosowanie odpadowej krzemionki funkcjonalizowanej silanami do sonifikacji pierwiastków toksycznych w glebie na terenach przemysłowych*. Przem. Chem. 2014, **93**, 1991-1996.
27. Grzesiak P., Łukaszyk J., Kurczewska J. Schroeder G.: *Zastosowanie funkcjonalizowanej krzemionki do immobilizacji pierwiastków toksycznych w glebie na terenach przemysłowych*. Przem. Chem. 2014, **93**, 1181-1185.

Professor Grzegorz SCHROEDER – Ph.D., D.Sc., is a graduate of the Faculty of Mathematics, Physics nad Chemistry, the specialization in chemistry, Adam Mickiewicz University in Poznań (1973). Received his Ph.D. in chemistry in 1977. Currently working at Adam Mickiewicz University in Poznań, Faculty of Chemistry. G. Schroeder has authored over 400 scientific papers in the field of supramolecular chemistry, nanotechnology, environmental chemistry, synthesis of bioactive compounds, NMR, FTIR spectroscopy, mass spectrometry (ESI, MALDI), and the kinetics in aqueous solutions and industrial processes.

e-mail: schroede@amu.edu.pl

Joanna KURCZEWSKA – Ph.D., is a graduate of the Faculty of Chemistry, Adam Mickiewicz University in Poznań (2003). Since 2007, tutor at the Department of Supramolecular Chemistry, Faculty of Chemistry, Adam Mickiewicz University in Poznań. She is the co-author of about 50 scientific papers. Nowadays, her research studies concentrate on the modification of different inorganic supports (magnetic or nonmagnetic) by various organic systems of diverse application.

Aktualności z firm

News from the Companies

Dokończenie ze strony 84

Grupa TAURON: Zmiany w zarządach Wydobycia i Dystrybucji

Rady nadzorcze TAURON Wydobycie oraz TAURON Dystrybucja dokonały 26 stycznia br. zmian w składzie zarządów spółek. W TAURON Wydobycie rezygnację z pełnienia funkcji złożyli: Łukasz Brzózka (dotychczasowy prezes zarządu) oraz Grzegorz Czornik (wiceprezes). W związku z tym – po decyzjach rady nadzorczej – zarząd będzie pracował w składzie: Zdzisław Filip (prezes zarządu), Łukasz Gębala i Tomasz Cudny (wiceprezesi zarządu). W TAURON Dystrybucja rezygnacje złożyli: Paweł Cygan i Janusz Kurpas (dotychczasowi wiceprezesi) oraz Marek Kleszczewski (z pełnienia funkcji prezesa zarządu). W efekcie decyzji rady nadzorczej, w skład zarządu spółki wchodzą: Robert Zasina (prezes zarządu) oraz wiceprezesi: Tomasz Jachna, Marek Kleszczewski i Jerzy Rzemyszkiewicz (dotychczasowy wiceprezes).

Zmiany w funkcjonowaniu zarządów spółek, to efekt wdrożonej w Grupie TAURON koncepcji poprawy efektywności zarządczej oraz optymalizacji kosztowej organów korporacyjnych poszczególnych spółek zależnych. Będzie to możliwe m.in. poprzez zmiany ich struktur organizacyjnych, w tym ograniczenie składu osobowego zarządów. Członkowie zarządów, którzy złożyli rezygnacje, otrzymali oferty kontynuacji współpracy na poziomie menedżerskim w spółkach Grupy TAURON. *(kk)*

(http://media.tauron.pl/, 26.01.2016)

Zmiana w zarządzie Grupy Azoty SA

Rada Nadzorcza Spółki na posiedzeniu w dniu 19 lutego 2016 r. dokonała zmian w składzie Zarządu Spółki. Rada Nadzorcza Spółki na posiedzeniu w dniu 19 lutego 2016 r. dokonała zmian w składzie Zarządu Spółki. Ze składu Zarządu Spółki został odwołany Prezes Zarządu, Pan Paweł Jarczewski oraz Wiceprezesi Zarządu, Panowie: Krzysztof Jałosiński, Marek Kapłucha, Marian Rybak.

Uchwałą Rady Nadzorczej funkcję Prezesa Zarządu obejmie Pan Mariusz Bober.

Wszystkie uchwały wchodzą w życie z dniem podjęcia.

Mariusz Bober jest absolwentem Szkoły Głównej Handlowej w Warszawie (1989) i kursu dla członków Rad Nadzorczych spółek z udziałem Skarbu Państwa (1996). Odbył liczne szkolenia z zakresu zarządzania firmą i zespołem, skutecznej komunikacji i zarządzania zespołem. Doświadczenie zawodowe: Prezes Zarządu – Fundacja Rosa (2013–2014); Dyrektor Zarządzający – Fundacja Rosa (2012–2013); Prezes Zarządu – Trinity AdVenture sp. z o. o. (2012–2013); Dyrektor Inwestycyjny – Trinity AdVenture sp. z o. o. (2010–2011); Prezes Zarządu – KGHM ECOREN SA (2006–2010); Wiceprezes Zarządu – KGHM ECOREN SA (2006); Prezes Zarządu – SUPRA Agrochemia sp. z o. o. (2006); Prezes Zarządu – Auto Śląsk sp. z o. o. (2002–2003); Dyrektor Finansowy – Fundusz Inwestycji Kapitałowych KGHM METALE SA w Lubinie (2001–2002); Wiceprezes Zarządu – Warszawska Fabryka Platerów HEFRA SA w Warszawie (2001–2002); Wiceprezes Zarządu – INTERFERIE Sp. z o.o. w Lubinie(1998–1999); Członek Zarządu – Dyrektor ds. Finansowo-Ekonomicznych Przedsiębiorstwo Systemów Komputerowych i Telekomunikacji CUPRUM 2000 Sp. z o.o. w Lubinie (1997–1998); Członek Zarządu – Dyrektor ds. Restrukturyzacji Walcownia Metali „Łabędy" SA w Gliwicach (1997–1998); Kierownik Działu Restrukturyzacji – Polskie Górnictwo Naftowe i Gazownictwo SA w Warszawie (1996); Wiceprezes Zarządu – Dolnośląska Spółka Inwestycyjna SA w Lubinie (1995–1996); Członek Zarządu – Dolnośląska Spółka Inwestycyjna SA w Lubinie (1994–1995); Dyrektor – Pełnomocnik ds. Inwestycji Kapitałowych i Nadzoru Właścicielskiego – KGHM Polska Miedź SA w Lubinie, Biuro Zarządu (1994–1995); Dyrektor Departamentu Finansów i Nadzoru Kapitałowego – KGHM Polska Miedź SA w Lubinie, Biuro Zarządu (1992–1994);Naczelnik Zespołu Nadzoru Kapitałowego – KGHM Polska Miedź SA w Lubinie, Biuro Zarządu (1992). *(abc)*

(http://grupaazoty.com/pl 19.02.2016; http://www.bankier.pl 21.02.2016)

Dokończenie na stronie 93