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Modified PAMAM dendrimers as matrix for photostabilization of curcumin

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Six recently synthesised poly(amidoamine) (PAMAM) dendrimers from zero, first and second generations modified with 1,7-bis(4-hydroxy-3-methoxyphenyl)-1,6- heptadiene-3,5-dione (curcumin) and 2,4- dihydroxybenzophenone (CU-1, CU-2, CU-3, CU-4, CU-5 and CU-6) have been investigated in water/dioxane (4:1) (v/v) solution by absorption and fluorescence spectroscopy in order to determine their photostability. It has been found that the photostability of curcumin is enhanced upon its incorporation into the dendrimer molecule, and a new additional stabilization is achieved by bonding of 2,4-dihydroxybenzophenone as a UV absorber to the dendrimer molecule. It has also been established the dendrimers generation impact upon this parameter as the photostabilizing effect enhances at a higher dendrimer generation. The photostability of dendrimers have also been investigated after their deposition onto a polyethylene terephthalate (PET) fabric.

Keywords: Curcumin; 2,4-dihydroxybenzophenone; Photostability; Fluorescence; PAMAM.

Introduction

Curcumin is a natural yellow fluorescent dye extracted from the root of the dry *rhizomes* and has many applications in health care as a design of fluorescence chemosensor, food and beverages colorant, and in dyeing of textile fibres.^{1–8} Nevertheless, the poor photostability of curcumin has limited its application in the aforementioned areas.^{9–11} Therefore, to continue expanding its usage and areas of application, it has been essential to develop procedures aiming at improvement of its photostability.^{11–14} In this connection the extensive efforts have been made to photostabilize the curcumin^{11,13,17–18} including complexation with proteins,¹⁷ liposome and phospholipid,¹⁸ encapsulation into baker's yeast cells, β -cyclodextrin and starch,¹⁹ polymeric nanoparticles,^{20,21} copolymer micelles,²² and hydrogels.²³ Most of the above mentioned approaches have been

considered unavailing for practical purposes due to the complicated preparation procedure, limited efficience online and insufficient accessibility. Accordingly, the attempts to find a more suitable procedure to improve the photostability of curcumin are still greatly appreciated.

PAMAM dendrimers are a special class of hyperbranched polymers with a wide range of applications.^{24,25} Different modified PAMAM dendrimers have been find application in the biomedicine,^{26,27} sensors,^{28–31} dyes,^{32–34} and textiles.^{35,36} To the best of our knowledge, thus far, the modification of dendrimers with curcumin for enhancing their photostability have not been investigated. With this regard, recently we have synthesised new PAMAM dendrimers from zero, first and second generation, modified with curcumin and UV-absorber. They have been used as days for polyethylene terephthalate fabrics.^{1,2} Their photostability of such sensor systems, containing curcumin as signalling fragment is very important, for which are known to have low light resistance.

The aim of this work is to investigate the effect of the PAMAM dendrimer generation influence upon the photostability of the chemically bonded curcumin to the dendrimers. The effect of 2,4-dihydroxybenzophenone, on curcumin photostability has also been investigated. The light resistance of dyed polyethylene terephthalate fabrics with dendrimers have also been evaluated.

Materials and Methods

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All chemicals and instruments used in this study are listed in Table S1 and Table S2, respectively.

Results and discussion

Modified PAMAM dendrimers with curcumin

PAMAM dendrimers of zero, first and second generations were synthesized by a divergent synthetic method employing the reagent excess method starting from ethylenediamine by consecutive Michael addition and ester amidation reaction according to our previous reports.^{29,35} To synthesize the complete generation of PAMAM dendrimer, ethylenediamine was dissolved in methanol and cooled down. Methyl acrylate was then added drop-wise at stirring condition and under nitrogen atmosphere. The mixture was kept at ambient temperature for 168 h. The surplus of methyl acrylate and solvent was removed under vacuum at the temperature below 50°C resulting in a nearly colourless viscous solution of dendrimers. The synthesized dendrimers were modified with curcumin and 2,4-dihydroxybenzophenone by the method described recently.^{1,2} Modified with curcumin and benzophenone PAMAM dendrimers of various generations were obtained in a three-step synthesis. 2,4,6-Trichloro-1,3,5-triazine (Cyanuric chloride) has been used as a bridging agent between them, and its possibility of a gradual replacement of chlorine atoms depending on the thermal conditions has been used.

