Self-assembled Supramolecular Rigid Rods

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The self-assembly of the complementary components AP_2 and AU_2, through hydrogen bonding *via* uracil and 2,6-diacylaminopyridine groups, yields polymeric supramolecular rigid rods $(AP_2, AU_2)_n$ that present a lyotropic mesophase.

Molecular recognition induced polyassociation of complementary molecular components through hydrogen bonding has been shown to yield polymeric species of supramolecular type, that may also possess liquid crystalline properties.[1] In a broad perspective, one may envisage building up a supramolecular polymer chemistry that could translate to the supramolecular level the features of molecular, covalent polymer chemistry, such as the formation of copolymers, reticulation and, incorporation of rigid blocks.[2]

On the other hand, the development of molecular and supramolecular devices[3] comprises *inter alia* the synthesis of species of nanometric dimensions for the positioning of functional components in well-defined arrangements. The preparation of rigid linear or starshaped species such as molecular lines,[4] dendrimers,[5] arborols[6] and branched polyacetylenes[7] represents molecular approaches to such nanostructures. Again the possibility exists to translate these considerations to the supramolecular level by designing molecular components endowed with the ability to spontaneously build up such species through molecular recognition-directed self-assembly. Several studies have been concerned with the controlled formation of various superstructures through hydrogen bonding in the solid state or in solution.[8–11]

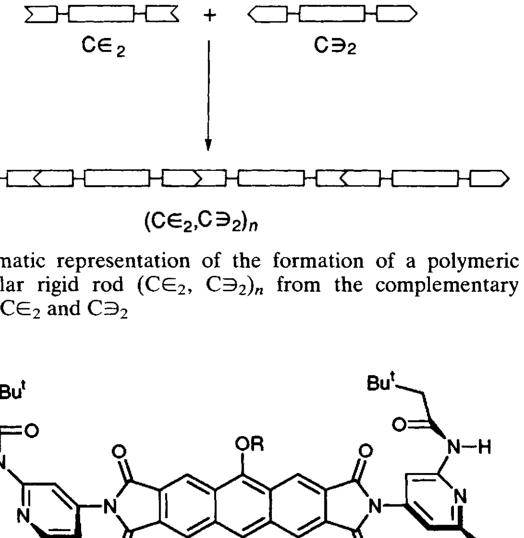


Fig. 1 Schematic representation of the formation of a polymeric supramolecular rigid rod $(C\in_2, C\ni_2)_n$ from the complementary components $C\in_2$ and $C\ni_2$

We report here the self-assembly of the complementary components AU_2 and AP_2 to form supramolecular species $(AU_2, AP_2)_n$ that present at the same time the features of polymeric entities and of linear rods based on rigid components.

If two complementary units $\in$ and $\ni$ are grafted onto a rigid core C, mixing $C\in_2$ with the complementary $C\ni_2$ may lead to the self-assembly of a linear polymeric rigid rod (Fig. 1). This new material may present liquid crystalline properties if suitable side-chains are introduced onto the components.

In the present study the 9,10-dialkoxyanthracenic derivative A was chosen as the central rigid core whereas uracil U and 2,6-diacylaminopyridine P groups were used as complementary units $\in$ and $\ni$. The formation of triply hydrogen-bonded complementary pairs by these units is well documented (see for instance refs. 1, 12–14). In order to assure the rigidity of the system the U and P subunits are grafted onto the anthracene moiety by an imid function that strongly hinders rotation around the C–N bond between the core A and the attached U and P groups.

AP_2 and AU_2 were synthesized by reacting respectively the diacylaminopyridine **1** and the commercially available 6-amino-1-propyl uracil **2** with the anthracenic dianhydride **3**.

Compound **1** was obtained *via*: (*a*) protection of the amine function of the dimethyl ester of 4-amino 2,6-pyridine dicarboxylic acid **4**[15] with di- *tert*-butyl dicarbonate to **5** (mp: 173–176 °C decomp., 72% yield), (*b*) formation of the diamide **6** with methanolic ammonia (mp: 160–165 °C decomp., 71% yield), (*c*) conversion of **6** to **7** (mp: 146 °C then 180 °C, 67%

