

LUBRICANTS FOR MAGNETIC RECORDING MEDIA

Cross-Reference to Related Application

[0001] This application claims the benefit of priority of Singapore Patent Application No. 201205893-9, filed August 8, 2012, the contents of which being hereby incorporated by reference in its entirety for all purposes.

Technical Field

[0002] The invention relates to lubricants for magnetic recording media, and in particular, to such lubricants containing cyclotriphosphazene.

Background

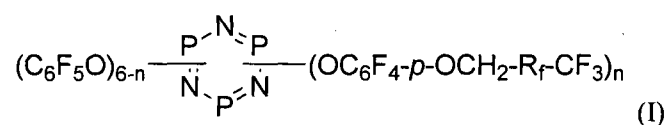
[0003] Heat assisted magnetic recording (HAMR) or thermal assisted magnetic recording (TAMR) are promising solutions for continuously increasing data storage recording density. Under the HAMR or TAMR conditions, the temperature of the recording medium surface will reach as high as or above the Curie temperature of the magnetic layer. This therefore requires thermally stable lubricant which can survive at 350 °C, or even higher. Meanwhile, not only reliable tribological performance in hard disk drive is very critical, but also the highly thermally stable lubricant with comparable tribological properties to the commercial lubricants is an essential and critical requirement for HAMR application.

[0004] Currently, there are limited commercial lubricants which have decomposed temperatures above 300 °C, such as X1-p (Dow Company) and A20H (Moresco (Matsumura Oil Research Corporation)). However, these lubricants are not quite appropriate for HAMR application mainly due to relatively low thermal stability and poor laser resistance.

Summary

[0005] Present inventors have surprisingly found that by first substituting a cyclotriphosphazene moiety with six pentafluorophenoxy groups, followed by substituting the *para* fluorine atom of at least one of the six pentafluorophenoxy group with a perfluoropolyether (PFPE) group, the resultant lubricants show significant improvement in thermal stability as evidenced by isothermal testing at 300 °C and 350 °C. Experimental results further show that about 82 % of the present lubricant remained after 8 h of heating at 300 °C while all other tested conventional lubricants had about 40% or less left remaining. Most importantly, present lubricant can still withstand decomposition when exposed to heating at 350 °C for 65 min while all other tested conventional lubricants rapidly decompose with more than 90 % weight loss within a very short period of time. Additionally, the laser testing demonstrated better thermal resistance than commercial lubricants under the laser irradiation, which is a necessary prerequisite for HAMR technology. In other words, present lubricants show much more reliable tribological performance in comparison with the existing commercial lubricants, further highlighting the potential application for HAMR (TAMR) systems.

[0006] Thus, in a first aspect of the disclosure, there is provided a compound of formula (I)



wherein

n is 1 to 6;

R_f is selected from the group consisting of CF₂CF₂O(CF₂CF₂CF₂O)_mCF₂CF₂ wherein m is 2 to 30 and CF₂(OCF₂CF₂)_rO(CF₂)_s wherein r is 2 to 30 and s is 0, 1, 2, or 3.

[0007] In a second aspect of the disclosure, a method for forming the compound of formula (I) is provided. The method may include:

reacting hexakis(pentafluorophenoxy)cyclotriphosphazene with a perfluoropolyether in a mixture of an organic solvent and a perfluorinated solvent in the presence of cesium carbonate at a temperature range of about 50 to 250 °C,

wherein the perfluoropolyether is a hydroxyl-terminated perfluoropolyether selected from the group consisting of $\text{HOCH}_2\text{-R}_f\text{-CF}_3$,

wherein R_f is selected from the group consisting of $\text{CF}_2\text{CF}_2\text{O}(\text{CF}_2\text{CF}_2\text{CF}_2\text{O})_m\text{CF}_2\text{CF}_2$ wherein m is 2 to 30 and $\text{CF}_2(\text{OCF}_2\text{CF}_2)_r\text{O}(\text{CF}_2)_s$ wherein r is 2 to 30 and s is 0, 1, 2, or 3.

[0008] In a third aspect of the disclosure, use of the compound of formula (I) as a lubricant is disclosed.

Brief Description of the Drawings

[0009] In the drawings, like reference characters generally refer to the same parts throughout the different views. The drawings are not necessarily drawn to scale, emphasis instead generally being placed upon illustrating the principles of various embodiments. In the following description, various embodiments of the invention are described with reference to the following drawings.