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The peripheral primary amino groups of PAMAM dendrimers from different generations have been reacted with cyanuric chloride at low temperature (t = 0-5 °C). The nucleophilic substitution of the second chlorine atom of the triazine cycle with curcumin was carried out at a temperature of 30-35 °C, while the benzophenone

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moieties were introduced to the dendrimer structure at a higher temperature (70-75 °C). Thus, <u>six</u> modified tricle Online PAMAM dendrimers of zero (CU-1, CU-4), first (CU-2, CU-5), and second (CU-3, CU-6) generation with covalently bounded benzophenone and curcumin residues were synthesized (Table S3). Their chemical structures and synthesis route of these compounds are depicted in Scheme 1 and Scheme 2. Meanwhile, the chemical structure of modified dendrimers was analysed using analytical techniques including FTIR, ¹H-NMR, ¹³C-NMR, elemental analysis and DSC and results summarized in Table S4.



Scheme 2. Chemical structures of curcumin and 2,4-dihydroxybenzophenone conjugated to PAMAM dendrimer of first and second generations (CU-2, CU-3, CU-5, CU-6).

Photodegradation of curcumin and modified dendrimers in solution based on absorption and fluorescence measurements

Due to its photosensitivity, curcumin is easily degrading to the different compounds when exposed to the light.¹⁵ This research intends to find the photodegradation rate of the curcumin before and after its modification with PAMAM dendrimer and 2,4-dihydroxybenzophenone as a UV-absorber. Normalised absorption spectra of

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initial compounds: curcumin and 2,4-dihydroxybenzophenone were plotted in Figure 1. Both_composition of the spectral region: the absorption maximum of curcumin is at 419 nm, while benzophenone absorbs in the ultraviolet region with a maximum at 278 nm. The Figure 1 also shows considerable overlap between the two spectra. The coupling of these substances to the dendrimer structure does not significantly alter the spectral curve, as can be seen from the absorption spectrum of dendrimer CU-5 and CU-6 given as an example.



Figure 1. Normalised UV-vis absorption spectra of curcumin, 2,4-dihydroxybenzophenone, CU-5 and CU-6.

As can be seen from Schemes 1 and 2, the dendrimers tested contain different numbers of curcumin and 2,4dihydroxybenzophenone units. Figure 2A shows the dependence of the molar absorption coefficient (ϵ) of the dendrimer generation, compared to the monomeric units. The results show a progressive increase in the values of ε depending on the number of curcumin and 2,4-dihydroxybenzophenone units bonded to the dendrimer structure. The lower values of dendrimers CU-4-CU-6 are because in them the number of curcumin units is smaller due to the presence of 2,4-dihydroxybenzophenone units. These results show that in the dendrimer structures, the curcumin units are respectively as follows: 8 (CU-1), 16 (CU-2), 32 (CU-3), 4 (CU-4), 8 (CU-5) and 16 (CU-6), which has also been confirmed by the corresponding NMR spectra (Table S4). A similar dependence of the fluorescence intensity of dendrimers is recorded, as can be seen from Figure 2B. Dendrimers have different quantum yields (Curcumin: 0.302, CU-1: 0.414, CU-2: 0.638, CU-3: 0.747) and fluorescence intensities respectively.^{1,3} The changes in the fluorescence quantum yields and molar absorption coefficient of the modified curcumins in accordance with the generation of dendrimers revealed that the photo-induced electron transfer proceeded from the core of the dendrimer molecule to the curcumin fluorophores located in its periphery which obviously affect the energy transfer upon excitation, thus increasing the fluorescence intensity and molar absorption coefficient.²⁸ On the other hand, the values of these indicators may be influenced by different factors such as the polarity of organic solvents and possible dipole-dipole interactions. The formation of hydrogen bonds can also lead to a change in the polarization of the curcumin chromophore system and non-irradiative deactivation processes to predominate in the $S_1 \rightarrow S_0$ transition.³

