Asian Journal of Chemistry; Vol. 27, No. 7 (2015), 2587-2592

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2015.18414

Poly(aryl ether) Dendritic Structures Based on 1,4,8,11-Tetraazacyclotetradecane Core: Synthesis, Characterization, Photophysical Properties and Biological activity

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Received: 7 July 2014; *Accepted*: 17 September 2014; *Published online*: 30 March 2015; AJC-17085

This work describes the synthesis of two new dendrimers consisting of a 1,4,8,11-tetraazacyclotetradecane (cyclam) core appended with poly(aryl ether) dendritic structures carrying a donor (4-methyl-7-hydroxycoumarin) on the surface. Its structure was determined by ^{1}H NMR, ^{13}C NMR and elemental analysis. The photophysical properties of the series of poly(aryl ether) dendrimers have been determined and the effect of the generation number on the absorption and emission properties of the synthesized dendritic structures was investigated. As the chromophore group number on the surface of the dendritic structure increased, molar absorptivity coefficients and emission intensities of the structures were found to increase. The prepared dendritic structures were tested for their antimicrobial activity against, *Salmonella typhimurium* NRRLB, *Micrococcus luteus*, *Pseudomonas aeruginosa*, *Enterococcus fecalis* ATCC-29212, *Bacillus cereus* ATCC-117787, *Klepsiella pneumonia*, *Bacillus subtilis* NRS-744, *Proteus vulgoris*, *Yersinia enterolitica* and *Saccharomyces cereviciae*. Synthesized dendritic structures showed moderate activity against different strains of bacteria.

Keywords: Dendrimers, Photophysics, Absorption spectra, 1,4,8,11-Tetraazacyclotetradecane, Biological activity.

INTRODUCTION

Dendrimers have received considerable attention over the last 20 years due to the special properties by their unique physical property and structure, such as highly branched structure, monodispersed molecular weight, globular and symmetrical conformation and high density of peripheral functionalities[1-6]. These functional groups are reactive, thereby allowing modification of dendrimers. Their utility as molecular scaffolding in many applications, *e.g.*, liquid crystals, drug delivery systems, catalytic nanoreactors and light-harvesting systems[7-11]. A great deal of attention has been paid to this class of macromolecules owing to their new forms of structure organization which combines the properties of low and high molecular weight compounds. This utilization arises from the fact that dendrimers have the ability to concentrate a high number of end groups in high concentration in one molecule.

As the field of dendrimers rapidly grows[12], a few key architectures clearly stand out as the most attractive and best documented ones within the highly diverse pool of branched polymers described so far. Poly(aryl ether) dendrimers belong to this class because the simplicity, reability and flexibility of their convergent synthesis[13,14], together with the commercial availability of the monomer itself, strongly contribute to the prominent role of this structure within the dendrimer literature. Indeed, poly(aryl ether) dendritic macromolecules have been widely used by independent groups for a variety of applications[15-18] and their chemistry[19,20] and properties[21] are now well established.

Macrocyclic structures are extremely favorable for metal complexation and, thus, a large number of macrocyclic ligands have been synthesized because of their importance in coordination chemistry. Among the various ligands, the 1,4,8,11-tetraazacyclotetradecane (cyclam) is one of the most studied azamacrocycles[22-28]. 1,4,8,11-Tetraazacyclotetradecane fourteen membered tetraamine macrocycles show the ability to complex various transition metal cations and their complexes are often highly thermodynamically and kinetically stable with respect to metal ion dissociation[29]. 1,4,8,11-Tetraazacyclotetradecane and its derivatives have been studied as carriers of metal ions in antitumor, imaging applications and as anti-HIV agents[30,31]. In most cases, the cyclam derivatives contain pendant functionalities to increase complex stabilities or to allow attachment of other chemical species to the macrocyclic structure[31].

1,4,8,11-Tetraazacyclotetradecane is commercially available and its nitrogen atoms can be easily linked to functional units, thus paving the way to a large variety of derivatives. For

example, dendrons can be appended to the cyclam core. The synthesis of cyclam-cored dendrimers proceeds *via* a convergent approach, *i.e*., by coupling dendrons, containing appropriate functional units at the apical location, to the nitrogen atoms of the cyclam core[28].

