

Click Chemistry: Hexaadducts of C₆₀ which display columnar mesomorphism

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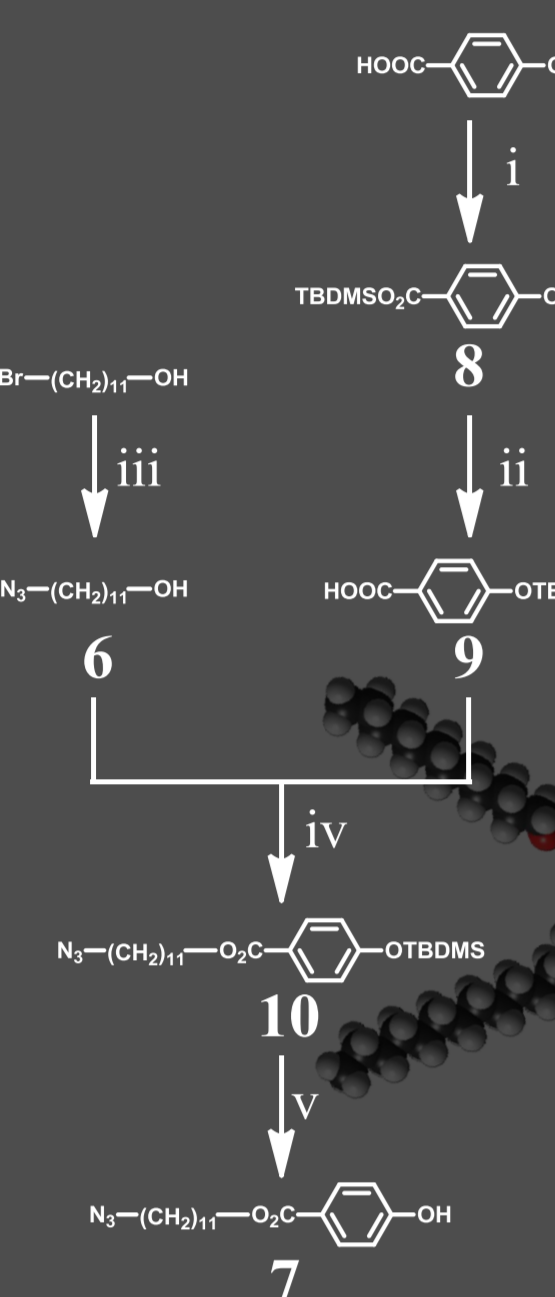
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Abstract

The synthesis of liquid-crystalline fullerene derivatives that self-organize into columnar phases are interesting materials from the point of view of electrochemical properties. However, hexaadditions of C₆₀ with dendrimers are challenging due to steric effect. We envisioned that click chemistry could be an elegant synthetic reaction to design such compounds.^[1,2]

