

# Nanomaterials Modification by Dendrimers – A Review

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**Abstract** - Following review summarizes the application of dendrimer-functionalized hybrid nanomaterials. Dendrimers are nano-sized, radially symmetric molecules with well-defined, homogeneous and monodisperse structure. Incorporation of dendritic structures onto surface of inorganic particles by covalent, ionic and van der Waals bonds introduces unique properties of the new material. Herein, we present structures and properties of silica, titania, carbon nanotubes and clays decorated with various dendrimers.

**Index Terms**- Clays, Dendrimer, Hybrid materials, Nanomaterials, PAMAM

Organic-inorganic hybrid materials are products, obtained by combining organic and inorganic chemicals [2]. Characteristic feature of such materials is demonstrated by their own, well-defined properties at the molecular level, significantly different from those of individual elements. Properties of hybrid materials depend on the nature of components which are built of, and, on the other hand, on their specific construction, creating a new quality of material that determines properties of the entire system. Attaching a dendrimer molecule to the surface of an inorganic support enables obtaining new materials with unique properties and a wide range of practical applications.

## I. INTRODUCTION

Dendrimers are sphere-like polymers characterized by a bifurcated, three-dimensional structure [1]. In structural construction, a multifunctional core can be distinguished, from which the "branches" (arms) of dendrimers, called dendrons, depart radially. At the end of dendrons there are free functional groups, which are tunable with various substituents, modifying the chemical and physical properties of the dendrimer molecule. Dendrimers construction determines presence of internal free spaces that can be used as a specific type of pockets as transport system for diverse kinds of molecules. The type of pockets, but also the number and type of terminal functional groups determine properties of polymer. In case of dendrimers, the branching process causes a multiplication of the number of functional groups. The dendrimer branch scale (Generation 0-10) is related to its properties and application.

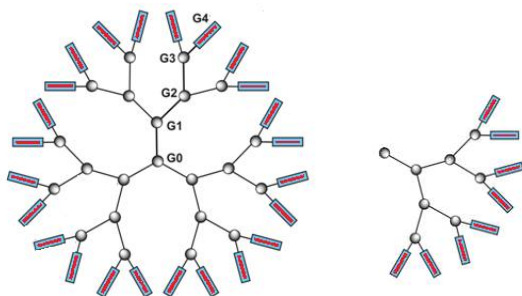


Fig. 1. Chemical structures of dendrimer and dendron

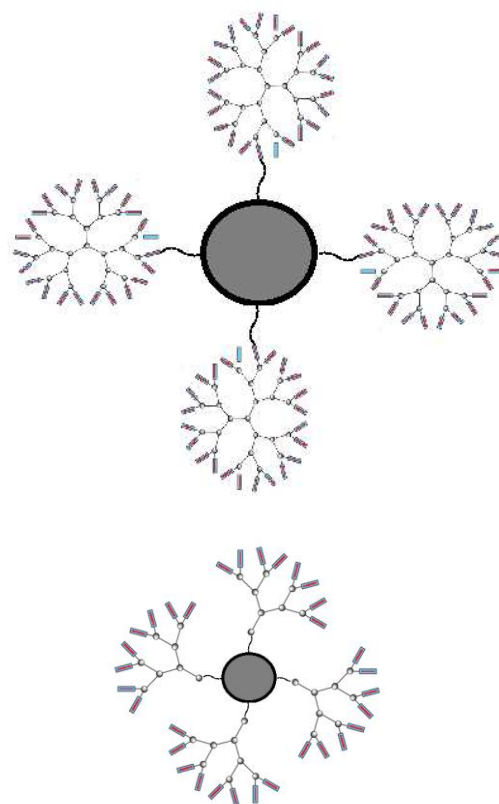


Fig. 2. Chemical structures of dendrimer/nanoparticles hybrid and dendrons/nanoparticles hybrid

The properties of hybrid materials such as chemical stability and functionalities (i.e. solvation, wettability), biocompatibility, optical and/or electronic properties can be mostly modified by the choice of organic substrates. The inorganic component can implement or improve electronic, magnetic and redox properties, density, refraction index and concentration of organic compounds on the surface of hybrid materials. The size and crystallinity of the inorganic phase in hybrid materials determine structure of

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materials. The synergistic effect between inorganic and organic components determines properties of hybrid materials.

## II. SILICA/DENDRIMER NANOHYBRIDS

Silica is one of the most popular inorganic-solid material used in chemistry and finds attractive applications as starting material for e.g. various adsorbents, column chromatography fillings, novel organic catalysts and promising nanomaterials [3]-[8]. Silica-family's characteristic feature is porosity. Therefore the most important differentiating of silica materials, as tunable materials, is based on size and shape of pores. In recent years, a few mesoporous silica materials have gained great attention due to their phenomenal structures (regular arrangement, size of pores and high surface area), e.g. MCM-41 [9], SBA-15 [10]-[11] or KIT-6 [12]. Parallely to exploration and researches on either amorphous or mesoporous silica, hyper-branched dendrimers, characterized by specific properties, gathered huge attention. The most applicable tree-like organic compound is poly(amidoamine) dendrimer (PAMAM), containing numerous amino groups and oxygen atoms, making it unique chelating agent (Fig. 3).

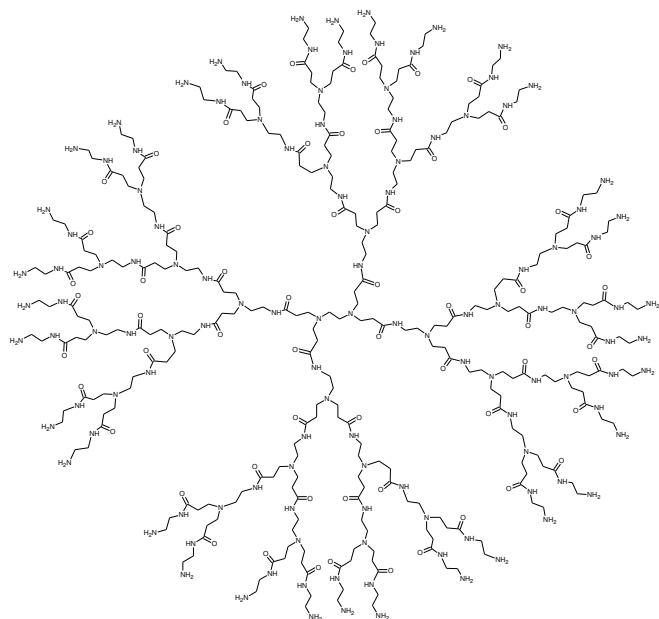


Fig. 3. The structure of PAMAM dendrimer

A creation of inorganic-organic hybrid material by combining those two species might find application in many fields. Silica particles functionalized with dendrimers might be obtained by two synthetic strategies: (1) incorporation of amino group onto silica surface, Michael addition of methyl acrylate and subsequent amidation with proper amine (size, volume and amount of branches depends on repeating Michael addition-amidation steps) (Fig. 4); (2) synthesis of desirable dendrimer, following functionalization with chloro-, isocyanato- or glycidyloxypropyl trimethoxysilane and coating of silica with silane-dendrimer intermediate (Fig. 5).

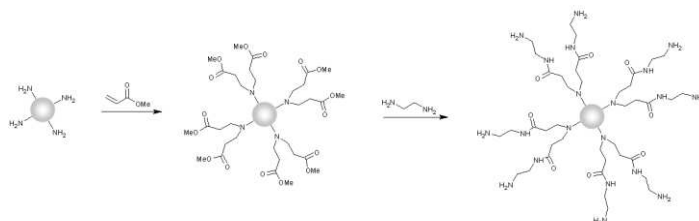


Fig. 4. The synthetic strategy of functionalization of nanoparticles surface

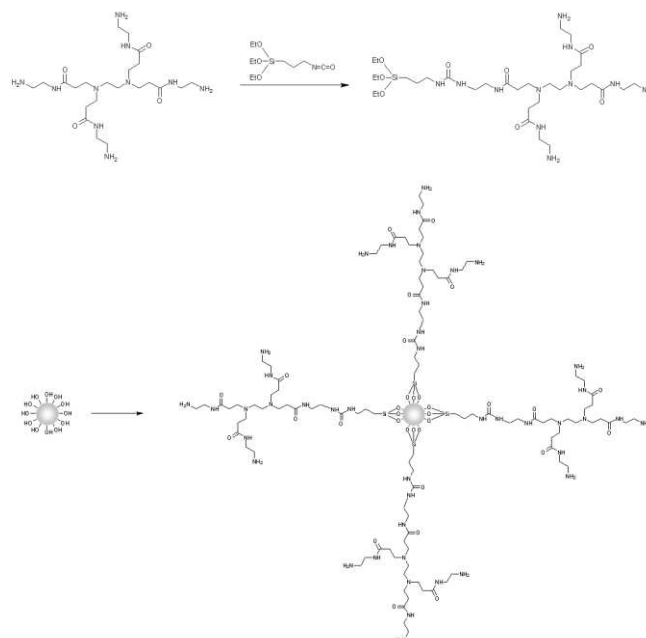


Fig. 5. The synthetic strategy of functionalization of nanoparticles surfaces by silanes

Both routes contain long-lasting steps of elongation/expansion dendrimeric structure [13]. However, Bu *et al.* [14] noticed some obstacles during expansion of dendrimer, which was especially manifested by losing of dendrimer arm and intramolecular cyclization. Such structural defects may indicate on suitability of obtaining hybrid via silica coating with silanized dendrimer. Additionally, widely-used microwave irradiation might be used as supportive factor to overcome time-problem, shortening of total synthesis several dozen times [15]. Silica-dendrimer hybrid materials may find application in High-Performance Liquid Chromatography (HPLC) as column fillings [16]-[17] or in Solid-Phase Extraction (SPE) [18]-[19] and Microextraction (SPME) [20]-[21] which are one of the method for pre-concentration and separation of trace metal ions and various organic compounds. Application of hybrid materials is more convenient than bare silica for metal ions adsorption, since such chemical entities are able to adsorb only to peripheral amine groups of dendrimer (due to the hindering of silica-surface by volumetric molecules), making them easier elutable [22].

