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Synthesis of Polyphosphazenes Bearing Covalently Linked Copper Phthalocyanine Units

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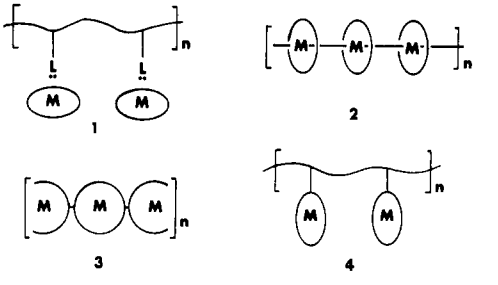
ABSTRACT: Soluble poly(organophosphazenes) bearing covalently bound copper phthalocyanine side groups have been synthesized. The synthesis pathway involved the preparation of a high molecular weight poly[bis(aryloxy)phosphazene] in which 90% of the side groups were phenoxy and 10% were *o*-dicyanoaryl units. Condensation of this species with a large excess of phthalonitrile, 1,2-dimethyl-4,5-dicyanobenzene, 1,2-dicyano-4,5-bis(phenoxymethyl)benzene, or 4,5-bis[(methoxyethoxy)methyl]-1,2-dicyanobenzene in DMF and in the presence of CuBr yielded open-chain polymers with phthalocyanine side groups covalently linked to the phosphazene chain. On the basis of UV/vis spectral data it was shown that the polymeric phthalocyanines did not aggregate in a variety of solvents. The synthesis of small-molecule, cyclic trimeric model analogues of these polymers has also been accomplished. The solubilities of these small-molecule cyclotriphosphazenyl phthalocyanines are much higher than those of the free phthalocyanines. The electrical conductivities of the iodine-doped trimeric and high-polymeric species, both as compressed pellets and as thin films, were in the range of 10^{-4} Ω^{-1} cm^{-1} for the cyclic trimers and 10^{-5}–10^{-8} Ω^{-1} cm^{-1} for the high polymers.

One of our interests is the synthesis and study of high molecular weight, linear, inorganic backbone polymers that bear large, planar side groups. Such macromolecules should have properties that are dominated by the ability of the side groups to stack in the liquid or solid states, a characteristic that, in different circumstances, could give rise to liquid crystallinity or electroactivity.

In the past we have pioneered the use of a substitutive synthesis method based on the reactions of poly(dichlorophosphazene), $(NPCl_2)_n$, or poly(difluorophosphazene), $(NPF_2)_n$, for the preparation of a wide range of poly(organophosphazenes).[1-4] Using this method we have been able to prepare macromolecules that bear alkoxy, aryloxy, amino, steroidal,[5] carboranyl,[6] metallocenyl,[7] and metalloporphyrinyl[8] side groups. In all cases, the properties of the polymers are determined by the backbone structure and by the side groups. Much of this macromolecular synthetic work has been preceded by model reactions and mechanistic studies with small-molecule counterparts, for example with phosphazene cyclic trimers or tetramers.[1,9]

Phthalocyanine compounds are of considerable interest because of their molecular stacking properties and because of their ability, when doped, to function as electronic conductors.[10,11] Photochemical and oxidative catalytic activity have also been described.[12] However, considerable difficulty has been reported in utilizing these properties, first because of the extreme insolubility of unsubstituted phthalocyanines, which hinders fabrication into useful devices, and second because the utility of stacked phthalocyanine systems is limited by crystal size and brittleness.

It has been recognized for some time that the incorporation of phthalocyanine units into a macromolecular system could avoid some of these problems. Four different conceptual approaches exist that might allow polymeric phthalocyanine systems to be prepared. These are illustrated in **1**–**4**.



Each of these approaches has its advantages and disadvantages. For example, systems of type **1** were explored by Zwart and co-workers,[13] who showed that phthalocyanines can be solubilized by coordination to poly(vinylamine) or polyacrylamide but that the macrocycle can be lost by dissociation in solution.

Polymeric systems of type **2**, in which the central metal or metalloid forms part of the macromolecular backbone system, have been explored extensively by Marks, Hanack,

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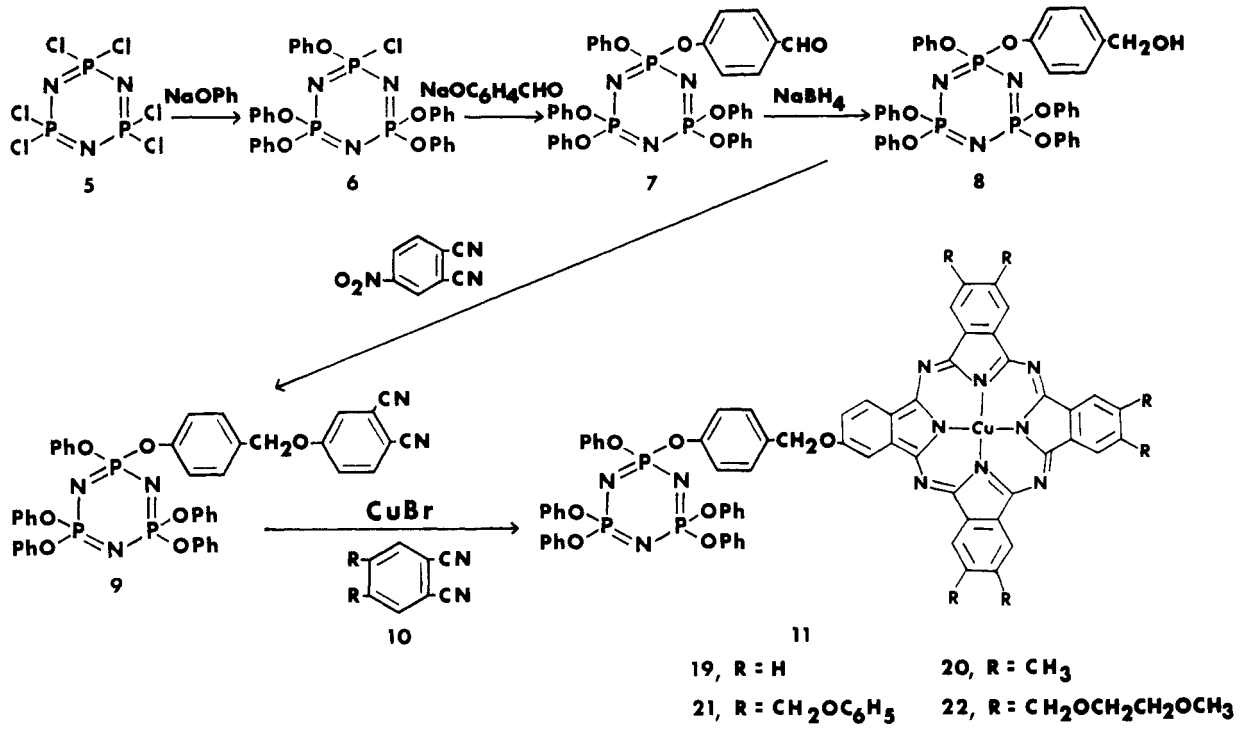
Scheme I



