Supplementary Data

Materials. Hexachlorocyclotriphosphazatriene (a gift from the Shin Nisso Kako Co Ltd) was purified by fractional crystallization from hexane prior to use. 2,2-Diphenyl-4,4,6,6-tetrachlorocyclotriphosphazatriene (**2**) was prepared by a literature method (Acock *et al.*, 1964). Sodium hydride, 60% dispersion in mineral oil (Merck); the oil being removed by washing with dry heptane followed by decantation prior to use. Tetraethylene glycol (Fluka) was dried over 4Å molecular sieves.

THF was distilled over a sodium-potassium alloy under an atmosphere of dry argon. Products were subjected to separation by column chromatography using silica gel (230-400 mesh Merck). All the solvents used throughout this work were purified by conventional methods. All the reactions were carried out under a dry argon atmosphere.

Preparation of 2,2-diphenyl-4,6-dichloro-4,6-[oxytetra(ethyleneoxy)]cyclo-triphosphazatriene, (3). 2,2-Diphenyl-4,4,6,6-tetrachlorocyclotriphosphazatriene (**2**) (Acock *et al*., 1964) (2.15 g, 5 mmol) and tetraethyleneglycol (**1)** (1.46 g, 7.5 mmol) were dissolved in 250 mL of dry THF in a 500 mL three-necked round-bottomed flask. The reaction mixture was cooled in an ice-bath and NaH (60% oil suspension, 0.6 g, 15 mmol) in 50 mL of dry THF was quickly added to a stirred solution under an argon atmosphere. The reaction was stirred for 2 h at room temperature and was followed on TLC silica gel plates using hexane-THF (1:1). The reaction mixture was filtered to remove the sodium chloride formed, the solvent removed under reduced pressure and the resulting colourless oil subjected to column chromatography, using THF-hexane (1:2) as eluant. 2,2-Diphenyl-4,6-dichloro-4,6-[oxytetra(ethyleneoxy)]cyclotriphosphazatriene, (**3**), was isolated as a colourless oil, which on crystallization from hexane-dichloromethane gave colourless crystals, m.p. 102^0C (yield 0.85 g, 31%). Analysis found: C, 43.31; H, 4.7; N, 7.34% ; M^+, 550.3. $C_{20}H_{26}Cl_2N_3O_5P_3$ requires: C, 43.50; H, 4.75; N, 7.61%; M 552.25.

Preparation of 2,2-diphenyl-4,6-bis(2',2',2'-trifluoroethoxy)-4,6-[oxytetra(ethyleneoxy)]cyclotriphosphazatriene, (4). 2,2,2-Trifluoroethanol (0.33 g, 3 mmol) and **(3)** (0.83g, 1.5 mmol) were dissolved in 30 mL of dry THF in a 50 mL three-necked round-bottomed flask. The reaction mixture was cooled in an ice-bath

and NaH (60% oil suspension, 0.12 g, 3 mmol) in 10 ml of dry THF was quickly added to a stirred solution under an argon atmosphere. The reaction was stirred for 48 h at room temperature and monitored on TLC silica gel plates using hexane-THF (1:1). The reaction mixture was filtered to remove the sodium chloride formed, the solvent removed under reduced pressure and the resulting colourless oil was subjected to column chromatography, using THF-hexane (1:1) as eluant. A colourless oil was obtained, which was dissolved in chloroform-light petroleum (1:2) from which crystallised 2,2-diphenyl-4,6- bis(2',2',2'-trifluoroethoxy)-4,6-[oxytetra(ethyleneoxy)]cyclotriphosphazatrienes, **(4),** as colourless crystals m.p. 74^0C. (yield 0.3g, 39%). Analysis found: C, 42.35; H, 4.38; N, 6.15% ; M^+, 680.1. $C_{24}H_{30}F_6N_3O_7P_3$ requires: C, 42.43; H, 4.45; N, 6.18%; M 679.43.

Preparation of 2,2-diphenyl-4,6-diphenoxy-4,6-[oxytetra(ethyleneoxy)]cyclotriphosphazatriene, (5). Phenol (0.188 g, 2 mmol) and **(3)** (0.55 g, 1 mmol) were dissolved in 20 mL of dry THF in a 100 mL three-necked round-bottomed flask. The reaction mixture was cooled in a ice-bath and NaH (60% oil suspension, 0.08 g, 2 mmol) in 10 mL of dry THF was quickly added to a stirred solution under an argon atmosphere. The reaction was stirred for 48 h at room temperature and monitored on TLC silica gel plates using hexane-THF (1:1). The reaction mixture was filtered to remove the sodium chloride formed, the solvent removed at reduced pressure and the resulting oil was subjected to column chromatography using THF-hexane (1:1) as eluant. The product was isolated as colourless oil, which dissolved in hexane-dichloromethane (2:1) and from which colourless crystals of 2,2-diphenyl-4,6-diphenoxy-4,6-[oxytetra(ethyleneoxy)]cyclotriphosphazatriene (**5)** were obtained, m.p. 83^0C (yield 0.39g, 58%). Analysis found: C, 57.97; H, 5.83; N, 6.34%; M^+, 667.58. $C_{32}H_{36}N_3O_7P_3$ requires: C, 57.57; H, 5.44; N, 6.29% M 669.