One of the first researches exploring cations adsorption onto dendrimer-grafted silica surfaces was ran by Qu [23], who demonstrated a comparison of adsorption capacities, using a set of amino- and ester-terminated dendrimer-containing adsorbents and eight metal ions. Adsorbates were divided into two groups: noble metals ( $\text{Au}^{3+}$ ,  $\text{Pd}^{2+}$ ,  $\text{Pt}^{4+}$ ,  $\text{Ag}^{+}$ ) and base metal ions ( $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Ni}^{2+}$ ). The experiments did not come along with common

conclusions. Adsorption capacity depends on many factors as: size of adsorbate, e.g.  $\text{Pt}^{4+}$  ion usually forms  $\text{PtCl}_6^{2-}$  in water solution making it less attachable onto adsorbents surface (especially ester-terminated); coordination ability of ester/amino group among each cation, e.g.  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions bind stronger to amino group than ester group what indicates on decreasing chelation by ester-terminated adsorbent; generation of grafted poly(amidoamine) molecules and percentage of grafting. In order to define hybrid adsorbents efficiency among binding metal ion, there were many studies dedicated to each metal. In 2008 the same research group focused on  $\text{Pd}^{2+}$  ion [24]. A number of tests on palladium ion bonding onto ester- or amino-terminated PAMAM-functionalized silica-gel brought important information, i.e. adsorption capacity of material is the most effective under the optimal pH -0.30 (2M HCl). This is explained by the nature of palladium ion in water solution – it appears as  $\text{PdCl}_4^{2-}$  ion. In acidic solution, primary and tertiary amino groups exist at their protonated states,  $\text{NH}_3^+$  and  $\text{NH}^+$  respectively, so that positively charged functional groups enhance adsorption of ion with electrostatic interactions. Nevertheless, adsorption in strongly acidic solution is sometimes difficult to carry out, so determination of adsorption capacities was made in neutral solution. The values increased with the increase of dendrimer generation up to G3.0 (the highest adsorption capacity  $q$ , was identified for  $\text{SiO}_2$ -G3.0,  $q = 1.01$  mmol/g). Those results convinced Qu to expand research with  $\text{Pb}^{2+}$  ion [25]. The optimal adsorption was obtained at pH 5.0 and the highest adsorption capacities for  $\text{SiO}_2$ -G2.0 and  $\text{SiO}_2$ -G3.0 were 0.80 and 0.76 mmol/g, respectively. Additionally, adsorption selectivity coefficients of binary systems were estimated indicating total selectivity of  $\text{Pb}^{2+}$  in the presence of  $\text{Mn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$ . Lead(II) ion was also a subject of studies using 5-sulfosalicylic acid derivative of PAMAM grafted on silica [23], achieving  $q = 0.12$  mmol/g. The hybrid material was used in micro-column enrichment. The results of studies showed that adsorbent was able to pre-concentrate 1.0 ng/ml  $\text{Pb}^{2+}$  solution, so that was used during establishing of ion content in sea water samples, using graphite furnace atomic absorption spectroscopy (GFAAS). Adsorption of  $\text{Pb}^{2+}$  was also investigated for  $\text{SiO}_2$ -PAMAM-thiomalic acid material, which showed an increase of adsorption capacity with increase of dendrimer generation (14.42 and 25.32 mmol/g for G1 and G4 dendrimer generations, respectively) [26]. Under pH 5.0, adsorption rate reached 95% and limit of detection was found at 2.9 ng/ml. Therefore, the adsorbent found application in column-enriching of tap and sea water samples, with GFAAS detection. Similar hybrid materials might be also used as auric ion adsorbent. It appears that second generation of dendrimers, having ethylenediamine (EDA) [27] or diethylenetriamine (DETA) [28] as a repeating amine-component, strongly chelate auric ion ( $\text{Au}^{3+}$ ,  $\text{AuCl}_4^-$  in water solution) – adsorption capacities are  $q_{\text{EDA}} = 2.45$  mmol/g and  $q_{\text{DETA}} = 1.45$  mmol/g. In 2016 Gerrans *et al.* [29] introduced sophisticated method of  $\text{Cu}^{2+}$  sensing with nanometer-sized silica LUDOX® combined with (1,1'-carbonyldiimidazole)-dendrimer-dye derivative. The experiments involved anchoring of two dyes: fluorescein isothiocyanate (FITC) and rhodamine B isothiocyanate (RITC), giving photoluminescence platforms. Finally, the ability of copper(II) ions, that bind near the

fluorophores, to perform fluorescence quenching was shown. The most significant change in fluorescent emission was observed for samples containing 0.066 mg/ml of the hybrid material with copper(II) solutions concentrated up to 20  $\mu\text{M}$ . Relative intensity of fluorescence observed with maxima peaks at 525 nm for FITC and 576 nm for RITC, decreased due to ions interactions with fluorescence source. Many other metal ions were examined as interrupters. Nevertheless, the results showed that only  $\text{Ag}^+$  ion had slight quenching ability, causing 5% difference in relative emission intensity. All above-described materials were based on amorphous silica as hybrid's inorganic-platform. However, regularly arranged silica particles are also used in the synthesis of ions adsorbents. For instance, SBA-15 silica was modified with third generation of PAMAM dendrimer and tested toward adsorption of four cations:  $\text{Cr}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Zn}^{2+}$  [30]. It was found that such material exhibits adsorption capacities on the level of 0.44, 0.21, 0.03, 0.21 mmol/g, respectively. The same silica material was also grafted with melamine, giving dendrimer-like outer surface [31]. The adsorbent was investigated in removal of  $\text{Pb}(\text{II})$ ,  $\text{Cu}(\text{II})$  and  $\text{Cd}(\text{II})$  ions from aqueous solution, as filling in fixed-bed column. An excellent efficiency of ion adsorption was observed, reaching adsorption capacities at 0.46, 1.42 and 0.63 mmol/g, respectively. Another mesoporous silica-type material is MCM-41, which was functionalized by ethylenediamine via triaziny linker [32]. The product performed selectivity toward  $\text{Ag}^+$  ions with remarkable, pH-independent adsorption capacity equals 1.57 mmol/g.

Nowadays, very important branch of chemical technology is based on still-growing development of biofuels [33]-[34]. One of the biofuels' biggest problem is the presence of metal ions, which enhance  $\text{CO}_2$  emission, decrease fuel quality and finally are emitted into the environment [35]. Hence, removal of metal ions plays a key role in ethanol fuel pre-treatment. Silica grafted with PAMAM and its sulfur-derivative appeared to be very effective adsorbent for metal ions such as  $\text{Hg}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Cu}^{2+}$  and  $\text{Co}^{2+}$ . Series of materials containing various poly(amidoamine) generations (G0 – G3) were tested and  $\text{SiO}_2$ -G2 sorbent was found to be the most efficacious, reaching adsorption capacities  $q = 0.61$ , 0.47, 0.84 and 0.46 mmol/g for listed metal ions, respectively [36]-[38]. Values of  $q$  coefficients are not relatively high, because alcoholated ions are relatively bigger than hydrated ones. Therefore steric hindrance hinders their diffusion into the structure of dendrimer [36].

