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## Design and Synthesis of Complementary Components for the Formation of Self-Assembled Supramolecular Rigid Rods

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**Abstract** : The complementary components  $AP_2$  and  $AU_2$ , resulting respectively from the linking of diacylaminopyridine and uracil derivatives to an anthracenic core, have been designed in order to self-assemble, through hydrogen bonding, into polymeric supramolecular rigid rods  $(AP_2, AU_2)_n$ . The synthesis of these compounds is reported.

Numerous supramolecular architectures resulting from the self assembly of suitably designed molecular components have now been reported.<sup>1</sup> Hydrogen bonding, electrostatic interactions, donor-acceptor effects and metal coordination, used as basic interactions between the components, make it possible to prepare a large variety of new structures in the solid state or in solution : extended arrays,<sup>2-4</sup> ribbons, <sup>2</sup> tapes,<sup>3</sup> cyclic species, <sup>3c,d,4-8</sup> cylindrical complexes,<sup>9</sup> double-helical complexes,<sup>10-14</sup> catenanes <sup>15-19</sup>, rotaxanes <sup>20-27</sup> and so on.

Polymeric species of supramolecular type have also been obtained from the molecular recognition induced polyassociation of complementary molecular components <sup>28,29</sup> and a supramolecular polymer chemistry may result from the combination of polymer chemistry with supramolecular chemistry.<sup>30</sup> As in covalent polymer chemistry one may envisage the formation of copolymers, the reticulation and the incorporation of rigid blocks.

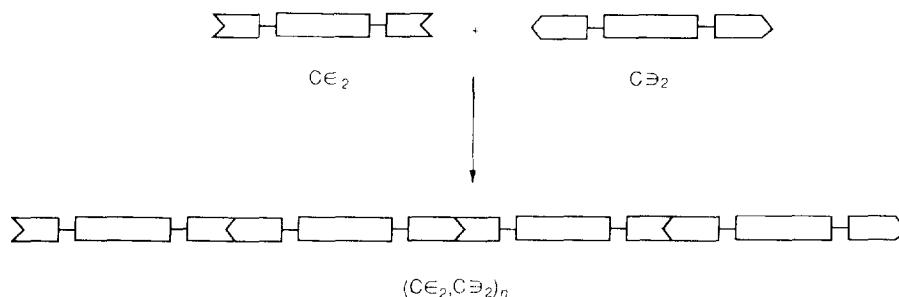
The molecular recognition directed self-assembly of complementary components may also represent an approach to the obtention of species of nanometric dimensions required for the development of molecular and supramolecular devices.<sup>1</sup> The molecular lines,<sup>31</sup> rod-shapes molecules<sup>32</sup>, dendrimers,<sup>33-36</sup> arborols,<sup>37</sup> and branched polyacetylenes<sup>38</sup> that represent molecular approaches to such nanostructures might be formed by polyassociation of complementary monomer species.

On the other hand, the introduction of rigid molecular units into polymers has been actively pursued in view of the novel physico-chemical properties that the resulting material may present. We have recently reported<sup>29</sup> that self-assembly may constitute a

novel approach to such a synthetic problem : the autoassociation of the complementary components  $AU_2$  and  $AP_2$  was shown 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. We report here the design and the synthesis of the complementary units  $AU_2$  and  $AP_2$ .

#### Design of the complementary components $AU_2$ and $AP_2$

It two complementary units  $\epsilon$  and  $\vartheta$  are grafted onto a rigid core C, mixing  $C\epsilon_2$  with the complementarity  $C\vartheta_2$  may lead to the self-assembly of a linear polymeric rigid rod (Scheme 1).



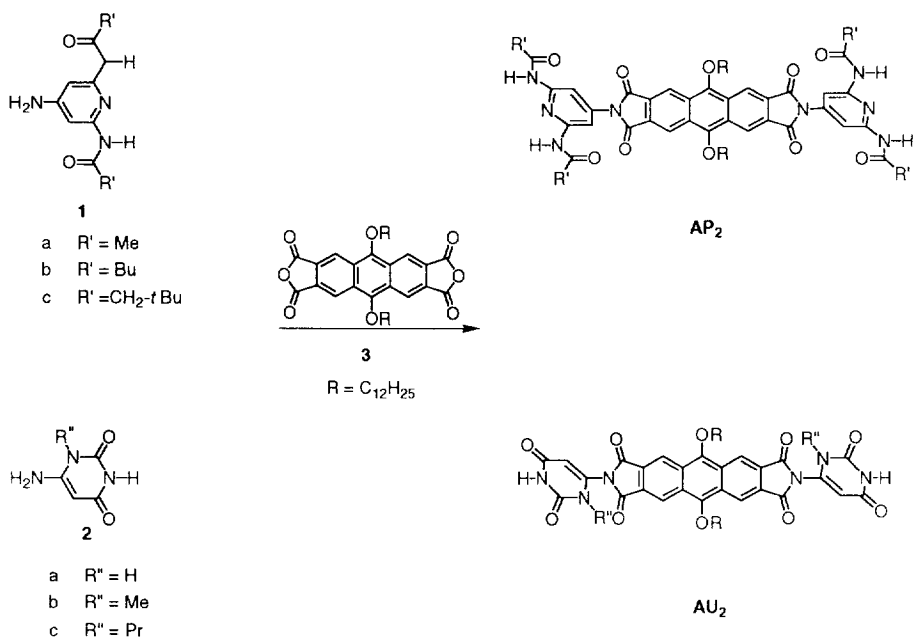
Scheme 1

In the present study, the 9,10-dialkoxyanthracenic derivative A was chosen as the central rigid core, the 9,10-disubstitution giving a certain solubility to the material. Directed hydrogen bonding was used as binding interactions between the components by the choice of uracil U and 2,6-diacylaminopyridine P groups as complementary units  $\epsilon$  and  $\vartheta$ , which are well known to form triply hydrogen-bonded complementary pairs<sup>28,39-41</sup> The whole system was made rigid by grafting the U and P subunits onto the anthracene moiety A by an imide function that strongly hinders rotation around the C-N bond between the core A and the attached U and P groups.

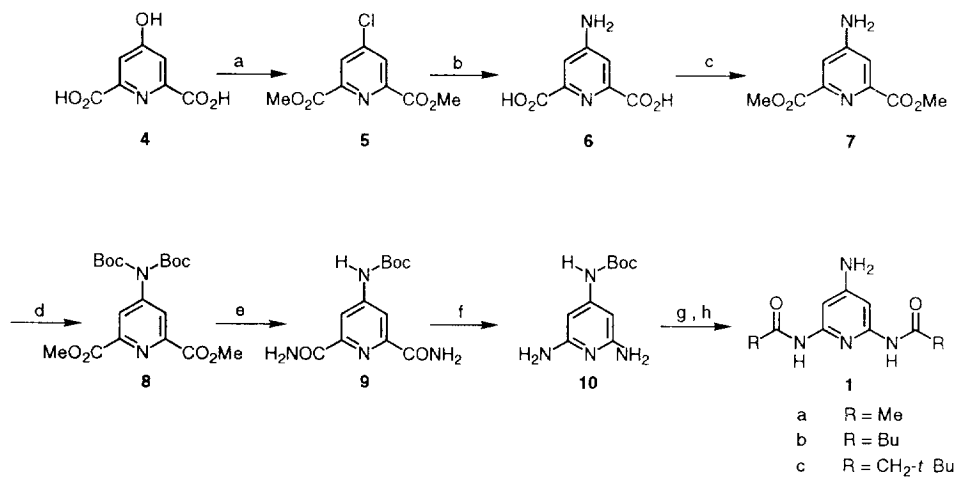
#### $AP_2$ and $AU_2$ Synthesis

$AP_2$  and  $AU_2$  were synthesized by reacting, respectively, the diacylaminopyridine **1** and the commercially available 6-amino-1-alkyl uracil **2** with the anthracenic dianhydride **3** (Scheme 2).