Wynne, and Kenney.[11,14] Systems of this type generate high electronic conductivities (up to 3.4 Ω^{-1} cm^{-1}) after doping but form brittle solids.

Polymers that consist of fused phthalocyanine rings (3) are well-known.[15] The syntheses are usually based on the template polymerization of 1,2,4,5-tetracyanobenzene or pyromellitic anhydride. Although soluble, high molecular weight polymers of this type have been reported,[16] most materials of this type are insoluble and difficult to characterize.

Alternative 4, in which phthalocyanine units are linked covalently to a soluble or moldable polymer, in principle could overcome many of these problems. It is known that replacement of the peripheral hydrogen atoms in phthalocyanine itself by bulky substituents increases the solubility dramatically. Moreover, because high polymers can often be converted to fibers or thin films by well-known solution- or melt-fabrication techniques, the possibility exists that species of type 4 might be of some interest in both research and technology.

Several research groups have prepared systems of type 4. Methods used for the phthalocyanine linkage include Friedel–Crafts alkylation[17] or dicyclohexylcarbodiimide or cyanuric chloride coupling to organic polymers.[18] Most of these systems have been designed and used for catalytic applications.

In this paper we discuss the synthesis, characterization, and study of several polyphosphazene–phthalocyanine systems based on structure 4. Our synthetic approach is different from those mentioned above. Specifically, it involves the synthesis of polyphosphazenes that bear side-group structures that function as phthalocyanine precursors, i.e., *o*-dicyanoaryl residues. Treatment of these precursor polymers with *o*-dicyanobenzene compounds then yields the polymer-bound phthalocyanines. We are aware of only one other attempt to use this methodology, specifically the use of a cross-linked insoluble polystyrene support as a template for the preparation of unsymmetrical phthalocyanines.[19] As in our previous studies, the synthesis pathways were explored first with the use of cyclic trimeric phosphazenes, which can be characterized structurally more easily than can the high polymers.

Questions that we wished to answer in this study were the following: (1) What influence does a cyclic trimeric phosphazene ring or a high-polymeric phosphazene chain have on the solubility of linked phthalocyanine residues? (2) What effects do the phthalocyanine units have on the physical properties of the phosphazene polymer? (3) Can the phthalocyanine units attached to the polymer chain undergo stacking phenomena even when "diluted" by non-phthalocyanine side groups? This question was of crucial importance because it was realized that steric factors would probably place a definite limit on the number of phthalocyanine units that could be attached to a given polymer chain.

Results and Discussion

Synthesis and Characterization of Cyclic Trimeric Phosphazenyl Phthalocyanines. The reaction pathway is illustrated in Scheme I. The phenoxy cosubstituent group was employed because of its solubilizing influence on a phosphazene ring and because it readily allows the isolation of the monochlorocyclotriphosphazene 6.

The conversion of 6 to 7 was monitored by the change in the ^{31}P NMR spectrum from an AB_2 spin system for 6 to a sharp singlet at 8.8 ppm for 7, by the appearance of a ^{1}H NMR resonance for the aldehydic proton at 9.8 ppm, and by the formation of a C=O stretching peak in the infrared spectrum at 1700 cm^{-1}. Reduction of 7 to 8 was accomplished by the use of excess sodium borohydride in methanol/THF. Species 8 was characterized by the appearance of a new methylene resonance in the ^{1}H NMR spectrum at δ 4.63 and by a loss of the C=O stretching peak in the infrared spectrum, together with the appearance of an OH stretching band at 3500 cm^{-1}.

The synthesis of compound 9 was accomplished by displacement of the nitro group from 4-nitro-*o*-dicyanobenzene, a reaction that is well documented in the literature.[19] The reaction could be carried out by two methods: either by first forming the tetra-*n*-butylammonium salt of compound 8, or by treatment of 8 with potassium carbonate/DMF. Compound 9 was characterized by a shift in

Table I
Characterization Data for Phthalocyanine Phosphazene Trimers and Polymers

PcCu(phos)(R_6) Trimers

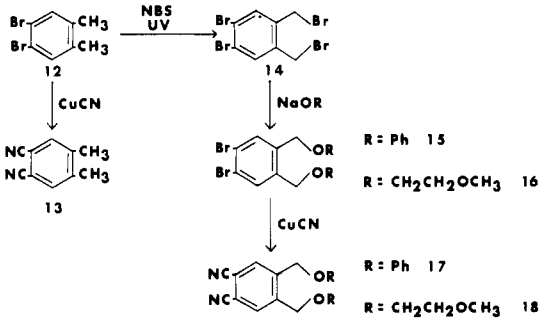
R	IR ν, cm^{-1}	^{31}P NMR δ, ppm	UV/vis[b] λ, nm	elem anal.	% C	% H	% N
H (19)	1610 (ArCH), 1170 (P=N)	8.25	666 (2.1)	calcd	63.84	3.55	11.87
				found	63.51	3.70	11.44
CH_3 (20)	2920 (aliphatic CH), 1600 (ArCH), 1175 (P=N)	8.60	668 (1.83), 604 (0.38)	calcd	65.17	4.20	11.15
				found	65.84	4.18	11.37
CH_2OPh (21)	1600 (ArCH), 1230 (C-O) 1180 (P=N)	8.30	670 (2.82), 604 (0.14), 332 (0.18)	calcd	68.83	4.24	7.96
				found	68.19	4.03	8.24
$CH_2OCH_2CH_2OCH_3$ (22)	1600 (ArCH), 1170 (P=N), 1100 (C-O)	8.70	681 (0.17)	calcd	61.11	5.14	8.43
				found	61.37	5.17	8.22