Silica-supported adsorbents may also find application in removal of other water contaminants, including organic dyes, aromatic hydrocarbons, etc. Combining dendrimer-grafted silica surface with hydrophobic carbohydrate chains may lead to obtaining amphiphilic PAMAM dendrimer. One of the examples is poly(amidoamine) dendrimer derivatized by octadecyl isocyanate [39]. It appeared to be very effective adsorbent toward negatively charged organic dyes or surfactants, as methyl orange and sodium dodecylbenzenesulfonate. Adsorption of positively charged molecules such as ethidium bromide or 1-dodecylpyridium chloride is not possible because of electrostatic repulsion between adsorbate and positively charged organically modified silica. Furthermore, dendrimer-assisted silica gained much attention as novel carbon dioxide adsorbents. There is a list of studies aimed to



such occurrence. Series of SBA-15 mesoporous silica grafted by melamine-based dendrimers were synthesized [40]-[41]. The only effective sorbents were those containing primary terminal amino groups. Moreover, generation of anchored dendrimer plays also important role, due to the sufficiency of space for CO<sub>2</sub> storage. One of the most active material was amorphous silica/tri(3-aminopropyl)amine dendrimer. It demonstrated huge adsorption capacity among CO<sub>2</sub>, that was 3.13 mmol/g with amine-loading at 50%. Moreover, recoverability and stability remained unchanged after 12 adsorption/desorption cycles. Another hybrid material dedicated for specific carbon dioxide capture contained melamine-tris(2-aminoethyl)amine dendrimer coated onto SBA-15 silica [42]. High adsorption capacity was achieved even with third dendrimer generation, but still was lower than theoretical one, as the effect of steric hindrance made by highly-branched aminoethyl chains and possible cross-linking or incomplete extension during dendrimer synthesis. However, material was reusable even after seventh adsorption/desorption cycle and its adsorption capacity was constant.

One of the most significant applications of silica-gel is found in chromatography (TLC or HPLC) as a stationary phase. Nowadays, RPC (Reversed-Phase Chromatography) variant is the most widely used in HPLC (High-Performance Liquid Chromatography), which is achieved by functionalization of silica with hydrophobic domains, such as phenyl and long-chain hydrocarbon group. However, there are many polar or ionic substances, e.g. drugs, nucleotides, carbohydrates or proteins, for which separation RP-mode is ineffective. One of the solution is synthesis of novel column fillings for ion-exchange chromatography [43]-[44]. Modification of silica surface with dendritic structure performs high density of functional groups. Moreover, it also might arise to role of analite traps used in size exclusion chromatography [45]. Silica-based adsorbents are characterized by higher efficiency and mechanical stability in contrast to the organic ones. The application of silica-dendrimer materials as ion-exchangers has been shown by many authors. Li *et al.* [46]-[47] presented anchoring of a dendrimer, based on 1,4-butanedioldiglycidyl ether and aniline, on amorphous silica and KIT-6 silica material. The hybrids were tested for their ion-exchangeability among nucleobases/nucleosides and acidic drugs (ibuprofen, ketoprofen and naproxen). The presence of three interaction types between sorbent and analite, i.e. polar (amine and hydroxyl groups), electrostatic (ternary ammonium cations) and hydrophobic (alkyl chains, phenyl rings) promotes high sensitivity and good separation. Applicability of KIT-6-based sorbent in detection of Nonsteroidal Anti-inflammatory Drugs (NSAIDs) in human urine samples was confirmed by validation of chromatography method. Similar material was also studied by another research group, who applied silica-dendrimer hybrid material to simultaneous determination of four nucleotide monophosphates in infant milk [48]. They concluded high selectivity and reusability of ion-exchanger, considering its development in routine application.

Silica-based hybrid materials containing dendritic structures find also great application as catalysts, however their catalytic properties are usually stimulated by appearance of metals (such as Cu, Pd, Pt, etc.) or their ions within

hyper-branched molecules [49]. Metallodendrimers are interestingly efficient, because they prevent nanoparticles against agglomeration and leaching. Moreover, nanoparticles are retained inside dendrimer mostly via steric effects, thus their reactive surfaces do not undergo passivation process [50]. Furthermore, modulation of dendrimer generation, affecting on the size of “access-gates”, leads to selectivity toward substrate access to metal trapped within tree-like structure [51]-[52]. The most popular way of obtaining metallodendrimers is diffusion of metal ions into the interior of dendritic structure. Mostly used PAMAM dendrimer consists of internal tertiary amine and amide groups, dramatically stabilizing retention and bonding of metal ions. Moreover, peripheral primary amine groups exhibit strong base character, but water solution of dendrimer must be acidic for synthesis, so it makes coordination of metal ions to periphery amine groups impossible [53]. While, they are fully extracted within dendrimer, reducing agent (most often sodium borohydride, NaBH<sub>4</sub>) is used, leading to zerovalent metal nanoparticles (Fig. 6).

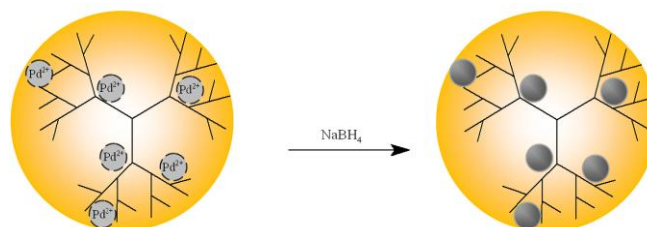


Fig. 6. The synthesis of zerovalent metal nanoparticles in structure of hybrid materials

So far, a number of studies have been carried out in order to confirm catalytic properties of silica-dendrimer-based materials toward many organic and inorganic reactions (Table 1).

Table 1. The silica/dendrimer nanomaterials as catalysts for various reactions

Catalyst		Reaction type	Ref.
Silica	Functionalization		
amorphous silica SiO <sub>2</sub>	polyallylamine/ G3-PPI/Pd	hydrogenation of various alkenes	[54]
	G4-G6-OH-PAM AM/Ru/ILL (Ionic Liquid Layer)	hydrogenation of toluene	[55]
	G4-PAMAM/Pd	hydrogenation of various alkenes and nitroalkenes	[56]
	G1-G3-PAMAM/ 5-methyl salicylaldehyde/ V(IV)	oxidative desulfurization of dibenzothiophene (as model fuel component) with tBuOOH	[57]
	G0-G4-PAMAM/ PPh <sub>2</sub> /Rh	hydroformylation of styrene and other various olefins	[58], [59]
	G0-G2-PAMAM/ PPh <sub>2</sub> /Pd	Heck Reaction	[60]
	G1-G2-PAMAM/ (1R, 2S)-ephedrine	enantioselective addition of diethylzinc to benzaldehyde	[61]

	G1-PAMAM/ PPh <sub>2</sub> /Pd	carbomethoxylation of iodoarenes	[62]
	PEI/Cu(II)	catalytic oxidation of pollutants from gasoline engine	[63]
	G0-G3-PAMAM/ Pd	intramolecular cyclocarbonylation in obtaining ring fused heterocycles and large-ring (12-18) O-, N- or S-containing macrocycles	[64], [65]
SBA-15	G4OH-PAMAM/ (Pt/Pd/Rh)	methylcyclopentane isomerisation	[66]
		dehydrogenation/hydrog enation of N-heterocycles (tetrahydroquinoline/ indoline, respectively)	[67]
	G4OH-PAMAM/ (Pt/Rh)	ethylene and pyrrole hydrogenation	[68]
	G4OH-PAMAM/ Pd	hydroalkoxylation of 2-phenylethynyl-phenol	[69]
	G4OH-PAMAM/ Au	diastereoselective and chemoselective cyclopropanation	[70]
	G1-G4-PAMAM/ Au	oxidation of aromatic and cycloaliphatic alcohols	[71]
	G4-OH-PAMAM/ Fe(III)	Michael addition to indole	[72]
	G4-PAMAM/Pt	electron transfer reaction (reduction: Fe(CN) <sub>6</sub> <sup>3-</sup> to Fe(CN) <sub>6</sub> <sup>4-</sup> ; p-nitrophenol to p-aminophenol	[73]
MCM-41	G0-G2-PAMAM/ PPh <sub>2</sub> /Rh	hydroformylation of various olefins	[74]
	G0.5-G2.5- PAMAM/ porphyrin/Fe(III)	oxidation of 2,3,6-trimethylphenol to trimethylbenzoquinone	[75]
nano-SiO <sub>2</sub>	G2-PAMAM/ phosphotungstic acid(PWA)	synthesis of 2H-indazolo[2,1-b] phthalazine- triones	[76]
	G2-thiolated- trimesic dendrimer/Ru	aliphatic alkene epoxidation and oxidation of various benzyl, aliphatic alcohols with tBuOOH	[77]
	G3-PAMAM/G3- PAMDMAM	Knoevenagel Reaction	[78]
	G1-triazine dendrimer/manga nese (III) salophen	oxidation of benzyl and aliphatic alcohols with NaIO <sub>4</sub>	[79]
	G2-PAMAM/Pd	phosphine-free Sonogashira cross coupling reaction	[80]
	G1-triazine dendrimer/Cu(II)	synthesis of un- and symmetrical 1,3-dynes	[81]
	G2-thiolated trimesic dendrimer/Cu(II)	synthesis of benzimidazoles and benzothiazoles	[82]
mesoporous benzene silica	G2-PAMAM/ Ti(IV)	synthesis of 3,4-dihydropyrimidin-2( 1H)-ones (Biginelli reaction) and pyranopyrazoles	[83]

large-pore Davisil silica	G0-G3-PAMAM/ Rh	hydroformylation of various olefins	[84]
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All above-presented hybrid materials perform high efficiency toward each reaction. Anchoring dendrimer-metal conjugates onto silica surface lead to novel, eco-friendly, economically beneficial and easy-recyclable heterogeneous catalysts, which might be used in many kind of reactors, e.g. fixed-bed flow reactors or continuous flow reactors [56]-[57],[85]. Moreover, there are several materials, where nanoparticles-PAMAM-silica conjugate plays a role of encapsulating agent among e.g. magnetic iron oxide Fe<sub>3</sub>O<sub>4</sub> or zinc oxide ZnO, so that materials perform common properties for each of component [86]-[90]. Dendrimers find also application in synthesis of dendrimer-free silica-based catalyst. Such protocol consists of depositing nanomaterial encapsulated in dendrimer onto silica surface and following thermal activation leading to dendrimer removal. Such technique provides stabilization and grafting of defined number of nanoparticles, so that size and distribution of nanomaterial over target catalyst might be predicted [91]-[92].

