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Article

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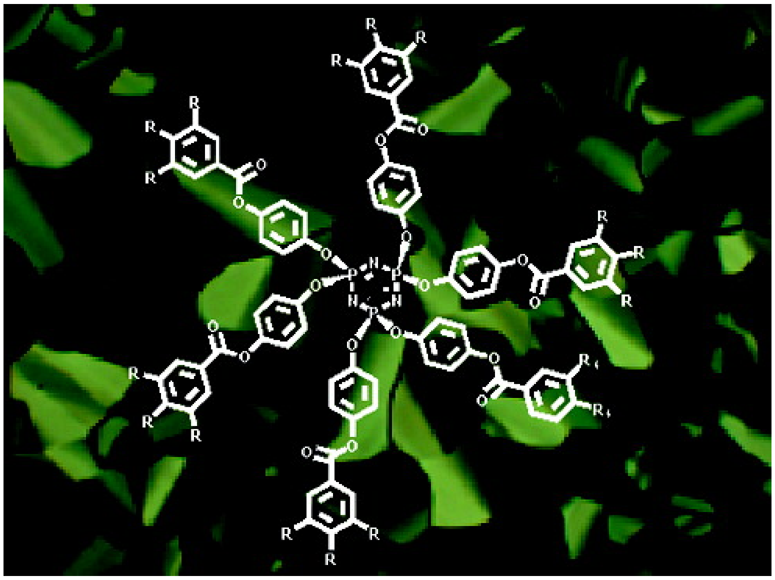

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Columnar Mesomorphic Organizations in Cyclotriphosphazenes

Joaquín Barberá,† Manuel Bardají,‡ Josefina Jiménez,*,‡ Antonio Laguna,‡
M. Pilar Martínez,‡ Luis Oriol,*,† José Luis Serrano,† and Irene Zaragozano‡

Contribution from the Polymer and Liquid Crystal Group—Departamento de Química Orgánica,
and Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón,
Universidad de Zaragoza-C.S.I.C., 50009 Zaragoza, Spain

Received February 18, 2005; E-mail: jjimvil@unizar.es; loriol@unizar.es

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Abstract: A synthetic strategy has been developed to prepare cyclotriphosphazenes that bear polycatenar aromatic esters as promesogenic units linked to phosphorus atoms. The microsegregation of the rigid and flexible parts of the system and the space-filling properties are the driving forces that determine the kind of mesomorphism exhibited by the organocyclotriphosphazenes. Mesogenic units that contain only one terminal alkyl chain give rise to calamitic mesomorphism, since the molecules are arranged to give a cylindrical superstructure with the aromatic promesogenic cores elongated in a manner approximately perpendicular to the cyclotriphosphazene ring. On the other hand, mesogenic units that contain three long terminal chains exhibit columnar mesophases. In this case, a discotic structure consisting of promesogenic cores arranged approximately parallel to the cyclotriphosphazene ring can explain the columnar organization. The X-ray diffraction patterns corresponding to the Col_h mesophase of the cyclotriphosphazene with dodecyloxy chains (**8**) indicate the presence of helical ordering, which was confirmed for a homologous compound bearing stereogenic centers on two of the terminal chains (**11**). All of the synthesized phosphazenes show a high thermal stability.

Introduction

A great deal of scientific and technological effort has been devoted to molecular columnar assemblies in recent years, mainly due to their applications as electronic materials.[1] In particular, discotic liquid crystals are a promising type of material, since their self-ordering facilitates the formation of one-dimensional columnar superstructures.[2] As a result, molecular systems with a high thermal stability, columnar mesomorphism at temperatures close to room temperature, and a high tendency to yield oriented monodomains are in great demand.

Phosphazenes comprise a broad class of molecules based on the repeating unit [NPR_2], including cyclic or linear oligomers and polymers. The most striking characteristic of this type of compound is the associated synthetic versatility, which enables the introduction of almost any side group R on phosphorus and allows the properties to be tailored by the choice of appropriate functional groups.[3] For example, in the case of polymers, it is possible to design materials with special properties such as electrical conductivity, catalytic properties, or biomedical activity.[3c,4] Other properties, such as the optical transparency of the skeleton from the near-infrared to about 210 to 190 nm in the ultraviolet, high flexibility, high thermal stability, and low flammability of the inorganic backbone, make them of considerable interest for both fundamental and applied materials research.[5]

Promesogenic units have also been attached to polyphosphazenes in an effort to obtain liquid crystals. However, since the first reported example of liquid crystallinity in side-chain polyphosphazenes in 1987,[6a,b] only a few exploratory examples have been described, and these incorporate calamitic promesogenic units (mainly azobenzene or biphenyl groups) with only one terminal chain, which are separated from the skeleton by a flexible spacer.[5a,6c] Previous works showed that specific polyphosphazenes, particularly those with fluoroalkoxy or simple aryloxy side groups, are capable of an unusual mesophase-like behavior, a phenomenon that is still not fully understood.[7]

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† Departamento de Química Orgánica.

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Cyclophosphazenes are also very attractive in this area because they are excellent models for structure−reactivity studies at a macromolecular level. Furthermore, the multiarmed rigid ring allows the exploration of nonconventional dendritic structures.[8] Several liquid crystalline cyclophosphazenes have also been described and, unlike polymers, mesomorphic phases were found even when the promesogenic unit (containing biphenyl,[9] Schiff bases,[9a−d] or azo[9b,c] groups, also with only one terminal chain) was directly linked to the rigid cyclophosphazene ring. Furthermore, despite the apparent D_{3h} symmetry of these derivatives, they exhibit calamitic phases that are mainly smectic in nature.

In this paper we report the molecular design, synthesis, and thermal and mesomorphic properties of a series of cyclotriphosphazenes with polycatenar promesogenic groups. Particular emphasis is given to the effect of the number and length of alkyloxy terminal chains in the promesogenic units linked to the phosphazene ring on the mesomorphic ordering. The space-filling properties of the cyclotriphosphazene derivatives lead to calamitic or columnar assemblies of these materials through conformational changes.

Results and Discussion

Synthesis and Structural Characterization. The reaction sequences used for the cyclic phosphazene trimers **3**−**11** are shown in Scheme 1. Hexachlorocyclotriphosphazene was reacted with excess 4-benzyloxyphenol in the presence of Cs_2CO_3 in acetone to yield trimer **1**. The 4-benzyloxyphenoxy units of trimer **1** were converted to 4-hydroxyphenoxy groups with cyclohexene in a mixture of THF/ethanol, in the presence of $Pd(OH)_2$ as a catalyst, to give **2**. Treatment of trimer **2** with an excess of the corresponding acid chloride (1.3 mol/mol of OH), in the presene of NEt_3 in THF, led to trimers **3**−**9**.