[0010] Fig. 1 shows a scheme of a chemical reaction process of forming exemplary embodiments of compounds of formula (I).

[0011] Fig. 2 is a bar graph showing lubricant film recovery for different lubricants measured with TOF-SIMS (Z-DOL is used for reference).

[0012] Fig. 3 shows the friction coefficient of IDL1 and selected commercial lubricants.

[0013] Fig. 4A shows the laser adsorption of IDL1 solution.

[0014] Fig. 4B shows the laser reflection of IDL1 thin film.

[0015] Fig. 5A and Fig. 5B show the thermal aging effect on the thermal stability of various lubricants measured by TGA at 350 °C and 300 °C, respectively.

[0016] Fig. 6 shows the laser irradiation on different lubricated disks. Laser irradiation: 200 ns and cooling down period: 30ms, 400 pulses of laser shined on every spot along a straight line.

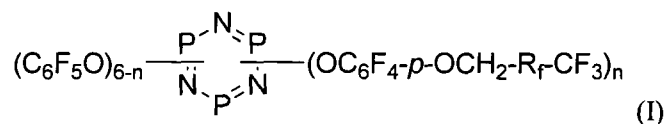
[0017] Fig. 7A and Fig. 7B show the laser irradiation with difference duration on IDL1 lubricated disks: (A) 200 ns on and 30 ms off laser, and 20 pulses of 5 ns on; and (B) 5 ns off laser shine on the same spot 400 times on IDL1 lubricated disk, respectively.

Description

[0018] The following detailed description refers to the accompanying drawings that show, by way of illustration, specific details and embodiments in which the invention may be practised. These embodiments are described in sufficient detail to enable those skilled in the art to practise the invention. Other embodiments may be utilized and structural changes may be made without departing from the scope of the invention. The various embodiments are not necessarily mutually exclusive, as some embodiments can be combined with one or more other embodiments to form new embodiments.

[0019] Among a variety of approaches to achieve high temperature enduring hard disk lubricants for heat assisted magnetic recording (HAMR) applications, chemically bonding perfluoropolyether (PFPE) to a cyclotriphosphazene moiety is one of the most effective methods. In addition, this type of lubricant is able to form thin and homogenous films on hard disks, providing good mobility, good bonding ratio, low surface energy, and improved thermal stability and laser resistance.

[0020] Thus, in a first aspect of the disclosure, there is provided a compound of formula (I)



wherein

n is 1 to 6;

R_f is selected from the group consisting of CF₂CF₂O(CF₂CF₂CF₂O)_mCF₂CF₂ wherein m is 2 to 30 and CF₂(OCF₂CF₂)_rO(CF₂)_s wherein r is 2 to 30 and s is 0, 1, 2, or 3.

[0021] As can be seen from formula (I), the compounds in formula (I) are PFPE covalently-linked cyclotriphosphazenes. Specifically, the compound is a cyclotriphosphazene which is substituted by pentafluorophenoxoy groups (C₆F₅O) and *p*-PFPE-tetrafluorophenoxy groups (OC₆F₄-*p*-OCH₂-R_f-CF₃).

[0022] The R_f used in this disclosure includes two types of hydroxy-terminated PFPEs. In exemplary embodiments, present compounds IDL1 have six substituted aromatic groups, and at least one PFPE chain attached to the *para* position of the tetrafluorophenoxy groups.

[0023] The term "perfluorinated" means an organic compound including all hydrogens replaced by fluorine on a carbon chain but the compound also contains at least one different atom or functional group.

[0024] In formula (I), R_f can be CF₂CF₂O(CF₂CF₂CF₂O)_mCF₂CF₂ and m is 2 to 30, such as 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, or 30. Thus, HOCH₂R_fCF₃ has a molecular weight from about 600 to about 5,500.

[0025] In various embodiments, R_f is CF₂CF₂O(CF₂CF₂CF₂O)_mCF₂CF₂ where m is 21.

[0026] Alternatively, in formula (I), R_f can be $CF_2(OCF_2CF_2)_rO(CF_2)_s$ and r is 2 to 30, such as 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, or 30, and s is 0, 1, 2, or 3. Thus $HOCH_2R_fCF_3$ has a molecular weight from about 400 to about 3,000.