In addition to adsorptive and catalytic performance of dendrimers, they find also plethora applications as biotargets. Their monodisperse structure, numerous functional groups (amine -NH<sub>2</sub>, amide -CO-NH- or hydroxyl -OH) and internal cavities make them good candidates as drug, therapeutic agent and gene delivery systems, contrast agents used in Magnetic Resonance Imaging (MRI), as well as enzymes immobilizers [93]-[97]. However, among those applications, drug delivery gained the biggest attention due to the complicity of finding suitable therapeutic-targeted systems. Drug conjugating into dendritic structure improves hydrophilicity (especially important in case of insoluble hydrophobic drugs), circulation time and balanced release of an active substance [98]-[99]. Dendrimers as large-size, hyper-branched compounds perform an enhanced permeability and retention effect (EPR), i.e. enlarged affinity of dendrimer-drug complex toward tumor tissues than healthy ones, what is vital for targeted anticancer treatment with decreased side effects [100]-[101]. So far, there are many studies focused on ability of dendrimeric structures, such as poly(amidoamine) dendrimers, PPI, triazine dendrimer for targeted delivery of anticancer drugs, e.g. 5-fluorouracil, paclitaxel, camptothecin or metothrexate [100]. In recent few years, much attention was drawn to a new class of bioactive macromolecules – dendrimer-silica hybrid materials, which demonstrate either free-dendrimer features or astonishingly high biocompatibility and large capacity for therapeutics loadings [102]. In 2009, Gonzalez *et al.* [103] presented comparison of ibuprofen adsorption and its controlled release by 3 materials based on SBA-15 silica material, decorated with G1, G2 and G3 PAMAM dendrimer. Ibuprofen has been chosen as a model molecule, according to its widespread usage as Nonsteroidal Anti-Inflammatory Drug (NSAID).

The results showed that adsorption capacity increased gradually with dendrimer's generation, achieving 288 mg/g and 480 mg/g for SBA-15 grafted with G1- and G3-PAMAM,

respectively. Such trend results from increase of electrostatic attractions between carboxylic groups of drug and higher amount of amino groups in dendritic structure of G3 compared to G1. Afterwards, kinetics of drug release process was examined, keeping probes in simulated body fluid at 37°C, as physiological conditions [104]. The amount of released drug – which is tightly connected with adsorption capacity – increased with either generation of used tree-like structure or incubation time. Studies showed that full drug release is achieved after ~72 hours, 270 mg/g and 465 mg/g for G1- and G3-modified silica surface respectively. Interestingly, first stages of release experiments can be described with Higuchi model, assuming amount of released (diffused) drug from solid porous carrier as a linear function of square root of time, making drug dosage designable and predictable by the dendrimer generation and time of residing in bloodstream [105]. Another very attractive modification of hybrid material based on mesoporous silica grafted with G0-G3 PAMAM dendrimer and curcumin as a model drug was introduced, giving self-fluorescent, pH-sensitive platform for drug delivery [106]. The amount of loaded and released curcumin was examined by measuring its fluorescent absorption at wavelength  $\lambda = 488$  nm. The highest adsorption rate was achieved for G3-PAMAM-derivative – 31.1%, which results from increase of amino groups and then formation of hydrogen bonding between hybrid material and curcumin. Drug release studies were conducted in phosphate buffered saline at pH 5.0 and pH 7.4. Curcumin release in slightly acidic environment was slower than at pH 7.4, what indicated on higher efficacy of retaining drug in material's pores at pH 5.0, preventing drug overdosing. Release equilibrium could have not been achieved even after 24 hours, what makes the material a great drug delivery system with prolonged release. Moreover, cytocompatibility (standard procedure using 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl-tetrazolium bromide, i.e. MTT assay) of obtained materials was established, using HeLa cells (commonly used human cell line) – there was no significant influence of systems on cells viability. Silica-based platforms transporting drugs can be sensitive not only to pH, but also to presence of selected bonds. For instance, disulfide bond might play a role of stimulus in drug delivery, which reduction is induced by redox-active, widely distributed in animal tissues glutathione, which concentration in the plasma is much lower than in intracellular fluid. Thus, glutathione-sensitive drug delivery systems retain unaltered during transport and only release bioactive molecule while incorporated into the targeted cell [107]. Such mechanism was utilized during obtaining of mesoporous silica encapsulated with G1-G5 poly(propylene imine) dendrimer (PPI) disulfide-derivative and following entrapment of two fluorescent dyes: fluorescein disodium salt (FSS) and 5(6)-carboxyfluorescein (CF) as drug-mimic molecules [108]. According to *in vitro* instability of glutathione, dithiothreitol (DTT) was used as stimulus for releasing tests. The highest concentrations of adsorbed dyes were achieved for samples containing G1- and G2-PPI dendrimers, what is connected with increasing steric hindrance. Therefore, the highest amount of released cargo FSS was achieved for G2-PPI-silica material (~9.5  $\mu\text{mol/l}$ ) and slightly lower for its G1-variant (~9  $\mu\text{mol/l}$ ). The same trend was observed during CF-release experiments, where amounts of dye were ~22  $\mu\text{mol/l}$  and ~13.5  $\mu\text{mol/l}$ ,

respectively. Release tests were carried out for 380 minutes in the presence of DDT; dyes concentration was determined with fluorescent measurements at  $\lambda = 520$  nm, using excitation wavelength  $\lambda = 490$  nm. To confront, whether all dyes were derived from hybrid system, DDT-free samples were also investigated in the matter of dye presence (leakage). Platforms consisting of G1- and G2-PPI dendrimer assisted with FSS exhibited leakage on the level of approximately 5%, but CF-containing ones exhibited leakage at 40% and 24%, respectively. Moreover, the key feature of synthesized materials is functionalization of mesoporous silica material, while amorphous is not able to generate dye/drug delivery tool. Poly(propylene imine) dendrimer was also used as mesoporous silica grafting in synthesis of levofloxacin delivery system [109]. Combination of 3G-polycationic dendrimer, which is able to penetrate through negatively charged bacteria walls with antimicrobial drug lead to obtain “nano-antibiotic”. Levofloxacin loading on hybrid material was achieved at 7.8%, with full release after 72 hours. However, even at the initial stage of release (1 hour, 3 hours of incubation), concentration of drug is several times higher than its minimum inhibitory concentration for *E. coli* [110]. Confocal microscopy studies were conducted in order to demonstrate the ability of obtained material toward penetrating through bacteria walls and internalization of nanosystem into the Gram-negative bacteria cells has been proven. In general, silica-PPI-levofloxacin material might gain huge attention as novel nanomaterial, capable for antibiotic transport. Described silica-dendrimer systems find also application as anticancer drug delivery platforms. Recently, there was another study using poly(amidoamine) dendrimer as capping agent for anthocyanin [111]. Anthocyanin is bioactive molecule, present in black carrot extract, which exhibits selective cytotoxicity against Neuro 2A cells – fast-growing neuroblastoma cell line. The nanoparticles of anthocyanin-decorated silica-G2-PAMAM were tested for drug release against neuroblastoma cell culture. The results showed that after 6 hours 10% of anthocyanin was released, which is connected with drug molecules adsorbed on the material's surface, and full-release was achieved after 6 days. The most important *in vitro* MTT study concerned anthocyanin-doped nanomaterial's cytotoxicity against cancer cells. After 2 days of nanomaterial interaction with cell line, inhibition reached 40.2%. Gradual increase of inhibition leveled out after 6 days, reaching approximately 87.9%. Bioactivity of nanosystem was compared with bare silica nanoparticle, which exhibited no inhibitory effect. Above-described nanoparticles have gained attention by the fact of drug's directed transport. However, there are known a few materials delivering two or more bioactive molecules. For instance, mesoporous silica was grafted with chondroitin sulfate, polysaccharide possessing activity toward binding over expressed hyaluronic acid receptors on cancer cells and curcumin-PAMAM conjugate with layer-by-layer technique (LbL) [112]. Before grafting, silica mesopores were filled with anti-cancer drug doxorubicin. Release studies were conducted in three different environments – high acidic pH 3.0, slightly acidic pH 5.0 and neutral pH 7.4. Percentage of released drugs were achieved by UV-Vis spectra at wavelength  $\lambda = 428$  nm for curcumin and  $\lambda = 495$  nm for doxorubicin. The results concluded that the more acidic the sample environment,



the faster the drug release. Moreover, amounts of released drugs are not the same, but their ratio remains equally. Additionally, the research studies also concerned the impact of hyaluronidase (lysosome enzyme which cause fragmentation of silica shell's component, chondroitin sulphate – the most widely found enzyme in tumor cells) onto doxorubicin and curcumin release. In case of both drugs, enzyme presence had a slight impact on their released amount, causing approximately 2% value changes. Finally, obtained nanomaterials were proved for their *in vitro* cytotoxicity by either MTT study or confocal imaging of nanosystem-cell samples.

