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New cyclen-cored dendrimers functionalized with pyrene: Synthesis characterization, optical and photophysical properties

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ABSTRACT

New cyclen (1,4,7,10-teraazacyclododecane) cored dendrimers up to the second generation, functionalized with 4, 8 and 16 pyrene units, respectively, were synthesized following a convergent procedure. All new compounds were characterized by NMR spectroscopies and ESI or MALDI TOF mass spectrometry. The optical and photophysical properties of the new dendrimers were studied in THF solution. Absorption spectra showed the typical absorption bands of pyrene moieties. In the fluorescence spectra, monomer as well as excimer emission were observed for all compounds. An increased proportion of excimer emission was observed in the dendrimer of the highest generation.

Introduction

Dendrimers are macromolecules presenting a well-defined structure which have been extensively studied in the last decades due to the large amount of potential applications in materials and biological science.[1–7] Among them, photoactive dendrimers, able to give light harvesting, changing the initial wavelength of the incident light like the antennas of photosystems do during the photosynthesis, are presenting a special interest.[8–10] Specific photophysical properties, such as excimer and exciplex formation, charge transfer (CT) or resonance energy transfer (RET), are observed in photoactive dendrimers, depending on the nature of the different types of chromophore placed in their structures. The incorporation of photoactive metals in dendrimers have been achieved through the incorporation of porphyrin or bipyridine based ligands and have found applications in sensors, catalysis or nanomaterials for drug delivery.[11–13]

Other metals were incorporated at the core of dendrimers by means of coordination with aza-macrocycles. This kind of ligand is very effective due to its chelating effect.[14,15] Moreover, the ability of complexation of aza-macrocycles towards various metal ions have been reviewed.[11,16] Among them, 1,4,7,10-teraazacyclododecane (cyclen), has shown good coordination ability for a large range of metals.[17–20] This has lead to various applications in ion sensing, ion carriers and medical diagnosis.[14,21–28] Dendrons have been appended to a cyclen core[14,29–32] and sensitization of lanthanide complexed with cyclen based ligands have been observed from various chromophores.[33–35]

In our research group we have been focusing on pyrene as chromophore, studying its ability to transfer energy to chromophores such as porphyrins and fullerenes.[33,36] The special interest in pyrene emission is due to its ability to form excimers. Dendrimers built with numerous pyrene units at the periphery are therefore presenting various types of photophysical processes.[37] A linear dependence between the excimer formation and the generation number has been previously reported for a series of pyrene labeled dendrimers.[38] Since only a few reports about energy transfer from pyrene to lanthanides are available,[39–42] we have designed novel series of cyclen cored dendrimers with an increasing number of pyrene units at the periphery. In this work, we are presenting the synthesis as well as the optical and photophysical properties of the free cyclen dendrimers with 4, 8 and 16 pyrene units, respectively.

Results and discussion

Synthesis of the dendrimers

The synthesis of the cyclen-cored dendrimer of the zero generation (**2**) and first generation dendrimer (**5**) are illustrated in Scheme 1. Firstly, bromination of 1-pyrenebutanol was carried out in the presence of CBr_4 and PPh_3 in anhydrous THF to give the corresponding 1-(4-bromobutyl)pyrene **1**.[11] Afterwards, **1** was reacted with cyclen (1,4,7,10-tetraazacyclododecane) tetrahydrochloride salt to afford the desired compound **2**. For the