The synthesis of compounds **1** and **2** has been described previously, but this involved different, less efficient methods; **1** was prepared using $NaOC_6H_4OCH_2Ph$-4 as the nucleophile instead 4-benzyloxyphenol,[10] and **2** was synthesized by treating hexakis(4-methoxyphenoxy)cyclotriphosphazene with boron tribromide[10a,b] or by deprotection of benzyl ether groups in **1** by hydrogenation under pressure in the presence of a Pd catalyst.[10c]

It is worth pointing out that the commonly used method of nucleophilic substitution of aryl oxides on the cyclic halophosphazene trimer[11] did not give the target compounds. The reaction of hexachlorocyclotriphosphazene [$N_3P_3Cl_6$] with the alcohol R′OH [OR′ = $OC_6H_4\{OC(O)C_6H_2(3,4,5\text{-}OC_{12}H_{25})_3\}$-4] in a 1:6 molar ratio in the presence of Cs_2CO_3 in acetone gave substitution of the chlorine atoms. However, after 2 days under reflux, the $^{31}P\{^1H\}$ NMR spectrum showed incomplete substitution, with signals corresponding to the pentasubstituted compound [$N_3P_3Cl(OR')_5$] [22.57 (t) and 7.34 (d) ppm, $^3J(P-P) = 83.1$ Hz] and the hexasubstituted derivative **8**.[12] The addition of an excess of the alcohol to the reaction mixture and extended heating under reflux did not yield **8** as a single compound. The $^{31}P\{^1H\}$ NMR spectrum of the crude of reaction indicated a mixture of compounds with very similar phosphorus atoms (with signals between 9 and 10 ppm), probably due to reactions involving side groups. This mixture could not be purified by conventional chromatographic techniques.

As will be discussed below, the interesting structural features of compound **8** encouraged us to synthesize an organocyclophosphazene having nonequivalent mesogenic groups, as well as stereogenic centers in terminal chains. With this purpose, the synthesis of **11** was accomplished. The use of a smaller amount of acid chloride (1.08 mol/mol of OH) in the esterification reaction led to a mixture containing not only the hexasubstituted derivative but also the compound with five promesogenic groups and one 4-hydroxylphenoxy unit (**10**), which was carefully purified by chromatography using a silica gel column and hexane/ethyl acetate (20/1) as eluent. By treatment of **10** with an excess of the corresponding acid chloride, in the presence of NEt_3 in THF, it was possible to isolate compound **11** containing ca. 4% of **10** (as measured by ^1H NMR data), which could not be purified, even by chromatographic techniques.

All cyclic phosphazene trimers (**1**−**11**) were characterized by IR; ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy; mass spectrometry (LSIMS or MALDI-TOF techniques); and microanalysis. All these data are summarized in the Experimental Section (for **1**, **2**, **8**, **10** and **11**) and in the Supporing Information (for **3**−**7** and **9**). The IR spectra of all of these compounds feature peaks at around 1200 cm^{-1} (br) (P═N)[13] (due to the phosphazene ring), and the $^{31}P\{^1H\}$ NMR spectra consist of a singlet for **1**−**9** and an AB_2 pattern for **10**, with signals at similar positions to those observed for other (phenoxy)cyclotriphosphazenes.[14] In the case of **11**, this last spectrum also showed a single resonance, which is due to the similarity between the P environments in this compound. The ^1H and $^{13}C\{^1H\}$ NMR spectra are also consistent with the formulas indicated. For example, in addition to signals for the protons in the aromatic ring (OC_6H_4O, AA′BB′ spin system), the ^1H NMR spectrum of **1** contains resonances for benzyloxy protons at 4.97 (s, OCH_2) and 7.39−7.30 (m, C_6H_5) ppm. These signals were replaced by a signal at 8.33 (s) due to OH protons after conversion to **2**. The ^1H NMR spectra of trimers **3**−**11** also showed resonances corresponding to the other aromatic protons and the protons of the terminal alkyl chains. In the case of **10**, the signal

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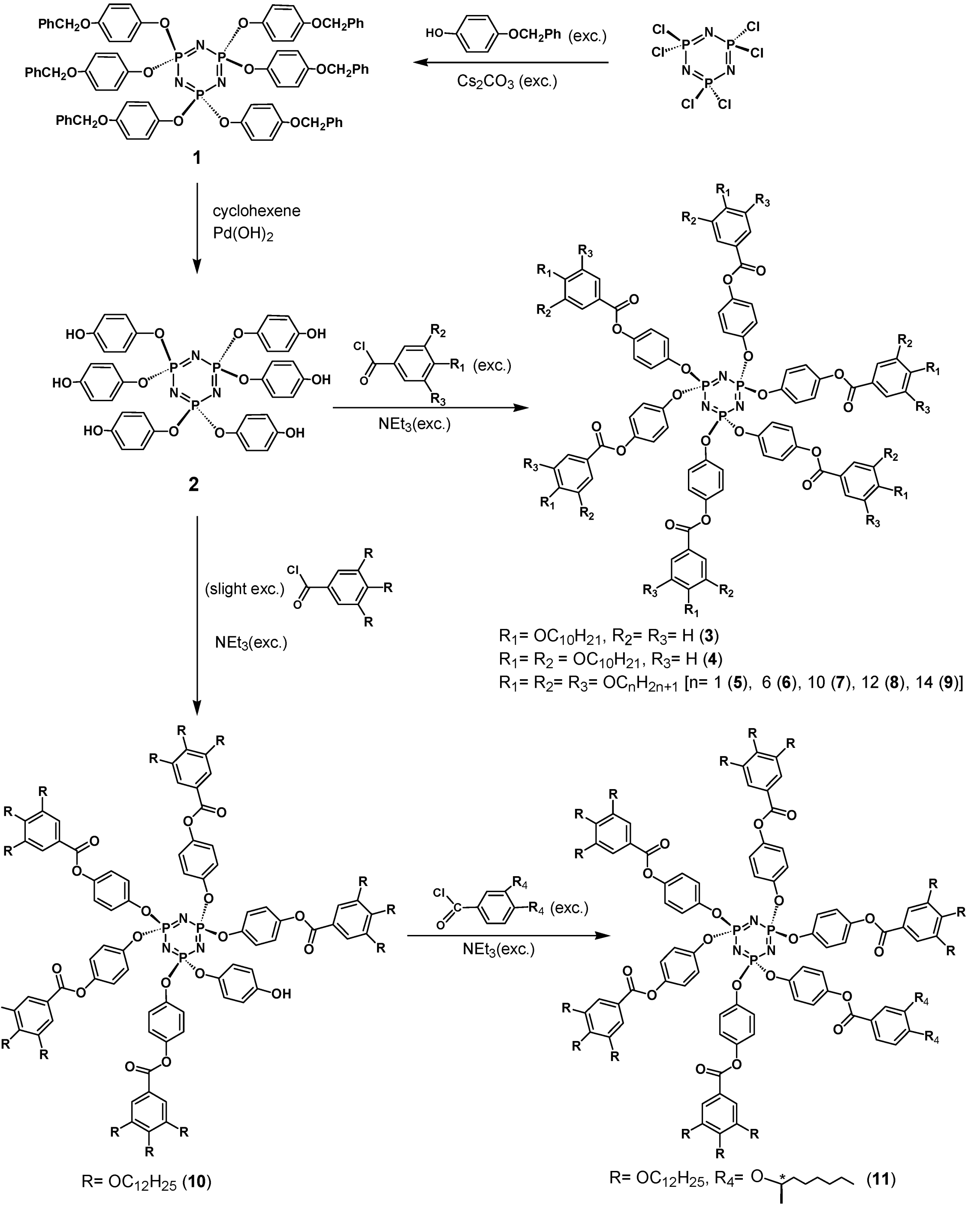
Scheme 1



corresponding to the OH proton was observed at 6.1 ppm. This last spectrum, along with that of **11**, was more complicated as a result of the nonequivalence of all the promesogenic groups.

