

## Fluorescence Phenomena -New Properties of Hexakis (4-Aminophenoxy) Cyclotriphosphazene

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**Abstract:** Investigations of the absorption and fluorescence spectra of hexakis (4-aminophenoxy)-cyclotriphosphazene at room temperature in three solvents of different polarity (N, N-dimethyl-formamide, tetrahydrofuran and toluene) have been conducted. And fluorescence lifetimes of these three solutions were also measured. Major reasons of such spectral behavior are discussed.

**Keywords:** Hexakis(4-aminophenoxy)cyclotriphosphazene, absorption, fluorescence, lifetime.

Hexakis(4-aminophenoxy)cyclotriphosphazene is an important intermediate for the preparation of resins with enhanced fire retardancy<sup>1</sup>. This amine and a number of its derivatives have been prepared by several groups of investigators<sup>2-12</sup> who have shown these materials to be useful both as polymer precursors and as model compounds in studies of polymeric phosphazene systems. Invariably, amine (**3**) has been prepared by catalytic reduction of hexakis(4-nitrophenoxy)cyclotriphosphazene (**2**). But so far we have not found any reports about the fluorescence phenomena of amine (**3**). The goal of the research presented herein is to investigate the spectral properties of hexakis (4-aminophenoxy)-cyclotriphosphazene. We hope to find new optical applications for this amine.

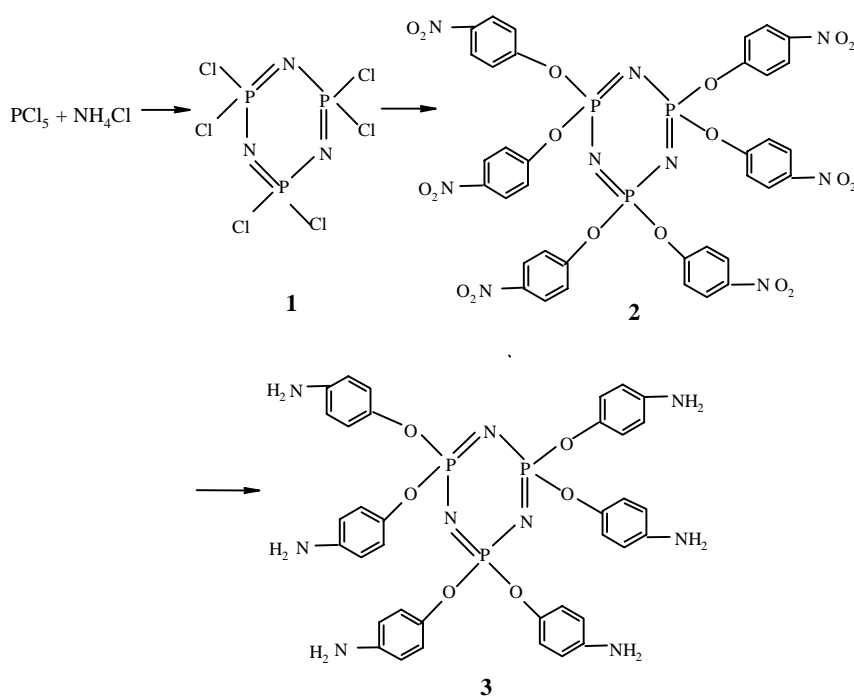
The melting points were measured by differential scanning calorimetry (METTLER-TOLEDO DSC 822) at a rate of 5°C/min under nitrogen atmosphere. Elemental analyses were performed on ElementarVario EL. <sup>1</sup>H NMR, IR and <sup>31</sup>P NMR were conducted respectively on JEOL FX-90Q, Nicolet 20SX FT-IR (KBr) and Bruker DRX400 spectrograph. The absorption spectra and the fluorescence spectra (and also lifetime) of the amine were measured respectively by U-3500 recording spectrophotometer and by ENDINBURGH FLS 920 fluorescence spectrograph with dilute solutions of  $1 \times 10^{-5}$  mol/L in three solvents of different polarity.

