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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 $\mathbf{AP_2}$ and $\mathbf{AU_2}$, 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 $(\mathbf{AP_2}, \mathbf{AU_2})_n$. The synthesis of these compounds is reported.

Numerous supramolecular architectures resulting from the self assembly of suitably designed molecular components have now been reported.[1] 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,[2-4] ribbons, [2] tapes,[3] cyclic species, [3c,d,4-8] cylindrical complexes,[9] double-helical complexes,[10-14] catenanes [15-19], rotaxanes [20-27] and so on.

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

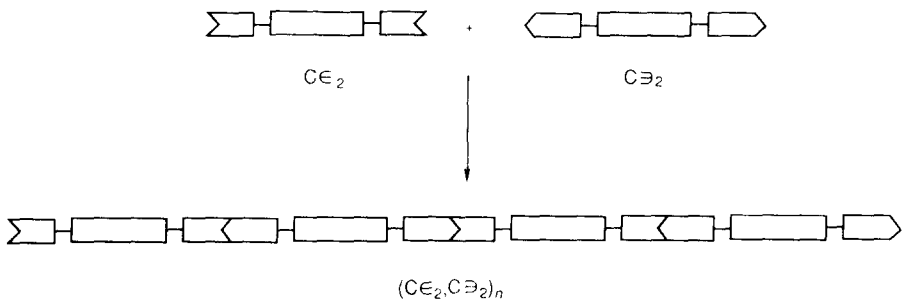
The molecular recognition directed self-assembly of complementary components may also represent an approach to the obtention of species of nanometric dimensions required for the development of molecular and supramolecular devices.[1] The molecular lines,[31] rod-shapes molecules[32], dendrimers,[33-36] arborols,[37] and branched polyacetylenes[38] 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[29] that self-assembly may constitute a

novel approach to such a synthetic problem : the autoassociation of the complementary components $\mathbf{AU_2}$ and $\mathbf{AP_2}$ was shown to form supramolecular species $\mathbf{(AU_2,AP_2)_n}$ 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 $\mathbf{AU_2}$ and $\mathbf{AP_2}$.

Design of the complementary components $\mathbf{AU_2}$ and $\mathbf{AP_2}$

It two complementary units $\in$ and $\ni$ are grafted onto a rigid core C, mixing $C\in_2$ with the complementarity $C\ni_2$ may lead to the self-assembly of a linear polymeric rigid rod (Scheme 1).

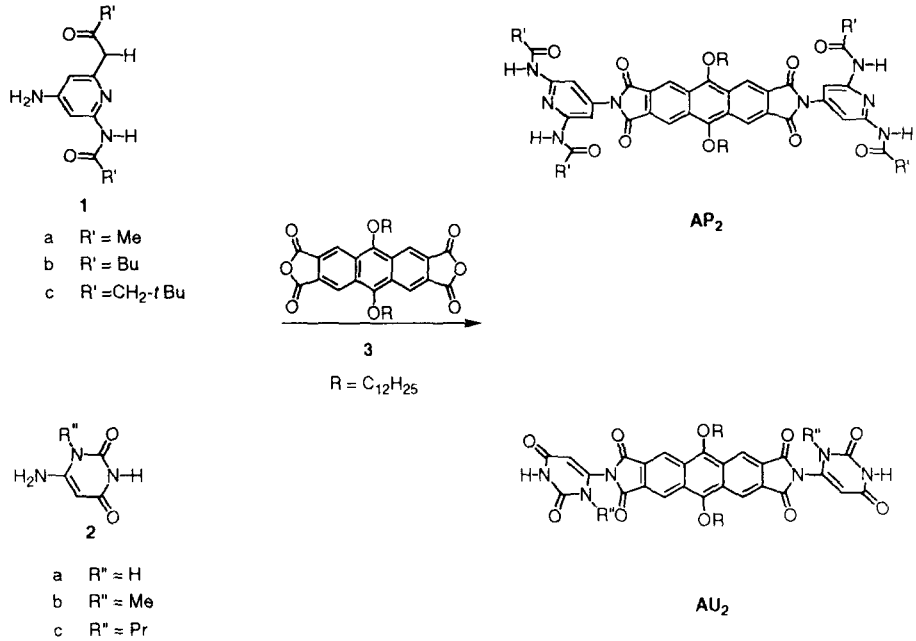


Scheme 1

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 $\in$ and $\ni$, which are well known to form triply hydrogen-bonded complementary pairs[28,39-41] 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.

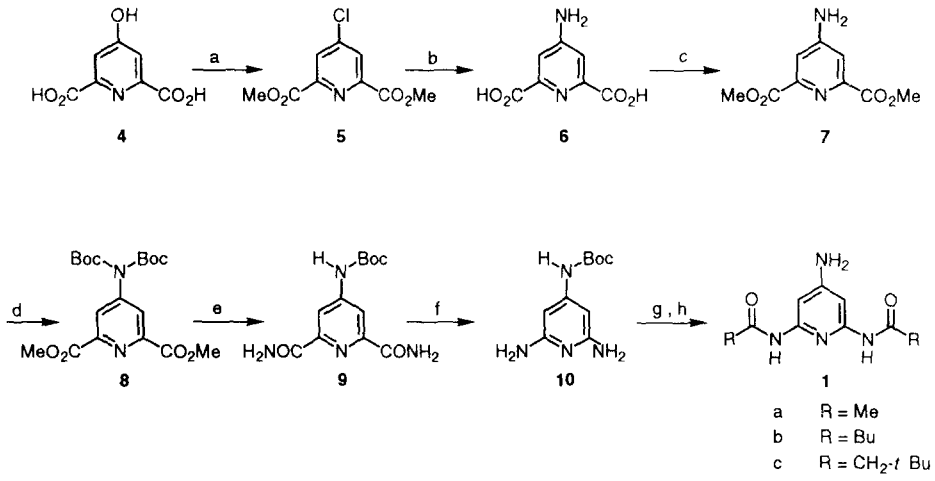
$\mathbf{AP_2}$ and $\mathbf{AU_2}$ Synthesis

$\mathbf{AP_2}$ and $\mathbf{AU_2}$ 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).