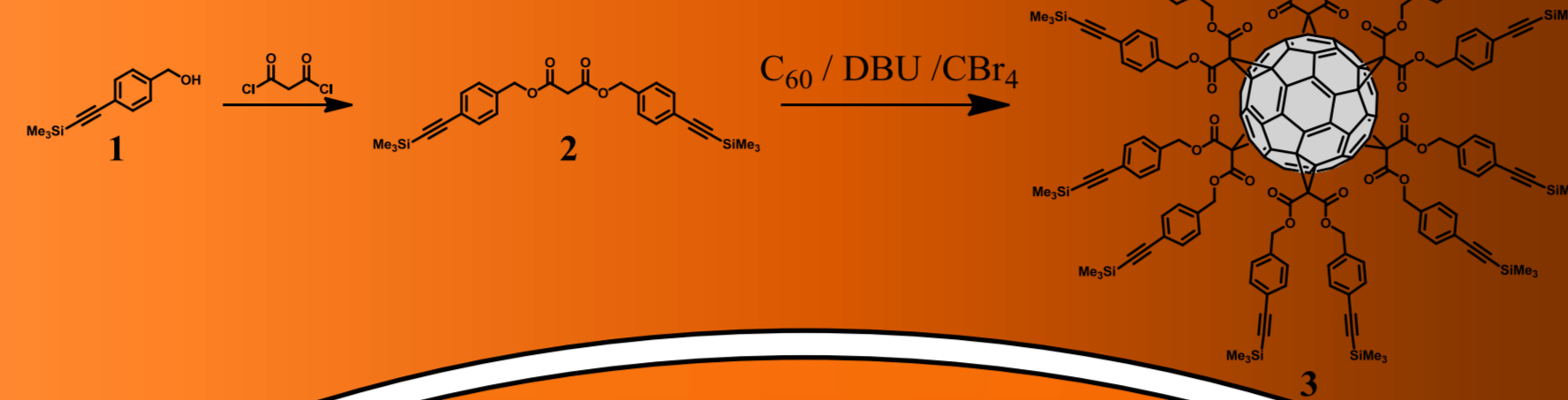
Synthesis

Azido-spacers

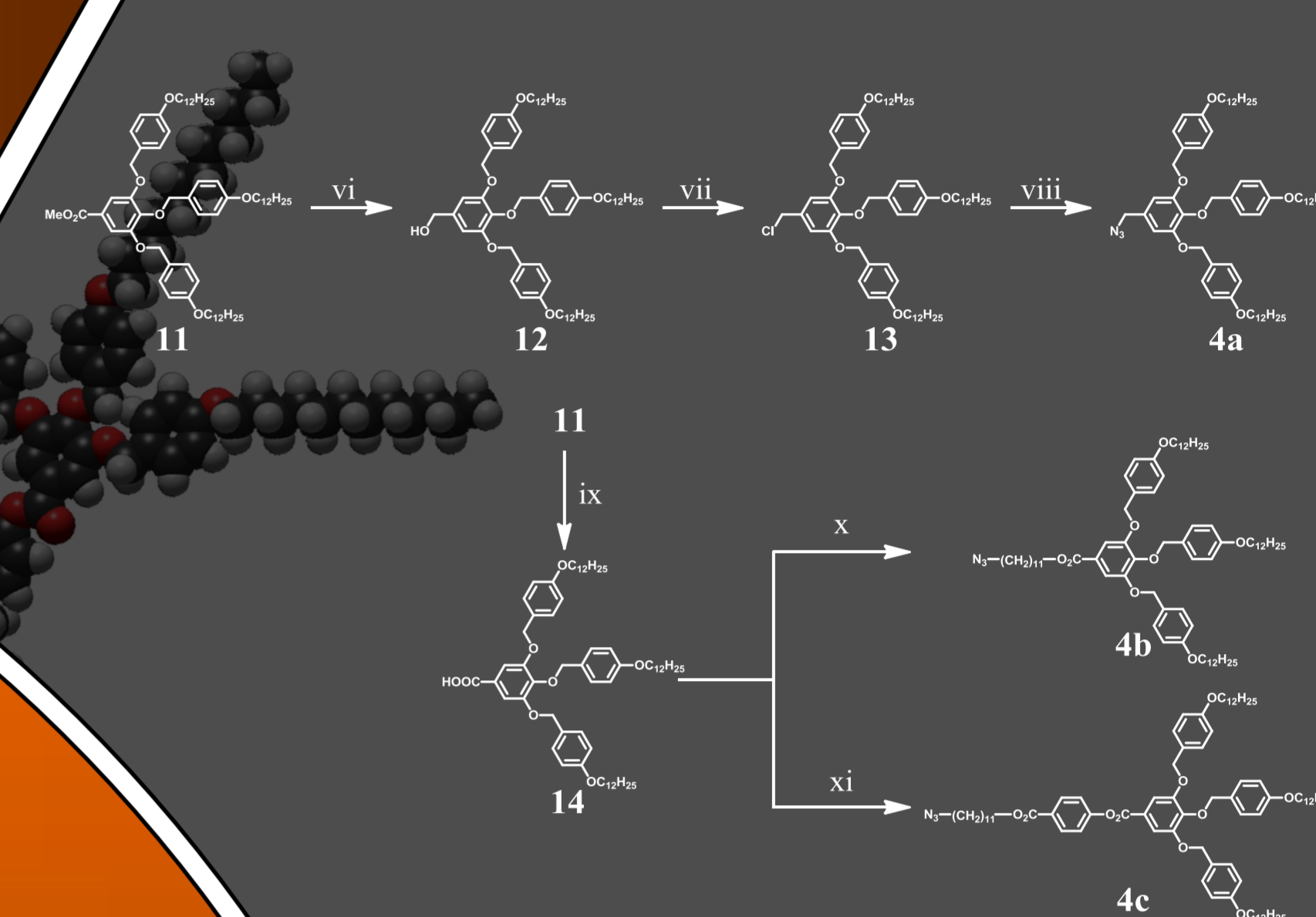


i) CH₂Cl₂, TBDMSCl, DMAP, Et₃N, rt, 24h, 99 %; ii) Acetic acid glacial, H₂O, rt, 3h, 81 %; iii) DMF, NaN₃, reflux, 24h, 88 %; iv) CH₂Cl₂, DPTS, EDC, rt, overnight, 47 %; v) THF/H₂O (9 : 1), Zn(BF₄)₂ · 6-7 H₂O, 50 °C, 24h, 95 %.