## Supramolecular rigid rods



Scheme 2

Synthesis of diacylamino pyridine derivatives 1

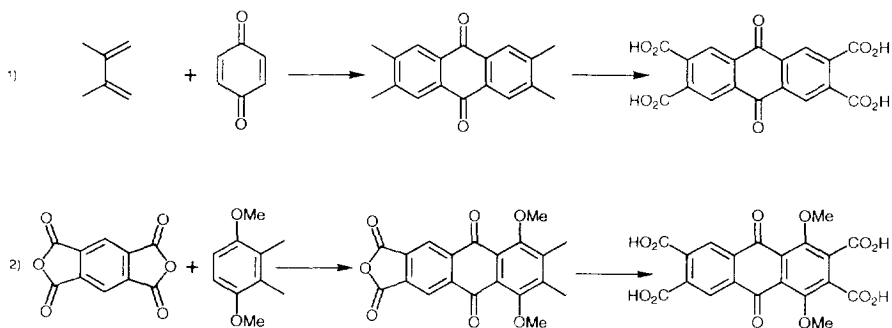
Scheme 3. a)  $\text{PCl}_5$ , then MeOH; b) NaOH then  $\text{NH}_3$  aq.,  $170^\circ\text{C}$ ; c) MeOH,  $\text{SOCl}_2$ ; d)  $\text{Boc}_2\text{O}$ , pyridine; e)  $\text{NH}_3$ , MeOH; f)  $\text{Br}_2$ , KOH; g)  $(\text{R}-\text{CO})_2\text{O}$  or *tert*-Bu- $\text{CH}_2\text{COCl}$ ; h)  $\text{CF}_3\text{CO}_2\text{H}$ .

The straightforward synthesis of derivative **1** starting from chelidamic acid **4** is outlined in Scheme 3. Other shorter synthetic paths were explored but could not be completed.

The dimethyl 4-amino-2,6-pyridinedicarboxylate **7** was prepared from chelidamic acid **4** through compounds **5**<sup>42</sup> and **6**<sup>43</sup>, according to slight modifications of literature procedures. The protection of the amine function of **7** with di-*tert*-butyldicarbonate, which gave the di-*Boc*-compound **8** (72%) was followed by the synthesis of the diamide **9** (71%) by treatment with methanolic ammonia; this step was accompanied by the cleavage of one of the two *Boc*-groups attached to the amine function of **8**. Submitted to Hofmann rearrangement (Br<sub>2</sub>,KOH), the diamide **9** yielded the diamino compound **10** (67%). The acylation of **10**, either by an anhydride (acetic or butyric) or by 3,3-dimethylbutyrylchloride, followed by CF<sub>3</sub>CO<sub>2</sub>H deprotection of the amine function, gave the compounds **1 a-c** (75-80%).

#### Synthesis of the anthracenic dianhydride **3**

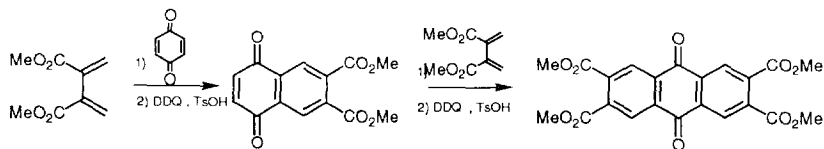
Most synthetic methods to obtain 2,3,7,8-anthracenetetracarboxylic acid derivatives use the same strategy shown in Scheme 4.



Scheme 4

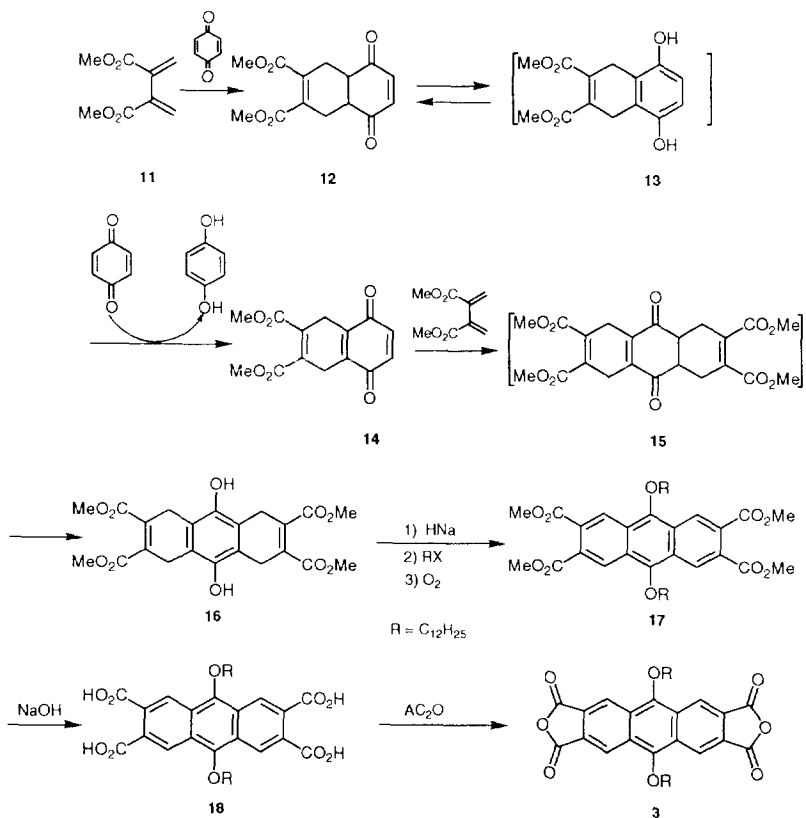
The anthracenic framework is obtained either by Diels-Alder reactions between benzoquinone and 2,3-dimethylbutadiene<sup>44</sup> or by Friedel-Crafts reactions of pyromellitic anhydride derivatives with *o*-xylene derivatives<sup>45</sup>. The KMnO<sub>4</sub> oxydation of the methyl anthraquinones thus obtained gives 2,3,7,8-anthraquinonetetracarboxylic acids<sup>44c,45</sup>; a reduction of these compounds, followed by an alkylation, then yields 9,10-dialkoxy-2,3,7,8-anthracenetetracarboxylic acids.

Starting from 2,3-dicarbomethoxy-1,3-butadiene, a more recent strategy avoids the tedious  $\text{KMnO}_4$  oxydation<sup>46</sup> (Scheme 5).



Scheme 5

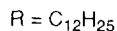
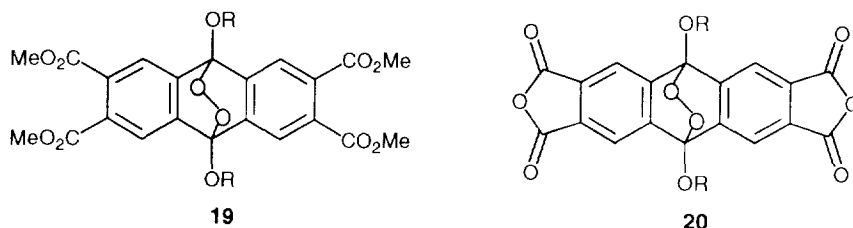
From the same starting materials, the method we describe here is shorter since the compound **16** was obtained in a one-pot reaction (Scheme 6).