Scheme 2

Synthesis of diacylaminopyridine derivatives **1**



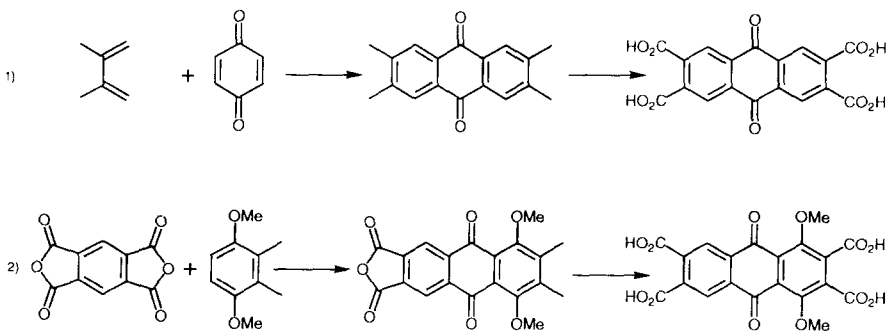
Scheme 3. a) PCl_5, then MeOH; b) NaOH then NH_3 aq., 170°C; c) MeOH, $SOCl_2$; d) Boc_2O, pyridine; e) NH_3, MeOH; f) Br_2, KOH; g) $(R\text{-}CO)_2O$ or *tert*-Bu-CH_2COCl; h) CF_3CO_2H.

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**[42] and **6**[43], 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_2,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_3CO_2H deprotection of the amine function, gave the compounds **1** a-c (75-80%).

Synthesis of the anthracenic dianhydride **3**

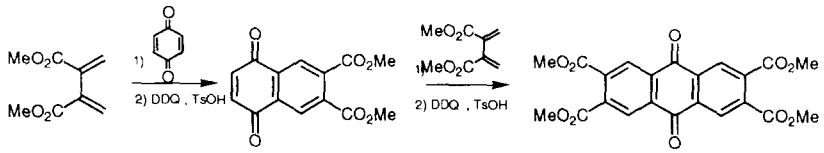
Most synthetic methods to obtain 2,3,7,8-anthracenetetracarboxylic acid derivatives use the same strategy shown in Scheme 4.



Scheme 4

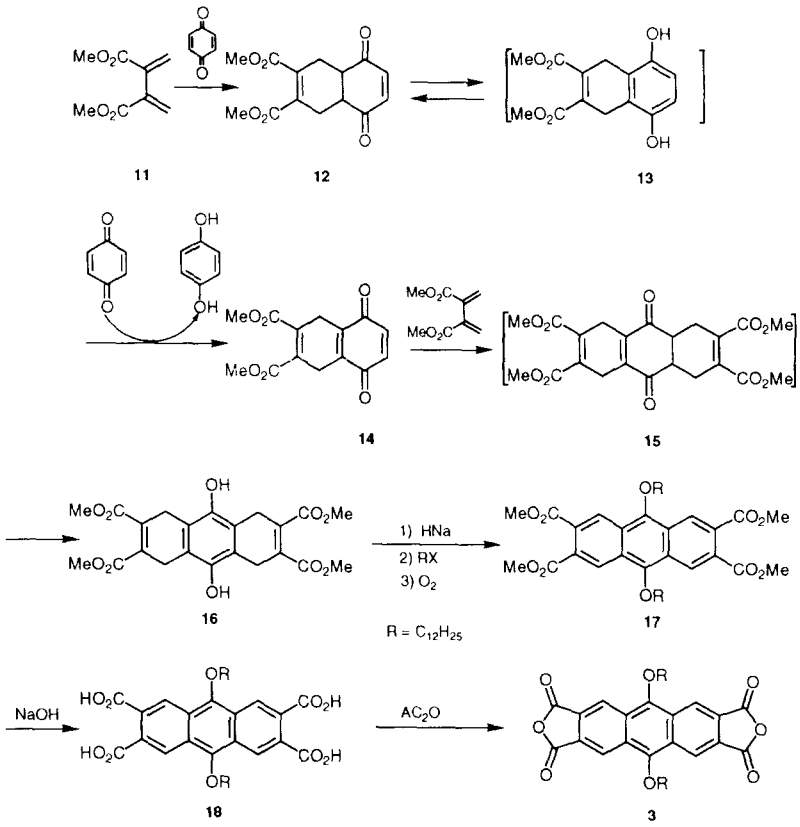
The anthracenic framework is obtained either by Diels-Alder reactions between benzoquinone and 2,3-dimethylbutadiene [44] or by Friedel-Crafts reactions of pyromellitic anhydride derivatives with *o*-xylene derivatives [45]. The $KMnO_4$ oxydation of the methyl anthraquinones thus obtained gives 2,3,7,8-anthraquinonetetracarboxylic acids [44c,45] ; 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 $KMnO_4$ oxydation [46] (Scheme 5).



Scheme 5

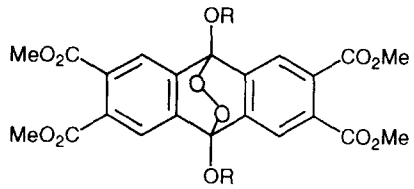
From the same starting materials, the method we describe here is shorter since the compound **16** was obtained in a one-pot reaction (Scheme 6).



