Synthesis, Structural Analysis and Self-Assembly Study of Supramolecular Janus Dendrimers

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Abstract

Janus-dendrimers represent a new class of supramolecular amphiphiles containing two structurally different dendritic building blocks attached to each other by chemical bonds.

In this research project, new libraries of Janus-dendrimers as well as twin-dendrimers were synthesized. Structural analysis, self-assembly mode and liquid crystalline (LC) behavior of these dendrimers were explored.

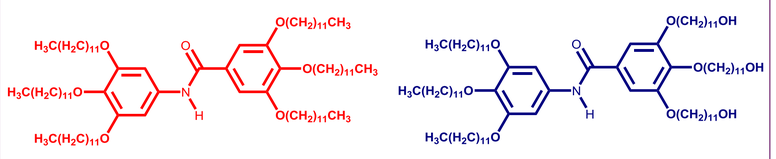


Figure 1. Examples of twin (left) and Janus-dendrimers (right).

Introduction

Dendrimers are perfectly branched monodisperse macromolecules with a regular and controlled three-dimensional topology. The primary structural unit or a fragment of a supramolecular dendrimer is known as **dendron**.

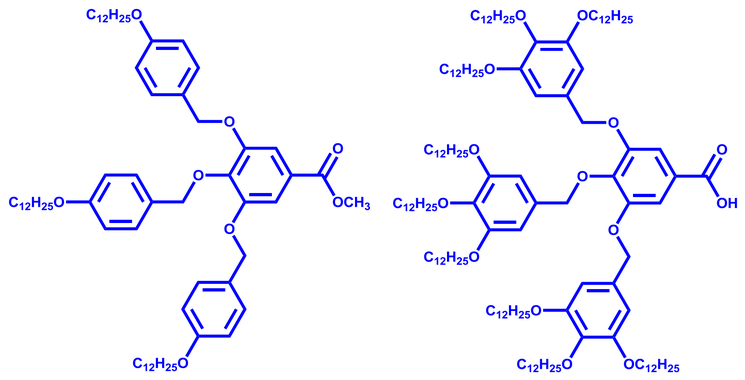


Figure 2. Examples of Percec's amphiphilic dendrons.

Wedge-shape amphiphilic dendrons containing long hydrophobic chains on the periphery and relatively small hydrophilic groups at the apex positions of the dendrons have the ability to self-assemble into supramolecular columns or spheres exhibiting LC properties that can self-organize into various two-dimensional columnar as well as three–dimensional cubic periodic arrays.

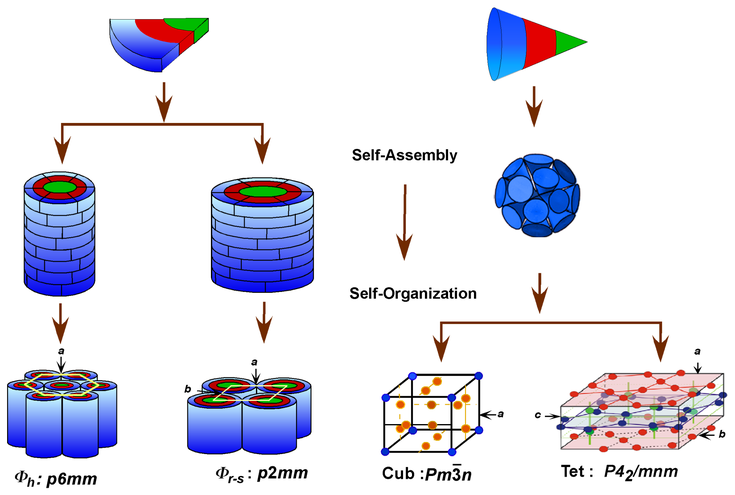
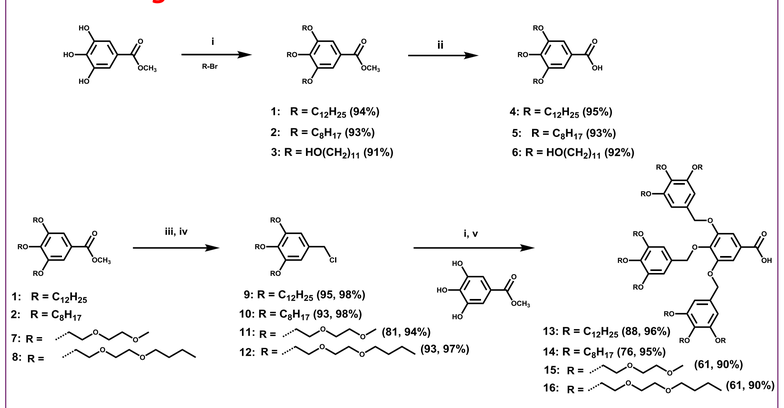


Figure 3. Schematic representation of the 2D and 3D periodic arrays self-organized from dendritic building blocks.