In continuation of our investigations on photoactive dendritic structures we thought that cyclam could be a suitable core for constructing dendrimers because they are less affected by steric constraints. These kinds of structures are promising candidates for variety of applications. Compounds derived from cyclams by appending suitable subunits having signaling functions have been devised to probe the important ionic guests and physical properties of system[32-34].

We have previously reported the synthesized poly(aryl ether) dendritic structures **1** and **2** bearing chromophore peripheral groups and *via* convergent methods and to determine their photophysical properties and fluorescence quantum yields[35]. Recently, we have synthesized two new dendrimers consisting of a calix[4]arene and we have carried out photophysical investigations[36,37]. In this paper, we report the synthesis of two new dendrimers consisting of a cyclam core and carried out photophysical and biological activity of the dendrimers.

EXPERIMENTAL

All commercially available reagents were used without further purification. K_2CO_3 was activated by heating at 150 °C overnight under vacuum and stored in a desiccator. Column chromatography was carried out with Merck silica gel 70-230 mesh. Preparative TLC plates were Merck aluminum sheets covered with silica gel 60 F_{254}. The FTIR spectra were recorded via the KBr pellet method by using a Perkin-Elmer 1605 FTIR spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a BRUKER DPX-400 High Performance Digital FT NMR, with tetramethyl silane (TMS) as the standard. The compounds were characterized by an Elementar Vario CHNS-932 (LECO) elemental analysis instrument. UV-visible absorption spectra were measured using a Shimadzu UV-1700 Pharma spectrophotometer. The photoluminescence were recorded on a VARIAN CARY ECLIPSE Fluorescence spectrophotometer.

Synthesis of compound 4: 1,4,8,11-Tetraazacyclotetradecane (1 eq., 0.032 g, 0.160 mmol); K_2CO_3 (40 eq., 0.885 g, 6.400 mmol), 4-(4-methylcoumarin-7-yl-oxymethyl)benzylbromide **1** (4.4 eq. , 0.253 g, 0.704 mmol) in dry chloroform (50 mL) was refluxed under N_2 for 72 h. After cooling, the solution was filtered and filtrate was evaporated. The residue was partitioned between H_2O and CH_2Cl_2 and the organic layer was washed with water. The separated organic layer was evaporated and the product was purified by column chromatography on silica gel (100:3.5 CH_2Cl_2/MeOH) to yield white solids. Yield, 59 %. m.p.: 139 °C. IR (KBr, ν_{max}, cm^{-1}): 1733 (C=O), 1611 (C=C), 1390 (CH_3), 1070 (C-N). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.78 (t, 4H, *J* = 10 Hz, C*H*$_2$), 2.4 (d, 12H, *J* = 0.88 Hz, C*H*$_3$), 2.55 (t, 8H, *J* = 6.4 Hz, C*H*$_2$N), 2.62 (s, 8H, C*H*$_2$N), 3.47 (s, 8H, Ar-C*H*$_2$), 5.09 (s, 8H, ArOC*H*$_2$), 6.14 (s, 4H, C*H*=C), 6.86 (d, *J* = 2.43 Hz, 4H, ArH, coumarin), 6.95-6.92 (m, 4H, ArH, coumarin), 7.31 (d, *J* = 17.72 Hz, 16H, Ar-H). 7,5 (d, 4H ArH, coumarin). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 18.66, 23.99, 50.59, 51.51, 59.06, 70.43, 101.82, 112.01, 112.89, 113.72, 125.58, 127.43, 129.19, 134.11, 140.42, 152.56, 155.18, 161.23, 161.74. Anal. calcd. for $C_{82}H_{80}O_{12}N_4$: C, 60.29; H, 4.94; N, 3.43; found: C, 61.09; H, 5.16; N, 3.80.