C₆₀ platform

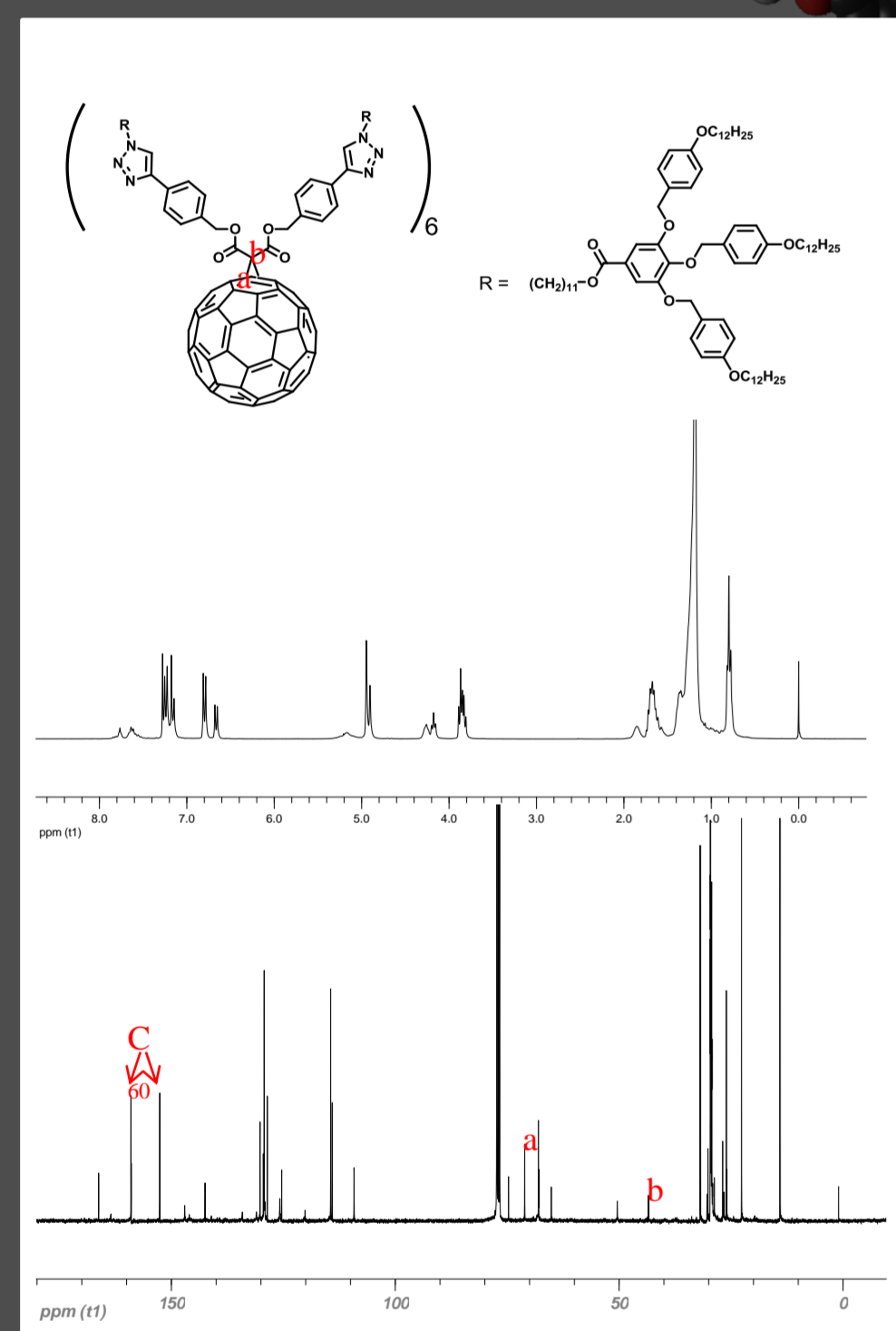


Dendrons [3, 4]



vi) THF, LiAlH₄, rt, 2h, 60 %; vii) CH₂Cl₂, DTBP, SOCl₂, rt, 30min, 98 %; viii) DMF, NaN₃, 70 °C, 24h, 97 %; ix) THF/EtOH (3 : 1), KOH, reflux, 3.5h, 78 %; x) CH₂Cl₂, 6, DPTS, EDC, 4-ppy, rt, 24h, 56 %; xi) CH₂Cl₂, 8, DPTS, EDC, 4-ppy, rt, 24h, 86 %.