In this project, a series of twin and Janus-supramolecular dendrimers were synthesized based on wedge-shape amphiphilic dendritic building blocks.

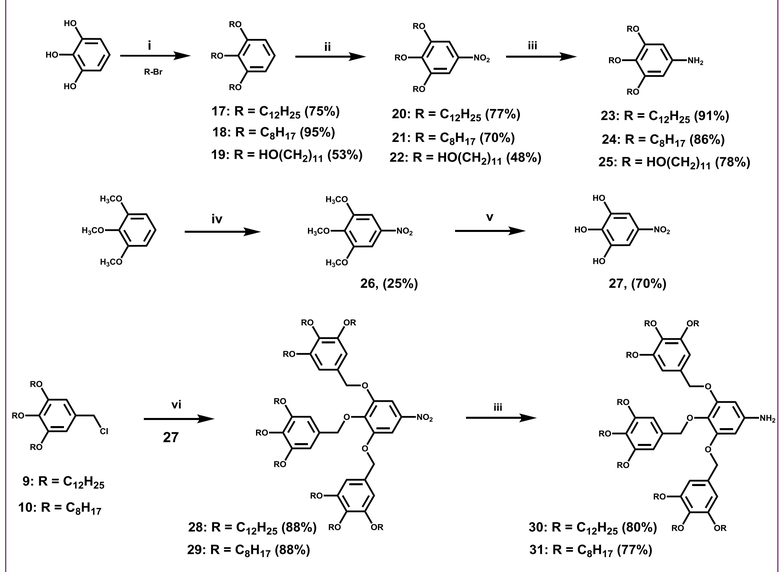
Synthesis

➢ ***Synthesis of dendritic precursors and dendritic building blocks***



Reagents and condition: (i) R-Br, K_2CO_3, DMF, 80 °C; (ii) KOH/ H_2O, EtOH, reflux, H^+; (iii) $LiAlH_4$, THF, 0-23 °C; (iv) $SOCl_2$, DTBMP, 0-23 °C; (v) KOH, EtOH-THF, reflux, H^+.

Scheme 1. Structures of dendritic acids.

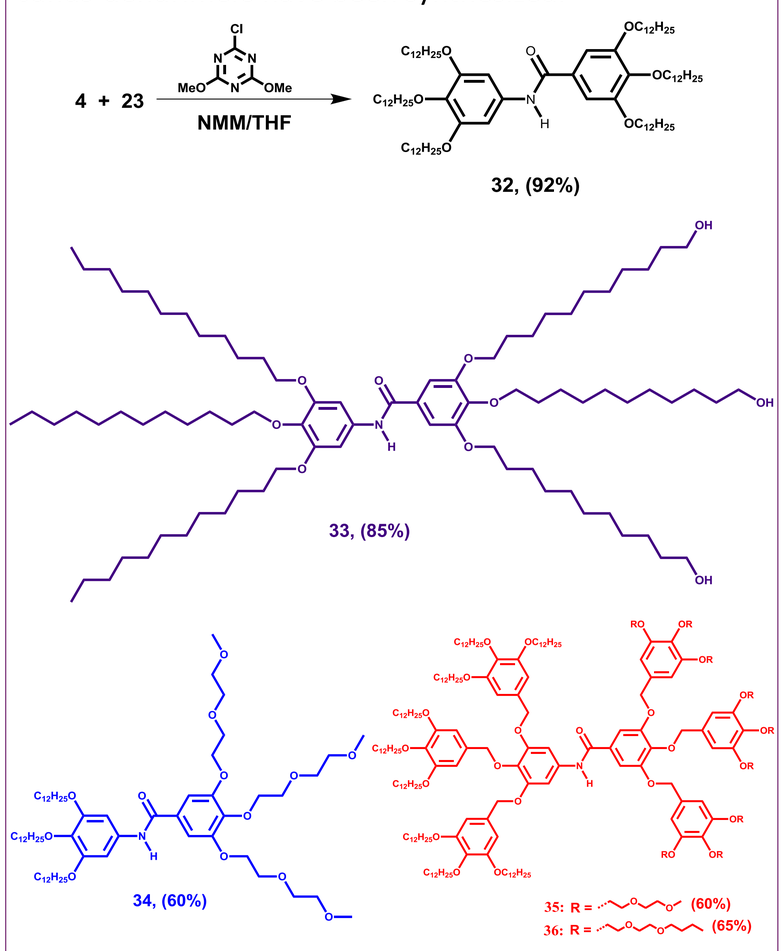


Reagents and condition: (i) R-Br, K_2CO_3, DMF, 80 °C; (ii) SiO_2-HNO_3, 25 °C, 5 min; (iii) NH_2-NH_2, graphite, EtOH, reflux; (iv) CH_2Cl_2, SiO_2-HNO_3, 25 °C, 15 min (v) Py-HCl, 200°C, 1 h; (vi) K_2CO_3, DMF, 80 °C.