Thermal and Mesomorphic Properties. The thermal and mesomorphic properties of the organocyclotriphosphazenes were studied by thermogravimetry (TGA), differential scanning calorimetry (DSC), polarizing optical microscopy (POM), and X-ray diffraction. The results are summarized in Table 1.

The polycatenar organocyclotriphosphazenes generally exhibit a high thermal stability according to thermogravimetric analysis, which shows a single, rapid decomposition at above 300 °C.

The study of the mesomorphic properties revealed liquid crystalline behavior that depended on the number and length of terminal chains. For example, compound **3**, which has promesogenic units with one terminal chain, displays an enantiotropic nematic phase. The calamitic nature of this compound is explained in terms of the model previously proposed by Moriya and co-workers.[15] In such a system, the mesogenic side groups are arranged approximately perpendicular to the cyclotriphosphazene ring, forming parallel triplets pointing upward and downward to give a calamitic superstructure capable of being organized in a nematic phase (see Figure 1).

However, when mesogenic units with a greater number of terminal chains are introduced, the organocyclotriphosphazenes

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Table 1. Thermal and Mesomorphic Properties of the Cyclotriphosphazenes

compd	2%[a]	T_{onset}[a]	T_{max}[a]	thermal transitions[b] (ΔH, kJ/mol)
3	364	393	407	K 125 (60.0) N 129 (1.6) I
4	313	387	399	K [61 (8.6) Col][c] 88 (81.0) I
5	338	403	411	g 75 I
6	303	381	387	K, $\mathrm{Col_r}$[d] 67 (26.4) I
7	361	384	400	K 38 (16.4) $\mathrm{Col_h}$ 67 (7.9) I
8	263	388	400	K 2 (68.0) $\mathrm{Col_h}$ 59 (7.8) I
9	361	395	406	K 32 (162.7) $\mathrm{Col_h}$ 65 (9.7) I
10	150	387	396	$\mathrm{Col_h}$ 54 (4.9) I
11	260	360	378	$\mathrm{Col_h}$ 54 (7.6) I

[a] Temperatures are in °C. 2% weight loss corresponds to the temperature that brings about 2% weight loss, T_{onset} corresponds to the onset of the decomposition detected on the weight loss curve, and T_{max} was read at the maximum of the derivative thermogravimetric curve (10 °C/min, under nitrogen atmosphere). [b] Temperature in °C detected by DSC and read at the maximum of the peak of the second scan (10 °C/min). ΔH values in kJ/mol are in parentheses. The nature of the mesophase was characterized by POM and X-ray diffraction. [c] Monotropic transition. [d] See the text for explanation.

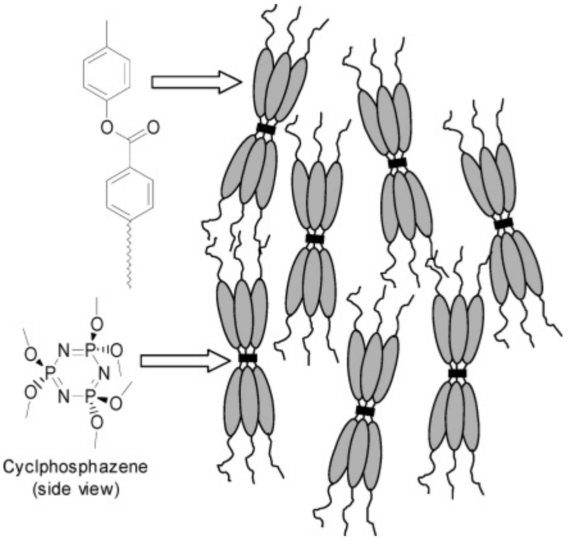


Figure 1. Nematic ordering 3 according to the model proposed by Moriya and co-workers.

tend to assemble in a columnar organization. Compound **4** contains mesogenic cores with two decyloxy terminal chains and is a crystalline material that melts at 88 °C to give a monotropic mesophase on cooling from the isotropic phase. However, this compound immediately crystallized, thus preventing the development of a well-defined texture. Nevertheless, a grainy texture with mosaic-like regions was observed, which became homeotropic under mechanical stress. On this basis, the mesophase has been tentatively assigned as columnar. The monotropic nature of this mesophase precluded an X-ray diffraction study as crystallization occurred during exposure to X-rays.

The incorporation of three terminal chains in each of the mesogenic cores (compounds **5**−**9**) eventually stabilizes the columnar mesomorphism. Compound **5** was synthesized in order to explore the possibility of obtaining monocrystals for X-ray measurements. However, this compound is an amorphous material that only exhibits a glass transition in both the first and second DSC scans. The presence of longer alkyl chains results in mesomorphism, but the thermal behavior depends on the length of these terminal chains. Compound **6** is a waxy material at room temperature and can be plastically deformed by mechanical stress. The study of **6** by POM did not show a well-defined birefringent texture, and the material became isotropic at above 70 °C. On cooling this compound (10 °C/min), an isotropic (I)−mesophase (M) transition occurred at around 35 °C and this was characterized by an ill-defined pseudo-fan-shaped texture with some dark regions, which is consistent with a columnar mesophase (Figure 2a). The texture was retained at room temperature. On the DSC traces only a peak was observed, both on heating and cooling processes. However, the enthalpy change corresponding to the endothermic peak detected at 67 °C in the heating scan (26.4) and to the exothermic peak detected at 34 °C on cooling (11.2) differs significantly. These findings are reproducible and point to partial crystallization of the sample, despite the fact that an exothermic crystallization peak was not clearly detected in the DSC curves or by optical microscopy.