[0027] In various embodiments, R_f is $CF_2(OCF_2CF_2)_rO(CF_2)_s$ where r is 2 and s is 2 or 3, preferably 3.

[0028] In various embodiments, n is 3.

[0029] It has been found by the inventors that compounds of formula (I) can be used as lubricants, and in particular, for lubricating magnetic recording medium. For example, lubricants containing compounds of formula (I) can have a high thermal stability, high bonding ratio and good mobility compared to conventional lubricants, and may be a good candidate for HAMR media. The compounds of formula (I) may also be potential as additives in existing lubricant system in order to improve the thermal stability, laser resistance and tribological properties.

[0030] Fig. 1 shows a scheme of a chemical reaction process of forming exemplary embodiments of compounds of formula (I). The method for forming the compound of formula (I) may include: reacting hexakis(pentafluorophenoxy)cyclotriphosphazene with a perfluoropolyether in a mixture of an organic solvent and a perfluorinated solvent in the presence of cesium carbonate at a temperature range of about 50 to 250 °C,

wherein the perfluoropolyether is a hydroxyl-terminated perfluoropolyether selected from the group consisting of $HOCH_2-R_f-CF_3$,

wherein R_f is selected from the group consisting of $CF_2CF_2O(CF_2CF_2CF_2O)_mCF_2CF_2$ wherein m is 2 to 30 and $CF_2(OCF_2CF_2)_rO(CF_2)_s$ wherein r is 2 to 30 and s is 0, 1, 2, or 3.

[0031] In various embodiments, the hydroxyl-terminated perfluoropolyether is

$\text{HOCH}_2\text{CF}_2(\text{OCF}_2\text{CF}_2)_3\text{OCF}_2\text{CF}_2\text{CF}_3$ or $\text{HOCH}_2\text{CF}_2(\text{OCF}_2\text{CF}_2)_3\text{O}(\text{CF}_2)_3\text{CF}_3$.

[0032] In various embodiments, the organic solvent is selected from the group consisting of tetrahydrofuran (THF), benzene, and methylbenzene. In certain embodiments, the organic solvent is THF.

[0033] In various embodiments, the precursor, hexakis(pentafluorophenoxy)cyclotriphosphazene, may be prepared by mixing hexachlorocyclotriphosphazene and a pentafluorophenoxide in a tetrahydrofuran solvent.

[0034] In further embodiments, the pentafluorophenoxide may be prepared by a reaction between a pentafluorophenol and a base solution including K_2CO_3 , Na_2CO_3 , KOH, NaOH or NaH in an organic solvent such as THF.

[0035] In one embodiment, a desired amount of hexachlorocyclotriphosphazene and sodium pentafluorophenoxide was placed into a reaction vessel to afford hexakis(pentafluorophenoxy)cyclotriphosphazene. The second step involved substitution of *para*-fluorine atom in the pentafluorophenoxy groups by one or several hydroxy-terminated PFPE chains in the presence of anhydrous cesium carbonate in a mixture of THF solvent and fluorinated solvent such as FC77. The THF may be replaced by another suitable solvent such as benzene, methylbenzene, or the like. The fluorinated solvent may be a perfluorinated solvent selected from FC-77™, HFE 7100™, PF5060™, and the like. Some of these solvents are commercially available from Dupont™ or 3M™ Novec™. A suitable solvent in the Vertrel™ family of solvents may also be used. The pure product may be obtained by simple separation processes including washing and centrifuging to remove the impurity.

[0036] In summary, present compounds and lubricants exhibit better thermal stability when compared with the currently available products. Present compounds and lubricants also show better laser resistance than the commercial lubricants under the same experimental conditions. This may address the thermal stability issue of the lubricant in HAMR and TAMR.

[0037] Furthermore, present compounds can be used as lubricants or additives in combination with commercial products to achieve even better performance such as higher thermal stability and better mobility.

[0038] In order that the invention may be readily understood and put into practical effect, particular embodiments will now be described by way of the following non-limiting examples.

Examples

[0039] Example 1: Preparation of Lubricant IDL1

[0040] The precursor hexakis(pentafluorophenoxy)cyclotriphosphazene may be prepared by the following method: To a dry tetrahydrofuran (THF) solution of pentafluorophenol (0.05 mol), sodium hydride (0.06 mol) was added. The reaction was stirred at 60 °C for 2 h.