Scheme 2. Structures of dendritic amines.

➢ ***Synthesis of Supramolecular Dendrimers***

By coupling reactions between dendritic acids and amines using CDMT and NMM, libraries of twin and Janus-dendrimers have been synthesized.



Scheme 3. Structures of supramolecular dendrimers.

Results and Discussion

- The structural analysis of supramolecular dendrimers was performed by a combination of NMR, IR, DSC, TOPM and XRD techniques .

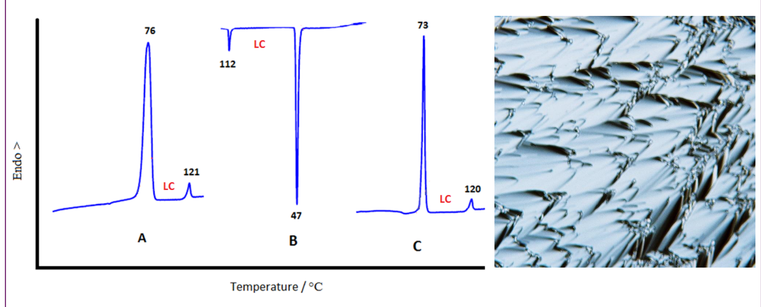


Figure 4. DSC traces of compounds **32** showing LC behavior (**A**, first heating; **B**, first cooling and **C**, second heating) and TOPM texture of LC phase as observed on cooling from isotropic liquid.

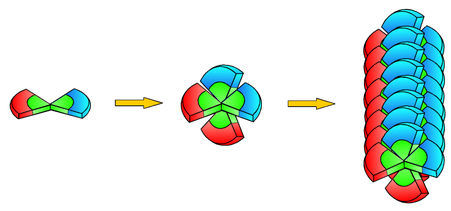


Figure 5. Schematic representation of self-assembly of Janus dendrimers into supramolecular columns.

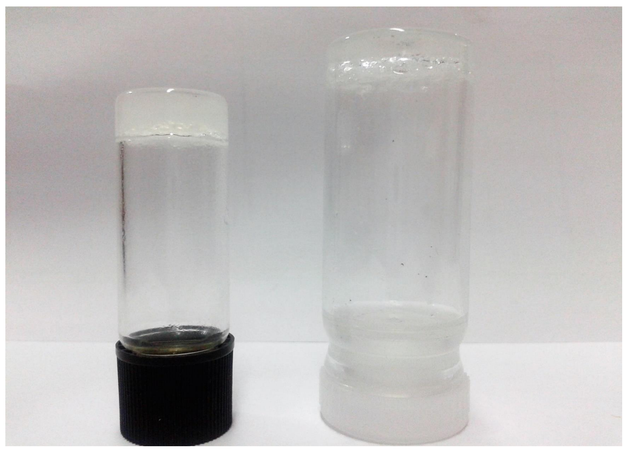


Figure 6. Gelation of compounds **33** (left) and **34** (right) in toluene (10 mg/1 mL).

- Potential applications for CO_2 capture by dendrimer 33 was explored using IR technique.

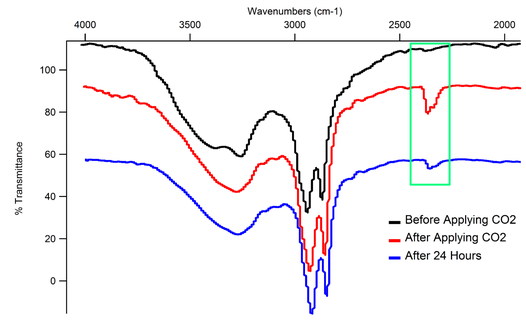


Figure 7. IR spectra of compound **33**.

Conclusions

- ❑ New libraries of twin and Janus-dendrimers have been synthesized and characterized.
- ❑ Structural analysis of these supramolecular dendrimers in isolated and self-assembled state has been performed.
- ❑ Preliminary results of some of these dendrimers showed that they have potential applications for CO_2 capture.

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