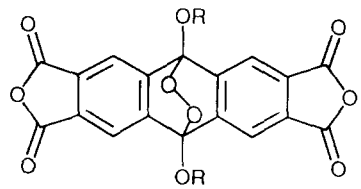
Scheme 6

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** [47] 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, $C_{12}H_{25}Br$) 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_2O 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.**



19



20

R = $C_{12}H_{25}$

Synthesis of **AP$_2$** and **AU$_2$** derivatives

The low solubility of **AP$_2$** and **AU$_2$** 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$_2$** and **AU$_2$** solvents of low polarity, where the hydrogen bonding is most efficient, must be used.

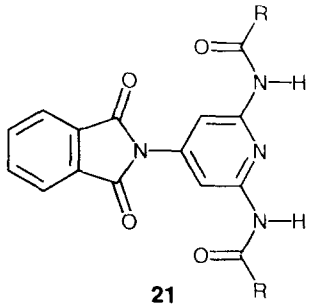
AP$_2$ derivatives were obtained by heating in 1-methyl-2-pyrrolidone (at 190-200°C for 40-60 mn) the amino derivatives **1 a-c** with the dianhydride **3** : 18-49% yield after recrystallization from a DMF-H_2O mixture. **AP$_2$-a** and **AP$_2$-b** were insoluble in $CHCl_3$ and all common solvents but their solubility drastically increased in presence of 1% of trifluoroacetic acid which allowed their characterization by ^1H and ^{13}C NMR. **AP$_2$-c** is more soluble and its ^1H-NMR spectra in $CDCl_3$ was obtained at low concentration (10^{-3} M) because line broadening, probably due to aggregation phenomena, was observed at higher concentration.

AU$_2$ 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 recristallization from DMF (**AU_2-a**) and DMF-H_2O (**AU_2-b**) or after chromatography on deactivated silica gel (**AU_2-c**). The solubility in $CHCl_3$ (null for **AU_2-a**) increased with the substitution on the uracil subunit. At concentrations higher than 10^{-3} M, the ^{1}H-NMR spectrum of (**AU_2-c**), in $CDCl_3$, 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 ^{13}C-NMR spectrum showed the same kind of splitting (Figure1).

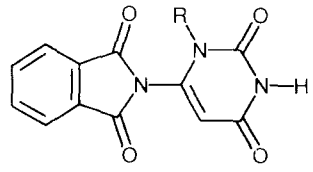
Like the compounds **3** and **17c**, **AU2-c** was readily converted under sunlight, in the presence of air, to the corresponding endoperoxide.

The PhtP and PhtU derivatives **21** and **22,** analogous to one half of **AP_2** and **AU_2**, were obtained in the same way that **AP_2** and **AU_2** compounds starting from phtalic anhydride.



21

R = CH_2-*t* Bu



22

R = Pr

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_2** and **AU_2** compounds were only obtained in moderate yield.

Mixing **AP_2** and **AU_2** yields polymeric supramolecular species **$(AP_2, AU_2)_n$**, corresponding to the structure schematically represented on scheme 7[29]. They were found to present a lyotropic mesophase, thus extending the generation of liquid crystalline phases by self-assembly [28,30] to rigid rod type substances.