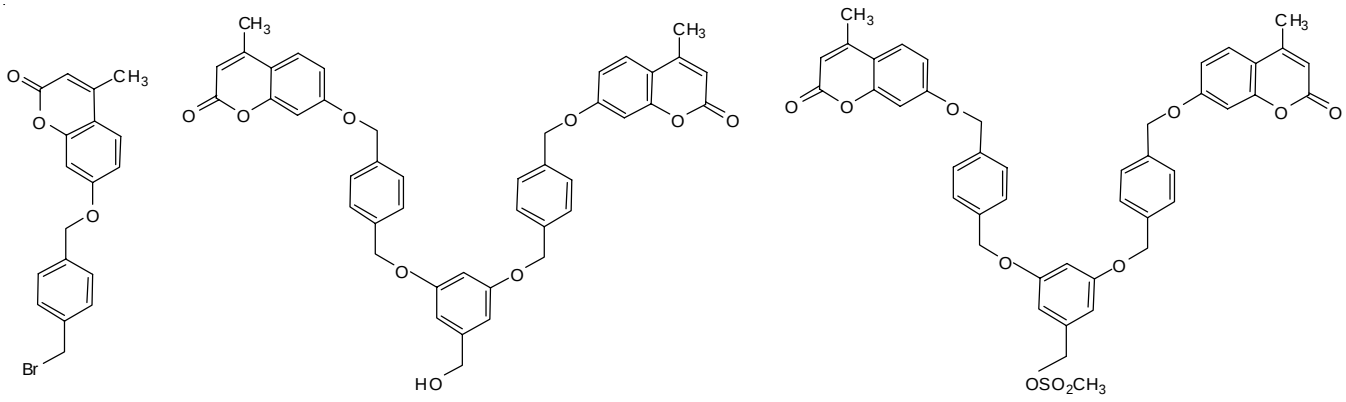
Synthesis of compound 5: 1,4,8,11-Tetraazacyclotetradecane (1 eq., 0.013 g, 0.065 mmol); K_2CO_3 (40 eq., 0.359 g, 2.600 mmol), compound **3** (4.4 eq., 0.222 g, 0.286 mmol) in dry chloroform (40 mL) was refluxed under N_2 for 72 h. After cooling, the solution was filtered and filtrate was evaporated. The residue was partitioned between H_2O and CH_2Cl_2 and the organic layer was washed with water. The separated organic layer was evaporated and the product was purified by column chromatography on silica gel (100: 3.5 CH_2Cl_2/MeOH) to yield white solids. Yield, 43 %. mp.: 132 °C. IR (KBr, ν_{max}, cm^{-1}): 1722 (C=O), 1612 (C=C), 1388 (CH_3), 1070 (C-N). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 1.83 (s, 4H, C*H*$_2$), 2.39 (s, 24H, C*H*$_3$), 2.54 (s, 8H, C*H*$_2$N), 2.61 (s, 8H, C*H*$_2$N), 3.39 (s, 8H, ArC*H*$_2$), 4.85 (s, 16H, ArC*H*$_2$O), 5.07 (s, 16H, OC*H*$_2$Ar, 6.12 (s, 8H, C*H*=C, coumarin), 6.42 (s, 4H, ArH, coumarin), 6.68 (d, *J* = 1.3 Hz, 8H, ArH), 6.82 (d, *J* = 2.36 Hz, 16H, ArH, coumarin) 6.93-6.90 (m, 8H, ArH, coumarin), 7.50-7.36 (m, 32H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 18.66, 44.93, 50.27, 51.69, 59.07, 69.38, 70.11, 100.70, 101.85, 107.65, 112.05, 112.79, 113.79, 125.63, 127.67, 127.75, 135.46, 137.23, 143.25, 152.53, 155.14, 159.70, 161.16, 161.56. Anal. calcd. for $C_{182}H_{160}O_{32}N_4$: C, 74.98; H, 5.53; N, 1.92; found: C, 74.19; H, 5.86; N, 1.71.

Antimicrobial screening: The biological activities of the dendritic structures were tested against different microorganisms with CH_2Cl_2 as the solvent. The sample concentration was 100 mg. In this study, *Salmonella typhimurium* NRRLB-4420, *Micrococcus luteus*, *Pseudomonas aeruginosa*, *Enterococcus fecalis* ATCC-29212, *Bacillus cereus* ATCC-117787, *Klepsiella pneumonia*, *Bacillus subtilis* NRS-744, *Proteus vulgaris*, *Yersinia enterocolitica*, *Saccharomyces cereviciae* were used as bacteria. YEPD medium cell culture was prepared as described by Connerton[38]. Ten milliliters of YEPD medium were inoculated with each cell from plate cultures. Yeast extract 1 % (w/v), bactopeptone 2 % (w/v) and glucose 2 % (w/v), was obtained from Difco. Microorganisms were incubated at 35 °C for 24 h. About 1.5 mL of these overnight stationary phase cultures were inoculated onto 250 mL of YEPD and incubated at 35 °C until OD600 reached 0.5. The antibiotic sensitivity of the polymers was tested with the antibiotic disk assay as described[39]. Nutrient agar (NA) was purchased from Merck. About 1.5 mL of each prepared different cell culture were transferred into 20 mL of nutrient agar and mixed gently. The mixture was inoculated into the plate. The plates were rotated firmly and allowed to dry at room temperature for 10 min. Prepared antibiotic discs (100 mg/disc) were placed on the surface of the agar medium[40]. The plates were kept at 5 °C for 30 min and then incubated at 35 °C for 2 days. If a toxic compound leached out from the disc, it means that the microbial growth is inhibited around the sample. The width of this area expressed the antibacterial or antifungal activity by diffusion. The zones of inhibition of microorganism growth of the dendritic structures were measured with a millimeter ruler at the end of the incubation period.