Cyclophosphazene **7** is a waxy compound that is susceptible to plastic deformation at room temperature. On heating the sample, the viscosity decreased and a mesophase was clearly observed. Finally, isotropization was detected at around 65 °C. On cooling of the sample from the isotropic state, the transition I−M was detected at a similar temperature, and well-defined textures were observed. The pseudo-focal-conic fan-shaped texture along with a homeotropic one exhibited by this compound at 60 °C is shown in Figure 2b. Both textures are compatible with a $\mathrm{Col_h}$ phase. On subsequent cooling, the texture observed by POM remained unchanged and the material appeared to be liquid crystalline at room temperature. However, the DSC study of this compound also reveals a phase transition at around 40 °C, both on heating and cooling cycles, and this transition has a relatively low ΔH. Compound **8**, which has dodecyloxy terminal chains, was clearly mesomorphic at room temperature. The phase became isotropic at around 60 °C. This material diplays similar textures to compound **7** but has a high tendency to orient homeotropically between glass substrates without any treatment. In fact, homeotropic monodomains can be obtained by slow cooling (<2 °C/min). The DSC traces show evidence of a transition at around 0 °C, which is most probably due to crystallization of the compound, according to the high enthalpy observed for this transition. However, only slight

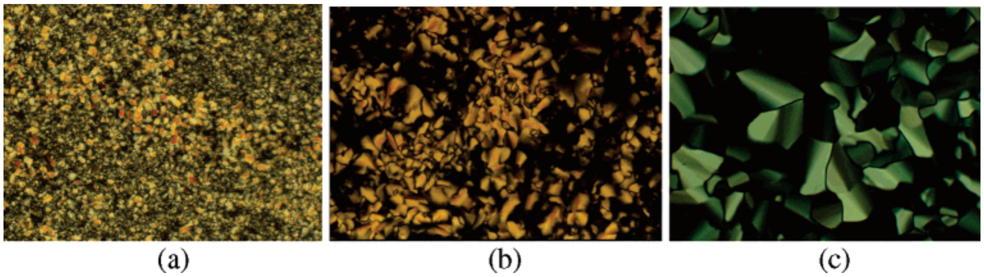

(a) (b) (c)

Figure 2. Microphotographs of compounds (cooled from the I phase at 10 °C/min): (a) **6** taken at 30 °C; (b) **7** taken at 60 °C; (c) **11** taken at 30 °C.

modifications of the mesomorphic texture were observed by POM study down to −20 °C (see Supporting Information).

Compound **9**, having the longest terminal alkyl chains, is a crystalline material at room temperature that melts into a columnar mesophase at 32 °C and finally becomes isotropic at around 65 °C. DSC and POM measurements of this compound put in evidence the tendency of this material to crystallize (with a high enthalpic change).

Finally, POM and DSC measurements of compounds **10** (synthetic precursor of **11**) and **11** indicated that both exhibit a similar thermal behavior to the homologous compound **8**: a $\mathrm{Col_h}$ mesophase at room temperature that becomes isotropic at approximately 54 °C. A typical texture observed for compound **11** is shown in Figure 2c. However, in contrast to compound **8**, evidence of crystallization was not detected on cooling from the isotropic phase on the DSC study.

Structural Characterization. In an effort to gain more information on the different phases, X-ray measurements were performed on samples of the columnar materials at different temperatures. First, diffraction experiments were performed at room temperature both in the virgin state and in samples cooled from the isotropic liquid. The diffraction patterns of virgin samples of **6**, **7**, and **9** indicate (at least partially) a crystalline structure, as revealed by the presence of a large number of sharp reflections over the whole angular range. Similar patterns were obtained from samples that had been heated to the isotropic liquid and then slowly cooled to room temperature. The above-mentioned softness observed for **6** probably arises from the persistence of some proportion of mesomorphic phase even at room temperature. In fact, crystallization on **6** can be avoided by a quick cooling from mesophase to room temperature (see below). However, the X-ray pattern of **7** at room temperature indicates that this phase must be crystalline in nature, as the crystallization could not be avoided and the DSC peak corresponding to this transition is reproducible regardless of the cooling rate. The softness of this phase at room temperature (it exhibits plastic deformation) suggests that the crystalline structure contains a large degree of disorder. This situation is supported by the presence in the X-ray patterns of a diffuse halo at about 4.5 Å, which is characteristic of the liquidlike arrangement of the chains (see Supporting Information). Finally, the X-ray diffraction patterns taken at room temperature for **9**, which contain a high number of sharp reflections in the whole angular range, also confirm the crystalline nature of this cyclophosphazene.

In contrast to this, when compound **8** was studied by X-ray diffraction at room temperature, both on virgin samples and samples cooled from the isotropic liquid, in all cases the patterns were consistent with a hexagonal columnar mesophase. The same type of pattern was found for the high-temperature phase of **7** and **9** and confirms that these compounds exhibit a $\mathrm{Col_h}$ mesophase (see Figure 3). The measured hexagonal lattice constant a is deduced from the d_{10} reflection observed in the patterns and calculated as $a = (2/\sqrt{3})d_{10}$. The cross-sectional area of a column (surface of the unit cell) is calculated as ad_{10}. All these values are gathered in Table 2. As expected, an increase in the lattice constant a and in the column cross-sectional area is observed upon increasing the chain length. In the high-angle region of the patterns, there is only a diffuse halo corresponding to a distance of about 4.5 Å. This halo is due to short-range correlations between the conformationally disordered hydrocarbon chains and confirms the liquid-crystalline character of the mesophases.

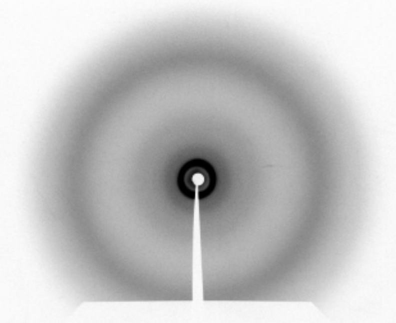
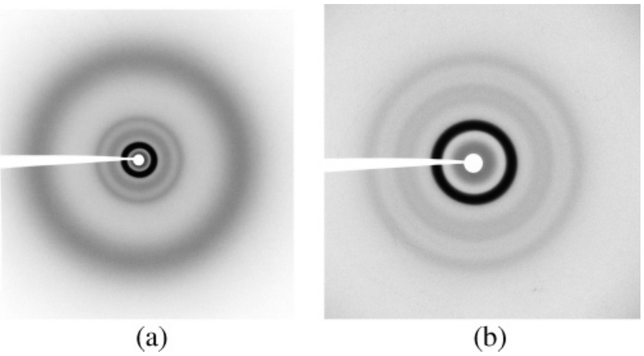


Figure 3. X-ray diffraction pattern of the $\mathrm{Col_h}$ mesophase of **7** taken at 48 °C.

Table 2. X-ray Diffraction Data for the Columnar Mesophases of Cyclophosphazenes

compd	*T* (°C)	phase	d_{hk} (Å)[b]	wave vector *q* (Å^{-1})	lattice constants (Å)	*S* (Å^2)[c]	S_0 (Å^2)[d]	*R* (Å)[e]
6[a]	rt	$\mathrm{Col_r}$	$d_{11} = 28.3$ (28.1)	0.224	$a = 62$	976.5	426	11.6
			$d_{31} = 17.3$ (17.3)	0.363	$b = 31.5$			
			$d_{22} = 13.8$ (14.0)	0.449				
			$d_{51} = 12.0$ (11.5)	0.546				
			d_{60}, $d_{13} = 10.2$ (10.3)	0.610				
7	48	$\mathrm{Col_h}$	$d_{10} = 32.5$	0.193	$a = 37.5$	1219	405	11.4
8	rt	$\mathrm{Col_h}$	$d_{10} = 35.0$	0.180	$a = 40.4$	1414	419	11.5
9	40	$\mathrm{Col_h}$	$d_{10} = 36.9$	0.170	$a = 42.6$	1572	421	11.6
10	rt	$\mathrm{Col_h}$	$d_{10} = 35.3$	0.178	$a = 40.7$	1433	457	12.1
11	rt	$\mathrm{Col_h}$	$d_{10} = 36.4$	0.173	$a = 42.0$	1529	483	12.4

[a] Sample quickly cooled from mesophase to room temperature. [b] Calculated spacings are in parentheses. [c] Column cross section. [d] Core cross section. [e] Core radius.