Recently, gene delivery is one of the most investigated therapy against cancer and genetic diseases, offering remarkably high effectiveness [113]-[114]. However, there are several conditions, which appropriate delivery system needs to meet. The main obstacle encountered during silica-based gene delivery system designing is strong electrostatic interaction between negatively charged nucleic acid and positively charged organic-silica composite [115]-[117]. Thus, novel transporting platforms must be able to selective and controlled gene release [118]. For instance, Du *et al.* [119] presented silica-(acetaldehyde-cysteine)-PPI hybrid as pH-sensitive (hydrolysis of fluorophoric imine group in acidic environment), GSH-sensitive (cleavage of disulfide bridge with intracellular glutathione high concentration) self-fluorescent gene delivery platform. A binding capability of synthesized nanohybrid was characterized with model nucleic acid - pEGFP-N1 pDNA, gene which encodes green fluorescent proteins. Electrophoresis allowed quantifying of loading capacity at the relatively high level of 30 mg/g. Using fluorescent assessment, it was revealed that stability of thenanomaterial decreased with increase of time, pH and GSH concentration. Moreover, its cytotoxicity was evaluated using MTT assay against three cell lines: HeLa, CHO (Chinese hamster ovary) and HEK 293 (Human embryonic kidney) cells. It appeared that maximal transfection efficiencies equaled 72.3%, 56.4% and 79.8%, respectively for cell lines, what indicated on high quality of designed multi-functional gene delivery system.

Silica-based dendrimer hybrid materials also find attractive applications in other biomedical fields. Multi-functional nanoparticles based on silica-G3-PAMAM grafted with indocyanine green and technetium-99m ( $^{99m}\text{Tc}$ ) were tested as fluorescent probes for molecular imaging of cancer cells occurring as the overexpression of human epidermal growth factor receptor (HER2) [120]. Dually-modified system turned out to be efficient imaging agent so its further optimization might have led to imaging/drug delivery bimodal vehicle. Moreover, dendrimer-silica hybrids can play a role of platforms for enzymes immobilization, performing high reusability, easy separation and increase in enzymes stability [121]. There are several studies, in which silica-poly(amidoamine) dendrimer nanocomposites were utilized as platforms for immobilization of glucose oxidase (GO) (EC 1.1.3.4), horseradish peroxidase (HRP) (EC 1.11.1.7) or cellulase (EC 3.2.1.4) [122]-[123]. The results showed improved stability and high efficiency of enzymes, dependently on solution pH, ionic strength, enzyme concentration and environment temperature.

### III. TITANIA/DENDRIMER NANOHYBRIDS

Titania ( $\text{TiO}_2$ ) is widely used metal oxide, as it performs several interesting properties which find applications in cosmetics or electrical and optical sciences [124]-[127]. However, titania also finds attractive application in surface science, therefore may be considered as efficient, easy functionalizable platform for synthesis of novel hybrid materials playing role of adsorbents or drug delivery systems, as well as photocatalytic nanocomposites.

$\text{TiO}_2$  has gained great interest as semiconductor, because of non-toxicity, high chemical stability and low-cost [128]. Additionally, it performs photocatalytic self-activity, what is connected with formation of photogenerated charge carriers under the UV-light irradiation [129]-[130]. However, titania's large band gap allows for utilizing of only 3% of solar light reaching earth surface [131]. Therefore, functionalization of  $\text{TiO}_2$  surface may lead to obtaining materials, which perform higher photocatalytic activity. Recently, there are many attempts to attach dendritic structures onto titania surface, which not only contributes to increase of hybrid material activity, but also protect  $\text{TiO}_2$  particles against aggregation process by forming protective spheres [132]. Titania-based photoactive materials find application in organic pollutants degradation process (described below) or in deactivation of bioorganic water pollutants [133]-[134]. One of the first studies exploring titania-dendrimer systems as photodegradative materials was conducted by Nakanishi *et al.* [132], whose research aimed to compare photoactivity of G4-PAMAM dendrimers with different terminal groups grafted onto  $\text{TiO}_2$  surface. It appeared that G4.5-COONa (carboxyl-terminated) and G4-OH (hydroxyl-terminated) dendrimers did not fully prevent titania nanoparticles against aggregation process in contrast to G4-NH<sub>2</sub> (amine-terminated) system, however all of them performed high activity against UV-stimulated photodegradation of model organic molecule: 2,4-dichlorophenoxyacetic acid. A time-dependent photoactivity of all products were measured with fluorescence spectra, observing decrease of emission band at  $\lambda = 357$  nm with excitation band at  $\lambda = 254$  nm, what indicated on pollutant photooxidation supported with each titania-PAMAM material. In comparison to bare  $\text{TiO}_2$ , all dendrimer-grafted particles were more efficient among photoreaction. Those findings brought many research groups to development of titania-dendrimer conjugate with other suitable compounds, due to improve material catalytic performance. One of such hybrid materials is titania grafted with melamine based dendrimer conjugated with Rhodamine B (RhB- $\text{TiO}_2$ ), where dye plays a role of switch between spirolactam (off) and ring-opened amide (on) equilibrium, manipulating photocatalytic process by change of solution pH [128]. The system was several times more efficient as photocatalyst for phenol degradation in aqueous medium than bare titania. The most interesting measurement was connected with pH-dependent switch off/on system mode. In order to determine material photoactivity, several samples with different pH were tested for phenol degradation. It appeared that the lower the solution pH, the higher the degradation rate. Low pH is favorable for spirolactam opening, transforming into open-amide, therefore photocatalytic activity of ring-opened material is much higher than ring-closed one, however ring-closed RD- $\text{TiO}_2$  is much more recyclable than

ring-opened RD-TiO<sub>2</sub> (after 8 successive cycles, phenol degradation rate for ring-closed and ring-opened material decreased by approximately 20 and 75%, respectively). Another compound which provides better photocatalytic properties of titania-dendrimer material is phthalocyanine. It is reported that phthalocyanines are very effective among degradation of organic water pollutants, however they easily self-aggregate, thus lose their catalytic activity [135]. Therefore, their incorporation into titania/dendrimer complex is reasonable way to obtain highly efficient degradative system. Xiao *et al.* [136] proposed novel synthesis of three-component hybrid material TiO<sub>2</sub>-dendrimer-zinc phthalocyanine as photocatalyst for Rhodamine B degradation, as model organic molecule. The nanocomposite was investigated for RhB degradation as time-dependent process. After 3 hours degradation rate reached 97%, while dendrimer-less system and bare titania reached 79 and 46%, respectively. Efficiency of described materials among photocatalytic degradation of organic pollutants is encouraging for combining them with easily removal iron oxide magnetic nanoparticles. One of the newest researches aimed to obtain magnetic nanoparticles grafted with PAMAM dendrimers (generation G0 up to G3) and covered with TiO<sub>2</sub>, which find applications in methyl orange degradation [137]. The results of the studies showed that dendrimer generation had big impact on material activity – G3-PAMAM-derivative appeared as the most effective catalyst for dye degradation, however, materials containing G0-G2-PAMAM still exhibited extremely better photoactivity than bare magnetic nanoparticles. Moreover, recyclability of the system obtained was measured. After five cycles of methyl orange degradation, activity of G0-, G1-, G2- and G3-PAMAM derivative decreased to 98, 94, 89 and 76% of the activity for the first degradation cycle, respectively.

Titania-based dendrimer-containing nanomaterials are not only used as photocatalysts, but also find applications as template for introducing metal nanoparticles onto titania surface. It is proved that metal nanoparticles are located in strict, highly-ordered manner, thus after dendrimer (template) removal well-defined metal arrangement on the platform surface is achieved, making obtained materials very efficient catalysts for several reactions [138]-[140].