RESULTS AND DISCUSSION

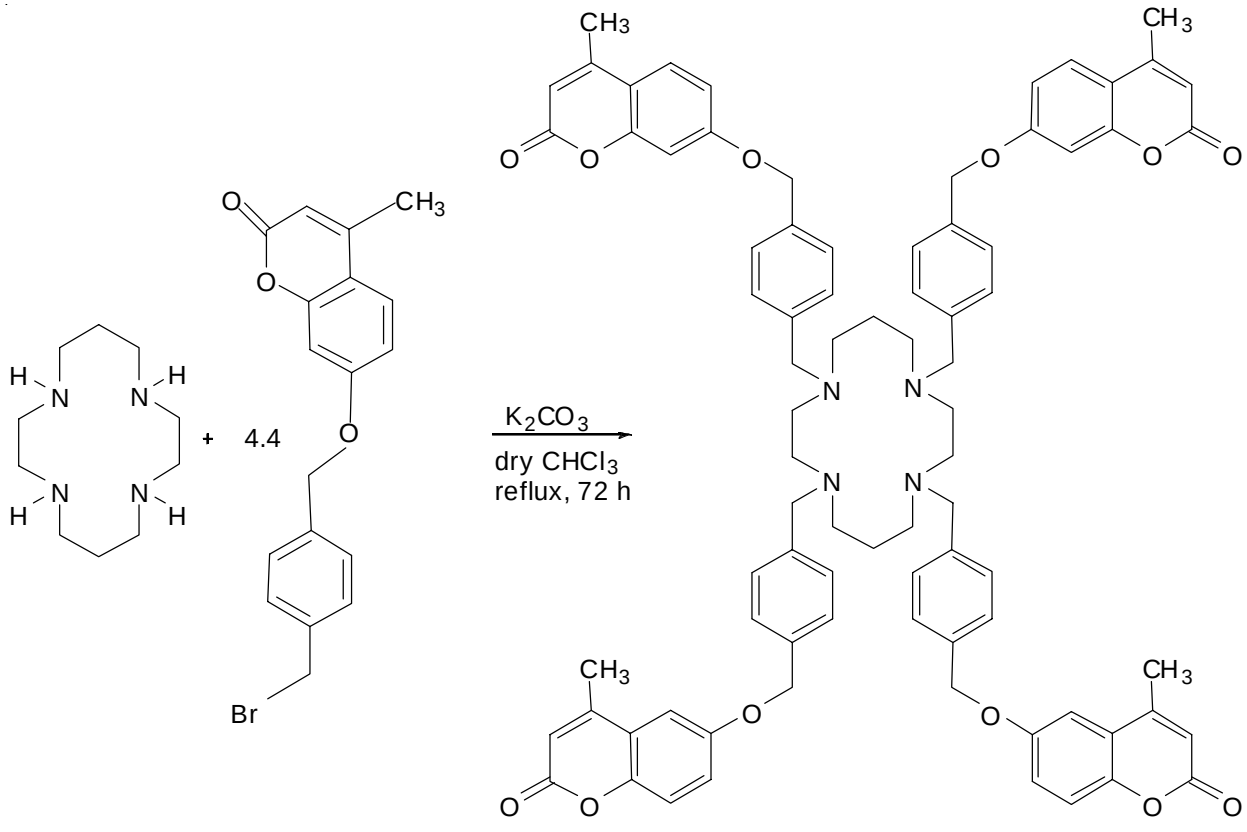
The synthesis initially involves the preparation of 4-(4-methylcoumarin-7-yl-oxymethyl)benzylbromide **1** and compounds **2**, **3** according to the literature procedures[35] (**Scheme-I**). Under typical Williamson ether synthesis conditions in the presence of K_2CO_3, 1,4-*bis*(bromomethyl)-benzene was reacted with 4-methyl-7-hydroxycoumarin to synthesize compound **1** in a yield[35] of 41 %. Following a standard convergent strategy, the first generation of benzyl alcohol (compound **2**) was prepared in 68 % yield through a coupling reaction of compound **1** and 3,5-dihydroxybenzyl alcohol monomer (**Scheme-I**)[35]. Compound **2** was converted to the compound **3** in 78 % yield using methane sulphonyl chloride in the presence of excess NEt_3 at -10 °C[35]. Following a standard convergent strategy, in the presence of K_2CO_3, cyclam was reacted compound **1** in chloroform at reflux temperature to give compound **4** in 59 % yield (**Scheme-II**). The ^{1}H NMR spectrum of compound **4** reflects several characteristic features of both cyclam and compound **1** systems: (i) the presence of two triplets and one singlet due to methylene groups (1.78, 2.55, 2.62 ppm, respectively) of cyclam; (ii) the presence of two singlet of $ArCH_2$ and $ArOCH_2$ groups at 3.47 and 5.09 ppm, respectively being clear evidence for a tetra-substituted conformation of cyclam. All in accordance with proposed structure of the whole system.