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Figure 2. A: Molar extinction coefficient of curcumin, 2,4-dihydroxybenzophenone and dendrimers (A): Fluorescence intensity of curcumin and CU-1– CU-3 (B).

The stability of curcumin and its derivatives, CU-1, CU-2, CU-3, CU-4, CU-5 and CU-6 was assessed by exposing their solutions (water/dioxane (4:1) (v/v), $c=5\times10^{-6}$ mol/L) to a UV lamp at 290-315 nm (peak at 302 nm) (9W, 240V) and ambient temperature and then the effect of light on their absorbance and fluorescence spectra investigated. Figure 3 shows the change of absorbance of curcumin and its dendrimer derivatives according to the irradiation time (Figure 3a-g). It is clear that the absorption decreases with the irradiation time due to the destruction of the chromophore system of curcumin. This effect was better pronounced in the case of monomeric curcumin. The smallest change in the absorption has been observed for CU-6 dendrimer, which contain sixteen fragments of curcumin and sixteen fragments of 2,4-dihydroxybenzophenone. Furthermore, the changes in the position of the absorption maximum have been observed. In this case during the irradiation, the absorption maximum of curcumin and modified dendrimers are hypsochomically shifted with approximately 40 nm. The highest change has been achieved for monomeric curcumin, which can be explained by different absorbance of the respective decomposed products. From the other hand the autooxidative transformation of curcumin via the mechanism described by Griesser et. al. might be the possible reason for the highest level of hypsochromic and hypochromic shifts for curcumin.¹⁶ Figure 3h plots the photodegradation rate (PR) of curcumin and modified dendrimers during irradiation based on absorption spectroscopy from which the linear dependence of the photodegradation process with following equations has been observed: PR (curcumin)(t)=3.67t-4.396 (R²=0.981), PR (CU-1)(t)=3.23t-3.256 (R²=0.986), PR (CU-2)(t)=2.71t-1.682 (R²=0.994), PR (CU-3)(t)=2.38t-4.342 (R²=0.988), PR (CU-4)(t)=1.45t-2.363 (R²=0.983), PR (CU-5)(t)=0.99t-3.613 (R²=0.953), PR (CU-6)(t)=0.56t-1.076 (R²=0.961).







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Figure 3. UV-vis absorption spectra of curcumin (a) and dendrimers CU-1 (b), CU-2 (c), CU-3 (d), CU-5 (f), CU-6 (g) in water/dioxane solution (4:1) (v/v) at concentration c=5×10⁻⁶ gl/L and dependence of photodegradation to the irradiation time (h).

After irradiation of 24 hours, 88% of curcumin, 77% of CU-1, 65% of CU-2, 57% of CU-3, 35% of CU-4, 24% of CU-5 and 12% of CU-6 have been degraded (Figure 4). This clearly shows that, after the binding of curcumin to the dendrimer periphery, its photodestruction has been reduced and this is proportional to the number of curcumin fragments. At dendrimers CU-1 - CU-3, the photostability of the CU-3, containing 32 photoactive curcumin fragments is highest i.e. the dendrimer structure affects the stability of curcumin. On the other hand, the incorporation of 2.4-dihydroxybenzophenone into the dendrimer molecule at a ratio of 1:1 to curcumin, stabilizes its photodestruction processes by 55-79%. This indicates that the 2,4-dihydroxybenzophenone has a strong influence on the photostability of curcumin, with the dendrimer generation also having a stabilizing impact. This effect is similar in the cases of dendrimer sensors, dendrimers with microbiological activity or drug delivery systems.37,38

Degradation (%) сизсие CU CU1CU4 CU2CU5 PAMAM Generation

Figure 4. Photodegradation of curcumin (CU) and PAMAM dendrimers (CU1-CU6) after 24h irradiation.