Titania, gained also much attention in the matter of efficient heavy-metal ions and dyes adsorbents synthesis. As dendritic structures perform highly effective chelating properties, they found great application as the grafting materials for TiO<sub>2</sub> particles. Additionally, titania is suitable inorganic platform for hybrid materials forming, because it performs high mechanical strength and already finds application as photocatalysts of organic pollutants in wastewater treatment [141]. There are several studies aiming heavy metal ions removal by titania/PAMAM-dendrimer composites. For instance, G4-OH-PAMAM grafted on titania surface was studied as adsorbent for Cu<sup>2+</sup>, Ni<sup>2+</sup> and Cr<sup>3+</sup> ions [141]. The experiments included investigation of adsorption properties depending on pH and ions concentration. It was revealed that high efficiency in metal ions removal was at pH 7.0 for Cu<sup>2+</sup>, Cr<sup>3+</sup> and at pH 9.0 for Ni<sup>2+</sup>, therefore adsorption dependency on metal ions concentration and adsorbent dosage were established in required pH solutions. The results of the studies showed that the highest efficiency of adsorption

process was for 1.0 g/l adsorbent concentration. Higher dosage resulted in decrease of adsorption capacities because of progressing titania/dendrimer hybrid aggregation. Moreover, efficiency of Cu<sup>2+</sup> and Cr<sup>3+</sup> removal remained almost constant even at their high concentration equaled 800 mg/l, in opposite to Ni<sup>2+</sup>, which exhibited strong decrease starting from 100 mg/l. The differences observed result from different tendencies of metal ions complexing with chelating agents. The same hybrid material (titania/G4-OH-PAMAM) was studied as adsorbent of Pb<sup>2+</sup> ions - models for the wastewater treatment [142]. The most efficient environment for lead(II) ions adsorption appeared to be at the range of pH 7.0-9.0, thus adsorption properties were examined at neutral pH 7.0. As mentioned above, adsorption properties are dependent on adsorbent and initial concentration of metal ions, as well as on reaction time. The hybrid material exhibited the greatest efficiency for Pb<sup>2+</sup> concentration up to 400 mg/l. The material concentration higher than 0.25 g/l performed >90% removal efficacy. The adsorbent studied was found to be very effective even at the first minutes of interactions, reaching 99.9% adsorption after 30 minutes. Another material tested as an extraordinary adsorbent for metal ions removal, based on titania/dendrimer structures, was TiO<sub>2</sub>/G4-NH<sub>2</sub>-PAMAM – similar to the one described above, varying in dendrimer's terminal group [143]. The material was found to be an attractive adsorbent for Pb<sup>2+</sup>, Cu<sup>2+</sup> and Cd<sup>2+</sup> ions. It was tested under various conditions (single and three-component samples were tested in different solution pH, temperatures and adsorbent concentrations), still performing high adsorptive properties for all desired cations. However, wastewater treatment does not include only heavy metal ions removal, but also organic compounds such as phenol [144] or organic dyes. Polycationic nature of PAMAM dendrimer grafted onto titania surface contributes to effective adsorption of anionic dyes, e.g. Direct Red 23 (DR23), Direct Green 6 (DG6) and Direct Red 31 (DR31). Those dyes were tested among their adsorption onto hybrid nanocomposite TiO<sub>2</sub>/G2-PAMAM [145]. The material obtained was verified in its adsorption capacity among three anionic organic dyes at different pH values and their initial concentration, reaching adsorption capacity at the level of 244, 189 and 234 mg/g, for DR23, DG6 and DR31, respectively. Adsorption progress was controlled with UV-Vis spectroscopy, observing characteristic peaks at  $\lambda = 500, 634$  and  $527$  nm, respectively. The highest adsorption efficiency was determined for acidic samples, at pH 2.0, which resulted from appearance of protonated dendrimeric terminal amino groups, enhancing electrostatic interactions between the adsorbent and the anionic dyes molecules. Decrease of adsorption properties was observed with increase of compounds initial concentrations, as the matter of rigid capacity of adsorbing material. Additionally, the studies involved defining the impact of competing salts (Na<sub>2</sub>SO<sub>4</sub>, NaHCO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub>) on dyes adsorption process. It was established that salts small molecules effectively compete with larger organic molecules, anchoring faster and easier onto adsorbent surface, making dyes adsorption decreased. The same research group conducted similar study using another two anionic dyes: Direct Blue 78 (DB78) and Direct Red 80 (DR80), as model adsorbate for TiO<sub>2</sub>/G4-PAMAM hybrid adsorbent [146]. Those two molecules exhibit maxima on UV-Vis spectra at wavelength



$\lambda = 598$  and  $540$  nm, thus adsorption process was easy to monitor. Tendency of effects on changeable solution pH and initial dyes concentrations stayed unaltered, correspondingly to their previous work [145], however maximum adsorption capacity increased radically to  $1250$  mg/g for DB78 and  $990$  mg/g for DR80.

Titania-based hybrid nanostructures might also play a role of bioactive composites, however up to now there are only a few reports regarding such application. Very attractive example of biological application was introduced by Torres *et al.* [147]. This research group focused on  $\text{TiO}_2$  nanotubes/G3-PAMAM dendrimer hybrid investigation as a dual system for encapsulation and long-term release of three model therapeutics: curcumin, methotrexate and silibinin. The results of the studies exhibited incorporation of drugs in the amount of  $0.33$ ,  $0.49$  and  $0.22$  mmol/g, respectively. *In vitro* tests of drug release were carried out in simulated body fluid and provided  $80\%$  of drug release in  $60$ ,  $130$  and  $250$  h for methotrexate, curcumin and silibinin, respectively, while dendrimer-less materials exhibited few times fold shorter time.

#### IV. CARBON NANOMATERIALS/DENDRIMER HYBRIDS

In past few decades, carbon nanotubes (CNTs), built of  $\text{sp}^2$ -hybridized carbon atoms, gained huge attention, according to their distinctive properties, which make them applicable in optics, electronics and chemistry [148]-[151]. However, CNTs-conjugates perform high hydrophobicity and low solubility in water and organic solvents, what leads to activity loss by aggregation process or even heterogeneous interaction with cell components, resulting in negative effects on organisms [152]. Thus, choice of functionalizing agent should be dictated with promoting of solubility increase, accomplished by breaking of the nanotubes bundles [153]. Such appearance is observable for grafting dendrimeric structures onto CNTs surface, which might be demonstrated with two pathways: non-covalent functionalization (based on  $\pi$ - $\pi$  stacking, van der Waals interactions, electrostatic attractions or physical entanglement) or covalent functionalization achievable by “grafting to” and “grafting from” approach [152]. The most attractive chemical applications of dendrimer-modified CNTs include especially electrochemical sensors and gene transfection nanoplatfroms.

For instance, one of the research groups synthesized multiwalled carbon nanotubes (MWCNTs) grafted with 4G-PAMAM/Pt-nanoparticles conjugate, in order to obtain electrocatalytic material [154]. UV-Vis-NIR spectrum of prepared material demonstrated a phenomenal observation connected with electron transfer to MWCNTs from dendrimer-encapsulated Pt-nanoparticles, resulting in enhanced electrochemical behavior of nanotubes-based material. Electrocatalytic performance was examined by anchoring of MWCNTs/PAMAM/Pt onto screen-printed circular gold (SPCG) working electrode and its analysis with cyclic voltammetry (CV). It appeared that the material obtained exhibited high reactivity, as the result of enlarged surface area of the working electrode by CNTs as well as electron transfer occurrence. Moreover, the material possessed high stability, hence the same research group used it as electrode-support for electrochemical reaction of methanol oxidation [155]. Voltammetry studies showed high

process efficiency and high electrode durability – it exhibited unchanged physical and chemical properties even after  $20$  cycles of CV scans. Another example of Pt-containing dendrimer/CNTs application is connected with preparation of biofuel cells, special kind of fuel cells which use bioorganic compounds as energy source [156]. A novel material was obtained by layer-by-layer assembly of 4G-PAMAM/nano-Pt and glucose oxidase onto carbon nanotubes, which was subsequently used as grafting material for indium tin oxide (ITO) electrode [157]. Electroactivity of obtained electrode toward glucose oxidation was studied with CV analysis and appeared to be very effective under physiological conditions, what may lead to a novel and successful application of new class of biofuel cells based on CNTs/dendrimer hybrid. Dendrimer-grafted carbon nanotubes are also applicable as electrode components for detection of biomolecules. For instance, Ahmar *et al.* [158] synthesized multiwalled carbon nanotubes grafted with poly(amidoamine) dendrimer as a matrix for encapsulation of Pd-nanoparticles. This nanohybrid was used as modifying agent for glassy carbon electrode (GCE), in order to obtain electrode designated for oxalic acid electrooxidation. Cyclic voltammetry analysis showed a great performance toward selective oxalic oxidation process, reaching limit of detection at  $0.02$  mM, as well as good repeatability, chemical stability (CV analysis stayed almost unchanged after electrode incubation in a supporting electrolyte for  $2$  weeks) and physical stability (surface remained constant even after  $130$  analysis) of electrode. Very promising results led to electrode application for fast determination of oxalic acid in spinach extract samples. Another example of an analyte which can be determined with MWCNTs/dendrimer-based electrode is metolcarb – *N*-methylcarbamate, widely used pesticide for fruit flies control [159]. Carbon nanotubes functionalized with various PAMAM-dendrimer generations (G1-G5) were immobilized onto gold electrode and subsequently metolcarb antibody was anchored on its surface, obtaining piezoelectric immunosensing platform. This kind of biosensors exhibit high selectivity and sensitivity for antigen-antibody interaction, what contributes to extraordinary properties of nanohybrid. The results of the studies showed that the dendrimer-assisted materials demonstrated significantly higher adsorption capacity for metolcarb antibody (especially G5-PAMAM dendrimer) than dendrimer-less products. Therefore, this immunosensor was evaluated for its metolcarb (antigen) detection performance with experiments based on the pesticide determination in apple and orange juice. It appeared that the material is highly recoverable (recoveries varied in the range of  $81.9\%$  to  $101.2\%$ ) and effective toward designated antibody-antigen interaction process, reaching limit of detection at  $0.019$  mg/l. Gold electrode might also play a role of electrode platform for anchoring MWCNTs co-grafted with chitosan immobilized with PAMAM/dsDNA (double stranded DNA chain acquired from herring sperm) for determination of dopamine and uric acid in coexistence of ascorbic acid [160]. Electrochemical detection of mentioned biomolecules is highly interfered with ascorbic acid presence, as its peak overlaps with other signals. However, this nanocomposite performed good separation of oxidation peaks of each compounds on cyclic voltammograms. The research studies consisted of a series of CV scans for  $1$  mM ascorbic acid samples, containing