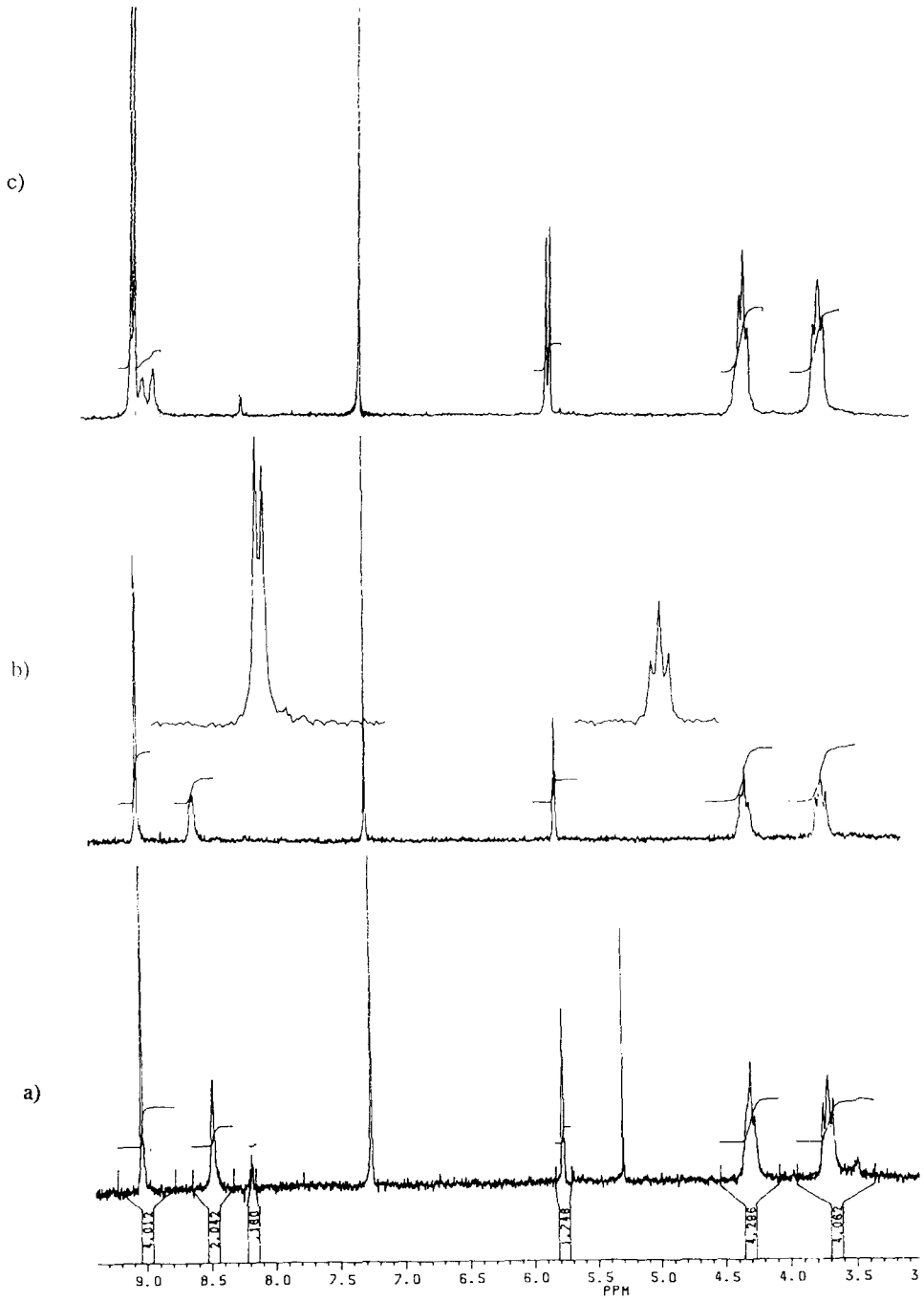
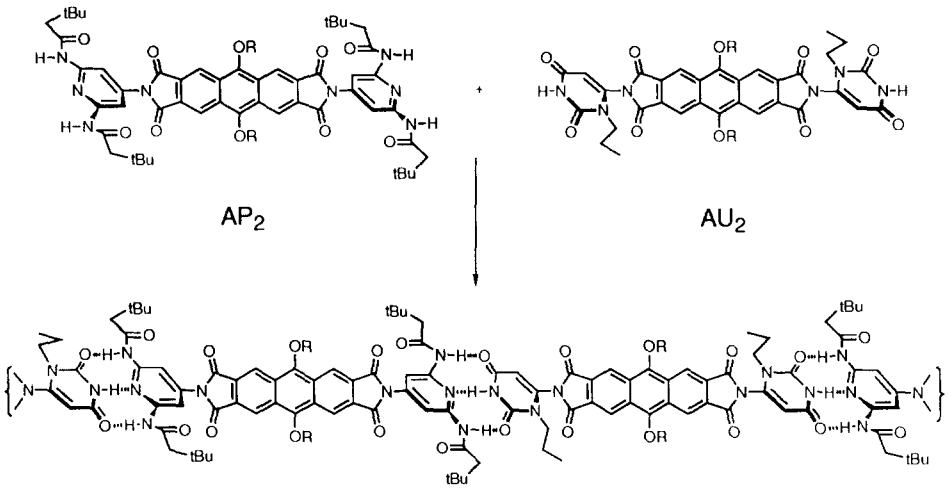


Figure 1- ^{1}H-NMR spectra of **AU_2-c** ($CDCl_3$) : a) 1 mg in 0.6 ml of $CDCl_3$. b) 3 mg in 0.6 ml. c) 6 mg in 0.6 ml.



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 (δ) are reported in ppm from tetramethylsilane as reference.

Mass spectra (MS) : FAB^+ 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**[36] (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_3 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 : $SOCl_2$ (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_2O (83.4 g, 0.382 mol), Et_3N (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; ^1H NMR ($CDCl_3$) : 1.46 (s,18H), 4.03 (s,6H), 8.12 (s,2H); Anal. Calcd for $C_{19}H_{26}N_2O_8$: 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_3 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_f 0.30

(CH_2Cl_2-10% MeOH).
IR : 3390, 3260, 1745, 1680, 1580, 1510, 1350, 1280, 1240, 1158, 1100. ^1H NMR (DMSO-d_6) 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 $C_{12}H_{16}N_4O_4$, 0.5 H_2O : 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_2O (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 dioxanne (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_2 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_2Cl_2. The organic layers were dried on Na_2SO_4 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_f 0.23 (CH_2Cl_2-10% MeOH). IR : 3450, 3400, 3370, 3200, 1715, 1615, 1520, 1440, 1380, 1370, 1313, 1250, 1168. ^1H NMR ($CDCl_3$) 1.49 (s,9H), 4.16 (br.s, 4H), 5.97 (s, 2H), 6.49 (br.s,1H). Anal. Cacld for $C_{10}H_{16}N_4O_2$: 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_2O (20 ml) at r.t. overnight. After removal of the solvents the residue was dissolved in CH_2Cl_2 and the solution passed through a SiO_2 column with CH_2Cl_2-7% 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_3CO_2H (5 ml) in CH_2Cl_2 (20 ml) at r.t. for 4 h. After evaporation of the solvents the residual oil was dissolved in CH_2Cl_2 (20 ml) and NEt_3 (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_2O_5. The aminopyridine **1**-a thus obtained was analytically pure but contains half a molecule of H_2O. (502 mg, 76%). R_f 0.42 (CH_2Cl_2-10% MeOH). IR : 3400, 3300, 3180, 3110, 1690, 1602, 1517, 1455, 1420, 1379, 1343, 1290, 1237, 1150, 1068. ^1H NMR (DMSO-d_6) : 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 $C_9H_{12}N_4O_2$, 0.5 H2O : 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_2, overnight. After evaporation of the pyridine, the residue was dissolved in ether (50 ml) and the etheral solution was washed twice with $NaHCO_3$ saturated aqueous solution (10 ml), dried over Na_2CO_3, 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_3CO_2H (2 ml) in CH_2Cl_2 (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_2O_5, at 60°C to give **1-b** (484 mg, 82%) which was used without further purification. mp 146-152°C. R_f 0.53 (CH_2Cl_2-10% MeOH). IR : 3480, 3440, 3370, 3240, 1688, 1625, 1580, 1520, 1270, 1220, 1190, 1145, 1090, 1033. ^1H NMR (DMSO-d_6) : 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 $C_{15}H_{24}N_4O_2$, 025 H_2O : 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*-Butylacetylamino)pyridine (**1-c**)