Scheme 6

When the Diels-Alder reaction was conducted in dioxane in presence of *p*-toluenesulfonic acid, the monoadduct **12** was oxidized to **14**, via the intermediate **13**, by an excess of benzoquinone. The compound **14**, a better dienophile than **12**, reacted then with a second equivalent of diene **11**<sup>47</sup> giving **16** via the intermediate **15**. Thus, the tetrahydroanthracenic derivative **16** was isolated in moderated yield (56 %) directly from **11**. The alkylation of **16** (HNa, DMF, C<sub>12</sub>H<sub>25</sub>Br) gave the tetramethyl-9,10-didodecyloxy-2,3,6,7-anthracenetetracarboxylate **17** since aromatization occurred at the same time in presence of air. The saponification of the tetraester **17** in a MeOH/THF mixture gave the corresponding acid **18** (100% yield) which was dehydrated in refluxing Ac<sub>2</sub>O to yield the dianhydride **3** (88%).

Chloroform solutions of compounds **17** and **3** when exposed to sunlight for a few hours gave endoperoxides **19** and **20**.



#### Synthesis of AP<sub>2</sub> and AU<sub>2</sub> derivatives

The low solubility of AP<sub>2</sub> and AU<sub>2</sub> compounds in common organic solvents made their isolation and purification very difficult. Moreover, in order to favour the self-assembly of the complementary components AP<sub>2</sub> and AU<sub>2</sub> solvents of low polarity, where the hydrogen bonding is most efficient, must be used.

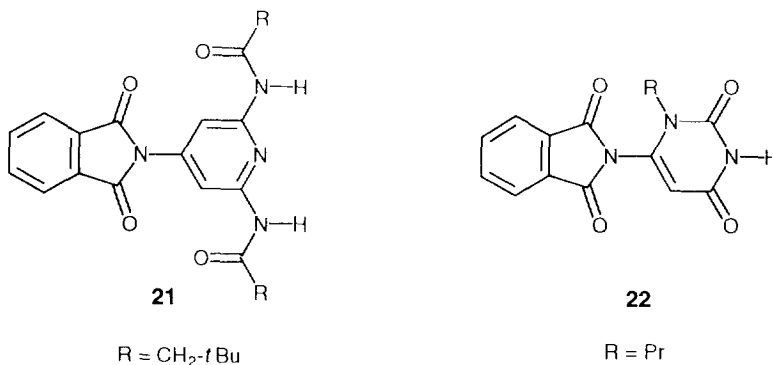
AP<sub>2</sub> derivatives were obtained by heating in 1-methyl-2-pyrrolidone (at 190-200°C for 40-60 mn) the amino derivatives **1 a-c** with the dianhydride **3**: 18-49% yield after recrystallization from a DMF-H<sub>2</sub>O mixture. AP<sub>2</sub>-a and AP<sub>2</sub>-b were insoluble in CHCl<sub>3</sub> and all common solvents but their solubility drastically increased in presence of 1% of trifluoroacetic acid which allowed their characterization by <sup>1</sup>H and <sup>13</sup>C NMR. AP<sub>2</sub>-c is more soluble and its <sup>1</sup>H-NMR spectra in CDCl<sub>3</sub> was obtained at low concentration (10<sup>-3</sup> M) because line broadening, probably due to aggregation phenomena, was observed at higher concentration.

AU<sub>2</sub> derivatives were similarly obtained by heating the amino uracil derivative **2 a-c** with the dianhydride **3** in 1-methyl-2 pyrrolidinone at 190-200°C but for a shorter

time (10-15 min); in this case it was necessary to proceed in presence of *N*-(*tert*-butyldimethylsilyl)-*N*-methyltrifluoroacetamide which transforms, *in situ*, the amino uracil compounds into a more reactive silyloxy species : 29-42% yield after recrystallization from DMF (**AU<sub>2</sub>-a**) and DMF-H<sub>2</sub>O (**AU<sub>2</sub>-b**) or after chromatography on deactivated silica gel (**AU<sub>2</sub>-c**). The solubility in CHCl<sub>3</sub> (null for **AU<sub>2</sub>-a**) increased with the substitution on the uracil subunit. At concentrations higher than 10<sup>-3</sup> M, the <sup>1</sup>H-NMR spectrum of (**AU<sub>2</sub>-c**), in CDCl<sub>3</sub>, showed several signal splittings with line broadening and downfield shifts. This may be attributed to the different ways the uracil groups may self-associate. The <sup>13</sup>C-NMR spectrum showed the same kind of splitting (Figure1).

Like the compounds **3** and **17c**, **AU<sub>2</sub>-c** was readily converted under sunlight, in the presence of air, to the corresponding endoperoxide.

The PhtP and PhtU derivatives **21** and **22**, analogous to one half of **AP<sub>2</sub>** and **AU<sub>2</sub>**, were obtained in the same way that **AP<sub>2</sub>** and **AU<sub>2</sub>** compounds starting from phthalic anhydride.



## Conclusion

The aminopyridine derivatives **1** were obtained in good yield by a rather long but reliable synthetic path (scheme 3) and an improvement of a known method made tetracarboxylic anthracene derivatives easily available in good yield. Due to their insolubility in common organic solvents which makes their isolation and purification very difficult, the **AP<sub>2</sub>** and **AU<sub>2</sub>** compounds were only obtained in moderate yield.

Mixing **AP<sub>2</sub>** and **AU<sub>2</sub>** yields polymeric supramolecular species (**AP<sub>2</sub>**, **AU<sub>2</sub>**)<sub>n</sub>, corresponding to the structure schematically represented on scheme 7<sup>29</sup>. They were found to present a lyotropic mesophase, thus extending the generation of liquid crystalline phases by self-assembly<sup>28,30</sup> to rigid rod type substances.