Following a standard convergent strategy, in the presence of K_2CO_3, cyclam was reacted compound **3** in chloroform at



1 **2** **3**

Scheme-I

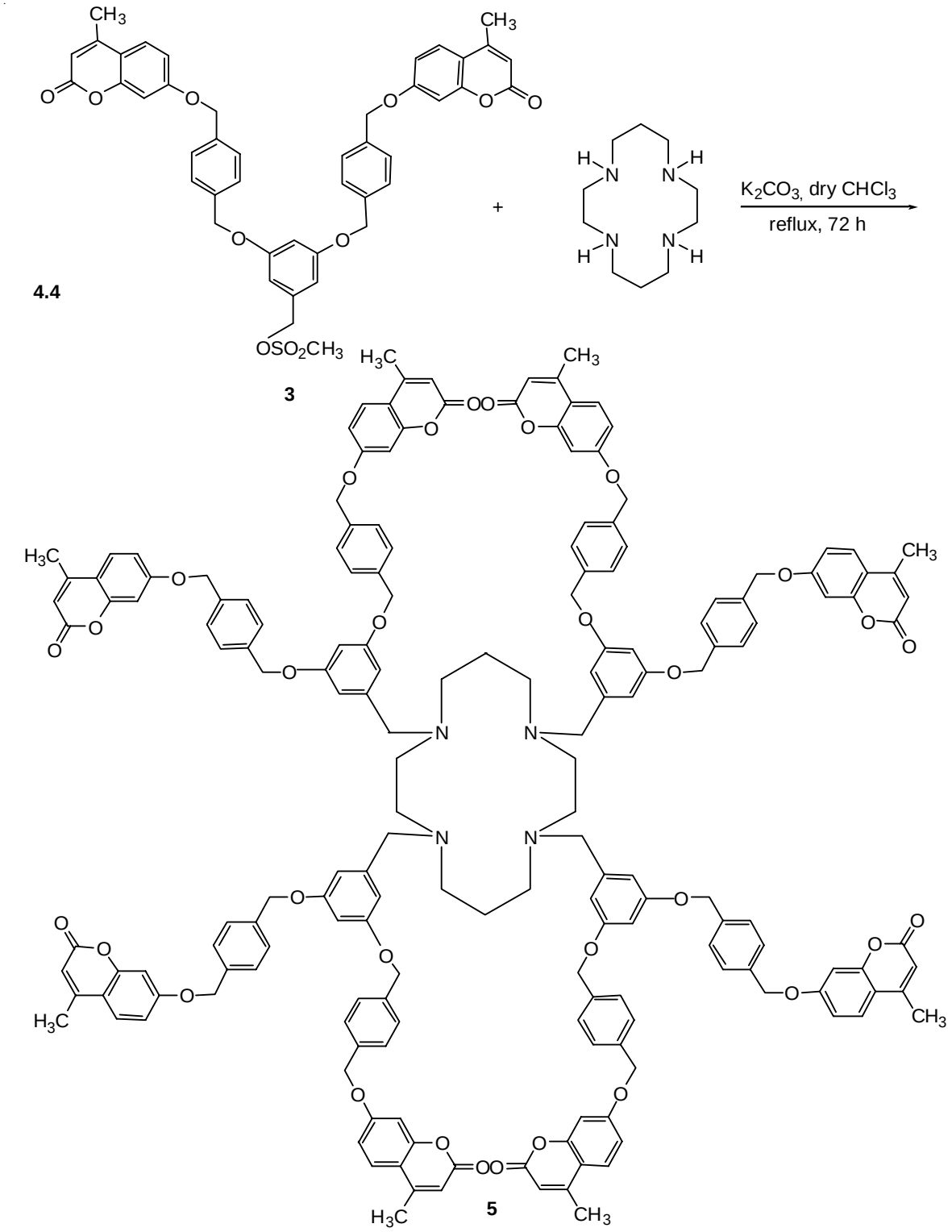


1 **4**

Scheme-II: Synthesis of dendrimer compound **4**

reflux temperature to give compound **5** in 43 % yield (**Scheme-III**). The ^{1}H NMR spectrum of compound 5 reflects several characteristic features of both cyclam and compound **1** systems: (i) the presence of three singlet due to methylene groups (1.83, 2.54, 2.61 ppm, respectively) of cyclam; (ii) the presence of three singlet of $ArCH_2$ and $ArCH_2O$, OCH_2Ar groups at 3.39, 4.85 and 5.07 ppm, respectively being clear evidence for a tetra-substituted conformation of cyclam. All in accordance with proposed structure of the whole system.

Photophysical properties: The investigated dendritic structures compounds **4** and **5** consist of four 4-methyl-7-hydroxycoumarin units (compound **4**), eight 4-methyl-7-hydroxycoumarin units (compound **5**), respectively. The absorption and fluorescence emission spectra of these compounds have been investigated[35] in CH_2Cl_2. In these measurement 1×10^{-5} M solutions of each compound was used. Fig. 1 illustrates the absorption properties of the dendrimers consisting of a cyclam core compounds **4** and **5**. Accordingly, the spectra