(a) (b)

Figure 4. (a) X-ray pattern of the rectangular columnar mesophase of compound **6** taken at room temperature; (b) small-angle region.

In the case of compound **6**, with the aim of obtaining the pure liquid crystal phase and precluding crystallization, a sample of the compound was heated to the isotropic liquid, slowly cooled to the mesophase transition temperature and then quickly cooled to room temperature. This procedure caused the mesophase to freeze for a sufficient period of time for study by X-ray diffraction prior to the onset of crystallization (Figure 4). This situation was confirmed by the absence of sharp reflections at high angles and the presence in this region of only the diffuse halo corresponding to a distance of about 4.4 Å, which is typical in disklike liquid crystals. Although long-exposure patterns could not be registered, due to the tendency of the compound to slowly crystallize, the X-ray photographs clearly indicate that the liquid crystal phase is of a columnar

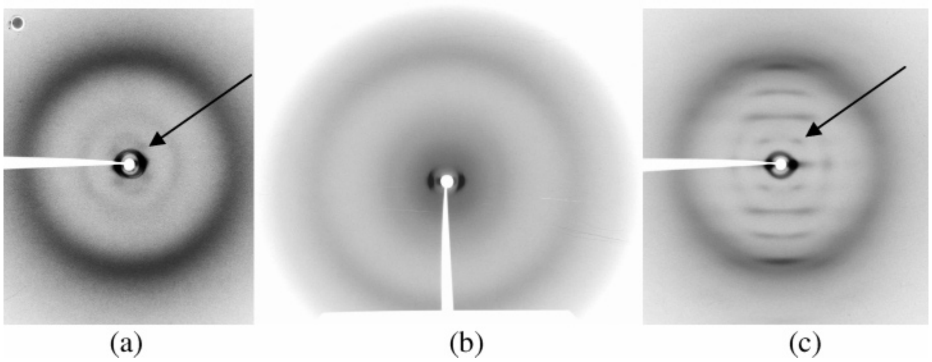

(a) (b) (c)

Figure 5. X-ray pattern of an aligned sample in the $\mathrm{Col_h}$ mesophase: (a) compound **8** taken at room temperature; (b) compound **9** taken at 40 °C; (c) compound **11** taken at room temperature. The capillary axis is vertical. Diffuse spots in the first layer line are indicated with an arrow.

nonhexagonal type. The structure is most probably rectangular columnar, and the proposed lattice constants, as deduced from the observed reflections, are gathered in Table 2. Assuming that there are two columns per unit cell, the cross-sectional area of each column is calculated as $ab/2$. This value appears consistent with those calculated for the columnar cross section of the rest of the compounds taking into account the differences in chain length.[16] Identical X-ray results were obtained within the experimental error when the sample was investigated at higher temperatures (52 and 60 °C).

Very interesting structural information is given by the X-ray patterns taken on aligned samples of compound **8**, which were obtained by mechanical alignment of the sample in the capillary tube. The resulting X-ray patterns contain a pair of low-angle strong arcs centered on the equator (direction perpendicular to the capillary axis)—these correspond to the d_{10} reflection—and a nearly isotropic diffuse halo at 4.5 Å (Figure 5a). A pattern such as this means that the mesophase is oriented with the column axes in the direction of the capillary axis (stretching direction), as it is usual in columnar mesophases, and the aliphatic chains remain disordered. The presence of only a maximum at low angles is not inconsistent with a hexagonal columnar mesophase.[17] In addition, several middle-angle diffuse spots are apparent, and these are not common in classical discotic liquid crystals. A diffuse spot is observed in the direction of the meridian (direction of the capillary axis) and this corresponds to a distance of about 15.5 Å. The presence of this scattering suggests some kind of modulation of the electronic density along the column axis. Moreover, a diffuse scattering maximum, split into four spots, is situated symmetrically with respect to the equator and the meridian. These spots correspond to a modulation of the electronic density with a period of about 28.5 Å in the direction of the column axes. The fact that these spots are off the meridian is probably consistent with some kind of helical order.[18] This feature is more clearly visible for compound **11** and will be discussed below. The diffuse spot at 15.5 Å centered on the meridian could be consistent with a structure in which the columns are "broken" into blocks of stacked molecules. A reasonable value for the mesophase density is obtained if we assume that each of these blocks contains three molecules (estimated density 1.08 g cm^{-3}). These defects in the columnar packing would be related to the peculiar geometry of the molecules, which have a 3-fold axis perpendicular to the cyclophosphazene ring that leads to a molecule with a star shape. The stacking of this kind of molecule would generate an empty space between the arms of the "star", and this mismatch can be compensated if two neighboring blocks are rotated with respect to each other. The fact that 28.5 Å is almost twice 15.5 Å suggests that the blocks are rotated by 60° with respect to each other. In this way the arms of each block would be able to locate themselves between the arms of the neighboring block, thus giving more efficient space filling. It is not clear why 15.5 Å thick blocks of three molecules act as units before making the 60° turn around the column axis. At first sight, for best space filling a turn would be expected to occur after each individual molecule, giving an alternating structure. The reason for the actual behavior may be that the benzoyloxyphenyl groups have tendency to stack parallel to each other, and the eclipsed stacking is left out every three molecules after being forced to rotate by the increasing overcrowding of the rigid arms and alkoxy chains. However, it should be borne in mind that the diffuseness of the maxima under discussion indicates that the described distribution in blocks and the alternating twist structure only extend over short distances.

Similarly to compound **8**, oriented patterns of the mesophases of **7** and **9** (as well as **10**) could be obtained by mechanical alignment of the samples. The resulting X-ray patterns contain a pair of low-angle strong arcs centered on the equator, which correspond to the d_{10} reflection, and a nearly-isotropic diffuse halo at 4.5 Å (Figure 5b). However, in contrast to compound **8**, no other features are observed in these diffractograms, and this means that there is no evidence of helical order in the mesophases of these compounds.

In an attempt to favor the helical order suggested for compound **8**, the synthesis of compound **11**, containing two

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(16) Estimations of packing density led to reasonable values if we consider two columns per unit cell. The relationship between the density (ρ) of the compounds and the number (Z) of molecules in the unit cell is given by the following equation: $\rho = (M/N)/(V/Z)$, where M is the molar mass (g) (3217 g for **6**), N the Avogadro number, and V the unit cell volume (cm^3). V (in cm^3) is calculated by the formula $V = abc \times 10^{-24}$ for a rectangular lattice, where a, b, c are the lattice constants in Å. Considering a density equal to 1 g cm^{-3}, this means that in the proposed rectangular columnar structure the average stacking distance (c constant) would be 4.5 Å for $Z = 2$. This distance is reasonable compared to those found in other columnar mesophases and are in agreement with the diffuse halo observed in the X-ray patterns.