PcCu(polyphos)(R_6) Polymers

R	IR ν, cm^{-1}	UV/vis[b] λ, nm	T_g(0 °C),[c] °C	% Cu[d]	mol wt (GPC)[e]
H (28)	1600 (ArCH), 1320–1100 (P=N)	668 (1.2)	44	2.14 (1:11)	$(0.8–1.1) \times 10^6$
CH_3 (29)	2930 (aliphatic CH), 1610 (ArCH), 1320–1100 (P=N)	666 (1.7)	52	2.07 (1:11)	$(1.0–1.1) \times 10^6$
(CH_2OPh) (30)	1600 (ArCH), 1300–1100 (P=N)	678 (2.97)	61	1.31 (1:14)	$(1.0–1.4) \times 10^6$
$CH_2OCH_2CH_2OCH_3$ (31)	1610 (ArCH), 1300–1100 682 (1.72) (P=N)	682 (1.72)	55	1.28 (1:12)	$(0.9–1.3) \times 10^6$

[a] All samples were proton decoupled. Chemical shift position were relative to aqueous 85% H_3PO_4. A D_2O capillary lock was used. [b] Spectra were recorded as 10^{-5}–10^{-6} M solutions in benzene. Values in parentheses are extinction coefficients × 10^{-5}. [c] By differential scanning calorimetry. [d] By atomic absorption spectrophotometry. Values in parentheses indicate the ratio of phthalocyanine macrocycles to P=N repeating units. [e] The range of values represents gel permeation results from different synthesis reactions.

Scheme II



the methylene resonance from 4.63 to 5.25 ppm in the ^1H NMR spectrum, by the appearance of nitrile carbon resonances in the ^{13}C NMR spectrum, and by strong CN stretching vibrations in the infrared spectrum at 2235 cm^{-1}. The mass spectra of compounds **7**, **8**, and **9** contained strong parent ions and the correct fragmentation patterns.

As shown in Scheme II, three different phthalonitriles (**13**, **17**, and **18**) were prepared for the reaction with **9**. These, together with phthalonitrile itself, provided a range of options for different phthalocyanine structures in species **11**. Phthalonitriles **17** and **18** were characterized by a combination of IR, UV, ^1H NMR, and ^{13}C NMR spectroscopy, mass spectrometry, and elemental microanalysis. Compounds **13**, **17**, and **18** all showed a strong CN stretching band at ~2230 cm^{-1} in the infrared spectrum. The mass spectra of **17** and **18** contained a strong peak for the parent ion, followed by the loss of successive cyano groups.

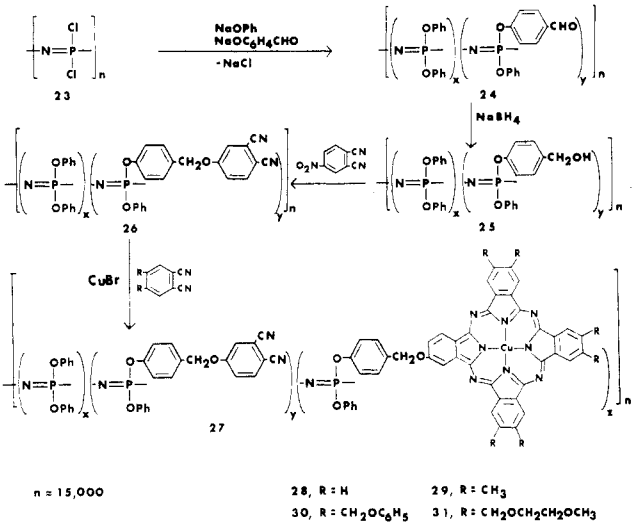
Treatment of **9** with CuBr and a large excess (>25 equiv) of **10** in a boiling solvent yielded deep blue solutions containing **11** and the free phthalocyanine derived from **10**.

Use of this procedure allowed the synthesis of four phosphazenyl phthalocyanines (**11**) from phthalonitrile to give **19**, from **13** to give **20**, from **17** to give **21**, and from **18** to give **22**. Products **19–22** were quite soluble in THF, acetone, or chloroform. The insolubility of the free phthalocyanines formed along with **19–21** allowed **19–21** to be separated by Soxhlet extraction. The free phthalocyanine formed with **22** was sufficiently soluble that chromatography over alumina was needed to effect a separation.

Compounds **19–22** were obtained as deep blue, red-reflecting powders and were characterized by a combination of ^{31}P NMR, IR, and UV spectroscopy, mass spectrometry, and elemental analysis. The results are summarized in Table I. All the compounds showed a strong P=N stretching vibration in the infrared spectrum at 1180–1200 cm^{-1}, which was an indication that the phosphazene ring remained intact during the condensation reaction. The UV/vis spectrum of each compound contained intense bands in the 600–700-nm region. The shape and significance of these bands are discussed later. Compounds **19–22** yielded a sharp singlet in the ^{31}P NMR spectrum. This result is consistent with the fact that the formation of the macrocycle occurs at too great a distance from the phosphorus atoms to cause perturbation and peak splitting. Satisfactory ^1H NMR spectra could not be obtained because of the paramagnetic nature of the compounds. Although the free phthalocyanines gave intense parent ions in the mass spectrum (with a copper isotope pattern), the phosphazene-substituted compounds yielded no spectra at probe temperatures below 400 °C. Above that temperature the compounds were fragmented into the phosphazene and phthalocyanine units and showed strong fragment ions for each.

Synthesis and Characterization of High-Polymeric Phosphazene–Phthalocyanine Compounds. The isolation and characterization of the small-molecule model species **19–22** indicated that the corresponding synthesis of the high-polymeric analogues was feasible. However, the macromolecular reactions presented several additional challenges. In particular, the possibility existed that two or more *o*-dicyanophenyl groups attached to the same or different polymer chains might become incorporated into the same phthalocyanine structure. This would cause cross-linking and insolubilization. For this reason the loading of *o*-dicyanophenoxy units was limited to 10% of the total side groups present, and a very large excess (~50 equiv) of the *o*-dicyanoaryl reagent was employed. Furthermore, the use of dilute reaction conditions and lower coupling temperatures than normal was expected to minimize this type of cross-linking.