Scheme-III: Synthesis of dendrimer compound **5**

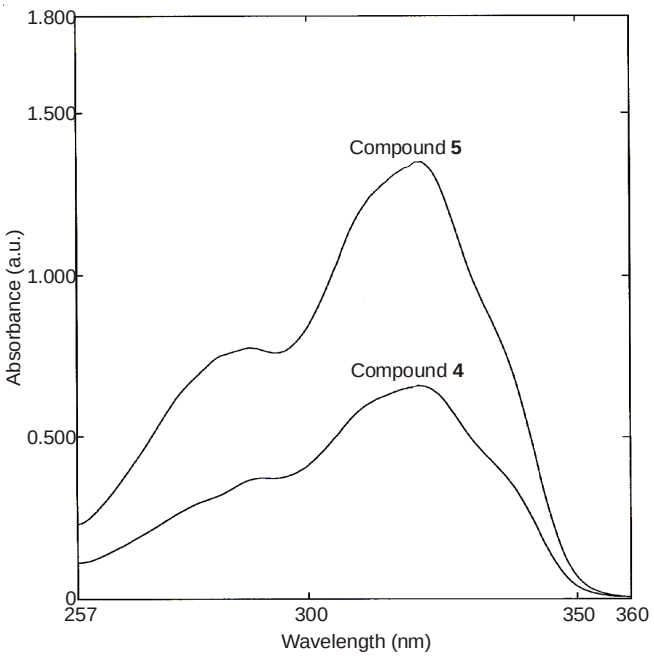


Fig. 1. Adsorption spectra of dendrimers having cyclan core compounds **4** and **5** in CH_2Cl_2

of these compounds show absorption maximum in the 288, 320 nm. As expected, an increase in the generation number leads an increase in the number of the peripheral chromophores and doubles the absorption from one to the next. Hence, with increasing generation number, the amount of light that the peripheral antenna is capable of harvesting is dramatically enhanced. Compound **4** contains 4-methyl-7-hydroxycoumarin and benzene chromophoric groups. Compound **5** contains dimethoxybenzene unit additionally. It is concluded that the absorption spectra of the examined compounds are those expected from the spectra of the component chromophoric units. Fig. 2 illustrates the emission properties of the dendrimers consisting of a cyclam core (compounds **4** and **5**). In these measurement 1×10^{-5} M solutions of each compound was used. Excitation of the dendrimers at $\lambda_{max} = 320$ nm (maximum absorption wavelength for peripheral chromophore) resulted in emissions at 381 nm (compound **4**), 384 nm (compound **5**).