Table 1. Photodegradation Rate (PR) of curcumin and dendrimers CU-1-CU-6 based on absorbance, fluorescence in solution and fluorescence on solid PET.

Compounds	Absorbance		Fluorescence		Fluorescence on PET	
	PR (%/h)	R ²	PR (%/h)	R ²	PR (%/h)	R ²
Curcumin	3.67	0.980	3.42	0.958	3.21	0.953
CU-1	3.23	0.986	3.07	0.957	2.55	0.963
CU-2	2.71	0.995	2.34	0.972	2.00	0.982
CU-3	2.38	0.988	2.15	0.966	1.78	0.983
CU-4	1.45	0.983	1.23	0.985	0.99	0.970
CU-5	0.99	0.873	0.83	0.929	0.53	0.950
CU-6	0.52	0.961	0.33	0.904	0.24	0.933

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The photodegradation of curcumin and dendrimers has also been investigated by fluorescence spectroscopy/denvolo2737E more precise analytic method. The fluorescence intensity of all compounds has been measured after their excitation at the absorption maxima. The photodegradation rate of dendrimers has also been evaluated on the basis of fluorescence intensity during the irradiation (Figure 5). The photodegradation process of curcumin had occurred easily and quickly in comparison to those of the modified dendrimers. The highest and lowest photodegradation rates were obtained for curcumin (3.42) and dendrimer CU-6 (0.33) respectively, what is in accordance with the results obtained by absorption spectroscopy (Table 1).



Figure 5. Dependence of photodegradation of curcumin and dendrimers CU-1–CU-6 to time in water/dioxane (4:1) (v/v) solution at concentration of 5×10^{-6} mol/L based on fluorescence intensity.

Figure 6 shows the change in the fluorescence spectra of curcumin and its dendrimer derivatives CU-3 and CU-6 as a typical example. The difference between the dendrimers is only in the nature of the substituents. Dendrimer CU-3, has thirty-two curcumin units, while for CU-6 they are sixteen and the remaining sixteen are substituted with 2,4-dihydroxybenzophenone. The three compounds have different quantum yields and fluorescence intensities respectively.^{1,3} The comparison of their properties gives us a good possibility for the explanation of the effect of substituents on curcumin photostabilization. It was observed that the photodegradation of the initial curcumin is the greatest extent (Figure 6A). After its binding to the dendrimer molecule, the destruction is delayed (Figure 6B). In the case of dendrimer CU-6 which molecule have sixteen 2,4-dihydroxybenzophenone units, this process was very low pronounced (Figure 6C).



Figure 6. Fluorescence spectra of curcumin (A) and dendrimers CU-3 (B), CU-6 (C), in water/dioxane solution (4:1) (v/v) (c=5×10⁻⁶ mol/L), depending on the irradiation time (λ_{ex} = 420 nm)

It is known that the hydroxyl group from 2,4-dihydroxybenzophenone is rapidly converted into a "phenol" form by absorption of light energy (Scheme 3). This phenomenon arises from its ability to undergo intramolecular proton transfer from the hydroxyl group to the adjacent carbonyl group following light absorption in the UV region. This is an internal conversion process, as the absorbed UV light energy dissipates as harmless heat, with almost 100% efficiency.³⁹ On the other hand, it might be attributed to the fact that during the absorption of the light, dendritic structure converts the light energy into fluorescence emission and reduced the destructive effect of light.⁴⁰



Scheme 3. Proposed internal conversion process of the 2,4-dihydroxybenzophenone with absorbing the UV light energy.