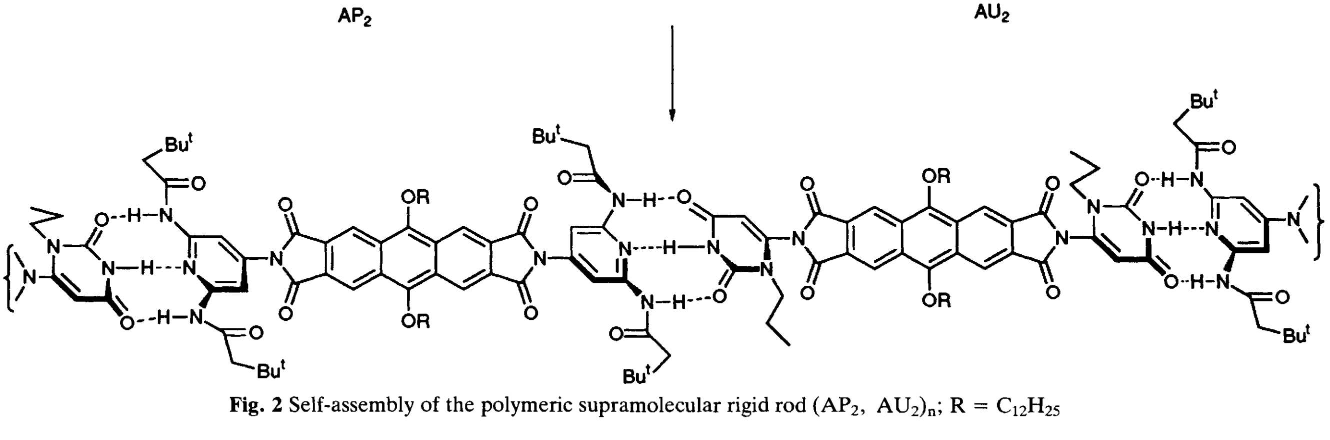


Fig. 2 Self-assembly of the polymeric supramolecular rigid rod $(AP_2, AU_2)_n$; $R = C_{12}H_{25}$

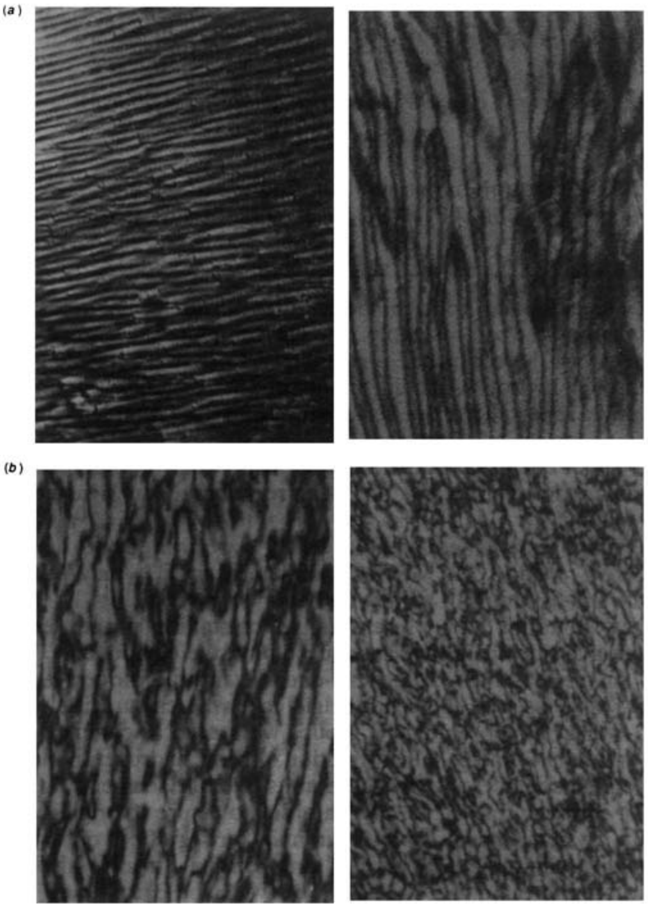
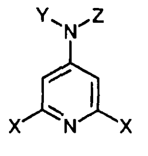
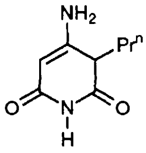


Fig. 3 Optical textures observed for different preparations obtained from a 0.05 mol dm^{-3} solution of (AP$_2$, AU$_2$) in 1,1,2,2-tetrachlorethane between crossed polarizers, at room temp., by: (*a*) slow evaporation of the solution deposited on a lamella (top), (*b*) confinement of the solution between two lamella (bottom)



1; X = NH–COCH$_2$Bu^t, Y = Z = H
4; X = CO$_2$Me, Y = Z = H
5; X = CO$_2$Me, Y = Z = Boc
6; X = CONH$_2$, Y = H, Z = Boc
7; X = NH$_2$, Y = H, Z = Boc
Boc = CO$_2$Bu^t



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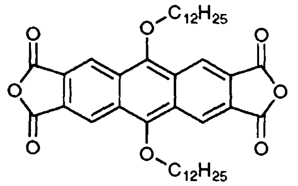