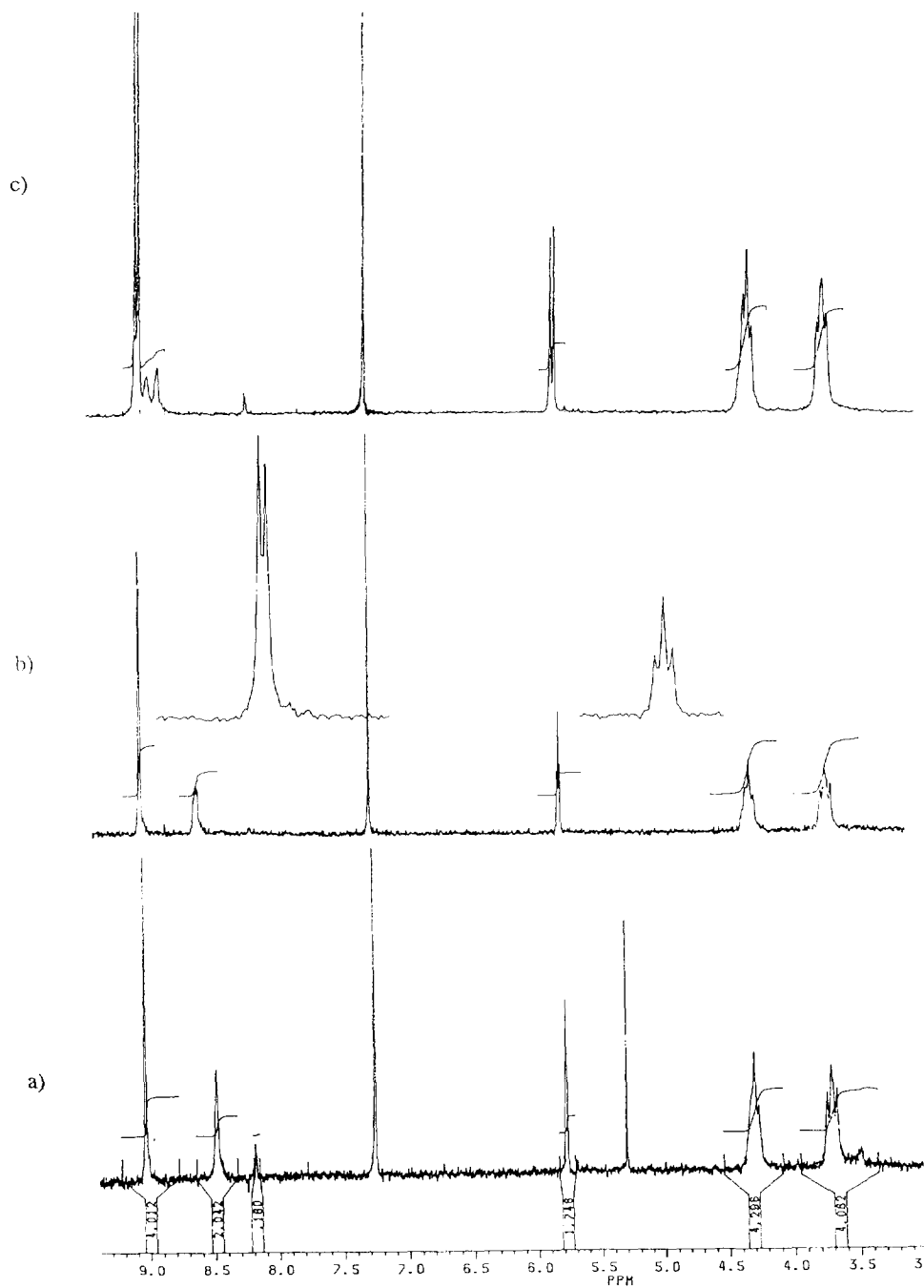
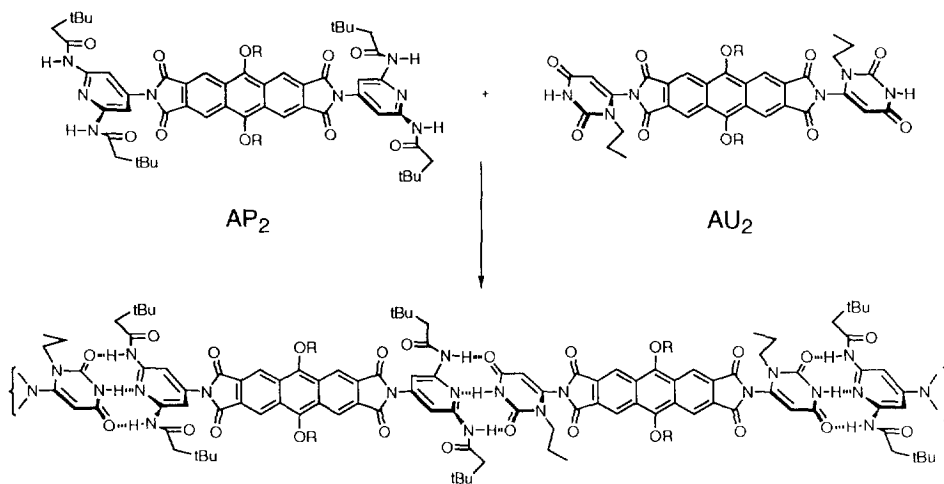


Figure 1-  $^1\text{H-NMR}$  spectra of  $\text{AU}_2\text{-c}$  ( $\text{CDCl}_3$ ): a) 1 mg in 0.6 ml of  $\text{CDCl}_3$ . b) 3 mg in 0.6 ml. c) 6 mg in 0.6 ml.





Scheme 7. Self-assembly of the polymeric supramolecular rigid rod  $(AP_2, AU_2)_n$ ;  
 $R=C_{12}H_{25}$

## EXPERIMENTAL SECTION

*General* - All commercially available chemicals employed were reagent grade and used without further purification. Melting points were determined on a Electrothermal digital melting point apparatus or on a Perkin-Elmer DSC 7 microcalorimeter. Infrared spectra (IR) were recorded on suspension in nujol using a Perkin-Elmer 297 spectrophotometer. IR spectra bands are reported in  $cm^{-1}$ . Absorption spectra (UV) were taken in  $CHCl_3$  solutions on a Perkin-Elmer 554 instrument; the spectral bands are reported in nm.  $^1H$  and  $^{13}C$  NMR spectra were recorded on a Bruker AC-200 spectrometer. Chemical shifts ( $\delta$ ) are reported in ppm from tetramethylsilane as reference.

Mass spectra (MS) : FAB<sup>+</sup> spectra were measured at the Laboratoire de Chimie Organique Structurale (J.-C. Tabet), Université Pierre et Marie Curie, Paris, using NBA (3-nitrobenzylalcohol) as matrix. Elemental analyses were performed at the Service Central de Microanalyse du CNRS, Lyon and at the Service Régional de Microanalyse de

l'Université Pierre et Marie Curie, Paris.

Column chromatographic separations and filtrations were performed over Merck silica gel 60 (0.040-0.063 mm). Analytical thin-layer chromatography (TLC) were carried out on Merck silica gel TLC plates F 254.

Dimethyl 4-(N,N-di-*ter*-Butyloxycarbonyl) amino-2,6-pyridinedicarboxylate (8).

A solution of diester **5**<sup>36</sup> (48.5 g, 0.211 mol) in 1N NaOH aqueous solution (500 ml) was heated at 50-60°C until complete dissolution. Upon addition of concentrated HCl (45 ml) a white solid precipitated. After cooling, the diacid was filtered off and washed with water. The humid cake was placed in a high pressure hydrogenation bomb and a 30% NH<sub>3</sub> aqueous solution was added (400 ml). The bomb was heated at 150°C for 12 h. After cooling the mixture was poured on water (300 ml) and the solvents were evaporated off. The solid residue was dissolved in 1N aqueous NaOH (600 ml) and reprecipitated by adding concentrated HCl (60 ml). After cooling the aminodiacid **6** was collected by filtration, washed with water and dried (39.5 g, 100%).

The above crude diacid was esterified as following : SOCl<sub>2</sub> (80 ml) was added dropwise to cooled MeOH (ice-bath, 300 ml); then crude **6** (39.5 g) was added slowly and the resulting suspension was refluxed for 2.5 h. The volatile materials were evaporated off and the residue was dissolved in 0.8 N HCl solution (500 ml). The insoluble material was filtered off and 10 N aqueous NaOH solution was added carefully until pH 8-9 (about 50 ml). The aminoester **7** was collected by filtration, washed with water and dried (36.5 g, 82%).

This compound (36.5 g, 0.174 mol) was treated with Boc<sub>2</sub>O (83.4 g, 0.382 mol), Et<sub>3</sub>N (9 ml) and pyridine (9 ml) in DMF (170 ml) at 80-90°C for 40 min. The mixture was poured into water (2 l) and the resulting slightly colored precipitate was collected by filtration, washed with water and dried at r.t. under vacuum to give **8** (51.6 g, 72%). This product was used without further purification.

m.p. 173-176°C (dec.). IR : 3105, 1808, 1718, 1605, 1370, 1290, 1255, 1157, 1132; <sup>1</sup>H NMR (CDCl<sub>3</sub>) : 1.46 (s, 18H), 4.03 (s, 6H), 8.12 (s, 2H); Anal. Calcd for C<sub>19</sub>H<sub>26</sub>N<sub>2</sub>O<sub>8</sub> : C, 55.60; H, 6.39; N, 6.83. Found : C, 55.4; H, 6.3; N, 6.8.

4-(N-*ter*-Butyloxycarbonyl)amino-2,6-pyridinedicarboxamide (9)

A suspension of diester **8** (51.6 g, 0.125 mol) in 5 N NH<sub>3</sub> methanolic solution (500 ml) was refluxed for 18 h. After evaporation of the solvents the solid residue was washed with water and dried under vacuum in presence of KOH for a day. The resulting white powder (38 g), still containing *ter*-butylcarbamate, was recrystallized from methanol to afford **9** (24.7 g, 71%) as a powder. m.p. 160-165°C (dec.). R<sub>f</sub> 0.30

(CH<sub>2</sub>Cl<sub>2</sub>-10% MeOH).