Hexachlorocyclotriphosphazene was added in one portion. The mixture was stirred for 12 h. Crude product was separated by silica gel column chromatography to give rise to a pure precursor. The chemical structure of the precursor was confirmed by ¹H nuclear magnetic resonance (NMR) and ³¹P NMR.

[0041] To a solution of hexakis(pentafluorophenoxy)cyclotriphosphazene, hydroxy-terminated PFPE (0.3 equivalent) was added. The reaction was stirred at a temperature of 50 - 250 °C for 5 - 48 h in the presence of anhydrous CsCO₃. ¹H NMR and ³¹P NMR were used to confirm the chemical structure of the final product.

[0042] Example 2: Viscosity Measurement

[0043] Similar to traditional lubricants, the viscosity of lubricant IDL1 has shown to behave like a Newtonian liquid. The dynamic viscosity of lubricants together with several commercially available lubricants for comparison at 25 °C is given in **Table 1**.

TABLE 1. Viscosity Data for IDL1 vs. Commercial Lubricants

Lubricants	Viscosity at 25 °C (mPa.s)	Viscosity at 40 °C (mPa.s)	Viscosity at 100 °C (mPa.s)
IDL1	625	337	79
X1-p	729	259	9
A20H	65 ^a	--- ^a	--- ^a
Z-Tetraol	500 ^a	--- ^a	--- ^a

^a. Not measured.

[0044] Example 3: Surface Free Energy of Thin Film and Carbon-Lubricant Bonding Ratio

[0045] Lubricant IDL1 forms uniform thin films on disk surfaces with a thickness of 0.8 – 2.4 nm.

Table 2 and **Table 3** show the surface energies and bonding ratios of lubricant films measured with the same thickness of IDL1 and commercial lubricants. It is observed that present lubricant shows comparable surface energy and, in some cases, higher bonding ratio than those of the commercial lubricants.

TABLE 2. Surface Energy Comparison of IDL1 and Commercial Products

Lubricants	Surface Energy @ 25 °C
Z-DOL(2K)	44
A20H	44
Z-Tetraol	25
IDL1	41

TABLE 3. Bonding Ratio of Lubricant IDL1 and Commercial Products

Lubricants	Bonding Ratio @ 25 °C
Z-DOL(2K)	2
A20H	20
Z-Tetraol	9
IDL1	13

[0046] Example 4: Mobility Measurement of Lubricant Thin Films

[0047] The mobility of the lubricants was tested using time-of-flight secondary ion mass spectroscopy (TOF-SIMS). In these tests, a film of each respective lubricant was formed uniformly on a disk surface. A local area in the film (a radial “stripe” approximately 40 μm wide) was depleted of the lubricant. The rate at which each lubricant film re-flew back into the depleted area on the disk surface was measured using TOF-SIMS. The recovery by the respective lubricant in the depleted area after 1 h was examined; the recovery rate was used to indicate the lubricant film mobility. As shown in **Fig. 2**, the mobility of A20H film was found to be much lower than that of Zdol 2000 film: the latter showed complete recovery while the former showed little recovery. In comparison, lubricant IDL1 showed a moderate mobility. As can be appreciated, excess mobility may lead to lubricant spin-off and lubricant film dewetting, decreasing the durability of the hard disk, while poor mobility may result in loss of lubrication in some areas on the disk surface. Thus, moderate mobility may be desirable for a lubricant used in magnetic recording applications.

[0048] Example 5: Fiction Coefficients Measurement of Lubricant

[0049] The dynamic friction coefficients of thin films of IDL1 along with Z-DOL, A20H and Z-Tetraol lubricants were measured. The films were deposited on the surfaces of magnetic hard disks and their friction coefficients were measured using CETR reliability tester (skew angle was 0° , vertical load was 2.5 g). As illustrated in **Fig. 3**, the results showed that lubricant IDL1 had comparable dynamic friction coefficients to those of the conventional lubricants, indicating that lubricant IDL1 has comparable tribological behavior to the existing commercial lubricants.