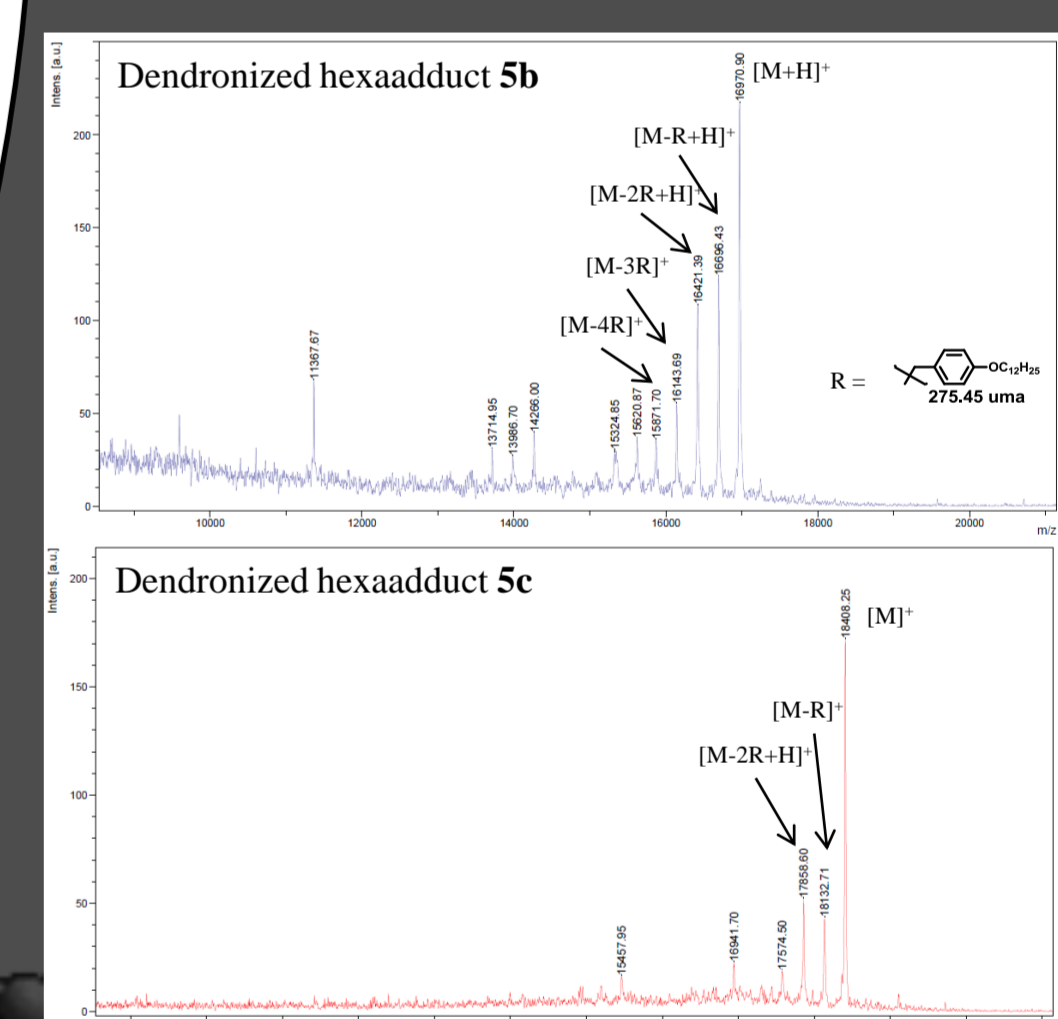
NMR Spectroscopy



¹H-NMR confirms the presence of the dendrons around the C₆₀ core and ¹³C-NMR allows to determine the octahedral symmetry of the hexaadducts of C₆₀.