Scheme III



The overall synthesis pathway is shown in Scheme III. The synthesis of mixed-substituent (aryloxy)phosphazene high polymers has been studied extensively in our own research group[20-22] and elsewhere.[23] Thus, treatment of the phenoxy(*p*-formylphenoxy)phosphazene high polymer **24** with sodium borohydride yielded macromolecule **25** that contained a primary hydroxyl group. Species **25** was characterized by its ^{31}P NMR spectrum (broad singlet at −18 ppm) and by the appearance of a strong OH band in the infrared spectrum at 3500 cm^{-1}. Treatment of **25** with excess 4-nitrophthalonitrile in the presence of base led to the formation of **26**.

Polymer **26** was characterized by a sharp CN absorption in the infrared spectrum and by the absence of the OH peak. High-field ^1H NMR spectra of **25** and **26** contained intense resonances in the aromatic region, together with weaker alkyl-proton resonances (δ 4.6 for **25** and δ 5.2 for **26**), assigned to the methylene proton. Polymers **24–26** are colorless to pale yellow, film-forming materials that are soluble in common organic solvents.

Treatment of polymer **26** with CuBr and a large excess (20–100 equiv) of *o*-dicyanoaryl reagent **10** yielded dark solutions from which the soluble, high-polymeric phosphazene phthalocyanines **27** could be recovered (see Experimental Section). The specific polymers isolated correspond to **28–31**. However, 60–90% of the product was an insoluble material. The conversion to insoluble material increased when lower concentrations of **10** were employed (below 20 equiv of **10** the yield of insoluble material approached 100%). Longer reaction times also favored the formation of insoluble products.

This finely divided, insoluble material, when suspended in DMF, was shown by UV analysis to contain phthalocyanine rings (intense absorption between 600 and 700 nm). The infrared spectrum contained a strong polyphosphazene absorption at 1300–1100 cm^{-1}. Thus, it appears that this type of product is formed by intermolecular coupling that involves *o*-dicyanoaryl groups on different polymer molecules.

The soluble fractions of polymers **28–31** could be isolated in two different forms, depending on the reaction conditions employed. For short reaction times (<2 h), the product was a dark blue elastomer that could be formed readily into fibers and films. This variant contained some residual nitrile functionality, as evidenced by the infrared spectrum. The phthalocyanine content was approximately 2.5% of all the side groups present. At longer reaction times (~5 h), darker colored polymers were obtained that

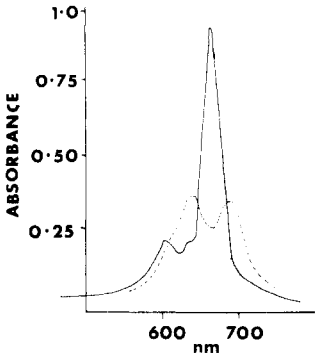


Figure 1. Comparison of spectra of benzene solutions of phthalocyanines showing effect on aggregation of linkage to the macromolecular carrier: (—) spectrum of **30**; (– – –) spectrum of octakis(phenoxymethyl)phthalocyanine.

were isolated as brittle films from THF. The phthalocyanine content of these products was 5–10% of the side groups present.

The general structure of both soluble forms of **28–31** was investigated by means of IR and UV spectroscopy, gel permeation chromatography (GPC), and microanalysis. The UV/vis spectrum of the polymers contained a characteristic intense band in the 600–700-nm region (see following section), while the IR spectrum of each contained an intense P=N absorption band at 1300–1100 cm^{-1}. For those polymers with the lowest concentrations of phthalocyanine, a residual CN stretch, of variable intensity, was also detected.

A criticism that could be leveled at a system of this type is that the phthalocyanines might be merely occluded in the polymeric matrices and not covalently attached. This is a particular concern in the present work because the paramagnetic character of the species does not allow meaningful NMR measurements to be obtained. Fractionation of the product polymers by gel permeation chromatography and analysis of the high molecular weight fractions were, therefore, vital. Separation of **28–31** from low molecular weight oligomers yielded intensely colored fractions with a GPC average molecular weight of $\simeq 10^5$. Analysis of these fractions by UV spectroscopy showed clearly the presence of phthalocyanine units.

Phthalocyanine Aggregation. The electronic absorption spectra of small-molecule phthalocyanines in solution are dominated by strong bands in the 600–720-nm region, the position and shape of which are highly dependent on the degree of aggregation. Although higher order complexes are known, copper phthalocyanines exist predominantly in a monomer–dimer equilibrium. The spectrum of monomeric phthalocyanine consists of a very intense π–π^* absorption ($\epsilon \simeq 10^5$ L mol^{-1} cm^{-1}) at approximately 670 nm, together with a weaker band at 605 nm ($\epsilon \simeq 10^{-4}$). The spectrum of the dimer consists of two bands of almost equal intensity in the region 620–700 nm. It has been shown that the tendency of the phthalocyanine to dimerize is greater in solvents of low dielectric constant and low solvation power such as benzene or carbon tetrachloride.

It was of interest to know the extent to which the monomer–aggregate equilibrium is affected by the presence of a bulky phenoxyphosphazene trimeric or high-polymeric component. It was found that in the concentration range 10^{-5}–10^{-6} M both the small-molecule compounds (**19–22**) and the high polymers (**28–31**) exist predominantly in a nonaggregated form. This is illustrated in Figure 1. The comparison in Figure 1 is between octakis(phenoxymethyl)phthalocyanine and the corresponding high-

Table II
Conductivities of Phthalocyanine Phosphazenes

compound	conductivity,[a] Ω^{-1} cm^{-1}	compound	conductivity,[a] Ω^{-1} cm^{-1}
19	3.13×10^{-3}	**28**	3.42×10^{-7}
20	7.14×10^{-3}	**29**	4.52×10^{-6}
21	1.19×10^{-3}	**30**	5.61×10^{-5}
22	0.48×10^{-3}	**31**	8.04×10^{-6}
PcCu (control)	4.2	$[NP(OPh)_2]_n$ (control)	$<10^{-12}$

[a] Conductivities were measured with a four-point probe as compressed pellets or as thin films on glass. All samples were exposed to iodine (vapor or solution in CCl_4) before measurements were obtained.

polymeric derivative, **30**. It is clear that while the free phthalocyanine yields substantial quantities of the dimeric aggregated product, the phthalocyanine units in **30** exist predominantly in the nonaggregated state. Only a small peak at 638 nm arises from the dimeric form. Thus, we conclude that the polymer chain in **30** effectively inhibits phthalocyanine agglomerization, at least at the concentration levels found in this system. Equally interesting is the fact that the presence of a pentaphenoxycyclotriphosphazene unit in **19–22** forces the equilibrium almost completely to the monomeric form. These results are summarized in Table I.