dopamine and uric acid at varying concentration in the ranges 0 – 200  $\mu\text{M}$  and 0 – 1000  $\mu\text{M}$ , respectively. The biosensor exhibited good-separation of three oxidation peaks, high stability, high reproducibility and it was very sensitive for dopamine and uric acid detection, reaching detection limit at 0.03  $\mu\text{M}$  and 0.07  $\mu\text{M}$ , respectively. MWCNTs/dendrimer conjugates are also useful for electrochemical detection of biomacromolecules, such as nucleic acids or proteins. Li *et al.* [161] introduced voltammetric biosensing of microRNA by glass carbon (GC) modified with MWCNTs/G4-PAMAM conjugate, then immobilized with DNA capture probe. Voltammetric biosensing of miRNA<sub>24</sub> as a model nucleic acid, extracted from HeLa cells was performed by hybridization of target RNA chain with DNA probe tethered at dendritic component of electrode and handled with Methylene Blue as a redox indicator. Differential pulse voltammetry (DPV) measurements indicated on high sensitivity of the material prepared (very low detection limit reached 0.5 fM), high specificity and reusability. Moreover, organic dye indicator affords overcoming obstacles connected with chemical labeling as well as facilitating and accelerating detection time. A similar approach based on hybridization of target nucleic chain with probe DNA on biosensor was introduced by Zhu *et al.* [162], who synthesized GC/MWCNTs/G2-PAMAM/ssDNA (single stranded DNA) electrode for a selective impedimetric detection of targeted DNA sample, using  $\text{Fe}(\text{CN})^{3-/4-}$  redox indicator, sensitive to charge-transfer caused by nucleic acids hybridization. The studies contained electrochemical impedance spectroscopy (EIS) analysis of the electrode and cyclic voltammetry for visualization of DNA biosensing, showing high effectiveness and low limit of DNA detection equaled 0.1 pM. Carbon nanotubes-based electrodes have been also employed for protein biosensing. One of the research groups has developed a new method of preparation of Au/MWCNTs/G4-PAMAM electrodes, immobilized with phthalamidoferrocene as the redox marker and biotinylated aptamers (short DNA/RNA fragments, selectively binding to target molecule) via biotin/streptavidin linker [163]. The material was designated as an electrochemical detector of human cellular prions  $\text{PrP}^{\text{C}}$ , as a model prion protein, based on the interaction of analyte with DNA aptamer receptors incorporated into biosensor. Interaction progress could be visualized with ferrocenyl redox label included in a platform structure. Very high sensitivity of aptosensor enabled detection of  $\text{PrP}^{\text{C}}$  even at the 0.5 pM concentration, in both buffer and spiked blood plasma, thus might introduce new approach for determination of pathological prions in human organisms.

Carbon nanotubes functionalized with dendrimers are also suitable platforms for biological applications [164]. The most important factor, which determines their biocompatibility and usefulness is increased dispersibility in water and physiological conditions [165]. Hence, CNTs/dendrimer nanosystems might be successfully introduced as efficient drug delivery platforms. However up to now there are very few reports aiming such application [166]. One of them was described by Wen *et al.* [167] and aimed synthesis of MWCNTs/G5-PAMAM dendrimer nanohybrid immobilized with fluorescein isothiocyanate (FITC) and folic acid (FA) as a platform for pH-sensitive doxorubicin delivery. Utilization of folic acid as functionalizing agent was

determined by its directing properties toward overexpressed folic acid receptors (FAR) of cancer cells [168]. Doxorubicin binds to nanocomposite surface mainly via  $\pi$ - $\pi$  stacking interactions, so its adsorption ability is pH-dependent. The results showed that acidic conditions decrease drug loading and subsequently enhanced its release from system, what is caused by increased water-solubility of protonated doxorubicin, contributing to prolonged drug release under physiological conditions. In order to establish permeability of the nanocomposite among cancer cells, confocal microscopy facilitated by fluorescence dye incorporation to hybrid material and MTT assay were conducted. Overall tests proved material's selectivity toward overexpressing FAR cancer cells and a high therapeutic efficiency of drug delivery system. Another example of targeted delivery of carbon nanotubes-based bioactive platforms was utility of MWCNTs/4G-PAMAM nanosystem functionalized with either bovine serum albumine fluorescein isothiocyanate (BSA-FITC) or fluorescein amidite-labeled DNA (Fam-labeled DNA) [169]. Both materials exhibited high permeability toward human osteosarcoma MG-63 cells, what was visualized by MTT assay and bright-field optical microscopy. Moreover, the modification of carbon nanotubes with PAMAM dendrimer affected on huge increase of its immobilization ability and simultaneous decrease of cytotoxicity, making it very promising tool for biomacromolecules delivery, such as protein or nucleic acids. Carbon nanotubes functionalized with dendrimers also found application as antimicrobial nanocomposites. In 2011, Murugan *et al.* [170] conducted preparation of MWCNTs immobilized with G2 amphiphilic poly(propyleneimine) dendrimer as the matrix for Ag-nanoparticles encapsulation. Antibacterial activity was examined on three types of microorganisms: *E. coli*, *B. subtilis* and *S. aureus*, resulting in their mortality at 93.1%, 99.8% and 99.7%, respectively, performing bioactivity increase in comparison to bare and dendrimer-only-modified MWCNTs. Similar approach was used by another research group, who synthesized multiwalled carbon nanotubes functionalized with Ag-nanoparticles spread within poly(amidoamine) dendrimer consisting of *p*-phenylenediamine as repeating amino-component [171]. Antimicrobial activity of this nanohybrid was estimated against three types of bacteria: *E. coli*, *P. aeruginosa* and *S. aureus*. The results showed that microbe reduction reached 93.7%, 69.7% and 56.7%, respectively, what indicated on high bioactivity toward microorganisms, in contrast to nonfunctionalized MWCNTs or even dendrimer-grafted ones. Another important application of CNTs/dendrimer platforms is directed gene delivery, related to ever-growing, highly promising gene therapy [172]. In 2009, Pan *et al.* [173] conducted pioneering studies aiming synthesis of MWCNTs functionalized with various generation G1-G5 of PAMAM dendrimers as vectors for a direct transport of FITC-labeled antisense c-myc oligonucleotides (asODNs). Penetrating efficacy of the nanosystems were investigated using breast cancer cells (MCF-7 and MDA-MB-435) and liver cancer cells (HepG2), visualized by standard MTT assay and fluorescent microscopy, enabled by fluorescent dye anchoring onto the nanoplatform. The material prepared performed great properties toward antisense therapy and overall gene delivery into mammalian cells. Furthermore, various CNTs (short and long multi-walled, and

single-walled CNTs) conjugated with PAMAM-dendrimer were considered for highly effective gene transfection property [174]-[175]. Diverse CNTs/dendrimer conjugates were studied among plasmid DNA of enhanced green fluorescence protein (pEGFP-N1) transfection into HeLa cells, visualized with fluorescence microscopy and MTT assays. Another study was concerned Cy3-labeled (orange-fluorescent dye) paragangliomas-3 (pGL-3) transfection, evaluated on HeLa cells and COS-7 cells (fibroblast-like cells derived from monkey kidney tissue) [176]. All mentioned analysis resulted in high efficiency and decreased cytotoxicity of obtained gene delivery materials.

Described nanomaterials are also useful tool, as hybrid material, for adsorption of metal ions or organic dyes. The mechanism of interactions between a nanoplatform and analytes is in the likeness to reported earlier silica and titania. For instance, MWCNTs grafted with G2-PPI dendrimer exhibited high affinity toward two organic dyes, Direct Blue 86 (DB86) and Direct Red 23 (DR23) with maximum absorbance wavelengths at  $\lambda = 631$  nm and  $\lambda = 504$  nm, respectively [177]-[178]. The adsorption experiments were carried out in two system: single and binary, resulting in satisfactory adsorption effectiveness reaching 95% and adsorption capacity equaled 666,66 mg/g for DB86 and 1000 mg/g for DR23. Moreover, G1-G5-PAMAM grafted MWCNTs might play a role of very super-efficient adsorbent among metal ions, such as  $Pb^{2+}$ ,  $Cu^{2+}$ ,  $Ni^{2+}$ ,  $Zn^{2+}$ ,  $As^{3+}$ ,  $Co^{2+}$ , exhibiting ultra-high adsorption capacities (even higher than 2500 mg/g), low toxicity and short contact-time for maximum pollutants removal [179]-[180].