IR : 3390, 3260, 1745, 1680, 1580, 1510, 1350, 1280, 1240, 1158, 1100. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) 1.49 (s,9H), 7.63 (br.s,2H), 8.26 (s,2H), 8.78 (br.s,2H), 10.24 (br.s,1H). Anal. Calcd for C<sub>12</sub>H<sub>16</sub>N<sub>4</sub>O<sub>4</sub>, 0.5 H<sub>2</sub>O : C, 49.82; H, 5.92; N, 19.37. Found : C, 49.8; H, 5.9; N, 19.2.

#### 4-(*N-ter* Butyloxycarbonyl)amino-2,6-diaminopyridine (10)

Pellets of 85% KOH (28 g, 0.4 mol) were dissolved in H<sub>2</sub>O (150 ml); to this cooled solution (0-5°C) bromine (12.7 g, 80 mmol) was added dropwise with stirring, then diamide **9** (40 mmol) rapidly. Upon slow addition of dioxane (50 ml) most of the solid was dissolved and the resulting solution was stirred for 30 min at r.t. then heated at 50-55°C for 45 mn. AcOH (20 ml) was added dropwise to the mixture : an exothermic reaction took place with CO<sub>2</sub> evolution. The mixture was further heated at 50-55°C for 20 mn then, after cooling at r.t., KOH (14 g) was added. The resulting white suspension was extracted three times with CH<sub>2</sub>Cl<sub>2</sub>. The organic layers were dried on Na<sub>2</sub>SO<sub>4</sub> and evaporated off to yield crude **10** (9.0 g). Recrystallization from AcOEt-*n* Hexane (1/1) afforded pure **10** (4.13 g, 46%). (Crude **10** may be used without further purification). m.p. 146°C then 180°C. R<sub>f</sub> 0.23 (CH<sub>2</sub>Cl<sub>2</sub>-10% MeOH). IR : 3450, 3400, 3370, 3200, 1715, 1615, 1520, 1440, 1380, 1370, 1313, 1250, 1168. <sup>1</sup>H NMR (CDCl<sub>3</sub>) 1.49 (s,9H), 4.16 (br.s, 4H), 5.97 (s, 2H), 6.49 (br.s,1H). Anal. Calcd for C<sub>10</sub>H<sub>16</sub>N<sub>4</sub>O<sub>2</sub> : C, 53.56; H, 7.19; N, 24.98. Found : C, 53.3; H, 7.1; N, 25.0.

#### 4-Amino-2,6-diacetylaminopyridine (1-a)

Crude diaminopyridine **10** (1.4 g, 5 mmol) was treated with pyridine (50 ml) and Ac<sub>2</sub>O (20 ml) at r.t. overnight. After removal of the solvents the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and the solution passed through a SiO<sub>2</sub> column with CH<sub>2</sub>Cl<sub>2</sub>-7% MeOH as eluent, to afford 4-(*N-ter* Butoxycarbonyl)amino-2,6 diacetylaminopyridine.

This latter (0.897 g, 2.91 mmol) was treated with CF<sub>3</sub>CO<sub>2</sub>H (5 ml) in CH<sub>2</sub>Cl<sub>2</sub> (20 ml) at r.t. for 4 h. After evaporation of the solvents the residual oil was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20 ml) and NEt<sub>3</sub> (5 ml) was added. The resulting suspension was sonicated for a while and stirred for 30 min. The precipitate was collected and dried under vacuum in presence of P<sub>2</sub>O<sub>5</sub>. The aminopyridine **1-a** thus obtained was analytically pure but contains half a molecule of H<sub>2</sub>O. (502 mg, 76%). R<sub>f</sub> 0.42 (CH<sub>2</sub>Cl<sub>2</sub>-10% MeOH). IR : 3400, 3300, 3180, 3110, 1690, 1602, 1517, 1455, 1420, 1379, 1343, 1290, 1237, 1150, 1068. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) : 1.45 (s,9H), 2.05 (s,6H), 7.87 (s,2H), 9.80 (br.s,1H), 9.84 (br.s,2H). Anal. Calcd for C<sub>9</sub>H<sub>12</sub>N<sub>4</sub>O<sub>2</sub>, 0.5 H<sub>2</sub>O : C, 49.76; H, 6.03; N, 25.79. Found : C, 50.2; H, 5.8; N, 25.6.

**4-Amino-2,6-dipentanoylaminopyridine (1-b)**

Diaminopyridine **10** (450 mg, 2.01 mmol) and valeric anhydride (830 mg, 4.46 mmol) were dissolved in pyridine (2 ml) and stirred at r.t., under N<sub>2</sub>, overnight. After evaporation of the pyridine, the residue was dissolved in ether (50 ml) and the ethereal solution was washed twice with NaHCO<sub>3</sub> saturated aqueous solution (10 ml), dried over Na<sub>2</sub>CO<sub>3</sub>, evaporated to give an oil which solidified by triturating with *n*-hexane (3 ml). After drying under vacuum this crude product (740 mg, 95%, mp 144°C) was treated with CF<sub>3</sub>CO<sub>2</sub>H (2 ml) in CH<sub>2</sub>Cl<sub>2</sub> (8 ml) for 6 h at r.t. After evaporation of the solvents, water (10 ml) was added to the oily residue and 1N NaOH solution (about 8 ml) was added slowly under stirring until pH 9-10. The white powder was filtered off, washed with water, dried under vacuum in presence of P<sub>2</sub>O<sub>5</sub>, at 60°C to give **1-b** (484 mg, 82%) which was used without further purification. mp 146-152°C. R<sub>f</sub> 0.53 (CH<sub>2</sub>Cl<sub>2</sub>-10% MeOH). IR : 3480, 3440, 3370, 3240, 1688, 1625, 1580, 1520, 1270, 1220, 1190, 1145, 1090, 1033. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>) : 0.94 (t, J=7Hz, 6H), 1.39 (sext., J=7Hz, 4H), 1.69 (quint., J=7Hz, 4H), 2.45 (t, J=7Hz, 4H), 4.35 (br. m, 2H), 7.27 (s, 2H), 7.5 (m, 2H). Anal. Calcd for C<sub>15</sub>H<sub>24</sub>N<sub>4</sub>O<sub>2</sub>, 0.25 H<sub>2</sub>O : C, 60.69; H, 8.32; N, 18.87. Found : C, 60.5; H, 8.1; N, 18.6.

**4-Amino-2,6-di-*t*-Butylacetylaminopyridine (1-c)**

*t*-Butylacetylchloride (1.15 g, 8.57 mmol) was added to a solution of diaminopyridine **10** (908 mg, 4.05 mmol) and NEt<sub>3</sub> (1.0 g, 10 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 ml) at r.t. After stirring for 1 h, the mixture was poured into Et<sub>2</sub>O (100 ml); the precipitated salt was filtered and washed with Et<sub>2</sub>O. The filtrate was evaporated to dryness to give crude N-Bocdiacylaminopyridine (1.92 g) which was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (16 ml). CF<sub>3</sub>CO<sub>2</sub>H (4 ml) was added and the mixture was stirred at r.t. overnight. After evaporation of the solvents, the oily residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (100 ml) and washed with a saturated solution of NaHCO<sub>3</sub> (50 ml). The aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 20 ml) and the combined organic phases were dried over Na<sub>2</sub>CO<sub>3</sub> and evaporated to give crude diacylaminopyridine (1.24 g). After purification by flash-chromatography on SiO<sub>2</sub> using CH<sub>2</sub>Cl<sub>2</sub>-10% MeOH as eluant pure **1-c** was obtained (1.02 g, 79%) mp. 225-226°C. R<sub>f</sub> 0.36 (CH<sub>2</sub>Cl<sub>2</sub>-10% MeOH). IR : 3512, 3490, 3450, 3360, 3220, 3160, 3130, 1750, 1690, 1640, 1580, 1515, 1460, 1380, 1370, 1350, 1257, 1232, 1215, 1144, 1120, 1028. <sup>1</sup>H NMR (CDCl<sub>3</sub>) : 1.09 (s, 18H), 2.19 (s, 4H), 4.29 (br. s., 2H), 7.29 (s, 2H), 7.34 (br. s., 2H). Anal. calcd for C<sub>17</sub>H<sub>28</sub>N<sub>4</sub>O<sub>2</sub> : C, 63.72; H, 8.81; N, 17.48. Found : C, 63.5; H, 8.7; N, 17.6.