t-Butylacetylchloride (1.15 g, 8.57 mmol) was added to a solution of diaminopyridine **10** (908 mg,,405 mmol) and NEt_3(1.0 g, 10 mmol) in CH_2Cl_2 (20 ml) at r.t. After stirring for 1 h, the mixture was poured into Et_2O (100 ml); the precipitated salt was filtered and washed with Et_2O. The filtrate was evaporated to dryness to give crude N-Bocdiacylaminopyridine (1.92 g) which was dissolved in CH_2Cl_2 (16 ml). CF_3CO_2H (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_2Cl_2 (100 ml) and washed with a saturated solution of $NaHCO_3$ (50 ml). The aqueous phase was extracted with CH_2Cl_2 (3 x 20 ml) and the combined organic phases were dried over Na_2CO_3 and evaporated to give crude diacylaminopyridine (1.24 g). After purification by flash-chromatography on SiO_2 using CH_2Cl_2-10% MeOH as eluant pure **1-c** was obtained (1.02 g, 79%) mp. 225-226°C. R_f 0.36 (CH_2Cl_2-10% MeOH). IR : 3512, 3490, 3450, 3360, 3220, 3160, 3130, 1750, 1690, 1640, 1580, 1515, 1460, 1380, 1370, 1350, 1257, 1232, 1215, 1144, 1120, 1028. ^1H NMR ($CDCl_3$) : 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 $C_{17}H_{28}N_4O_2$: 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**[41] (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_2 inlet, a reflux condenser, a magnetic stirrer and a thermometer. Under N_2 flow, dioxanne (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_2O (500 ml) and filtered to give a gray powder which was washed with acetone (**16** is pratically 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 dioxanne. mp 230-260°C (dec.). IR : 3450, 1700, 1660, 1315, 1295, 1240, 1227, 1195, 1150, 1075, 1055. ^{1}H NMR (DMSO-d_6) : 3.50 (s, 8H), 3.72 (s, 12H), 8.08 (s, 2H). Anal. Calcd for $C_{22}H_{22}O_{10}$: 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_2 inlet and anhydrous DMF (40 ml) was introduced. Under N_2, 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_2 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 mml) and extracted with Et_2O (5x50 ml). The combined organic phases were washed twice with 1M NH_4Cl solution (2x50 ml), dried on Na_2SO_4 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_f0.42 (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). ^{1}H NMR ($CDCl_3$) : 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). ^{13}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 $C_{46}H_{66}O_{10}$: C, 70.92; H, 8.54. Found : C, 71.0;H, 8.6. Caution : 9,10-Alkoxyanthracenes react readily with O_2 under daylight to give endoperoxides. Care must

be taken when making NMR and U.V measurements.

9,10-Didodecyloxyanthracene-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_2O (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. ^{1}H NMR (acetone-d_6) : 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 $C_{42}H_{58}O_{10}$: 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_2O (150 ml) at reflux temperature (140°C) and stood on cooling. After dilution Et_2O (500 ml) crystalline dianhydride **3** was collected, washed with Et_2O 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_2O 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). ^{1}H NMR : 0.88 (br.t., 6H, J=7Hz), 4.27 (t, 4H, J=7Hz), 9.07 (s, 4H). MS : FAB$^+$, 687 (M^+). Anal. Calcd for $C_{42}H_{54}O_8$: C,73.44; H, 7.92. Found : C, 73.4; H, 7.7.

Endoperoxyde (**19**)

Anthracene tetraester **17** (100 mg) was dissolved in $CHCl_3$ (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_f 0.29 (AcOEt-hexane : 20-80). IR : 1735, 1630, 1440, 1290, 1240, 1110. UV : 241 (log ε = 4.6). ^{1}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). ^{13}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$^+$, 778 [$(M-O_2)^+$]. Anal. Calcd for $C_{46}H_{66}O_{12}$: 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 ε = 4.85). ^{1}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}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$^+$, 719 (M^+), 687 [$(M-O_2)^+$]. Anal. Calcd for $C_{42}H_{54}O_{10}$: 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-didodecyloxyanthra [2,3-c ; 6,7 c']dipyrrole-1,3,7,9(2H,8H)tetrone **AU$_2$-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_2 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$_2$-c** (540 mg). This material was purified by flash chromatography on deactivated silicagel [(prepared by stirring SiO_2 (85 g) and H_2O (15 g) for 10 mn)] using CH_2Cl_2/MeOH, 97/3, as eluant to afford pure **AU$_2$-c** dried at 110°C under vacuum (245 mg, 50%). mp 240-250°C (dec.). R_f 0.35 (CH_2Cl_2-7.5% MeOH). IR : 3200, 1782, 1742, 1695, 1460, 1380, 1330, 1230, 1165, 1130, 1020. UV : 312 (log ε = 5.0), 406 (log ε = 3.8), 432 (log ε = 4.2), 458 ((log ε =4.3). ^{1}H NMR ($CDCl_3$, c=10^{-3}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}C ($CDCl_3$: 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$^+$, 990 (M^+). Anal. Calcd for $C_{56}H_{72}N_6O_{10}$: 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-didodecyloxyanthra [2,3,-c ; 6,7-c']dipyrrole-1,3,7,9(2H, 8H)tetrone (**AU$_2$-a**)