Changes in the solvent from benzene to THF or DMF (thereby raising the dielectric constant of the medium) caused little or no change to the spectra of the phosphazene-bound phthalocyanines but moved the monomer–dimer equilibrium for the unbound phthalocyanines toward higher monomer ratios.

Electrical Conductivity. The electrical behavior of iodine-doped phthalocyanines has been studied in detail, particularly by Marks and co-workers.[24] The electrical conductivities of the iodine-doped compounds prepared in this study are summarized in Table II.

The high-polymeric compounds **28–31** show low conductivities, in the range 10^{-5}–10^{-6} Ω^{-1} cm^{-1}. This probably reflects the low concentrations of phthalocyanine units in these polymers and the difficulty encountered by these units in approaching close enough to generate significant stacked structures. Nevertheless, the conductivities fall in the semiconductor range, between the value for polystyrene of 10^{-18} Ω^{-1} cm^{-1} and poly(sulfur nitride) of 10^{4} Ω^{-1} cm^{-1}.

The conductivities of the cyclotriphosphazene small-molecule derivatives (**19–22**) are 2–3 orders of magnitude higher than those found for the high polymers, being in the range of 10^{-3} Ω^{-1} cm^{-1}. However, these conductivities are markedly lower than that of copper phthalocyanine itself (~ 4 Ω^{-1} cm^{-1}). This difference probably reflects the way in which the bulky cyclotriphosphazene component interferes with the stacking of the phthalocyanine units.

No contribution to the conductivity resulted from iodine doping of the polyphosphazene carrier system. A control experiment was carried out in which poly(diphenoxyphosphazene), $[NP(OC_6H_5)_2]_n$ ($n \approx 15\,000$), was treated with iodine. The conductivity of this system was less than 10^{-12} Ω^{-1} cm^{-1}. Thus, the effects that are observed with **28–31** are connected with the presence of the phthalocyanine substituent groups only.

Electrochemical Behavior. The electrochemical oxidation potentials of polymers **29** and **31** were measured both as solutions in DMF and as thin films cast on a platinum working electrode. In each case an oxidation potential was detected at 0.9–1.1 ± 0.02 V (vs. a saturated calomel electrode). These values agree well with those reported for free copper(II) phthalocyanine in 1-chloronaphthalene.[25]

Experimental Section

Materials. Hexachlorocyclotriphosphazene (**5**) (kindly supplied by Firestone Tire and Rubber Co.) was purified by three crystallizations from heptane and three fractional sublimations at 60 °C. Tetrahydrofuran (THF) was dried over and distilled from sodium benzophenone ketyl. Dimethylformamide (DMF) was dried over and distilled from magnesium sulfate under reduced pressure and was stored over 4-Å molecular sieves. Column chromatography was carried out with silica gel (230–400 mesh, VWR) or neutral alumina as packing material. All reactions were carried out under an atmosphere of dry nitrogen (except where indicated) in standard Airless Ware. Cuprous bromide (Fisher), phthalonitrile (Aldrich), phthalimide (Aldrich), and sodium hydride (Aldrich) were used without further purification. Phenol and *p*-hydroxybenzaldehyde (Aldrich) were sublimed once before use. Monochloropentaphenoxycyclotriphosphazene[26] (**6**) (mp 68–71 °C) and 4-nitrophthalonitrile[27] (mp 142 °C. Anal. Calcd for $C_8H_3N_3O_2$: C, 55.49; H, 1.75; N, 24.27. Found: C, 55.46; H, 1.95; N, 24.22[27]) were prepared by literature procedures.

Equipment. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on Varian EM 360 and CFT-20 NMR and Bruker WP-200 and WH-360 FT NMR spectrometers. The ^{31}P NMR shifts are relative to aqueous 85% H_3PO_4, with positive shifts downfield from this reference. The ^1H and ^{31}P NMR shifts were referenced to internal $CHCl_3$. Infrared spectra (NaCl films or KBr disks) were recorded on a Perkin-Elmer 283B grating spectrometer. Electron-impact mass spectral results were obtained with an AEI MS 950 spectrometer and were tabulated by a linked computer. Mass spectral isotope patterns were also calculated and tabulated. Gel permeation chromatography (GPC) was carried out with a Waters Associates liquid chromatography system using Polymer Laboratories gel columns (10^6, 10^6, and 10^3 Å in series). UV/vis spectra were obtained by means of a Hewlett-Packard HP8450 model UV/vis spectrometer. Spectra were recorded in quartz cells (1-cm path length) fitted with Teflon stopcocks. Electrical conductivities of the phthalocyanine-bound phosphazenes were measured by a standard in-line four-probe technique with pressure contacts. Samples (70–100 mg) were compacted under 10 tons of pressure to give pellets with dimensions 0.5 mm × 13 mm diameter. Conductivity measurements were also obtained for polymeric samples in the form of thin films (solution case) on a glass substrate. Room-temperature measurements were obtained with a commercial probe (Alessie Industries Model ATP test probe fixture fitted with an A4P four-point probe) with 0.635-mm probe spacings. Conductivities were corrected for finite sample thickness, and no correction was considered necessary for boundary effects.[28] Currents were imposed with a Keithley Model 225 current source, and voltages were measured with a Keithley Model 614 electrometer.