## V. CLAYS/DENDRIMER HYBRIDS

Clay minerals, composed of particles with a diameter below 2  $\mu m$ , are defined as hydrous aluminosilicates that are dominant in clay-sized fraction of soil. The major elements of clay minerals are oxygen, silicon, aluminum, iron, magnesium, calcium, sodium and potassium. There are two structural features in their crystal structures – tetrahedron and octahedron, differing in number and arrangement of oxygen ions. The largest group of clay minerals are phyllosilicates (sheet silicates) that commonly are characterized by the presence of  $SiO_4$  tetrahedral sheets (structural units), while the octahedral sheets are slightly less frequent. Clay minerals, including phyllosilicates, are classified by the number and arrangement of tetrahedral and octahedral sheets in their structure. The 1:1 layer structure contains one octahedral and one tetrahedral sheet, and is represented by kaolinite and halloysite. The other structure type of minerals, 2:1 (two tetrahedral and one octahedral sheets), is more diverse and includes, e.g. pyrophyllite, micas, vermiculites and smectites [181]-[182].

The inorganic part of hybrid functional materials can be composed of various, including previously described, inorganic compounds, however layered ones (e.g. clay minerals, layered double hydroxide) are of great interest. The application of naturally occurring clay minerals for preparation of hybrid materials is extensively explored. Therefore, there are many reports concerning organo-clay materials for various applications. It also includes the large group of hybrids, based on dendritic molecules, improving the properties of obtained materials for specific purposes.

An interesting field of research is the preparation of materials that would have a significantly greater interlayer spacing and hydrophobic properties. Naturally layered silicates are characterized by about 10 Å interlayer spacing and hydrophilic nature. The intercalation of third generation polyurea/malonamide dendrons having phenyl end-groups (Fig. 7) into montmorillonite (MMT) results in preparation of highly ordered silicas with the interlayer distance in the range of 38-115 Å [183].

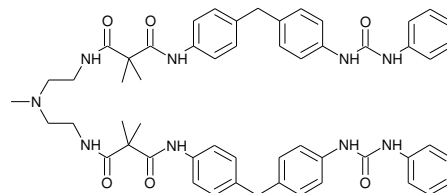


Fig. 7. Chemical structures of dendrons for generation G1 used in organo-clay hybrids

The distance is precisely controlled by the type of intercalating agents, i.e. the generation of selected dendrons. Moreover, these hydrophobic macromolecules allow the hybrid to be dispersed in organic solvents. A generation of dendrimer affects significantly on the arrangement of layers in the resulting hybrid. Clay nanocomposites synthesized from sodium montmorillonite and low-generation poly(amidoamine) dendrimer can be characterized by different structures [184]. The hybrids of generation G-0.0 always form monolayer structures (interlayer expansion of 0.42 nm), while G-2.0 - bilayered ones (interlayer expansion of 0.84 nm). Generation 1.0 of dendrimers yields to the formation of mixed-phase products. Interesting observations have been also made during intercalation of montmorillonite with polyglycerol dendrimers with different molecular weights, derived from soybean oil [185]. Thermal stability and hydrophilic character of the material increases in comparison to the pristine clay. As the number of hydroxyl groups in incorporated dendrimers increased, the affinity toward water and carbon dioxide arisen. Thus, this property of obtained hybrid material is related to the presence of polyglycerol dendrimers. Very promising results have been also demonstrated by using different dendrimers, terminated with a double bond or functional polar groups (-OH, -COOH), in order to form cloisite or montmorillonite nanocomposites, which show higher thermal stability than the original polymers [186]. On the other hand, carbosilane dendrimers with ammonium groups intercalated into MMT are able to increase interlayer space to 15 Å (first generation) and 20 Å (second generation) [187].

One of the application areas for dendrimer-modified clays is a production of flame-retardant materials. Dendrimers with phosphorous or boron components are used to mimic surfactant activity, at a clay surface (Fig. 8). In the next step, intermediate PAMAM organo-clays can interact with boric acid in order to obtain the material with expanded interlayer space, good thermal stability and flame-retardancy [188].



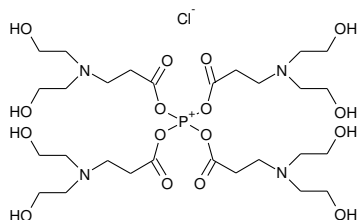


Fig. 8. Chemical structures of dendrons for generation G1 used in organo-clay hybrids

Another synthetic approach assumes the use of cyclophosphamide, with good thermal stability and flame-retardant ability, as a core for a preparation of PAMAM dendrimers introduced into MMT [189] (Fig. 9).

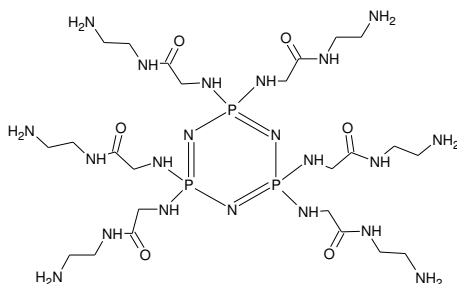


Fig. 9. Chemical structures of dendrons for generation G1 used in organo-clay hybrids

Any flame-retardant organo-clay can be used as an additive to materials of high flammability, e.g. natural rubber. The organo-clay functionalized with liquid crystal, affording thermal stability, and dendrimers with flame-retardant elements might be used to prepare natural rubber composites [190]-[191]. It causes increasing of horizontal burning time by about 69% and higher thermal stability.

Another area of potential dendrimer-modified clays applications is environmental protection. Nowadays, developing of such hybrid materials as adsorbents of gaseous pollutants, mainly  $\text{CO}_2$  and  $\text{NH}_3$ , became very popular. The effectiveness of gas binding depends especially on ionic nature of organoclays. Adsorption sites participating in the gas adsorption are situated on clay surfaces, clay interlayers, but also within dendrimers. Amino-terminated PAMAM dendrimer-loaded cation-exchange laponite and sericite are characterized as preferable  $\text{CO}_2$  adsorbent. On the other hand, carboxylate-terminated dendrimer-grafted anion-exchange hydrotalcite demonstrates reduced capacity for  $\text{CO}_2$  sorption process, in contrast to pristine clay [192]. Moreover, the amount of loaded dendrimers on clay surfaces depends on the surface area of the clay, what indicates that higher content of dendrimer is loaded on laponite than on sericite. Increased amount of a cationic dendrimer has a favorable effect on the  $\text{CO}_2$  adsorption [193]. Furthermore, the dendrimer-incorporated hydrotalcite demonstrates very good ability for  $\text{NH}_3$  gas adsorption. The adsorption ability increases with higher loading of dendrimer, as carboxyl terminated dendrimer moieties are responsible for the sorption properties of the organo-clay [194]. However, in case of amino - dendrimers, desorption and reuse of sorbent is more difficult because of a strength of acid-base interactions between the organoclay surface and  $\text{CO}_2$ . Therefore, polyol dendrimers are proposed for intercalation of MMT. These dendrimers are characterized by weak

basicity, so carbon dioxide is only adsorbed physically, making desorption process much easier [195]-[196]. Dendrimer-clay systems are also designed to remove impurities from waste water. Phosphorous-based dendrimers adsorbed by cation exchange on stevensite and montmorillonite form a suitable sorbent for Methylene Blue. The dye adsorption occurs physically and chemically [197]. Moreover, nanocomposites of phosphorous-based dendrimers and MMT are found to be effective in chromate removal [198]. Enhanced adsorption of anionic dye molecules has been also observed after functionalization of halloysite nanotube surfaces with amine-terminated dendritic structures [199]. Amine-terminated dendrimer of third generation is also a suitable solid sorbent for pre-concentration of cadmium and lead [200]. An interesting solution is the use of magnetic nanocomposites containing poly(amidoamine) dendrimer - MMT hybrids. These types of systems are characterized by high efficiency for sorption of ammonium cations, nitrate(V) anions, as well as the ability of xlenol orange degradation [201].

Organo-clays with incorporated dendrimers can also find many other applications. However, the possibility of their biomedical use seems particularly interesting. Both dendrimers and clay minerals are tested as drug carriers [202]-[203]. PAMAM dendrimer-functionalized halloysite is a suitable material for effective drug delivery. Such system is capable of increased adsorption and/or reduced release rate of a given drug compared to pristine clay [204]. This area of scientific research is not as widely developed as the previously described applications, but it has a great potential for development in the nearest future.

## VI. SUMMARY

Dendrimer/nanoparticles hybrid materials exhibit both great applicability and low toxicity to the natural environment, what makes them incredibly interesting field of surface science, needed to be explored in the coming years. However, their utility would be mostly determined by the availability of various types of dendrimers, but also by the preparation costs.

## ACKNOWLEDGMENT

This work was supported by Project no. POWR.03.02.00-00-I026/16.

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