Photodegradation of dyed polyethylene terephthalate (PET) fabrics

UV absorbers and antioxidant compounds could be used to neutralize the destructive effect of the energy absorbed from the UV light.³⁷ For this purpose, the UV absorbers and antioxidant could be applied on textiles materials by different procedures, while most of them need to be used in a separate process that is time and energy-consuming. The synthesised dendrimers in this research included a UV absorber which could be attached to the textiles at the same step of dyeing processes. To examine the photostability of the synthesized compounds, PET fabrics were dyed using curcumin, CU-1, CU-2, CU-3, CU-4, CU-5 and CU-6 according to our previous works.^{41,42} Then, the dyed fabrics were irradiated for 24 hours and their fluorescence spectra were recorded in dependence of irradiation time. The fluorescence spectra of dyed PET fabrics have also been studied

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during the irradiation and the results were plotted in Figure 7. The figure shows that upon irradiation and the results were plotted in Figure 7. The figure shows that upon irradiation and the fabrics decreases, and this decrease depends on the type of the dendrimer. The photodegradation rate of the PET fabrics dyed with curcumin and modified dendrimers during the irradiation was determined (Figure 7h).





Figure 7. Fluorescence spectra of PET fabrics dyed with curcumin (a) and synthesized compounds CU-1 (b), CU-2 (c), CU-3 (d), CU-4 (e), CU-5 (f), CU-6 (g), dependence of photodegradation rate from the irradiation time of curcumin and dendrimers CU-1–CU-6 on PET fabric (h).

It was of interest to compare the results from the photodestruction of curcumin and the corresponding dendrimers in solution and after deposition of the PET fabrics using absorption and fluorescence spectroscopy (Figure 8). In all cases the photodestruction rate of monomeric curcumin is the highest. Its degradation has been stabilised upon the attachment to dendrimer molecules. The introduction of more curcumin units leads to their stabilization. Further stabilisation has been achieved using 2,4-dihydroxybenzophenone as a photostabiliser, and the effect also depends on its amount into the dendrimeric structure. All calculated photodegradation rates constants in the solid state are lower, if compared with those in the solution. This is most likely due to the accelerated photodegradation process in humid environments which atmospheric humidity conditions play an important role in the photocatalysed degradation of curcumin and all dendrimers.⁴³



Figure 8. Photodegradation rate of curcumin and modified dendrimers in solution and on PET fabric by absorption and fluorescence spectroscopy

Conclusions

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The photostability of six recently synthetized PAMAM dendrimers from zero, first and second generation modified with curcumin and 2,4-dihydroxybenzophenone as UV-absorber has been investigated in solution and after their deposition on the PET fabric. The results have showed an increase in the photostability of curcumin

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after its binding to the dendrimer molecule. Further enhancement of photostability has been obtained in the dendrimer molecule. Further enhancement of photostability has been obtained in the dendrimer CU-6. It has been shown that, the dendrimer generation also influences on the photostability, which increases with the dendrimer generation. Curcumin and all dendrimers have been loaded on a polyethylene terephthalate fabric and their photostability has been investigated by measuring the fluorescence intensity before and after irradiation. The same dependence has been found as that from the investigations in solution, what indicates that the test compounds retain their properties after being applied to the textile matrix. On the other hand, it means the absence of negative influence of the textile matrix upon the dendrimers photostabilization. The good results indicate that binding of curcumin to dendrimers leads to its photostabilization. On the other hand, the multifunctionality of the dendrimer structures allows the introduction of compounds with UV absorber properties, thus further stabilizing the light resistance of curcumin. These results upgrade our previous studies of the same compounds and extend the possibility of using them as photostable sensors for metal ions and protons or dendritic dyes.

Conflicts of interest

There are no conflicts to declare.

Appendix A. Supplementary data

Supplementary data to this article can be found online at,,,,,,

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