Synthesis of 4,5-Bis(bromomethyl)-1,2-dibromobenzene[29] (14). 4,5-Dibromo-*o*-xylene (50 g, 0.19 mol) was dissolved in dry methylene chloride (1100 mL) to which was added *N*-bromosuccinimide (101.2 g, 0.57 mol). The solution was degassed by five freeze–pump–thaw cycles, and the solution was photolyzed for 8 h under an atmosphere of dry nitrogen. Aliquots were removed at intervals for analysis by ^1H NMR. When the reaction was complete, the organic layer was washed with water (3 × 500 mL), 10% sodium bisulfite in water (2 × 200 mL), and water (2 × 500 mL). The mixture was dried with magnesium sulfate, and the solvent was removed to yield **14** as an off-white solid. Recrystallization from heptane yielded **14** as colorless plates in 80% yield: ^1H NMR 7.6 (s, 2 H), 4.6 ppm (s, 4 H); mass spectrum, *m/e* calcd 422, found 422; mp 91–93 °C (lit.[29] mp 92.5 °C).

Synthesis of 4,5-Bis[(methoxyethoxy)methyl]-1,2-dibromobenzene (16). To 2-methoxyethanol (100 mL) in a 250-mL, three-necked, round-bottomed flask equipped with a condenser and a nitrogen inlet was added sodium metal (1.63 g, 0.07 mol). The solution was heated gently until all the sodium had dissolved. To this cooled solution was added **14** (10 g, 0.024 mol), and the solution was heated at reflux for 24 h. The progress of the reaction was monitored by TLC (silica, $CHCl_3$). The solution was cooled, and the excess alcohol was removed under reduced pressure.

Diethyl ether was added to the residue, and the organic layer was extracted with NaOH (5% aqueous, 3 × 200 mL) and water (3 × 200 mL). The organic layer was dried with magnesium sulfate, and the diethyl ether was removed under reduced pressure. The pale brown oil was chromatographed on neutral alumina to yield **16** as a pale yellow oil in 80% yield: IR 2950 (aliphatic CH), 1100 (vs, C–O), 650 cm^{-1} (m, C–Br); ^1H NMR ($CDCl_3$) 7.65 (s, 2 H), 4.55 (s, 4 H), 3.6 (s, 8 H), 3.41 ppm (s, 6 H); mass spectrum, *m/e* calcd 410, found 410 (M^+, 5.42%), 336 ($M^+ - OCH_2CH_2OCH_3$, 100). Anal. Calcd for $C_{14}H_{20}O_4Br$: C, 40.77; H, 4.85. Found: C, 40.69; H, 5.00.

Synthesis of 4,5-Bis[(methoxyethoxy)methyl]-1,2-dicyanobenzene (18). To a solution of **16** (3.5 g, 8.5 × 10^{-3} mol) in dry DMF (150 mL) was added CuCN (2.3 g, 3 equiv). The solution was heated at reflux for 4 h and the progress of the reaction was followed by TLC analysis. When all of **16** had been consumed, the solvent was removed under reduced pressure to yield a black tar. This was extracted with chloroform (8 × 100 mL) and then with water (2 × 200 mL). It was then dried with magnesium sulfate. The chloroform was removed to leave a dark yellow oil, which proved to be essentially pure **18** based on TLC and ^1H NMR analysis. Compound **18** was purified further by passing a solution of the compound in chloroform through a short column of neutral alumina. Product **18** was isolated as a yellow oil in 40% yield (based on **16**): IR 2950 (aliphatic CH), 2225 (vs, CN), 1600 (aromatic, m), 1100 cm^{-1} (vs, C–O); ^1H NMR ($CDCl_3$) 7.9 (s, 2 H), 4.65 (s, 4 H), 3.6 (s, 8 H), 3.4 ppm (s, 6 H); mass spectrum, *m/e* calcd 304, found 304 (M^+, 0.85%), 228 ($M^+ - OCH_2CH_2OCH_3$, 100%); high-resolution mass spectrum, *m/e* calcd for $C_{16}H_{20}O_4N_2$, 304.1423, found 304.1396.

Synthesis of 1,2-Dimethyl-4,5-dicyanobenzene (13). To a solution of 1,2-dimethyl-4,5-dibromobenzene (**12**) (10 g, 0.037 mol) in dry DMF (150 mL) was added CuCN (12.7 g, 0.15 mol, 4 equiv). The solution was heated at reflux for 6 h, cooled, and filtered. The filtrate was added to dilute aqueous ammonia (800 mL), and the mixture was stirred for 2 h. Filtration yielded a blue-black solid, which was Soxhlet extracted with diethyl ether for 48 h. Removal of the ether under reduced pressure yielded crude **13** as a yellow solid. Recrystallization from methanol gave **13** as white needles in approximately 35% yield: mp 174–177 °C (lit. mp 175–177 °C); IR (KBr) 3100 (w, aromatic CH), 2950 (m, aliphatic CH), 2235 (s, CN), 1600 cm^{-1} (s, aromatic C–C); ^1H NMR ($CDCl_3$) 7.6 (s, 2 H), 2.3 ppm (s, 6 H); mass spectrum, *m/e* calcd 156, found 156 (M^+, 100%), 141 ($M^+ - CH_3$, 87.3%). Anal. Calcd for $C_{10}H_8N_2$: C, 76.92; H, 5.12; N, 17.94. Found: C, 76.99; H, 5.27; N, 17.94.

Synthesis of $N_3P_3(OPh)_5(OC_6H_4CHO)$ (7). To a solution of 4-hydroxybenzaldehyde (22.5 g, 0.18 mol) in THF (200 mL) was added sodium hydride (7.4 g, 0.18 mol). Tetra-*n*-butylammonium bromide (1.0 g, 0.003 mol) was then added. To this solution was added rapidly a solution of **6** (90 g, 0.14 mol) in THF (300 mL). The reaction mixture was stirred at reflux temperature for 72 h. The mixture was then filtered hot, and the solvent was removed from the filtrate with a rotary evaporator to leave an oil. This oil was purified by HPLC using silica gel (50% methylene chloride/50% hexane as eluent). Removal of the solvent gave **7** as a white solid: yield 70%; mp 58 °C; ^{31}P NMR 9.4 ppm (s); ^1H NMR ($CDCl_3$) 9.93 (s, 1 H), 7.7–6.9 ppm (m, 29 H); mass spectrum, *m/e* calcd 721, bound 721; IR 2720 (w, CHO), 1690 (s, C=O), 1590 (s, Ar C–C), 1280–1250, 1200–1160 cm^{-1} (s, P=N). Anal. Calcd for $C_{37}H_{30}O_7N_3P_3$: C, 61.58; H, 4.16; N, 5.83. Found: C, 61.28; H, 5.01; N, 5.32.