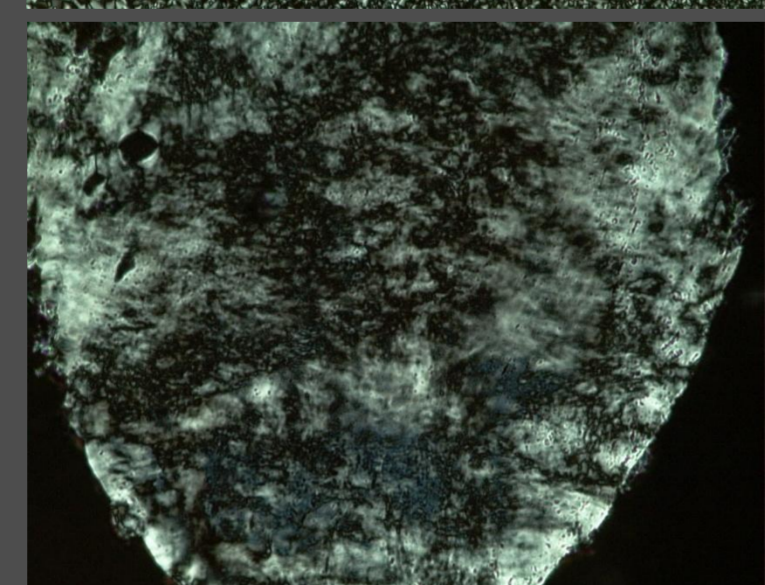
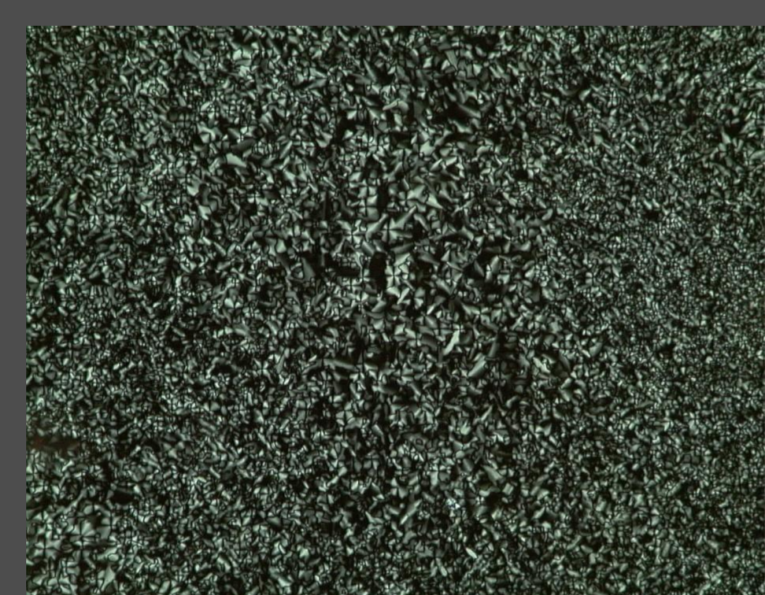
Mass Spectrometry

The mass spectrometry analysis allows to confirm the presence of the fully dendronized hexaadduct by the detection of the mono-cationic molecular peak.



Mesomorphism

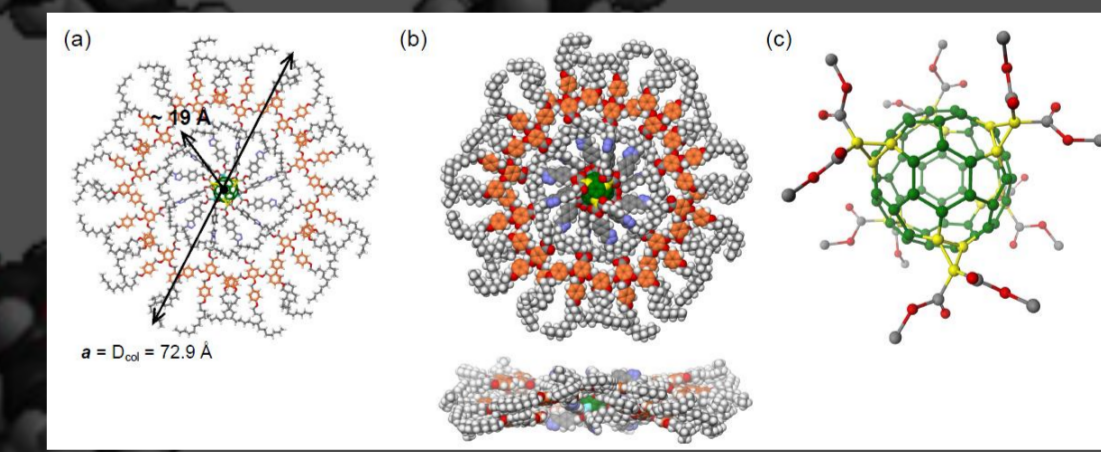
Compound	T _g ^a (°C)	Transition ^b	T _c ^c (°C)	ΔH (kJ/mol)
4a		Cr → Col _{cs} Col _{cs} → I	41 60	34.5 56.1
4b		Cr → I	34	79.5
4c		Cr → I	33	121.1
5a	^d	G → Col _h Col _h → I	160	13.9
5b		G → Col _h Col _h → I	114	13.4
5c		G → Col _h Col _h → Col _{cs} Col _{cs} → I	137 154	7.0 24.9



