Chiral Liquid-Crystalline Fullerodyads

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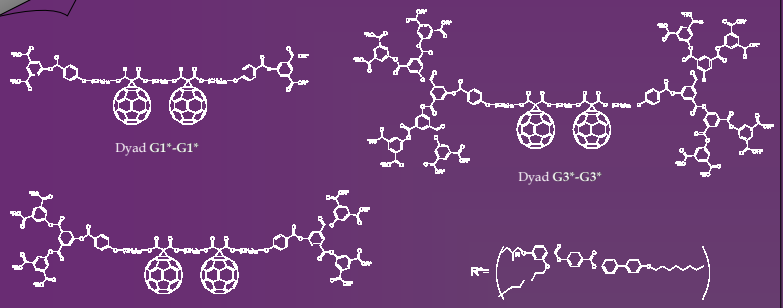
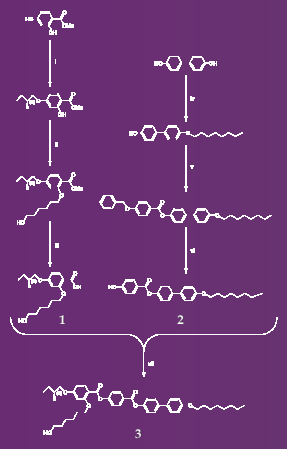
It was demonstrated that covalent functionalization of fullerene (C_{60}) with dendrimers prevented the formation of aggregates. The use of liquid-crystalline dendrimers allowed the design of thermotropic macromolecules with tailor-made mesomorphic properties.[1] Furthermore, the introduction of two C_{60} units into liquid-crystalline materials is of interest with the aim to better our understanding of the "structure-supramolecular organization" relationship for this class of compounds, and could serve as a model for the subsequent construction of main-chain polymers.

Target molecules



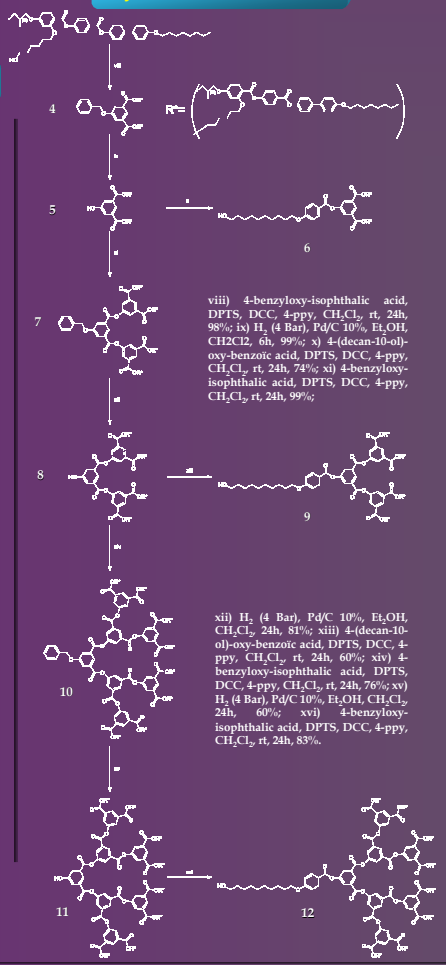
Synthesis

Synthesis of Goodby's mesogen



i) (S)-(+)-1-bromo–methylbutane, K_2CO_3, 18C6, butan-2-one, reflux, Ar, 36h, 70%; ii) 6-bromo-hexan-1-ol, K_2CO_3, KI, 18C6, DMF, Ar, 120°C, 24h, 76%; iii) NaOH, H_2O, MeOH, reflux, 3h, 96 %; iv) 1-bromo-octane, KOH, H_2O, Et_2OH reflux overnight, 58%; v) 4-benzyloxybenzoic acid, DCC, DPTS, 4-ppy, CH_2Cl_2, rt, overnight, 78%; vi) H_2 (4 Bar), Pd/C 10%, Et_2OH, CH_2Cl_2, 6h, 98%; vii) 1, 2, DPTS, DCC, 4-ppy, rt, 24h, 93%.