Preparation of the 2,2-diphenyl-4,6-dimethoxy-4,6-[oxytetra(ethyleneoxy)]cyclotriphosphazatrienes, (6). (3) (0.83 g, 1.5 mmol) was dissolved in 30 mL of dry MeOH in a 50 mL three-necked round-bottomed flask. The reaction mixture was cooled in an ice-bath and NaH (60% oil suspension, 0.3 g, 7.5 mmol) in 10 ml of dry THF was quickly added to a stirred solution under an argon atmosphere. The reaction was stirred for a further 48 h at room temperature and monitored on TLC silica gel plates using hexane-THF (1:1). The reaction mixture was filtered to remove the sodium chloride, the solvent removed under reduced pressure and the resulting colourless oil was subjected to column chromatography, using THF-hexane (1:1) as eluant. 2,2-Diphenyl-4,6-dimethoxy-4,6-

[oxytetra(ethyleneoxy)]cyclotriphosphazatrienes, **(6),** was isolated as a colourless oil. On dissolving this oil in chloroform-heptane (1:2) colourless crystals, m.p. 89^0C, were obtained (yield 0.53 g, 65%). Analysis found: C, 49.02; H, 5.9; N, 7.65% ; M^+,544. $C_{22}H_{32}N_3O_7P_3$ requires: C, 48.62; H, 5.94; N, 7.73%; M 543.44.

Preparation of 2,2-diphenyl-4,6-dianilino-4,6-[oxytetra(ethyleneoxy)]cyclotriphosphazatriene, (7). Aniline (5.58 g, 60mmol in 15 mL of dry THF) was added dropwise from an addition funnel to a solution of (**3)** (0.83 g, 1.5 mmol in 30 ml of dry THF) in a 250 mL three-necked round-bottomed flask. The reaction mixture was refluxed for 3 h and monitored by TLC. The reaction mixture was cooled to room temperature, filtered and the solvent removed under reduced pressure. 100 mL of distilled water was added and the mixture extracted with dichloromethane. The organic layer was dried over anhydrous Na_2SO_4 and concentrated to 5 mL. The crude product was dropped into 100 mL of pentane and the product precipitated, filtered off and dissolved in methanol from which 2,2-diphenyl-4,6-dianilino-4,6-[oxytetra(ethyleneoxy)]cyclotriphosphazatriene, (**7**) was obtained as colourless crystals, m.p. 158^0C (yield 0,76g, 76%). Analysis found: C, 57.64; H, 6.14; N, 10.34.% ; M^+, 666. $C_{32}H_{38}N_5O_5P_3$ requires: C, 57.74; H, 5.75; N, 10.52%; M 665.61

Preparation of 2,2-diphenyl-4,6-bis(t-butylamino)-4,6-[oxytetra(ethyleneoxy)]cyclotriphosphazatrienes, (8). t-Butylamine (1.46g, 20 mmol) and **(3)** (0.55 g, 1 mmol) were dissolved in 20 mL of dry THF in a 50 mL three-necked round-bottomed flask. The reaction mixture was refluxed for 3 days and monitored by TLC. The reaction mixture was cooled to room temperature, filtered and the solvent removed under reduced pressure. 100 mL of distilled water was added and the mixture was extracted two times with 20 mL of dichloromethane. The organic layer was dried over anhydrous Na_2SO_4 and concentrated to 5 mL. The resulting colourless oil was subjected to column chromatography, using THF-hexane (1:1) as eluant. A colourless oil was isolated, which was dissolved in hexane-dichloromethane (2:1) from which it gave colourless crystals of 2,2-diphenyl-4,6-bis(t-butylamino)-4,6-[oxytetra(ethyleneoxy)]cyclotriphosphazatriene, **(8),** m.p. 106^0C (yield 0,12g 19%). Analysis found: C, 53.67; H, 7.43; N, 11.00% ; M^+, 626.2. $C_{28}H_{46}N_5O_5P_3$ requires: C, 53.76; H, 7.41; N, 11.19%; M 625.63.

Reference:

Acock, K.G., Shaw, R.A. & Wells, F.B.G. (1964) *J. Chem. Soc.*, 121-130.