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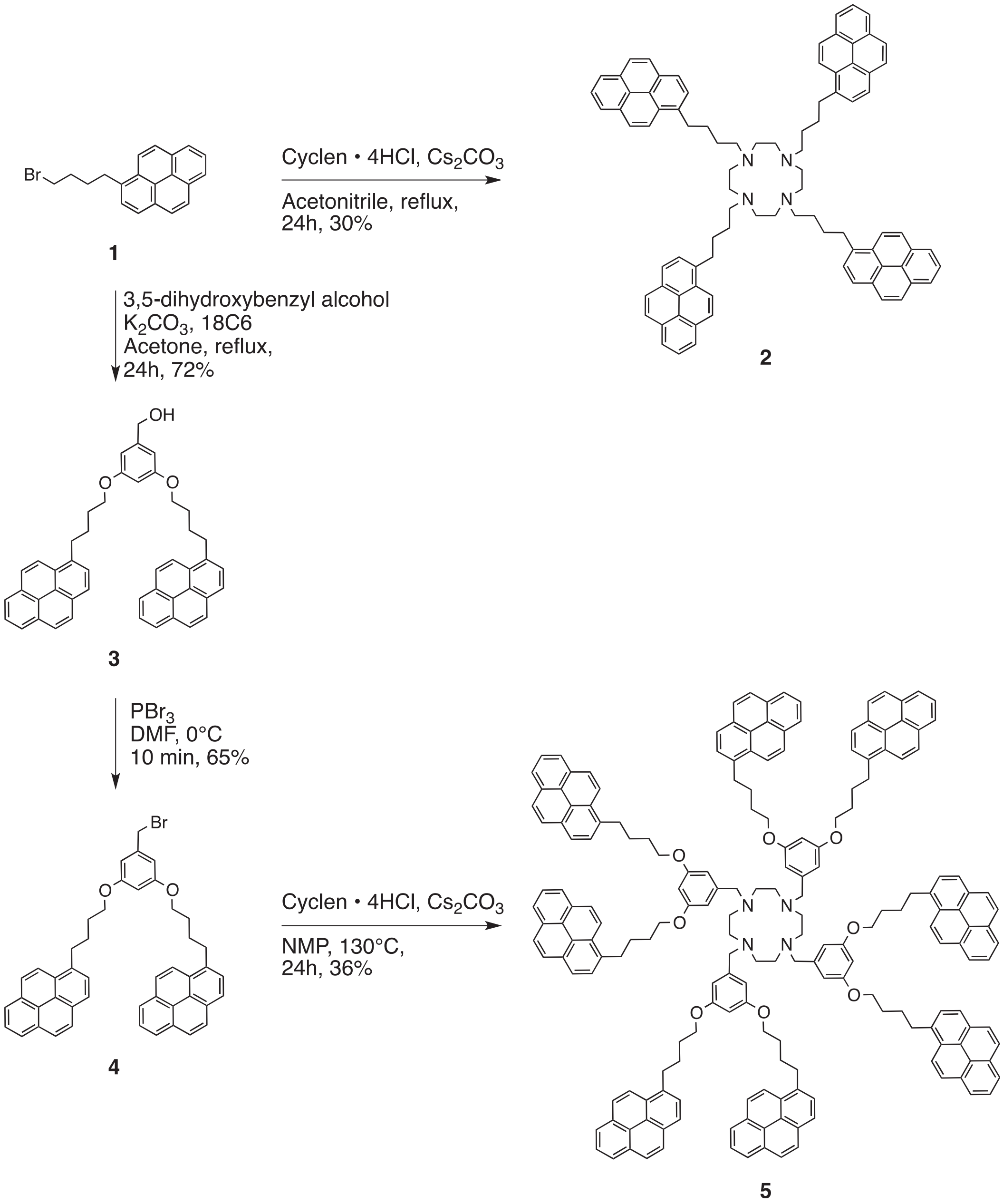

Scheme 1. Synthesis of compound **2** and first generation dendrimer **5**.

synthesis of the first generation dendrimer **5**, the brominated intermediate **1** was reacted in the presence of 3,5-dihydroxybenzyl alcohol and a catalytic amount of 18-crown-6 in anhydrous acetone to give the first generation alcohol **3**. Bromination of **3** in the presence of PBr_3 in DMF at 0 °C lead to the corresponding brominated dendron **4**.[43] Finally, **4** was reacted with cyclen tetrahydrochloride salt using Cs_2CO_3 as base and NMP as solvent to obtain the desired first generation dendrimer **5** in moderate yield.

The second generation dendrimer **8** was prepared similarly, using the convergent approach as depicted in Scheme 2. The brominated first generation dendron **4** was reacted in the presence of 3,5-dihydroxybenzyl alcohol, potassium carbonate and a catalytic amount of 18-Crown-6 in DMF to obtain the second generation benzyl alcohol **6**. This compound was brominated to give the corresponding alkyl bromide **7**, using the same reaction conditions employed for the bromination of compound **3**. Brominated dendron **7** was further reacted in the presence of cyclen tetrahydrochloride salt using Cs_2CO_3 as base and NMP as solvent to give the second generation dendrimer **8** in moderate yield.

Characterization of the dendrimers

All obtained dendrimers were fully characterized by ^{1}H and ^{13}C NMR spectroscopies and the structures were confirmed by ESI or MALDI-TOF mass spectrometry. In the ^{1}H NMR spectrum of the cyclen-cored dendrimer of generation zero (**2**), a broad singlet at 2.61 ppm indicating the presence of the aliphatic protons CH_2-N- of the cyclen core was seen. The ^{13}C NMR of compound **2** showed signal at 51.7 ppm attributed to the carbon of the cyclen, which indicated a full substitution of the four nitrogen atoms of the cyclen core. The MALDI-TOF spectrum of **2** exhibited a molecular ion peak at $C_{88}H_{84}N_4$ $[M]^+$ $m/z = 1197.67$ g/mol, which is very close to the calculated value ($m/z = 1197.76$ g/mol). This confirmed that