Antimicrobial activity of the dendritic structures: The dendritic structures thus obtained, were tested against different microorganisms that are commonly employed in biodegradability examinations. The results were standardized against

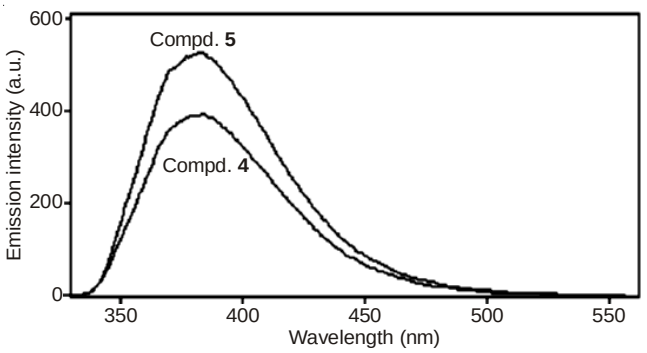


Fig. 2. Emission spectra of dendrimers having cyclano core compounds **4** and **5** in CH_2Cl_2

Ciprolfoxacin, Chloramphenicol, Eritromycin, Penicillin G and Amikacin and under the same conditions. The data reported in Table-1 and are the average data of three experiments. The results show that the investigated dendritic structures have moderate biological activity comparable with that of standard drugs such as Ciprolfoxacin, Chloramphenicol, Eritromycin, Penicillin G and Amikacin. These results may be traced to nitrogene content of this dendritic structures. As expected compound **4** is less effective to inhibit the growth of microorganisms. Although the nitrogen content of the dendritic structures are the same compound **4** is less effective to inhibit the growth of microorganisms. Although the lipophilic portion of the substance is important to biological function in general, the polar group contributes to biological activity. Thus, the activity of these compounds may allow to design antimicrobial systems specifically effective against certain microorganisms and for probably certain health care a great deal of practical applications.

Conclusion

We have synthesized two new dendritic structures bearing cyclam as a core through convergent synthetic strategy. It can be seen from the absorption and emission spectra (Figs. 1, 2) that as the number of peripheral chromophores double from one generation to the next, the amount of absorbed and emitted light also nearly doubles[35]. The synthesized dendritic structures have good biological activity comparable with that of standard drugs as Ciprolfoxacin, Chloramphenicol, Eritromycin, Penicillin G and Amikacin.

In conclusion, cyclam (1,4,8,11-tetraazacyclotetradecane) can be easily functionalized with dendrons at each one of its

TABLE-1
ANTIMICROBIAL EFFECTS OF THE COMPOUNDS (mm OF ZONES)

	Standards of antibiotic discs					Compound **4**	Compound **5**
	CIPS	C30	E15	P10	AM10	100 µg	100 µg
Salmonella typhimurium	32	28	9	4		11	14
Micrococcus luteus	-	-	-	-	19	10	16
Pseudomonas aeruginosa	-	-	-	-	-	13	17
Enterococcus fecalis	32	0	-	8	-	16	22
Bacillus cereu	-	-	-	-	11	12	19
Klepsiella pneumonia	39	36	-	-	-	20	24
Bacillus subtilis					-	18	24
Proteus vulgoris	36	32	6	0	20	12	14
Yersinia enterocolitica	-	-	-	-	-	19	23
Saccharomyces cereviciae	31	34	-	-	-	11	15

CIPS (Ciprolfoxacin), C30 (Chloramphenicol), E15 (Eritromycin), P10 (Penicillin G.), AM10 (Amikacin)

four nitrogen atoms. It is very interesting core for constructing dendritic structures. These dendrimers have potential as the construction of mixed (dendritic) ligand complexes and molecular recognition materials.

ACKNOWLEDGEMENTS

The authors thank Afyon Kocatepe University Research Fund (Grant No. 07.FENED.08) for financial support of this work. The authors are also indebted to Assoc. Prof. S. Elif Korcan for the biological activity studies.

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