Synthesis of $N_3P_3(OPh)_5(OC_6H_4CH_2OH$-*p*) (8). To a solution of compound **7** (24 g, 0.03 mol) in THF/methanol (200 mL, 90/10 (v/v)) was added sodium borohydride (1.26 g, 0.033 mol) as small solid portions. The solution was stirred for 24 h at room temperature as the mixture became pink. This mixture was added dropwise to dilute HCl (10 mL, 3 N). A white solid precipitated from the solution and was collected and washed to neutrality with ethanol. Compound **8** was recrystallized from ethanol as white needles in 88% yield: mp 58–59 °C; IR 3300–3600 (vs, OH), 2900 (ms, aliphatic CH), 1600 (s, aromatic C–C), 1200–1150 cm^{-1} (vs, P=N); ^1H NMR ($CDCl_3$) 7.3–6.9 (m, 29 H), 4.63 ppm (s, 2 H), OH proton not located; ^{31}P NMR ($CDCl_3$) 8.3 ppm (s); mass spectrum, *m/e* calcd 723, found 723 (M^+, 9.48%), 707 (M^+ – OH, 17.64%), 600 ($M^+ - OC_6H_4CH_2OH$, 100%). Anal. Calcd for $C_{37}H_{32}O_7N_3P_3$: C, 61.41; H, 4.42; N, 5.80. Found: C, 61.06; H, 4.52; N, 5.68.

Synthesis of $N_3P_3(OPh)_5[OC_6H_4CH_2OC_6H_3(CN)_2]$ (9). To a solution of **8** (4 g, 5.5 × 10^{-3} mol) in dry dioxane (200 mL) were added sodium hydride (0.13 g, 1 equiv) and tetra-*n*-butylammonium bromide (1 g, excess). The solution was stirred at room temperature for 2 h, followed by the addition of 4-nitrophthalonitrile (1 g, 5.53 × 10^{-3} mol). The solution was brought to reflux, and heating was continued for 24 h, after which time the reaction mixture was filtered and the solvent was removed under reduced pressure. The residual yellow oil was dissolved in chloroform and chromatographed on silica gel using chloroform as solvent. 4-Nitrophthalonitrile eluted first, followed by **9**. Removal of the solvent yielded **9** as colorless crystals in 75% yield: mp 120–122 °C; IR 2900 (m, aliphatic CH), 2235 (vs, CN), 1600 (vs, aromatic C–C), 1200–1150 cm^{-1} (s, P=N); ^1H NMR $CDCl_3$ 7.9–7.1 (m, 32 H), 5.3 ppm (s, 2 H); ^{31}P NMR ($CDCl_3$) 8.5 ppm (s); ^{13}C NMR ($CDCl_3$) 161.29, 150.13, 129.21, 128.81, 127.89, 124.74, 120.69, 120.66, 119.59, 119.34, 116.98, 115.48, 115.06, 107.07 (Ar, CN), 70.10 ppm ($ArCH_2O$); mass spectrum, *m/e* calcd 849, found 849 (M^+, 33.95%), 756 ($M^+ - OC_6H_5$, 100%); high-resolution mass spectrum, *m/e* calcd for 849.1671, found 849.1651.

General Synthesis of Phthalocyanine-Bound Phosphazene Trimers. Synthesis of 20. To a solution of **9** (1 g, 1.17 × 10^{-3} mol) in dry DMF (20 mL) were added **13** (4.59 g, 2.9 × 10^{-2} mol, 25 equiv) and CuBr (1.40 g, 9.8 × 10^{-3} mol). The solution was heated by means of a mineral oil heating bath for 4 h at 165 °C to yield a deep blue-black mass. After heating was discontinued, the contents of the flask were washed from the flask with excess absolute ethanol, and the crude product was collected on a coarse fritted funnel, washed with absolute ethanol, and dried. The deep blue product was placed in a cellulose thimble and was extracted with hot chloroform for 72 h. The blue solution was concentrated and added to *n*-pentane, whereupon **20** precipitated. Further purification was carried out by dissolution of **20** in THF, precipitation twice into absolute ethanol, and precipitation from THF into *n*-pentane. The product was recovered in approximately 15% yield (based on **9**). The material remaining in the extraction thimble was found to be essentially pure $CuPc(CH_3)_8$, characterized by IR and mass spectrometry. Characterization data for **20** are listed in Table I.

General Procedure for the Synthesis of Octasubstituted Free Phthalocyanines. Synthesis of $CuPc(CH_3)_8$. To a solution of **13** (4 g, 2.56 × 10^{-2} mol) in dry DMF (20 mL) was added CuBr (2 g, 1.4 × 10^{-2} mol). The solution was heated at reflux for 20 h. The blue-black, immobile mass was washed from the flask with absolute ethanol and was collected on a medium frit. It was then washed thoroughly with 0.1 N NaOH, water, ethanol, and diethyl ether. The crude product was dissolved in the minimum amount of concentrated sulfuric acid, filtered through a coarse frit, and precipitated by the addition of ice water. This procedure was repeated a second time to yield the product as a deep blue powder after drying in vacuo at 60 °C: yield ≃42%; mass spectrum, *m/e* calcd 687, found 687 (M^+, 100%, Cu isotope pattern), 672 ($M^+ - CH_3$, 30.5%); UV/vis (DMF) 678 nm.