This compound was prepared similarly to **AU$_2$-c** and purified by recrystallization from DMF(29% yield). mp > 260°C. ^{1}H NMR (DMSO-d_6) : 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$^+$, 905 $(M)^+$. Anal. Calcd for $C_{50}H_{60}N_6O_{10}$: 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_2-b**)

This compound was prepared similarly to **AU_2-c** and purified by recrystallization from DMF-H_2O (42% yield). mp 290-300°C (dec.). ^1H NMR ($CDCl_3$) : 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$^+$, 933 (M^+). Anal. Calcd for $C_{52}H_{64}N_6O_{10}$: 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_2-c**).

A mixture of anthracenedianhydride **3** (344 mg, 0.501 mmol) and diacylaminopyridine **1c** (318 mg, 0.992 mM) in 1-methyl-2-pyrrolidinone (1 ml) was heated for 1h, under N_2 with stirring, at 200°C. After cooling the reaction mixture was poured into MeOH/H_2O, 80/20 (50 ml). The precipitate was collected, washed with aqueous MeOH and dried to give crude **AP_2-c** (520 mg). This material was purified by flash chromatography on deactivated silicagel [(prepared by stirring SiO_2 (68 g) and water (12 g) for 15 mn)] using CH_2Cl_2/CH_3COCH_3, 98/2, as eluant to yield pure **AP_2-c** (359 mg, 56%) which was further purified by recrystallization from DMF (35 ml) and H_2O (4 ml) to afford analytically pure **AP_2-c** (310 mg, 48%). mp 350° (dec.). R_f 0.42 (CH_2Cl_2, 5% acetone). IR : 3440, 3350, 1780, 1735, 1700, 1612, 1583, 1430, 1370, 1350, 1305, 1228, 1138, 1030. UV (CH_2Cl_2) : 428 (log ε = 4.2), 455 (log ε = 4.3). ^1H NMR ($CDCl_3$, c=10^{-3} 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). ^{13}C NMR ($CDCl_3$-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$^+$, 1292 (M^+). Anal. Calcd for $C_{76}H_{106}N_8O_{10}$: 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_2-a**).

This product was obtained similarly to **AP_2-c** and purified by recrystallization from DMF-H_2O, without chromatography. (18% yield). mp : around 350°C (dec.). ^1H NMR ($CDCl_3$-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$^+$, 1068 (M^+). Anal. Calcd for $C_{60}H_{74}N_8O_{10}$: C, 67.52; H, 6.99, N, 10.50. Found : C, 67.3; H, 7.0; N, 10.6.

2,8-bis(2,6-dipentanoylamino-4-pyridyl)-5,11-didodecyloxyanthra[2,3-c : 6,7-c']dipyrrole-1,3,7,9 (2H,8H)tetrone (**AP_2-b**).

This product was obtained similarly to **AP_2-c** and purified by recrystallization from DMF-H_2O (35% yield). mp : around 330°C (dec.). ^1H NMR ($CDCl_3$) : 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$^+$, 1068 (M^+). Anal. Calcd for $C_{60}H_{74}N_8O_{10}$: C, 67.5; H, 6.99; N, 10.50. Found C, 67,3; H, 7.0; N, 10.6.

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

A mixture of phtalic anhydride (140 mg, 0.945 mmol) and acylamino-aminopyridine **1c** (161 mg, 0.502 mmol) in 1-methyl-2-pyrrolidinone was heated, under N_2, at 200°C for 30 mn. After cooling the mixture was dissolved in MeOH (2 ml) and poured in water (3 ml). A saturated $NaHCO_3$ 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_2 with 15% H_2O) using CH_2Cl_2/acetone, 97/3, as eluant. Recrystallization from MeOH-H_2O yielded pure **22** (92 mg, 43%). mp 210°C. R_f 0.30 (CH_2Cl_2, 5% acetone). IR : 3440, 3340, 1795, 1730, 1705, 1610, 1585, 1500, 1430, 1370, 1309, 1279, 1230, 1210, 1135, 1110, 1088, 1055, 1040, 1030. ^1H NMR ($CDCl_3$) : 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 $C_{25}H_{30}N_4O_4$ - 0.25 H_2O : 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 phtalic 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_2, 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_f 0.28 (CH_2Cl_2-20% acetone). IR 3180, 3050, 1798, 1700, 1630, 1460, 1420, 1370, 1350, 1335, 1227, 1170, 1079, 1026. ^1H NMR ($CDCl_3$) : 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 $C_{15}H_{13}N_3O_4$: C, 60.20; H, 4.38; N, 14.04. Found : C, 60.15; H, 4.3; N, 14.1.