[0050] **Example 6: Characterization of Laser Adsorption**

[0051] Laser adsorption measurement was performed using the lubricant solution and the lubricant film on hard disk surface. As shown in **Fig 4**, IDL1 shows the similar laser performance to commercial lubricants, which no noticeable adsorption was observed in the laser wavelength range of 380 to 800 nm for both IDL1 solution and IDL1 film. The photo-effect is completely negligible, however, thermal effect is expected be dominated particularly for red light laser source which is now being used by many researchers for HAMR application.

[0052] **Example 7: Characterization of Lubricant Thermal Stability**

[0053] TGA experiments were conducted to study the relative thermal stability in the air. The temperatures at which weight loss of 5 % and 20 % occurs are given in **Table 4**.

TABLE 4. Decomposition Temperatures of Lubricants

lubricants	Temp. at weight loss @ 5% (°C)	Temp. at weight loss @ 20% (°C)
IDL1	305	421
Z-DOL(2K)	183	-- ^a
Z-DOL(4K)	200	-- ^a
X1-P	304	336
A20H(3K)	319 ^b	-- ^a
Z-tetraol	230 ^b	-- ^a

^a. no data ^b. Reference data

[0054] The effect of the heating rate on the decomposition temperature of lubricant was studied and the data are summarized in **Table 5**. As the lubricant is heated up to a very high temperature within a very short period, for instance, 1 second, by using a laser source in HAMR, this experiment is likely to provide evaluation on whether the lubricant on the surface of a disk can survive at very high heating rate. In an experiment, if the heating rate is increased to be 200 °C/min, the recorded decomposition temperature of IDL1 can reach up to 350 °C.

TABLE 5. Heat Rate vs. Decomposition Temperature of IDL1

Heating rate (°C/min)	Temp. at weight loss @ 5% (°C)	Temp. at weight loss @ 20% (°C)
20	304.6	420.9
50	310.7	425.2
100	332.2	453.1
150	342.5	466.4
200	350.3	476.0

[0055] The thermal aging tests were also conducted at 250 °C, 300 °C and 350 °C for about 8 h. The weight loss under such conditions may indicate the long term thermal stability of the lubricant (Fig. 5). Table 6 gives the comparison data of IDL1 and commercial products. The results indicated that under 300 °C, IDL1 still has more than 80 % left. However, less than 40 % was retained for all the commercial lubricants. Even if IDL1 was heated at 350 °C, it still can survive for 65 min with less than around 20 % weight loss. In contrast, A20H quickly lost more than 90 % weight within 30 min.

TABLE 6. Comparison of Thermal Stability of IDL1 and Commercial Products at 250, 300, and

350 °C for 480 min

Lubricants	Weight % after 480 min @		
	250 °C	300 °C	350°C
IDL1	89	82	32
Z-DOL(2K)	25	11	--
Z-DOL(4K)	68	39	-- ^a
X1-P	48	0	-- ^a
A20H(3K)	92	6	0

[0056] Example 8: Thermal Effect Induced by Laser on the Thermal Stability of Lubricant Film

[0057] A laser light with a wavelength of 785 nm was focused onto 1 μm size beam and irradiated on different lubricated disks. Fig. 6 shows the film optical surface analysis images after laser irradiation at power of 120 mW, 80 mW and 40 mW. Z-DOL lubricant film started to be affected with 40 mW power as a faint line was observed. It was completely damaged under laser with a power of 120 mW. However, other lubricant films are intact under 40 mW laser irradiation. At 120

mW and 80 mW power, the damage order is Z-DOL > Z-Tetraol > A20H >> IDL1. TOF-SIMS analysis showed that IDL1 decreased only slightly in lubricant thickness, while the other lubricant films showed significant lubricant degradation and decomposition. On the above experiment, the laser pulse width and size are purposely set much bigger than the laser beam on hard disk drive for practical HAMR application, since laser irradiation duration in hard disk drive is in fact at a nanosecond level. Using more practical laser irradiation conditions, the laser experiments of lubricant film of IDL1 were carried out and optical surface analysis images are shown in **Fig. 7**. IDL1 lubricant films are intact under the 40 mW and 80 mW laser irradiation for 5 ns.

[0058] By "comprising" it is meant including, but not limited to, whatever follows the word "comprising". Thus, use of the term "comprising" indicates that the listed elements are required or mandatory, but that other elements are optional and may or may not be present.

[0059] By "consisting of" is meant including, and limited to, whatever follows the phrase "consisting of". Thus, the phrase "consisting of" indicates that the listed elements are required or mandatory, and that no other elements may be present.