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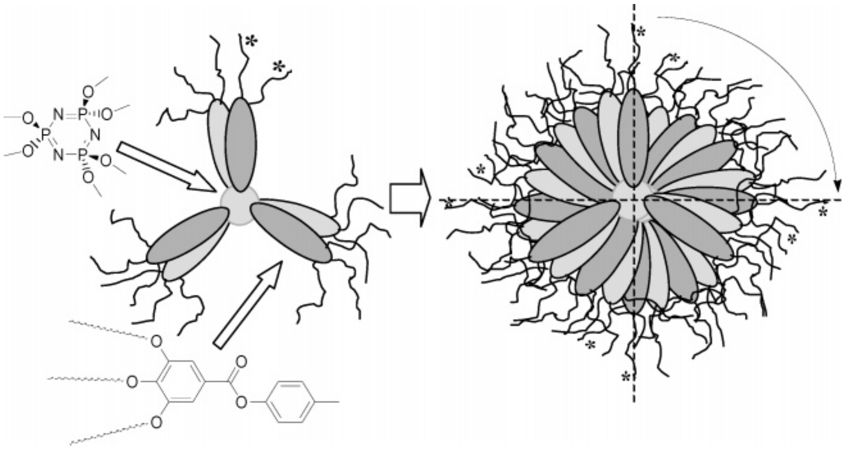

Figure 6. Schematic model for the helical columnar assembly of cyclotriphosphazene **11**. Four molecules rotated by 90° are needed to complete a full turn (chiral terminal chains are indicated with asterisks).

stereogenic centers, was carried out. In a first approach, the incorporation of a promesogenic unit with branched terminal chains having two stereogenic centers may hinder regular stacking of the organocyclotriphosphazenes and could consequently favor helical ordering. The X-ray patterns taken on compound **11**, as well as on its precursor **10**, confirm that the mesophase of these compounds is columnar hexagonal (Table 2). The measured d_{10} spacing and hence the hexagonal lattice constant *a* are slightly larger for **11** than those for **8**, despite the fact that the number of aliphatic carbons—and hence the molecular mass—is smaller in **11**. This suggests that the molecular conformation adopted by each compound is different and therefore the packing is also different. X-ray patterns of aligned samples of **11** show certain peculiar features (Figure 5c). Apart from the small-angle d_{10} reflection centered on the equator and the almost isotropic large-angle diffuse halo, the diffraction patterns contain a set of diffuse spots located on equally spaced layer lines parallel to the equator. The innermost maxima on the first and second layers lie approximately on straight lines radiating from the origin, producing a cross-like pattern. These features are consistent with a helical structure with the axis of the helix parallel to the columns (meridian direction), as it has been described for other chiral compounds.[18] The helical pitch, deduced from the spacing between the layer lines, is 18.4 Å. The number of molecules per helical turn can be deduced from the pattern, bearing in mind that on the fourth layer line (located at 4.60 Å) there is a strong scattering maximum centered on the meridian. This indicates that there are exactly four molecules per turn of the helix, and these are separated on average by a stacking distance of 4.60 Å. The density calculated for this structure is 1.04 g cm^{-3}. The existence of a hexagonal columnar mesophase with a helical organization in this compound can be described as follows: the molecules stack with their main planes parallel to each other, and they rotate around the column axis in such a way that two neighboring molecules are mutually rotated by an angle of $\pi/2$ (360°/4). Therefore, four molecules of compound **11** are needed to complete a full turn, the helical pitch being $4.6 \times 4 = 18.4$ Å. It is noteworthy that the helical order for this compound extends for longer distances than in the case of compound **8**. This fact is deduced from the above-mentioned presence of several layer lines of spots and by the higher intensity of these spots.

The model proposed by Moriya et al. to explain the calamitic mesomorphism in cyclotriphosphazenes with a terminal chain does not account for the columnar mesomorphism exhibited by these columnar cyclotriphosphazenes. When the number of terminal chains increases, there is a significant change in the relationship between the volumes of the hard part (cyclotriphosphazene ring and mesogenic cores) and the soft part (aliphatic terminal chains) of these multiarmed dendritic molecules. The segregation of the two parts of the molecule and the space-filling properties create a tendency for the molecules to adopt a discotic structure, which allows a higher degree of interaction between the neighboring molecules and explains the cross-sectional area of columns measured by X-ray diffraction. In this discotic structure, the aromatic promesogenic cores tend to arrange themselves in two levels: three promesogenic units are located in a plane above the phosphazene ring (upper level) and the other three in a plane below (lower level) as a consequence of the orientation of the P—O bonds. This situation gives rise to a supramolecular organization that is reminiscent of two three-arm star-shaped compounds forced to pack in columns.[19] Figure 6 displays the columnar organization of compound **11** according to this model and the X-ray data. The aliphatic chains surround the rigid central core and allow efficient packing of the molecules. Estimations about the radius of the columnar core, i.e., the inner part of the columns, which includes the cyclotriphosphazene ring and the benzoyloxyphenyl units, are listed in Table 2. On the basis of the percentage contribution of the central core to the molar mass and assuming that the density is similar in the central core and in the aliphatic chains, we calculate the fraction of the column cross section corresponding to the central core (S_0). From S_0 the core radii *R* are deduced and compared with the theoretical radius of the core. Using Dreiding stereomodels and ChemBats3D software, this theoretical radius is estimated to be about 13 Å. As the *R* values shown in Table 2 are smaller (especially in the case of compounds **6**−**9**), it is deduced that the rigid branches are tilted with respect to the lattice plane, i.e., the plane perpendicular to the column axis. These dendritic molecules show mesomorphic behavior resembling that exhibited by mesomorphic calamitic

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[19] (a) Lehmann, M.; Gearba, R. I.; Koch, M. H. J.; Ivanov, D. A. *Chem. Mater.* **2004**, *16*, 374. (b) Ryu, S. Y.; Kim, S.; Seo, J.; Kim, Y. W.; Kwon, O. H.; Jang, D. J.; Park, S. Y. *Chem. Commun.* **2004**, 70.

or columnar materials derived from the flexible DAB or PAMAM dendrimers,[20] despite the fact that these cyclophosphazenes have a rigid core. However, both calamitic and discotic models are compatible in these compounds as a consequence of the different conformations adopted by the molecules (conformational freedom on the P−O−C bonds) in an effort to optimize space filling.