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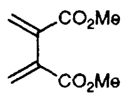

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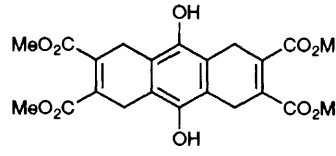

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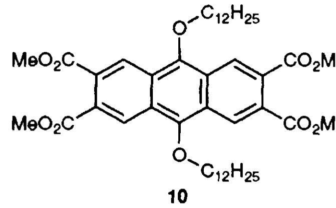

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yield) through Hofmann rearrangement (Br$_2$, KOH), (*d*) acylation of **7** with 3,3-dimethylbutyryl chloride (NEt$_3$, CH$_2$Cl$_2$, room temp.) followed by deprotection of the amine function (CF$_3$CO$_2$H, room temp.) to **1** (mp: 225–226 °C, 79% yield).

The dianhydride **3** was prepared by: (*a*) double Diels-Alder reaction (TsOH, dioxane, 70–75 °C) of benzoquinone with diene **8** to give the tetrahydroanthracene **9** (mp: 230–260 °C decomp., 56% yield), (*b*) alkylation (NaH, DMF, C$_{12}$H$_{25}$I, 80 °C) and oxidation at air of **9** to **10** (mp: 102 °C, 71% yield), (*c*) hydrolysis (NaOH in THF–MeOH, 1 : 1, v/v, reflux) of **10** followed by dehydration (Ac$_2$O, reflux) to give **3** (mp: 225 °C, 88% yield).[16]

AP$_2$ and AU$_2$ were obtained (mp: decomposition around 350 °C and 240–250 °C, 49 and 30% yield respectively) by heating in 1-methyl-2-pyrrolidinone (190–200 °C for 10–15 min) the amino derivatives **1** and **2** with the dianhydride **3**. In the case of **2** it was necessary to proceed in presence of *N*-(*tert*-butyldimethylsilyl)-*N*-methyltrifluoroacetamide which transforms, *in situ*, amino uracil **2** into a more reactive silyloxy species.‡

The 1 : 1 mixture of the complementary pairs AP$_2$ and AU$_2$ yielded a compound different from its components, in the solvent free state as well as in solution. In CDCl$_3$ (2×10^{-4} mol dm^{-3}) it showed downfield shifts (of about 0.2–0.3 ppm) for the NH ^{1}H NMR signals with respect to the pure substances, as expected[1,13,14] if association occurs. Larger shifts of 1–1.5 ppm were found with stoichiometric mixtures of the complementary pairs (PhtP + PhtU) and (AP$_2$ + 2 Pht U).§ This, and the broadness of the ^{1}H NMR signals at larger concentration, may indicate that the present substances undergo autoassociation to some extent.

The thermal and optical properties of the 1 : 1 mixture (AP$_2$, AU$_2$) have been studied by differential scanning microcalorimetry and with a polarizing microscope; it presents no thermotropic mesophase and melts with decomposition around 295 °C. In contrast, cooling a hot solution of (AP$_2$, AU$_2$) 1 : 1 in 1,1,2,2-tetrachloroethane (5×10^{-2} mol dm^{-3}) yields a viscous material at room temp. which presents an anisotropic texture when it is observed between crossed polarizers (Fig. 3). In the same conditions AP$_2$ and AU$_2$ give isotropic solutions. By heating the viscous material under the polarizing microscope one can observe a reversible transition between a mesomorphic phase and an isotropic phase around 90–100 °C. As the solvent evaporates, patterns appear that are similar to the structures described for oriented lyotropic polymers.[17] Preliminary X-ray patterns indicate that the mesophase is nematic.[18] A study of the appearance of the lyotropic phase at different concentrations will be performed in order to further characterize this phase.

The present results are in agreement with the structure schematically represented on Fig. 2: the overall process may be described as the self-association of a supramolecular lyotropic liquid crystalline polymer based on molecular recognition between complementary rigid subunits.

Further work is in progress in order to characterize the polymeric superstructure, to elucidate the mesophase arrangement and to study the properties of these new self-assembled rigid rod supramolecular species. The formation of rigid/flexible copolymeric entities also may be envisaged by mixing rigid and flexible[1] components.

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Footnotes

† UPR 285 of the CNRS.

‡ All new compounds gave correct elemental analyses and had spectroscopic data that were in accord with the reported structures.

§ PhtP and PhtU: derivatives (analogous to one half of AP$_2$ and AU$_2$) resulting from condensation of **1** and **2** with phthalic anhydride.

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