**Tetramethyl-1,4,5,8-tetrahydro-9,10-dihydroxyanthracene-2,3,6,7-tetracarboxylate (16).**

2,3-Dicarbomethoxy-1,3-butadiene **11**<sup>41</sup> (9.36 g, 55.0 mmol), benzoquinone (12.5g, 116 mmol) and *p*-toluenesulfonic acid (0.5 g) were placed in a three necked round bottom flask equipped with a N<sub>2</sub> inlet, a reflux condenser, a magnetic stirrer and a thermometer. Under N<sub>2</sub> flow, dioxane (20 ml) was added and the mixture was heated at 70-75°C, with stirring for 10 hours. Diene **11** (7.33 g, 43 mmol) was then added to the resulting dark suspension and the mixture was further heated at 70-75°C for 18 h. After cooling the suspension was poured into Et<sub>2</sub>O (500 ml) and filtered to give a gray powder which was washed with acetone (**16** is practically insoluble in acetone). The beige powder thus obtained was almost pure and used without further purification (12.2 g, 56%). An analytical sample was obtained by recrystallization from dioxane. mp 230-260°C (dec.). IR : 3450, 1700, 1660, 1315, 1295, 1240, 1227, 1195, 1150, 1075, 1055. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) : 3.50 (s, 8H), 3.72 (s, 12H), 8.08 (s, 2H). Anal. Calcd for C<sub>22</sub>H<sub>22</sub>O<sub>10</sub> : C, 59.19; H, 4.97. Found : C, 59.1; H, 5.0.

**Tetramethyl-9,10-didodecyloxyanthracene-2,3,6,7-tetracarboxylate (17).**

NaH (60% oil dispersion, 1.0 g, 25 mmol) was weighted in a 100 ml three necked round bottom flask and washed with pentane (3x30 ml) by a stirring-decantation sequence. The flask was fitted with a thermometer, a reflux condenser and a N<sub>2</sub> inlet and anhydrous DMF (40 ml) was introduced. Under N<sub>2</sub>, dihydroxyanthracene **16** (4.46 g, 10 mmol) was rapidly added. The resulting dark violet-blue solution was heated at 80°C for 40 mn before adding rapidly dodecyl iodide (5.6 ml, 21.6 mmol) with a syringe. The mixture was kept at 80°C for 1 h; then the N<sub>2</sub> flow was stopped and a flow of air was passed through the solution for 20 mn at 80°C. After cooling to r.t. the mixture was poured on water (300 ml) and the resulting aqueous suspension was acidified with 2N HCl (10 ml) and extracted with Et<sub>2</sub>O (5x50 ml). The combined organic phases were washed twice with 1M NH<sub>4</sub>Cl solution (2x50 ml), dried on Na<sub>2</sub>SO<sub>4</sub> and evaporated to give a yellow solid (8.0 g). Recrystallization of this crude material from hot methanol gave the didodecyloxyanthracene **17** (5.56 g, 71%). mp 102°C. R<sub>f</sub> 0.42 (AcOEt-hexane : 20-80). IR 1735, 1725, 1623, 1442, 1395, 1378, 1350, 1278, 1265, 1241, 1190, 1120; 1100. U.V. : 289 (log ε = 5.02), 405 (log ε = 3.89), 430 (sh). <sup>1</sup>H NMR (CDCl<sub>3</sub>) : 0.88 (br.t., 6H, J=6Hz), 1.1-1.6 (m, 32H), 1.67 (m, 4H), 2.04 (q, 4H, J=7Hz), 4.00 (s, 12H), 4.19 (t, 4H, J=7Hz), 8.70 (s, 4H). <sup>13</sup>C NMR : 167.6, 150.1, 128.6, 125.9, 126.0, 77.8, 52.5, 31.8, 30.4, 29.5, 29.4, 29.2, 26.1, 22.5, 13.9. Anal. Calcd for C<sub>46</sub>H<sub>66</sub>O<sub>10</sub> : C, 70.92; H, 8.54. Found : C, 71.0; H, 8.6. Caution : 9,10-Alkoxyanthracenes react readily with O<sub>2</sub> under daylight to give endoperoxides. Care must

be taken when making NMR and U.V measurements.

#### 9.10-Didodecyloxanthracene-2,3,6,7-tetracarboxylic acid (18)

To a solution of anthracenetetraester **17** (5.56 g, 7.14 mmol) in THF (80 ml) a methanolic 1N NaOH solution (80 ml) was added. The mixture was heated to reflux for 2h during which a yellow powder precipitated. After cooling it was poured into H<sub>2</sub>O (300 ml) and filtered through a cotton wad. The yellow filtrate was acidified with 2N HCl solution (80 ml) and the resulting yellow precipitate was collected, washed with water and dried (at 80°C under vacuum in presence of KOH pellets) to afford tetraacid **18** (5.13 g, 100%). mp > 250°C (dec.). IR : 1690, 1350, 1290. <sup>1</sup>H NMR (acetone-d<sub>6</sub>) : 0.82 (br.t., 6H, J=7Hz), 1.1-1.5 (m, 36H), 1.63 (m, 4H), 1.96 (quint., 4H, J=7Hz), 4.18 (t, 4H, J=7Hz), 8.61 (s, 4H). Anal. Calcd for C<sub>42</sub>H<sub>58</sub>O<sub>10</sub> : C, 69.78; H, 8.09. Found : C, 69.7; H, 8.1.

#### 5.11-Didodecyloxy-1H,3H-anthra[2,3-c : 6,7]difuran-1,3,7,9-tetrone (3)

Anthracenetetracarboxylic acid **18** (5.13 g, 7.14 mmol) was dissolved in Ac<sub>2</sub>O (150 ml) at reflux temperature (140°C) and stood on cooling. After dilution Et<sub>2</sub>O (500 ml) crystalline dianhydride **3** was collected, washed with Et<sub>2</sub>O and dried (4.29 g, 88%). The heating is not necessary for the transformation of the tetraacid **18** to the dianhydride **3** : complete transformation of **18** to **3** was observed on standing of a suspension of **18** in Ac<sub>2</sub>O at r.t.. The heating allowed to obtain a crystalline material instead of a powder. mp 245°C. IR : 1850, 1780, 1355, 1268, 1239, 1125. UV : 304 (log ε = 5.15), 445 (log ε = 4.18). <sup>1</sup>H NMR : 0.88 (br.t., 6H, J=7Hz), 4.27 (t, 4H, J=7Hz), 9.07 (s, 4H). MS : FAB<sup>+</sup>, 687 (M<sup>+</sup>). Anal. Calcd for C<sub>42</sub>H<sub>54</sub>O<sub>8</sub> : C, 73.44; H, 7.92. Found : C, 73.4; H, 7.7.