**Scheme 1** shows the preparation scheme of amine (**3**). Cyclotriphosphazene (**1**) was synthesized by PCl<sub>5</sub> and NH<sub>4</sub>Cl (mp:112-113°C). Hexakis (4-nitrophenoxy) cyclo-triphosphazene (**2**) was synthesized by an improved method<sup>13,14</sup> (mp:249 and 262°C)<sup>10</sup>. Hexakis(4-aminophenoxy)cyclotriphosphazene(**3**) was synthesized as

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Scheme 1

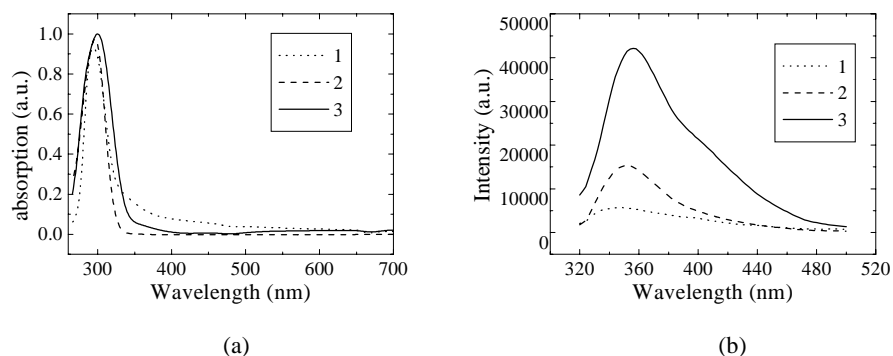


(mp:170-171°C)<sup>10,15</sup>. From the absorption and fluorescence spectra (**Figure 1**), the maxima of absorption bands ( $\lambda_a^{\max}$ ) and the maxima of fluorescence bands ( $\lambda_{a'}^{\max}$ ) (shown in **Table 1**) exhibited only a small red shift with the increase of solvent polarity. But their full-width at half-maximum ( $\Delta\lambda_a$  and  $\Delta\lambda_{a'}$ ) did not obey any rule. The absorption at  $\lambda_a^{\max}$  for amine (**3**) increased slightly with the increase of solvent polarity, while the fluorescence intensity and the lifetime exhibited a considerable increase with the increase of solvent polarity. The increase of lifetime means on the excited state, the molecule was more stable in the solvent of strong polarity than in the solvent of weak polarity.

**Table 1** Lifetime,  $\lambda_a^{\max}$  and  $\Delta\lambda_a$ (nm) of absorption and fluorescence spectra

solvents	Absorption		Fluorescence		
	$\lambda_a^{\max}$ (nm)	$\Delta\lambda_a$ (nm)	$\lambda_{a'}^{\max}$ (nm)	$\Delta\lambda_{a'}$ (nm)	Lifetime (ns)
1	294	34	348	82	1.73
2	296	36	350	52	2.02
3	300	47	356	68	5.93

**Figure 1** The absorption (a) and fluorescence (b) spectra for amine (3) in three solvents of different polarity: 1-toluene; 2- tetrahydrofuran; 3- N, N- dimethylformamide



Analyzing the structure of amine (3), we preliminarily drew this conclusion: because cyclotriphosphazene (1) was aromatic<sup>16, 17</sup>, the phosphazene N<sub>3</sub>P<sub>3</sub> skeleton of amine (3) can offer delocalized  $\pi$  electrons. What is more, the aminophenoxy groups are electron donors, so the delocalized  $\pi$  electrons can undergo a transition from the ground state to the excited state with the molecule excited by light.

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### References and Notes

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14. <sup>1</sup>HNMR (DMSO-d<sub>6</sub>/D<sub>2</sub>O,  $\delta$  ppm) : 8.21(d, 12H, J=9.3, Ar-H), 7.36 (d, 12H, J=9.3, Ar-H); <sup>31</sup>P NMR: 7.8519 (s); IR: 1590 (aromatic), 1525.3 and 1348.9 (asymmetrical and symmetrical nitro group stretching), 1204, 1183 and 1163 (cyclotriphosphazene ring P=N); Elemental analysis: Calcd : C, 44.65%; H, 2.51%; N, 13.0%; P, 9.61%; Found : C, 44.61%; H, 2.75%; N, 13.16%; P, 9.53%.
15. <sup>1</sup>HNMR (DMSO-d<sub>6</sub>/D<sub>2</sub>O,  $\delta$  ppm) : 6.50 and 6.46 (each s, 24H, Ar-H), 4.75 (s, 12 H, amino,

exchangeable with D<sub>2</sub>O); <sup>31</sup>P NMR: 10.593(s); IR: 3424, 3349 and 3216 (NH<sub>2</sub> stretching), 1619 (NH<sub>2</sub> bending), 1503 (aromatic), 1220, 1196 and 1169 (cyclotriphosphazene ring P=N, 956, 877, 832 (NH wagging); Elemental analysis: Calcd :C, 55.18; H, 4.60; N, 16.09; P, 11.87; Found: C, 55.17; H, 4.77; N, 15.79; P, 11.50.

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