Conclusions

The synthesis of a series of organocyclotriphosphazenes has been successfully achieved by esterification of the corresponding 4-hydroxyphenoxy derivatives. The mesomorphic properties of the cyclotriphosphazenes strongly depend on the number of terminal alkyl chains. Incorporation of the mesogenic unit with one terminal chain gives rise to calamitic mesomorphism, which is explained in terms of a cylindrical superstructure. However, the presence of a larger number of terminal chains causes the molecule to adopt a discotic structure in order to optimize the space-filling properties and the interactions of soft and rigid parts of the molecules. Evidence of helicity in the columnar mesophase of compound **8** has been detected by X-ray diffraction. The incorporation of stereogenic centers in the alkyl chains allowed confirmation of the helical columnar ordering in the mesophase by X-ray diffraction measurements of aligned samples. The great synthetic versatility of cyclotriphosphazenes, as templates for the design of supermolecular liquid crystals,[21] opens up new possibilities for the preparation of novel dendritic columnar assemblies at room temperature for optical and electronic applications.

Experimental Section

General Data. Instrumentation and general experimental techniques (elemental analysis, IR, NMR, thermogravimetry, and optical microscopy) were as described earlier.[22] MALDI-TOF mass spectrometry was carried out on a REFLEX III Bruker instrument using dithranol as matrix. DSC was performed using a DSC 2910 from TA Instruments with samples (2−5 mg) sealed in aluminum pans and a scanning rate of 10 °C/min under a nitrogen atmosphere. In general, the peaks obtained were broad and the transition temperatures were therefore read at the maximum of the peaks. The X-ray diffraction patterns were obtained with a pinhole camera (Anton-Paar) operating with a point-focused Ni-filtered Cu Kα beam. The samples were held in Lindemann glass capillary tubes (1 mm diameter) and heated, when necessary, with a variable-temperature oven. The patterns were collected on flat photographic films. The capillary axis and the film were perpendicular to the X-ray beam. Spacings were obtained using Bragg's law. Aligned samples were achieved by scratching the inner wall of the capillary in the direction of its axis with a metal rod at a temperature at which the mesophase is sufficiently fluid.

Acid chlorides[23] were prepared by literature methods. All of the reactions were carried out under a dry argon atmosphere.

Synthesis of $[N_3P_3(OC_6H_4OCH_2Ph\text{-}4)_6]$ (1). A mixture of $[N_3P_3Cl_6]$ (0.348 g, 1 mmol), 4-benzyloxyphenol (1.321 g, 6.6 mmol), and Cs_2CO_3 (4.88 g, 15 mmol) in acetone (50 mL) was heated under reflux and stirred for 15 h. The volatile materials were evaporated under vacuum, and the residue was extracted with dichloromethane (3 × 10 mL). Evaporation of the solvent to ca. 1 mL and addition of hexane led to the precipitation of **1** as a white solid. Yield: 1.105 g, 83%.

Anal. Calcd (%) for $C_{78}H_{66}N_3O_{12}P_3$ (1330.32): C, 70.42; H, 5.0; N, 3.16. Found: C, 70.74; H, 4.71; N, 3.26. IR (Nujol): 1193 (s, br), 1175 (s, br) (P═N); 952 cm^{-1} (s) (P−O). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 10.05$ (s, 3P; N_3P_3 ring). ^1H NMR ($CDCl_3$): $\delta = 7.39{-}7.30$ (m, 5H; C_6H_5), 6.85 ("d", $J = 9$ Hz, 2H; OC_6H_4O), 6.76 ("d", $J = 9$ Hz, 2H; OC_6H_4O), 4.97 (s, 2H; OCH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta =$ 155.98, 144.74, 137.05, 128.72, 128.10, 127.58, 122.06, 115.56 (12C; aromatic carbons); 70.66 (1C; OCH_2). MS (LSIMS$^+$) m/z (%): 1330 (100) [M$^+$] and peaks derived from the sequential loss of OCH_2Ph, $C_6H_4OCH_2Ph$, and $OC_6H_4OCH_2Ph$.

Synthesis of $[N_3P_3(OC_6H_4OH\text{-}4)_6]$ (2). To a solution of $[N_3P_3(OC_6H_4OCH_2Ph\text{-}4)_6]$ (**1**) (1.33 g, 1 mmol) in dry THF (10 mL) were added cyclohexene (6 mL), palladium hydroxide (20 wt % on carbon, 0.4 g), and ethanol (6 mL). The mixture was heated under reflux for 6 h and filtered. The solvent was evaporated and subsequent addition of dichloromethane (20 mL) led to the precipitation of the product as a white solid. Yield: 0.734 g, 93%.

Anal. Calcd (%) for $C_{36}H_{30}N_3O_{12}P_3$ (789.57): C, 54.76; H, 3.83; N, 5.32. Found: C, 54.36; H, 3.72; N, 5.61. IR (Nujol): 3274 (m, br), 3203 (m, br) (O−H); 1187 (s), 1175 (s, br) (P═N); 950 cm^{-1} (s) (P−O). $^{31}P\{^1H\}$ NMR [$(CD_3)_2CO$]: $\delta = 11.62$ (s, 3P; N_3P_3 ring). ^1H NMR [$(CD_3)_2CO$]: $\delta = 8.33$ (s, 1H; OC_6H_4OH), 6.72 (s, 4H; OC_6H_4OH). $^{13}C\{^1H\}$ NMR [$(CD_3)_2CO$]: $\delta = 155.35$, 144.57, 122.72, 116.66 (6C; OC_6H_4O). MS (LSIMS$^+$) m/z (%): 790 (100) [M$^+$] and peaks derived from the sequential loss of OC_6H_4OH.

Synthesis of $[N_3P_3(OC_6H_4\{OC(O)C_6H_2(3\text{-}R_2,4\text{-}R_1,5\text{-}R_3)\text{-}4\})_6]$ [$R_1 = n\text{-}OC_{10}H_{21}$, $R_2 = R_3 = H$ (3); $R_1 = R_2 = n\text{-}OC_{10}H_{21}$, $R_3 = H$ (4); $R_1 = R_2 = R_3 = n\text{-}OCH_3$ (5); $R_1 = R_2 = R_3 = n\text{-}OC_6H_{13}$ (6); $R_1 = R_2 = R_3 = n\text{-}OC_{10}H_{21}$ (7); $R_1 = R_2 = R_3 = n\text{-}OC_{12}H_{25}$ (8); $R_1 = R_2 = R_3 = n\text{-}OC_{14}H_{29}$ (9)]. These compounds were prepared in a similar manner. The following procedure is typical (see Supporting Information for details of the rest of compounds). A mixture of $[N_3P_3(OC_6H_4OH\text{-}4)_6]$ (**2**) (0.158 g, 0.2 mmol), $ClC(O)C_6H_2(3,4,5\text{-}OC_{12}H_{25})_3$ (1.56 mmol, 1.081 g), and NEt_3 (0.84 mL, 6 mmol) in freshly distilled, dry THF (10 mL) was stirred for 48 h at room temperature. The precipitated $[NHEt_3]Cl$ was filtered off and washed with THF (2 × 3 mL). The volatile materials were evaporated in vacuo. The resulting pale yellow oil was purified by chromatography using a silica gel column and hexane/ethyl acetate (20/1) as eluent. Compound **8** was finally dried in vacuo at 40 °C for 48 h.