[0060] The inventions illustratively described herein may suitably be practiced in the absence of any element or elements, limitation or limitations, not specifically disclosed herein. Thus, for example, the terms "comprising", "including", "containing", etc. shall be read expansively and without limitation. Additionally, the terms and expressions employed herein have been used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed. Thus, it should be understood that although the present invention has been specifically disclosed by preferred embodiments and optional features, modification and variation of the

inventions embodied therein herein disclosed may be resorted to by those skilled in the art, and that such modifications and variations are considered to be within the scope of this invention.

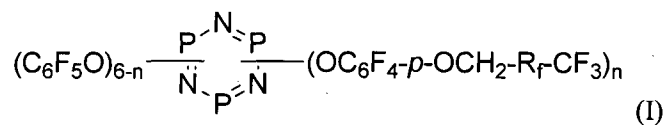
[0061] By "about" in relation to a given numerical value, such as for temperature and period of time, it is meant to include numerical values within 10% of the specified value.

[0062] The invention has been described broadly and generically herein. Each of the narrower species and sub-generic groupings falling within the generic disclosure also form part of the invention. This includes the generic description of the invention with a proviso or negative limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically recited herein.

[0063] Other embodiments are within the following claims and non- limiting examples. In addition, where features or aspects of the invention are described in terms of Markush groups, those skilled in the art will recognize that the invention is also thereby described in terms of any individual member or subgroup of members of the Markush group.

Claims

1. A compound of formula (I)

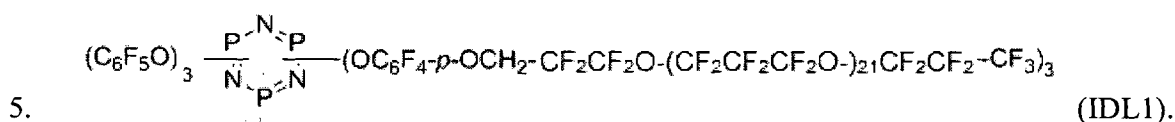


wherein

n is 1 to 6;

R_f is selected from the group consisting of CF₂CF₂O(CF₂CF₂CF₂O)_mCF₂CF₂ wherein m is 2 to 30 and CF₂(OCF₂CF₂)_rO(CF₂)_s wherein r is 2 to 30 and s is 0, 1, 2, or 3.

2. The compound of claim 1, wherein n is 3.
3. The compound of claim 1 or 2, wherein R_f is CF₂CF₂O(CF₂CF₂CF₂O)_mCF₂CF₂, and wherein m is 21.
4. The compound of claim 1 or 2, wherein R_f is CF₂(OCF₂CF₂)_rO(CF₂)_s, and wherein r is 2 and s is 3.



6. A method for forming the compound of formula (I), comprising:

reacting hexakis(pentafluorophenoxy)cyclotriphosphazene with a perfluoropolyether in a mixture of an organic solvent and a perfluorinated solvent in the presence of cesium carbonate at a temperature range of about 50 to 250 °C,

wherein the perfluoropolyether is a hydroxyl-terminated perfluoropolyether selected from the group consisting of HOCH₂-R_f-CF₃,

wherein R_f is selected from the group consisting of $CF_2CF_2O(CF_2CF_2CF_2O)_mCF_2CF_2$

wherein m is 2 to 30 and $CF_2(OCF_2CF_2)_rO(CF_2)_s$ wherein r is 2 to 30 and s is 0, 1, 2, or 3.

7. The method of claim 6, wherein the hydroxyl-terminated perfluoropolyether is $HOCH_2CF_2(OCF_2CF_2)_3OCF_2CF_2CF_3$ or $HOCH_2CF_2(OCF_2CF_2)_3O(CF_2)_3CF_3$.
8. The method of claim 7, wherein the organic solvent is selected from the group consisting of tetrahydrofuran, benzene, and methylbenzene.
9. The method of claim 6, wherein the hexakis(pentafluorophenoxy)cyclotriphosphazene is prepared by mixing hexachlorocyclotriphosphazene and a pentafluorophenoxide in a tetrahydrofuran solvent.
10. Use of the compound of any one of claims 1-5 as a lubricant.
11. The use of claim 10 for lubricating a magnetic recording medium.