Synthesis of dendrons

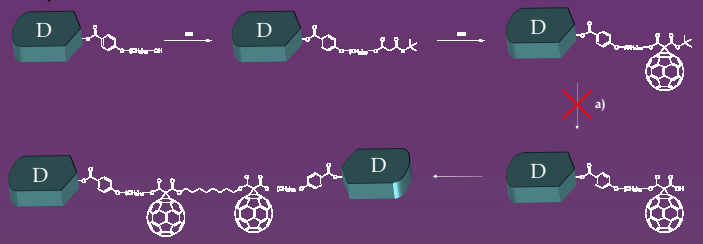


viii) 4-benzyloxy-isophthalic acid, DPTS, DCC, 4-ppy, CH_2Cl_2, rt, 24h, 98%; ix) H_2 (4 Bar), Pd/C 10%, Et_2OH, $CH2Cl2$, 6h, 99%; x) 4-(decan-10-ol)-oxy-benzoïc acid, DPTS, DCC, 4-ppy, CH_2Cl_2, rt, 24h, 74%; xi) 4-benzyloxy-isophthalic acid, DPTS, DCC, 4-ppy, CH_2Cl_2, rt, 24h, 99%;

xii) H_2 (4 Bar), Pd/C 10%, Et_2OH, CH_2Cl_2, 24h, 81%; xiii) 4-(decan-10-ol)-oxy-benzoïc acid, DPTS, DCC, 4-ppy, CH_2Cl_2, rt, 24h, 60%; xiv) 4-benzyloxy-isophthalic acid, DPTS, DCC, 4-ppy, CH_2Cl_2, rt, 24h, 76%; xv) H_2 (4 Bar), Pd/C 10%, Et_2OH, CH_2Cl_2, 24h, 60%; xvi) 4-benzyloxy-isophthalic acid, DPTS, DCC, 4-ppy, CH_2Cl_2, rt, 24h, 83%.

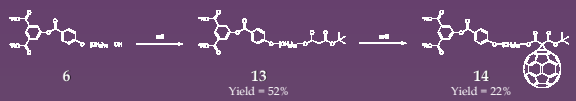
Attempted deprotections

Herein, dendrons are represented by « D ».



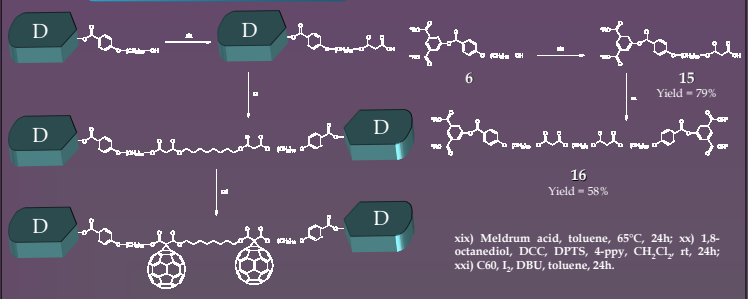
a) Attempted deprotections
1) TFA, CH_2Cl_2, rt, overnight : *Degradation;*
2) TFA, CH_2Cl_2, 0°C, 1h : *no reaction;*
3) TFA, CH_2Cl_2, rt, 1h : *Degradation;*
4) *p*-TsOH, toluene, rt, 8h : *no reaction;*
5) *p*-TsOH, toluene, reflux, 2h : *Degradation.*

xvii) mono-*t*-butyl-malonic acid, DPTS, DCC, 4-ppy, CH_2Cl_2, rt, 24h; xviii) C60, I_2, DBU, toluene, 24h.



Novel strategy

The « Meldrum acid » route



xix) Meldrum acid, toluene, 65°C, 24h; xx) 1,8-octanediol, DCC, DPTS, 4-ppy, CH_2Cl_2, rt, 24h; xxi) C60, I_2, DBU, toluene, 24h.

Molecular data

Phase-Transition Temperatures and Enthalpy Changes of the Compounds

Compound	T_g/°C	Transition	Temperature/°C	ΔH/kJ mol^{-1}
3	-	Cr → N*	100,2[b]	-
		N* → I	137,8[b]	-
4	6	N* → I	102	1,4
5	23	N* → I	129	1,8
6	12	N* → I	103	1,9
7	33	N* → I	99	2,7
8	37	N* → I	101	1,7
9	31	N* → I	88	1,7
10	44	N* → I	92	2,5
11	41	N* → I	87	2,3
12	42	N* → I	88	2,9
13	7	N* → I	85	1,5
14	-	Cr → I	55	9,0
15	20	N* → I	105	3,1
16	55	N* → I	98	-

Temperatures are given as the onset of the peaks; Tg = glass transition temperature, I = isotropic liquid, N* = chiral nematic phase, Cr = crystal. [b] After Goodby et *al.* [2]

Conclusion

In spite of the problems encountered to obtain the target molecules *via* the first synthetic way, the novel strategy should offer *in fino* the desired products.
The fullerodyads and their properties will lead to exceptional electron acceptor tanks.
Optically-active mesophases (our mesogen is chiral) open opportunities in the development of devices for optical-storage information.

References

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