REFERENCES

1. Lehn, J.-M. *Angew. Chem.,Int.Ed.Engl.* 1990, **29**, 1304.
2 *(a)* Lehn, J.-M.; Mascal, M.; DeCian, A.; Fischer, J. *J. Chem.Soc.,Chem Commun.* 1990,479. *(b)* Lehn, J.-M.; Mascal, M.; DeCian, A.; Fischer, J. *J.Chem.Soc.,Perkin Trans. 2* 1992, 461.
3. *(a)* Zerkowski, J.A.; Seto, C.T.; Wierda, D.A.; Whitesides, G.M. *J. Am. Chem. Soc.* 1990, **112,** 9025. *(b)* Seto, C.T.; Whitesides, G.M. *J. Am. Chem. Soc.* 1911, **113**, 712. *(c)* Zerkowski, J.A.; Seto, C.T.; Whitesides, G.M. *J. Am. Chem. Soc.* 1992, **114**, 5473.(*d*) Mathias, J.P.; Seto, C.T.; Simanek, E.C.; Whitesides, G.M. *J. Am. Chem. Soc.* 1994, **116**, 1725.
4. *(a)* Ducharme, Y.; Wuest, J.D. *J. Org. Chem.* 1988, **53**, 5787. *(b)* Gallant, M.; Viet, M.T.P.; Wuest, J.D. *J. Org. Chem.* 1991, **56**, 2284.
5. *(a)* Etter, M.C.; Parker, D.L.; Panunto, T.W.; Ruberu, S.R.; Britton, D. *J. Incl. Phenom.* 1990, **8**, 395.(*b*) Russel, V.A.; Etter, M.C.; Ward, M.D.; *J. Am. Chem. Soc.* 1994, **116**, 1941.
6. Zimmerman, S.C.; Duerr, B.F. *J. Org. Chem.* 1992, **57**,2215.
7. Drain, C.M.; Fischer, R.; Nolen, E.G.; Lehn, J.-M. *J. Chem. Soc., Chem. Commun.* 1993, 243.
8. Yang, J.; Fan, E.; Geib, S.J.; Hamilton, A.D. *J. Am. Chem. Soc.* 1993, **115**, 5314.
9. Baxter, P.; Lehn, J.-M.; DeCian, A.; Fischer, J. *Angew. Chem. Int. Ed. Engl.* 1993, **32**, 69.
10. Pfeil, A.; Lehn, J.-M. *J. Chem. Soc. Chem. Commun.* 1992, 838.
11. *(a)* Lehn, J.-M.; Rigault, A.; Siegel, J.; Harrowfield, J.; Chevrier, B.; Moras, D. *Proc. Natl. Acad. Sci. USA* 1987, **27**, 2565. *(b)* Lehn, J.-M.; Rigault, A. *Angew. Chem. Int. Ed. Engl.* 1988, **27**, 1095.
12. Garrett, T.M.; Koert, U.; Lehn, J.-M.; Rigault, A.; Meyer, D.; Fischer, J. *J. Chem.Soc.Chem. Commun.* 1990, 557.
13. *(a)* Constable, E.C. *Tetrahedron* 1992, **48**, 10013 and references therein. *(b)* Constable, E.C.; Edwards, A.J.; Raithby, P.R.; Walker, J.V. *Angew. Chem. Int. Ed. Engl.* 1993, **32**, 1465.
14. Carina, R.F.; Bernardinelli, G.; Williams, A.F. *Angew. Chem. Int. Ed. Engl.* 1993, **32**, 1463.
15. *(a)* Nierengarten, J .F.; Dietrich-Buchecker, C.O.; Sauvage, J.-P. *J. Am. Chem. Soc.* 1994, **116**, 355 and references therein. *(b)* Dietrich-Buchecker, C; Fromberger, B.; Lüer, I.; Sauvage, J.-P.; Vögtle, F. *Angew. Chem. Int. Ed. Engl.*

1993, **32**, 1434.

16. Vögtle, F.; Müller, W.M.; Müller, U.; Bauer, M.. Rissanen, K. *Angew. Chem. Int. Ed. Engl.* 1993, **32**, 1295.
17. *(a)* Amabilino, D.B.; Ashton, P.R.; Tolley, M.S.; Stoddart, J.F.; Williams, D*J. Angew. Chem. Int. Ed. Engl.* 1993, **32**, 1297. *(b)* Amabilino, D.B.; Ashton, P.R.; Reder, A.S.; Spencer, N.; Stoddart, J.F. *Angew. Chem. Int. Ed. Eng.* 1994, **33**, 433 and references therein. *(c)* Ashton, P.R.; Reder, A.S.; Spencer, N.; Stoddart, J.F. *J. Am. Chem. Soc.* 1993, **115**, 5286.
18. Hunter, C.A. *J. Am. Chem. Soc.* 1992, **114**, 5303.
19. *(a)* Gunther, M.J.; Johnston, M.R. *J. Chem. Soc., Chem. Commun.* 1992, 1163. *(b) ibid.* 1994, 829.
20. *(a)* Stoddart, J.F. *Angew. Chem. Int. Ed. Engl.* 1992, **31**, 846 and references therein. *(b)* Ballardini, R.; Balzani, V.; Gandolfi, M.T.; Prodi, L.; Venturi, M.; Philp, D.; Ricketts, H.G., Stoddart, J.F. *Angew. Chem. Int. Ed. Engl.* 1993, **32**, 1301
21. Manka, J.S.; Lawrence, D.S. *J. Am. Chem. Soc.* 1990, **112**, 2440.
22. Isnin, R.; Kaifer, A.E. *J. Am. Chem. Soc.* 1991, **113**, 8188.
23. Wenz, G.; Keller, B. *Angew. Int. Ed. Engl.* 1992, **31**, 197.
24. Harada, A.; Li, J.; Kamachi, M. *Nature*, 1992, **356**, 325.
25. Benniston, A.C.; Harriman, A. *Angew. Chem. Int. Ed. Engl.* 1993, **32**, 1459.
26. Chambron, J.-C.; Heitz, V.; Sauvage, J.-P. *J. Am. Chem. Soc.* 1993, **115**, 12378.
27. Shen, Y.X.; Xie, D.; Gibson, H.W. *J. Am. Chem. Soc.* 1994, **116**, 537.
28. *(a)* Fouquey, C.; Lehn, J.-M.; Levelut, A.-M. *Adv. Mater.* 1990, **2**, 254. *(b)* Gulik-Krzywicki, T.; Fouquey, C.; Lehn, J.-M. *Proc. Natl. Acad. Sci. USA* 1993, **90**, 163.
29. Kotera, M.; Lehn, J.-M.; Vigneron, J.P. *J. Chem. Soc., Chem. Commun.* 1994, 197.
30. Lehn, J.-M. *Makromol. Chem., Makromol. Symp.* 1993, **69**, 1.
31. *(a)* Thomas, D.A.; Miller, L.L. *J. Org.Chem.* 1986, **51**, 4160. *(b)* Christopfel, W.C.; Miller, L.L. *J. Org. Chem.* 1986, **51**, 4169. *(c)* Chiba, T.; Kenny, P.W.; Miller, L.L. *J. Org. Chem.* 1987, **52**, 4327. *(d)* Kenny, P.W.; Miller, L.L.; Rak, S.F.; Jozefiak, T.J.; Christopfel, W.C. *J. Am. Chem. Soc.* 1988, **110**, 445. *(e)* Dietz, T.M.; Stallman, B.J.; Kwan, W.S.V.; Penneau, J.-F.; Miller, L.L. *J. Chem. Soc., Chem. Commun.* 1990, 367. *(f)* Cammarata, V.; Kolaskic, C.J.; Miller, L.L.; Stallman, B.J. *J. Chem. Soc.,Chem. Commun.* 1990,1290.
32. Grösser, T.; Hirsch, A. *Angew. Chem. Int. Ed. Engl.* 1993, **32**, 1340.