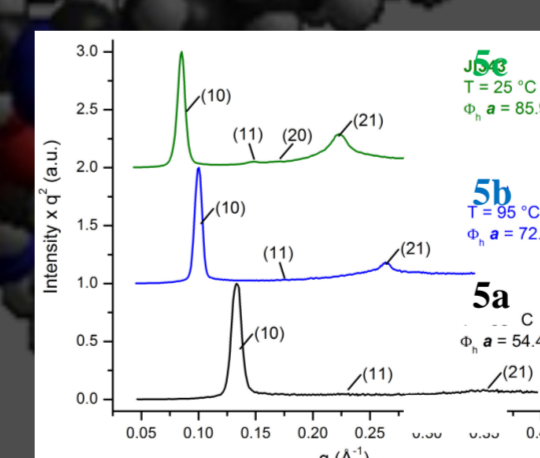
Micrograph of the unresolved texture of the Col_h phase of 5c at 125 °C.

^a T_g = glass transition temperature determined during the first cooling. ^b Cr = semicrystalline solid, G = glass, Col_h = columnar hexagonal phase, Col_{cs} = columnar single rectangular phase, Col_{cc} = columnar centered rectangular phase, I = isotropic liquid. ^c T = transition temperature given at the onset value taken from the second heating run. ^d Transition not detected.