#### Endoperoxyde (19)

Anthracene tetraester **17** (100 mg) was dissolved in CHCl<sub>3</sub> (50 ml) and exposed to sunlight for 8 h until the yellow color faded. After evaporation of the solvent, the residual solid was recrystallized from MeOH to give **19** (64 mg, 64%). mp 68°C. R<sub>f</sub> 0.29 (AcOEt-hexane : 20-80). IR : 1735, 1630, 1440, 1290, 1240, 1110. UV : 241 (log ε = 4.6). <sup>1</sup>H NMR : 0.88 (t, 6H, J=7Hz), 1.2-1.6 (m, 36H), 1.86 (quint., 4H, J=7Hz), 3.91 (s, 12H), 4.24 (t, 4H, J=7Hz), 7.84 (s, 4H). <sup>13</sup>C NMR : 167.1, 141.1, 131.6, 121.7, 101.3, 67.5, 52.8, 31.8, 30.9, 29.6, 29.5, 29.3, 25.8, 22.6, 14.0. MS : FAB<sup>+</sup>, 778 [(M-O<sub>2</sub>)<sup>+</sup>]. Anal. Calcd for C<sub>46</sub>H<sub>66</sub>O<sub>12</sub> : C, 68.13; H, 8.20; O, 23.67. Found : C, 67.8; H, 8.3; O, 23.8.

**Endoperoxide (20).**

**20** was prepared similarly to **19** (41% yield). mp 158°C. IR : 1860, 1803, 1300, 1248, 1198. UV : 241 (log  $\epsilon$  = 4.85).  $^1\text{H}$  NMR : 0.88 (br.t., 6H, J=7Hz), 1.2-1.7 (m, 36H), 1.92 (quint., 4H, J=7Hz), 4.29 (t, 4H, J=7Hz), 8.17 (s, 4H).  $^{13}\text{C}$  NMR : 161.5, 146.0, 131.4, 118.8, 101.1, 68.0, 31.8, 30.8, 29.5, 29.2, 25.7, 22.6, 14.0. MS : FAB<sup>+</sup>, 719 (M<sup>+</sup>), 687 [(M-O<sub>2</sub>)<sup>+</sup>]. Anal. Calcd for C<sub>42</sub>H<sub>54</sub>O<sub>10</sub> : C, 70.17; H, 7.57; O, 22.26. Found : C, 70.4; H, 7.7; O, 21.5.

**2.8-Bis(1.2.3.6-tetrahydro-2.6-dioxo-3-propyl-4-pyrimidinyl)-5.11-didodecyloxanthra [2.3-c : 6.7 c']dipyrrole-1.3.7.9(2H.8H)tetrone AU<sub>2</sub>-c.**

A mixture of anthracenedianhydride **3** (342 mg, 0.498 mmol), 6-amino-1-propyluracil (203 mg, 1.20 mmol) and N-(*tert*-Butyldimethylsilyl)-N-methyltrifluoroacetamide (638 mg, 2.64 mmol) in 1-methyl-2-pyrrolidinone (1.3 ml) was heated for 15 mn, under N<sub>2</sub> with stirring, in an oil bath preheated at 190-195°C. The hot resulting dark solution was added dropwise to 2N HCl (50 ml) and the precipitate was collected, washed with 2N HCl (50 ml) then with water (50 ml) and dried to yield crude AU<sub>2</sub>-c (540 mg). This material was purified by flash chromatography on deactivated silicagel [(prepared by stirring SiO<sub>2</sub> (85 g) and H<sub>2</sub>O (15 g) for 10 mn)] using CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 97/3, as eluant to afford pure AU<sub>2</sub>-c dried at 110°C under vacuum (245 mg, 50%). mp 240-250°C (dec.). R<sub>f</sub> 0.35 (CH<sub>2</sub>Cl<sub>2</sub>-7.5% MeOH). IR : 3200, 1782, 1742, 1695, 1460, 1380, 1330, 1230, 1165, 1130, 1020. UV : 312 (log  $\epsilon$  = 5.0), 406 (log  $\epsilon$  = 3.8), 432 (log  $\epsilon$  = 4.2), 458 (log  $\epsilon$  = 4.3).  $^1\text{H}$  NMR (CDCl<sub>3</sub>, c=10<sup>-3</sup>M) : 0.7-1.0 (m, 12H), 1.2-1.8 (m, 40H), 2.16 (m, 4H), 3.71 (t, 4H, J=7Hz), 4.30 (br.t., 4H, J=7Hz), 5.77 (br.s, 2H), 8.48 (br.s, 2H), 9.03 (s, 4H).  $^{13}\text{C}$  (CDCl<sub>3</sub>) : 11.05, 14.0, 22.1, 22.6, 26.0, 29.3, 29.5, 30.5, 31.8, 46.1, 76.3, 76.9, 77.5, 79.4, 104.2, 123.4, 126.7, 128.7, 143.0, 154.1, 161.4, 164.0. MS : FAB<sup>+</sup>, 990 (M<sup>+</sup>). Anal. Calcd for C<sub>56</sub>H<sub>72</sub>N<sub>6</sub>O<sub>10</sub> : C, 67.99; H, 7.34; N, 8.50. Found : C, 67.8; H, 7.5; N, 8.4.

**2.8 Bis(1.2.3.6-tetrahydro-2.6-dioxo-4 pyrimidinyl)-5.11-didodecyloxanthra [2.3.-c : 6.7-c']dipyrrole-1.3.7.9(2H. 8H)tetrone (AU<sub>2</sub>-a)**

This compound was prepared similarly to AU<sub>2</sub>-c and purified by recrystallization from DMF (29% yield). mp > 260°C.  $^1\text{H}$  NMR (DMSO-d<sub>6</sub>) : 0.84 (t, 6H, J=7Hz), 1.1-1.5 (m, 32H), 1.6 (m, 4H), 2.05 (m, 4H), 4.3 (t, 4H, J=7Hz), 5.82 (d, 2H, J=1.6Hz), 8.84 (s, 4H), 11.5 (br.m, 4H). MS : FAB<sup>+</sup>, 905 (M<sup>+</sup>). Anal. Calcd for C<sub>50</sub>H<sub>60</sub>N<sub>6</sub>O<sub>10</sub> : C, 66.36; H, 6.68; N, 9.29. Found : C, 66.3; H, 6.7; N, 9.3.

2,8-Bis(1,2,3,6-tetrahydro-2,6-dioxo-3-methyl-4-pyrimidinyl)-5,11-didodecyloxyanthra[2,3-c : 6,7-c']dipyrrole-1,3,7,9(2H, 8H)tetrone (AU<sub>2</sub>-b)

This compound was prepared similarly to AU<sub>2</sub>-c and purified by recrystallization from DMF-H<sub>2</sub>O (42% yield). mp 290-300°C (dec.). <sup>1</sup>H NMR (CDCl<sub>3</sub>) : 0.88 (t, 6H, J=7Hz), 1.1-1.8 (m, 36H), 2.16 (m, 4H), 3.33 (s, 6H), 4.28 (t, 4H, J=7Hz), 5.83 (2d, 2H), 8.25 (br.s, 2H), 9.03 (s, 4H, J=7Hz). MS : FAB<sup>+</sup>, 933 (M<sup>+</sup>). Anal. Calcd for C<sub>52</sub>H<sub>64</sub>N<sub>6</sub>O<sub>10</sub> : C, 66.93; H, 6.91, N, 9.01. Found : C, 66.8; H, 6.9; N, 9.1.

2,8-Bis[2,6-di(*tert*-butylacetylamino)-4-pyridyl]-5,11-didodecyloxyanthra[2,3-c : 6,7-c']dipyrrole-1,3,7,9(2H,8H)-tetrone (AP<sub>2</sub>-c).