33. Ottaviani, M.F.; Bossmann, S.; Turro, N.J.; Tomalia, D.A. *J. Am. Chem. Soc.* 1994, **116**, 661 and references therein.
34. Wooley, K.L.; Hawker, C.J.; Fréchet, J.M.J. *J. Am. Chem. Soc.* 1993, **115**, 11496 and references therein.
35. *(a)* Wörner, C.; Mülhaupt, R. *Angew. Chem. Int. Ed. Engl.* 1993, **32**, 1306. *(b)* De Brabander-van den Berg, E.M.M.; Meijer, E.W. *Angew. Chem. Int. Ed. Engl.* 1993, **32**, 1308
36. Xu, Z.; Moore, J.S. *Angew. Chem. Int. Ed. Engl.* 1993, **32**, 1354.
37. Newkome, G.R.; Baker, G.R.; Arai, S.; Saunders, M.J.; Russo, P.S.; Theriot, K.J.; Moorefield, C.N.; Rogers, L.E.; Miller, J.E.; Lieux, T.R.; Murray, M.E.; Phillips, B.; Pascal, L. *J. Am. Chem. Soc.* 1990, **112**, 8458 and references therein.
38. Boese, R.; Green, J.R.; Mittendorf, J.; Mohler, D.L.; Vollardt, K.P.C. *Angew. Chem.,Int.Ed.Engl.*, 1992, **31**,1643.
39. *(a)* Simundza, G.; Sakore, J.D.; Sobell, H.M. *J. Mol. Biol.* 1970, **48**, 263. (b) Scarbrough, F.E.; Shieh, H.-S.; Voet, D. *Proc. Natl. Acad. Sci. USA.* 1976, **73**, 3807.
40. *(a)* Feisbush, B.; Figueroa, A.; Charles, R.; Onan, K.D., Feisbush, P.; Karger, B.L. *J. Am. Chem. Soc.*, 1986, **108**, 3310. *(b)* Feisbush, B.; Saka, M.; Onan, K.; Karger, B.; Giese, R. *J. Am. Chem. Soc.* 1987, **109**, 7531.
41. *(a)* Hamilton, A.D.; Van Engen, D. *J. Am. Chem. Soc.*, 1987, **109**, 5035. *(b)* Hamilton, A.D. *J. Incl. Phenom. Molec. Reco. Chem.*, 1989, **7**, 27 and references cited therein. *(c)* Hamilton, A.D., *J. Chem. Educ.* 1990, **31**, 2401. *(d)* Hamilton, A.D.; Little, D. *J. Chem. Soc., Chem. commun.*, 1990, 297. *(e)* Chang, S.-K.; Van Engen, D.; Fan, E.; Hamilton, A.D. *J. Am. Chem. Soc.* 1991, **113**, 7640. *(f)* Park, T.K.; Schroeder, J.; Rebek, J.,Jr. *J. Am. Chem. Soc.* 1991, **113**, 5125. *(g)* Goodman, M.S., Rose, S.D.; *J. Am. Chem. Soc.* 1991, **113**, 9380.
42. Markees, D.G.; Kidder, G.W. *J. Amer. Chem. Soc.*, 1956, **78**, 4130.
43. Koenigs, E.; Kinne, G.; Weiss, W. *Berichte*, 1924, **57 B**, 1172.
44. *(a)* Morgan, G.; Coulson, E. *J. Chem. Soc.* 1931, 2323. *(b)* Hinshaw,*J. Organic preparations and procedures int.* 1972, **4**, 211. *(c)* Gangneux, P.; Marechal, E. *Bull. Soc. Chim. Fr.* 1973, **4**, 1466.
45. Japaneese patents. *Chem. Abstr.* 1984, **100**, 6119a, 34294x; *ibid.* 1975, **83**, 58548q.
46. Tarnchompoo, B.; Thebtaranonth, C.; Thebtaranonth, Y. *Tetrahedron Lett.* 1987, **28**, 6671.
47. Hamon, D.P.G.; Spurr, P.R. *Synthesis*, 1981, 873.

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