Yield: 0.674 g, 75%. Anal. Calcd (%) for $C_{294}H_{486}N_3O_{36}P_3$ (4732.03): C, 74.62; H, 10.35; N, 0.89. Found: C, 75.03; H, 9.82; N, 0.83. IR (Nujol): 1732 cm^{-1} (s) (C═O); 1201 (s, br), 1172 (vs, br) (P═N); 954 cm^{-1} (s) (P−O). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 9.21$ (s, 3P; N_3P_3 ring). ^1H NMR ($CDCl_3$): $\delta = 7.31$ [s, 2H; $C_6H_2(OC_{12}H_{25})_3$], 7.11 (m, 4H; OC_6H_4O), 4.01 [t, $^3J(H,H) = 5.9$ Hz, 2H; OCH_2], 3.94 [t, $^3J(H,H) = 5.6$ Hz, 4H; OCH_2], 1.77−1.26 (m, 60H; CH_2), 0.87 (br, 9H; CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 164.95$ [1C; $C(O)$]; 153.00, 148.09, 143.10, 123.75, 123.02, 121.89, 108.48 (12C; aromatic carbons); 73.60, 69.23 (3C; OCH_2), 32.02, 29.87, 29.76, 29.58, 29.47, 26.22, 22.78 (30C; CH_2), 14.19 (3C; CH_3). MALDI-TOF (9-nitroanthracene with silver triflate): m/z 4839 (M$^+$ + Ag).

Synthesis of $[N_3P_3(OC_6H_4\{OC(O)C_6H_2(3,4,5\text{-}OC_{12}H_{25})_3\text{-}4\})_5(OC_6H_4OH\text{-}4)]$ (10). A mixture of $[N_3P_3(OC_6H_4OH\text{-}4)_6]$ (**2**) (0.316 g, 0.4 mmol), $ClC(O)C_6H_2(3,4,5\text{-}OC_{12}H_{25})_3$ (2.6 mmol, 1.80 g), and NEt_3 (1.6 mL, 11.4 mmol) in freshly distilled dry THF (25 mL) was stirred for 72 h at room temperature. The precipitated $[NHEt_3]Cl$ was filtered off and washed with THF (3 × 5 mL). Evaporation of the solvent gave a pale yellow oil, which proved to be a mixture of **8**, **10**, and ClC(O)-

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$C_6H_2(3,4,5\text{-}OC_{12}H_{25})_3$. The resulting pale yellow oils of **8** (0.214 g, 11.3%) and **10** (0.361 g, 22.1%) were purified by chromatography using a silica gel column and hexane/ethyl acetate (20/1) as eluent and dried in vacuo at 40 °C.

The data for **10** follow. Anal. Calcd (%) for $C_{251}H_{410}N_3O_{32}P_3$ (4074.95): C, 73.98; H, 10.14; N, 1.03. Found: C, 74.03; H, 10.00; N, 1.02. IR (Nujol): 1732 (s) (C═O); 1201 (s, br), 1172 (vs, br) (P═N); 955 cm^{-1} (s) (P−O). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 10.70$ (1P), 9.19 (2P) (AB_2 system, $^2J_{AB} = 87.9$ Hz; N_3P_3 ring). ^1H NMR ($CDCl_3$): $\delta = 7.35$ [s, 4H; $C_6H_2(OC_{12}H_{25})_3$], 7.33 [s, 2H; $C_6H_2(OC_{12}H_{25})_3$], 7.32 [s, 4H; $C_6H_2(OC_{12}H_{25})_3$], 7.20−7.12 (m, 12H; OC_6H_4O), 7.09−7.02 (m, 8H; OC_6H_4O), 6.72 ("d", $J = 8.8$ Hz, 2H; OC_6H_4O), 6.51 ("d", $J = 8.8$ Hz, 2H; OC_6H_4O), 6.1 (br, 1H; O*H*), 4.06−3.94 (m, 30H; OCH_2), 1.84−1.26 (m, 300H; CH_2), 0.87 (m, 45H; CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 165.68$, 164.96 [5C; *C*(O)]; 153.1, 153.04, 148.12, 148.02, 147.76, 143.49, 143.21, 123.79, 123.47, 122.98, 122.85, 121.94, 121.52, 108.72, 108.62 (66C; aromatic carbons); 73.63, 69.34 (15C; OCH_2), 32.01, 29.76, 29.56, 29.47, 26.21, 22.78 (30C; CH_2), 14.17 (15C; CH_3). MALDI-TOF (dithranol): *m/z* 4075.1 ($M^+ + 1$).

Synthesis of $[N_3P_3(OC_6H_4\{OC(O)C_6H_2(3,4,5\text{-}OC_{12}H_{25})_3\text{-}4\})_5\text{-}(OC_6H_4\{OC(O)C_6H_3[3,4\text{-}O(R)\text{-}CH(CH_3)(CH_2)_5CH_3]_2\text{-}4\})]$ (11). 3,4-$\{CH_3(CH_2)_5(R)\text{-}CH(CH_3)O\}_2C_6H_3C(O)Cl$ (0.26 mmol, 0.103 g) and NEt_3 (0.3 mL, 2 mmol) were added to a solution of **10** (0.074 mmol, 0.301 g) in THF (25 mL), and the mixture was stirred for 4 d at room temperature. The precipitated $[NHEt_3]Cl$ was filtered off and washed with THF (3 × 5 mL). Evaporation of the solvent gave a pale yellow oil, which was washed with acetone (2 × 10 mL) and dried in vacuo at 40 °C for 48 h. The resulting pale yellow oil obtained of **11** contained ca. 4% of **10**. Yield: 0.227 g, 69.3%.

Anal. Calcd (%) for $C_{274}H_{446}N_3O_{35}P_3$ (4435.49): C, 74.20; H, 10.14; N, 0.95. Found: C, 74.15; H, 11.60; N, 0.74. IR (Nujol): 1732 (s) (C═O); 1201 (s, br), 1172 (vs, br) (P═N); 954 cm^{-1} (s) (P−O). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 9.35$ (s, 3P; N_3P_3 ring). ^1H NMR ($CDCl_3$): $\delta =$ 7.66−6.99 (m, 37H; aromatic protons), 4.40 (m, 1H; OC*H*), 4.31 (m, 1H; OC*H*), 4.03−3.93 (m, 30H; OCH_2), 1.85−1.26 (m, 326H; CH_2), 0.87 (m, 51H; CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 164.92$ [6C; *C*(O)]; 152.93, 148.11, 143.21, 123.80, 122.98, 121.88, 108.63 (72C; aromatic carbons); 73.61, 69.33 (17C; OCH), 32.0, 30.52, 29.75, 29.57, 29.47, 26.21, 25.51 22.77, 19.84, 19.72 (162C; CH_2), 14.15 (17C; CH_3). MALDI-TOF (dithranol): *m/z* 4435.5 (M^+).

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Supporting Information Available: Synthesis and structural characterization of **3**−**7**, **9**; NMR spectra of **9**; thermal behavior and micrographs of **8**; X-ray pattern of **7** at room temperature. This material is available free of charge via the Internet at http://pubs.acs.org.

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