Synthesis of $[NP(OPh)_{1.9}(OC_6H_4CHO)_{0.1}]_n$ (24). To a solution of poly(dichlorophosphazene) (**23**) (13.3 g, 0.116 mol) dissolved in dioxane (1000 mL) was added dropwise a solution of sodium phenoxide, prepared from sodium hydride (8.35 g, 0.21 mol) and phenol (19.4 g, 0.21 mol) in dioxane. The ratio of reactants was designed to bring about replacement of 90% of the chlorine atoms by phenoxy groups. The mixture was stirred at reflux for 48 h, cooled to 25 °C, and treated dropwise with a solution of sodium 4-formylphenoxide, prepared from 4-hydroxybenzaldehyde (7.07 g, 0.058 mol) and sodium hydride (2.32 g, 0.058 mol) in dioxane (150 mL). Tetra-*n*-butylammonium bromide (1 g) was added to the reaction vessel as a phase-transfer catalyst.[30] The reaction mixture was then stirred for an additional 48 h, cooled to 25 °C, and filtered to remove sodium chloride. The polymer was purified by dropwise addition of the reaction mixture into water and by three subsequent reprecipitations of the solid product from THF into water, from THF into absolute ethanol (twice), and from THF into *n*-pentane (twice). Drying in vacuo yielded 14.7 g (53.4%) of **24** as a white, elastomeric material: ^{31}P NMR (THF) −16, −21 ppm (ratio ~1:9); ^1H NMR ($CDCl_3$) 9.8 (s), 7.06–6.8 ppm (bs); IR 3100 (ArCH), 1705 (s, C=O), 1300–1100

cm^{-1} (s, P=N); M_n(GPC) = 1.5×10^5. Anal. Calcd for $[NP(OPh)_{1.9}(OC_6H_4CHO)_{0.1}]_n$: C, 61.15; H, 4.06; N, 5.68; P, 12.58. Found: C, 61.12; H, 4.08; N, 5.62; P, 12.50.

Synthesis of $[NP(OPh)_{1.9}(OC_6H_4CH_2OH)_{0.1}]_n$ (25). To a solution of $NP(OPh)_{1.9}(OC_6H_4CHO)_{0.1}]_n$ (6 g, 5.12×10^{-4} mol with respect to C=O content) in THF/methanol (9:1, 300 mL) was added sodium borohydride (0.38 g, 1.0×10^{-3} mol) in one portion. The solution was stirred at 25 °C for 12 h after which time a clear homogeneous solution was obtained. The solution was concentrated under reduced pressure to 100 mL and precipitated into dilute HCl (500 mL, 0.1 M). The polymer was purified by two successive reprecipitations from THF into water, from THF into absolute alcohol (twice), and from THF into *n*-pentane (twice). The product was obtained as a white elastomer in 85% yield after drying in vacuo: IR 3600 (OH), 3050 (w, ArCH), (aliphatic CH), 1600 (aromatic C–C), 1300–1100 cm^{-1} (s, P=N); ^{31}P NMR (THF) −18 ppm (bs); ^1H NMR ($CDCl_3$) 7.2–6.9 (b, m), 4.5 ppm (s). Anal. Calcd for $[NP(OPh)_{1.9}(OC_6H_4CH_2OH)_{0.1}]_n$: C, 60.23; H, 3.86; N, 5.41; P, 11.97. Found: C, 58.13; H, 3.99; N, 5.74; P, 12.42. M_n(GPC) = 1.5×10^5.

Synthesis of $[NP(OPh)_{1.9}(OC_6H_4CH_2OC_6H_3(CN)_2)_{0.1}]_n$ (26). To a solution of **25** (2 g, 1.70×10^{-4} mol with respect to the hydroxyl content) in dry DMF (60 mL) was added 4-nitrophthalonitrile (0.30 g, 1.7×10^{-3} mol) at 25 °C. Potassium carbonate (100 mg) was added and the solution was heated to reflux for 10 h, with successive portions of K_2CO_3 (100 mg per portion) being added every 2 h. Heating was discontinued, and the solution was cooled and poured into dilute HCl (200 mL, 0.1 M), whereupon the polymer precipitated. The crude polymer was purified by successive precipitations from THF into absolute ethanol, followed by two precipitations from THF into *n*-pentane. The polymer was then extracted for 48 h with *n*-pentane. Compound **26** was obtained as a pale yellow elastomer in approximately 60% yield: IR 3020 (w, ArCH), 2960 (m, aliphatic CH), 2225 (CN), 1600 (aromatic C–C), 1300–1100 cm^{-1} (bs, P=N); ^{31}P NMR (THF) −18.3 ppm (bs); ^1H NMR ($CDCl_3$) 7.9–6.9 (b, m), 5.2 ppm (s); M_n(GPC) = 1.8×10^5. Anal. Calcd for $(NP(OPh)_{1.9}(OC_6H_4CH_2OC_6H_3(CN)_2)_{0.1}]_n$: C, 61.24; H, 3.70; N, 9.8. Found: C, 60.94; H, 3.89; N, 10.15.

Typical Synthesis of Polymeric Phthalocyanines. Synthesis of Polymer 28. To a solution of **26** (0.5 g, 4.25×10^{-5} mol with respect to *o*-dicyanophenyl) in DMF (20 mL) were added phthalonitrile (0.54 g, 4.25×10^{-3}, 100 equiv) and CuBr (0.20 g, 1.41×10^{-3} mol) in a one-necked, round-bottomed flask equipped with a reflux condenser. The flask was immersed in a mineral oil heating bath set at 165 °C, and heating was continued for 3.5 h. The contents of the flask turned successively from yellow to green to blue to blue-black. Heating was discontinued and the flask was cooled to room temperature. The contents of the flask were poured into absolute ethanol (100 mL), and the precipitated material was collected on a coarse frit. It was then washed with absolute ethanol and dried. The blue-black residue was extracted with hot THF for 2 days to yield a deep blue solution. The solution was concentrated to 5 mL and added to *n*-pentane to precipitate an elastomeric blue product. The crude polymer was purified further by successive precipitations from THF into *n*-pentane. Characterizations data are listed in Table I. Polymers **29**–**31** were prepared by similar procedures.

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Registry No. **6**, 5032-39-3; **7**, 101671-97-0; **8**, 101671-98-1; **9**, 101671-99-2; **12**, 24932-48-7; **13**, 36360-43-7; **14**, 6425-67-8; **16**, 101671-96-9; **18**, 101671-95-8; **19**, 101695-56-1; **20**, 101695-54-9; **21**, 101695-57-2; **22**, 101695-58-3; $CH_3OCH_2CH_2OH$, 109-86-4; $4\text{-}HOC_6H_4CHO$, 123-08-0; 4-nitrophthalonitrile, 31643-49-9; octamethylcopper phthalocyanine, 10695-44-0.

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