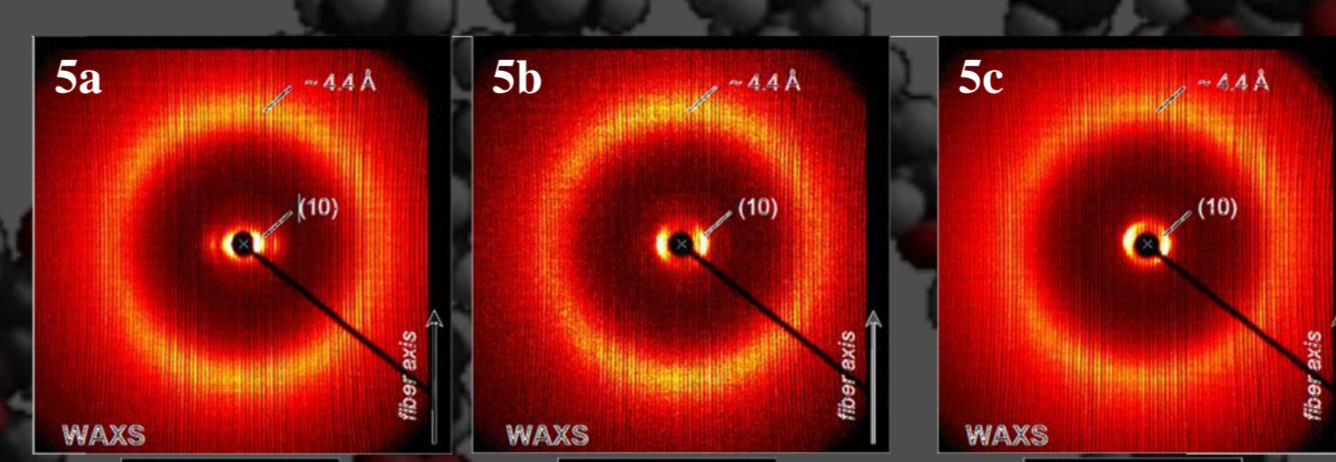
Organization



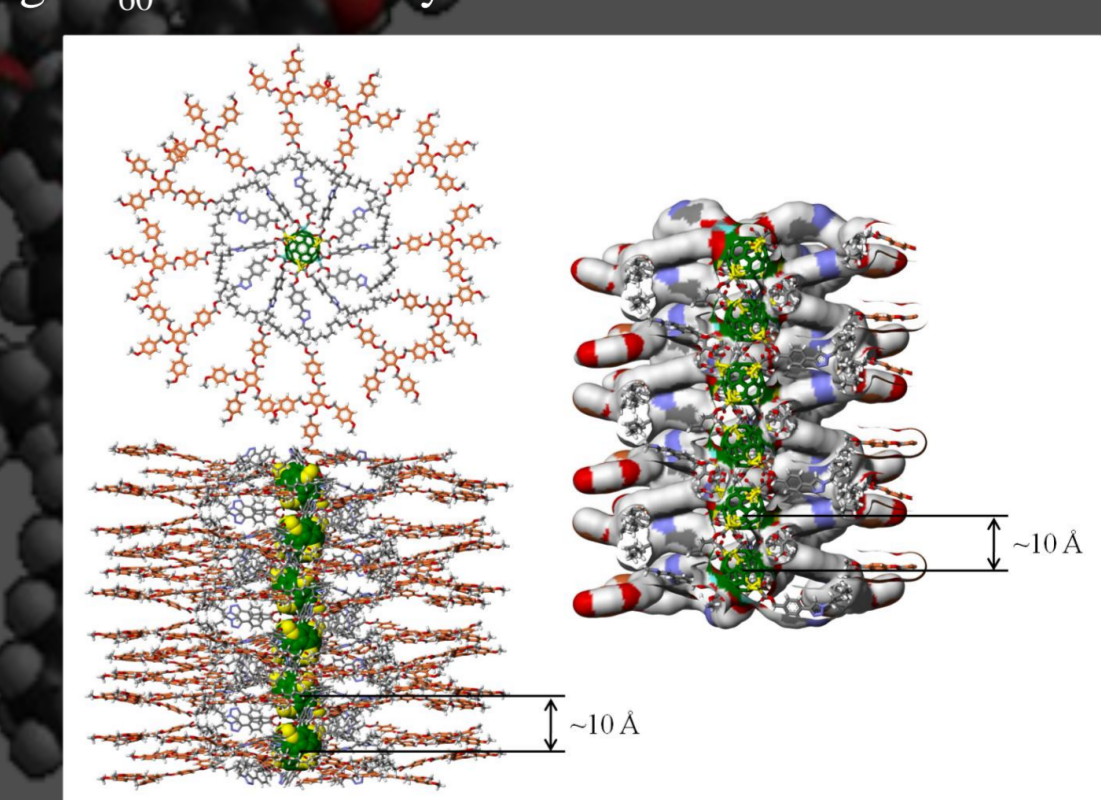
Small angle X-ray powder diffraction plots of dendronized C₆₀ in columnar hexagonal phase.



Molecular model of the dendronized C₆₀ 5b: top view of the column strata (a), top and side views of the column strata shown in space filling (b), and detailed view of the core region (c). Color code: C –gray, H –white, O –red, N –blue, dendron aromatic rings –orange, C₆₀ core –green, and the C atoms linkage C₆₀-dendrons –yellow.



Wide and small angle X-ray diffraction patterns collected from the oriented fibers of the dendronized C₆₀ in columnar phase at 25 °C.



Molecular model of the dendronized C₆₀ 5c.

Conclusions

In this project, hexaadducts of C₆₀ were fully functionalized with non-mesomorphic dendrons by click chemistry. Surprisingly, all the dendronized C₆₀ rise not to cubic phases as expected, but into columnar phases where the C₆₀ cores are perfectly aligned in the center of the column strata.

References

- [1] J. Iehl, R. Pereira de Freitas, B. Delavaux-Nicot, J.-F. Nierengarten, *Chem. Commun.* **2008**, 2450.
- [2] J. Iehl, I. Osinka, R. Louis, M. Holler, J.-F. Nierengarten, *tetrahedron Letters*, **2009**, 50, 2245.
- [3] V. Percec, W.-D. Cho, M. Möller, S. A. Prokhorova, G. Ungar, D. J. P. Yearley, *J. Am. Chem. Soc.* **2000**, 122, 4249.
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