A mixture of anthracenedianhydride **3** (344 mg, 0.501 mmol) and diacetylaminopyridine **1c** (318 mg, 0.992 mM) in 1-methyl-2-pyrrolidinone (1 ml) was heated for 1h, under N<sub>2</sub> with stirring, at 200°C. After cooling the reaction mixture was poured into MeOH/H<sub>2</sub>O, 80/20 (50 ml). The precipitate was collected, washed with aqueous MeOH and dried to give crude AP<sub>2</sub>-c (520 mg). This material was purified by flash chromatography on deactivated silicagel [(prepared by stirring SiO<sub>2</sub> (68 g) and water (12 g) for 15 mn)] using CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>COCH<sub>3</sub>, 98/2, as eluant to yield pure AP<sub>2</sub>-c (359 mg, 56%) which was further purified by recrystallization from DMF (35 ml) and H<sub>2</sub>O (4 ml) to afford analytically pure AP<sub>2</sub>-c (310 mg, 48%). mp 350° (dec.). R<sub>f</sub> 0.42 (CH<sub>2</sub>Cl<sub>2</sub>, 5% acetone). IR : 3440, 3350, 1780, 1735, 1700, 1612, 1583, 1430, 1370, 1350, 1305, 1228, 1138, 1030. UV (CH<sub>2</sub>Cl<sub>2</sub>) : 428 (log ε = 4.2), 455 (log ε = 4.3). <sup>1</sup>H NMR (CDCl<sub>3</sub>, c=10<sup>-3</sup> M) : 0.87 (t, 6H, J=7Hz), 1.11 (s, 36H), 1.2-1.8 (m, 36H), 2.2 (m, 4H), 2.27 (s, 8H), 4.29 (t, 4H, J=7Hz), 7.69 (br.s, 4H), 8.22 (s, 4H), 8.92 (s, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>-1% trifluoroacetic acid), 14.0, 22.6, 25.8, 29.3, 29.5, 29.6, 30.1, 31.7, 31.9, 50.2, 76.3, 76.9, 77.5, 79.5, 102.0, 122.69, 125.5, 127.7, 145.3, 147.9, 153.2, 163.5, 175.2. MS : FAB<sup>+</sup>, 1292 (M<sup>+</sup>). Anal. Calcd for C<sub>76</sub>H<sub>106</sub>N<sub>8</sub>O<sub>10</sub> : C, 70.67; H, 8.27, N, 8.67. Found : C, 70.5; H, 8.2; N, 8.7.

2,8-bis(2,6-diacetylamino-4-pyridyl)-5,11-didodecyloxyanthra[2,3-c : 6,7-c']dipyrrole-1,3,7,9 (2H,8H)tetrone (AP<sub>2</sub>-a).

This product was obtained similarly to AP<sub>2</sub>-c and purified by recrystallization from DMF-H<sub>2</sub>O, without chromatography. (18% yield). mp : around 350°C (dec.). <sup>1</sup>H NMR (CDCl<sub>3</sub>-1% trifluoroacetic acid) : 0.88 (t, 6H, J=7Hz), 1.2-1.8 (m, 36H), 2.1 (m, 4H), 2.45 (s, 12H), 4.04 (t, 4H, J=7Hz), 7.46 (s, 4H), 8.44 (s, 4H), 11.3 (br.s, 4H). MS : FAB<sup>+</sup>, 1068 (M<sup>+</sup>). Anal. Calcd for C<sub>60</sub>H<sub>74</sub>N<sub>8</sub>O<sub>10</sub> : C, 67.52; H, 6.99, N, 10.50. Found : C, 67.3; H, 7.0; N, 10.6.



2,8-bis(2,6-dipentanylamino-4-pyridyl)-5,11-didodecyloxanthral[2,3-c : 6,7-c']dipyrrole-1,3,7,9 (2H,8H)tetrone (AP<sub>2</sub>-b).

This product was obtained similarly to AP<sub>2</sub>-c and purified by recrystallization from DMF-H<sub>2</sub>O (35% yield). mp : around 330°C (dec.). <sup>1</sup>H NMR (CDCl<sub>3</sub>) : 0.88 (t, 6H, J=7Hz), 0.99 (t, 12H, J=7Hz), 1.3-1.8 (m, 52H), 2.10 (m, 4H), 2.63 (t, 8H, J=7Hz), 4.04 (br.t, 4H, J=7Hz), 7.45 (s, 4H), 8.42 (s, 4H), 11.06 (br.s, 4H). MS : FAB<sup>+</sup>, 1068 (M<sup>+</sup>). Anal. Calcd for C<sub>60</sub>H<sub>74</sub>N<sub>8</sub>O<sub>10</sub> : C, 67.5; H, 6.99; N, 10.50. Found C, 67.3; H, 7.0; N, 10.6.

2-(2,6-Di(*tert*-butylacetyl-amino)-4-pyridyl)-1H-isoindole-1,3 (2H)dione (21).

A mixture of phthalic anhydride (140 mg, 0.945 mmol) and acylamino-aminopyridine **1c** (161 mg, 0.502 mmol) in 1-methyl-2-pyrrolidinone was heated, under N<sub>2</sub>, at 200°C for 30 mn. After cooling the mixture was dissolved in MeOH (2 ml) and poured in water (3 ml). A saturated NaHCO<sub>3</sub> solution (1 ml) was added to the suspension and, after stirring for 5 mn, the solid was filtered and dried to afford crude **22** which was purified by flash chromatography on deactivated silicagel (prepared by stirring SiO<sub>2</sub> with 15% H<sub>2</sub>O) using CH<sub>2</sub>Cl<sub>2</sub>/acetone, 97/3, as eluant. Recrystallization from MeOH-H<sub>2</sub>O yielded pure **22** (92 mg, 43%). mp 210°C. R<sub>f</sub> 0.30 (CH<sub>2</sub>Cl<sub>2</sub>, 5% acetone). IR : 3440, 3340, 1795, 1730, 1705, 1610, 1585, 1500, 1430, 1370, 1309, 1279, 1230, 1210, 1135, 1110, 1088, 1055, 1040, 1030. <sup>1</sup>H NMR (CDCl<sub>3</sub>) : 1.10 (s, 18H), 2.24 (s, 4H), 7.60 (br.s, 2H), 7.78-7.82 (m, 2H), 7.94-7.98 (m, 2H), 8.12 (s, 2H). Anal. Calcd for C<sub>25</sub>H<sub>30</sub>N<sub>4</sub>O<sub>4</sub> - 0.25 H<sub>2</sub>O : C, 65.99, H, 6.76; N, 12.31. Found : C, 66.1; H, 6.7; N, 12.5.

2-(1,2,3,6-Tetrahydro-2,6-dioxo-3-propyl-4 pyrimidyl)-1H-isoindole-1,3 (2H)-dione (22).

A mixture of phthalic anhydride (744 mg, 5.02 mmol), 6-amino-1-propyluracil (850 mg, 5.02 mmol), bis(trimethylsilyl)acetamide (2.0 g, 10 mmol) in 1-methyl-2-pyrrolidinone (5 ml) was heated, under N<sub>2</sub>, at 150-160°C for 15 mn. After cooling the reaction mixture was poured into water (50 ml). The precipitate was filtered, washed with water and dried to afford a crude product (1,0 g, 66%) which was recrystallized from MeOH to afford pure **21** (603 mg, 40%). mp 228-230°C. R<sub>f</sub> 0.28 (CH<sub>2</sub>Cl<sub>2</sub>-20% acetone). IR 3180, 3050, 1798, 1700, 1630, 1460, 1420, 1370, 1350, 1335, 1227, 1170, 1079, 1026. <sup>1</sup>H NMR (CDCl<sub>3</sub>) : 0.80 (t, 3H, J=7.6Hz), 1.58 (sext., 2H, J=7.6 Hz), 3.64 (t, 2H, J=7.6 Hz), 5.72 (d, 1H, J=2.2 Hz), 7.88-8.03 (m, 4H), 9.6 (br.s, 1H). Anal. Calcd for C<sub>15</sub>H<sub>13</sub>N<sub>3</sub>O<sub>4</sub> : C, 60.20; H, 4.38; N, 14.04. Found : C, 60.15; H, 4.3; N, 14.1.

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