

A New Fullerene Complexation Ligand: N-Pyridylfulleropyrrolidine

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The subject of this paper is a new fullerene building block design with the potential for defined geometry and good electronic communication. The synthesis and characterization of a new pyridinofullerene ligand capable of forming axially symmetric complexes with metalloporphyrins is reported. X-ray structural and molecular modeling studies, ¹H NMR, UV–vis spectroscopy, electrochemistry studies, and fluorescence quenching data support the formation of a strong complex between the new ligand and the metal center of ZnTPP. On the basis of computational studies, the highest occupied molecular orbital (HOMO) of this ligand is significantly different from a model compound with insulating carbons between the pyridine and the fullerene. The N-pyridinium fulleropyrrolidine salts of the new ligand and model compound were also prepared and their spectral and electrochemical properties are reported.

Introduction

Supramolecular Architectures using Fullerene-Pyridine Ligands. Noncovalent supramolecular systems displaying photochemically induced energy and electron transfer processes have recently attracted considerable attention, and have played an important role both as models for the naturally occurring photosynthetic reaction centers and for the development of artificial molecular devices.¹ Fullerenes are particularly suitable building blocks for the construction of such multicomponent systems because of their unique three-dimensional structure, low reduction potentials, electronic absorption bands throughout the UV–vis spectral region, and strong electron acceptor properties.² In recent years, the preparation of various non-covalently linked donor–acceptor systems by coordination of fullerene derivatives bearing a pyridine unit to zinc porphyrins have been reported in the literature.³ Fullerene-C₆₀ is an excellent electroactive material, reversibly accepting up to six electrons.⁴ Modulation of the electronic properties of C₆₀ is a major goal in the synthetic organic chemistry of fullerenes.^{5,6} The improvement of the electron-accepting features of C₆₀, coupled with the versatile organic chemistry of fullerenes,

may lead to more efficient behavior in charge-transfer processes.^{7,8}

Two key principles for the creation of fullerene-based materials involve (1) creation of key building blocks and (2) design of electrical connectors with good conductivity

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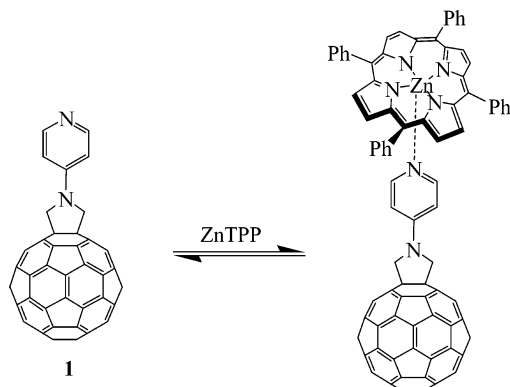


FIGURE 1. Compound **1** and its complex with ZnTPP.

and capability for metal–fullerene bonding. Considerable efforts have been devoted—with limited success—to extending fullerene conjugation with the possibility of providing modified electronics at the fullerene core.⁹ In our own approach, we were drawn to the well-known properties of *p*-(dimethylamino)pyridine (DMAP). Protonation on the pyridyl nitrogen atom of DMAP is greatly enhanced by the *p*-amino group. In addition, the pyrrolidine analogue is known to be even more basic.¹⁰ Because the fulleropyrrolidine nitrogen has good communication with the fullerene core,¹¹ we decided to employ a combination of these structural elements for the bridge between fullerene and the metal center.

Recently, we reported our preliminary results on the synthesis and photophysics of such a ligand: *N*-pyridyl-fulleropyrrolidine. We also showed this derivative is capable of forming a stable complex with zinc tetraphenylporphyrin (ZnTPP) via axial ligation¹² (Figure 1). We describe herein the details of the synthesis, photochemical, and electrochemical properties of this new class of ligand, as well as X-ray crystallographic and computational studies. We have also examined the related pyridinium salts as a further probe of the electronic communication between the pyridyl nitrogen and the fullerene.

Results

Synthesis of *N*-(*p*-Pyridyl)-3,4-fulleropyrrolidine.

Fullerene ligand **1** was prepared by azomethine ylide cycloaddition to C₆₀ (the Prato reaction). A mixture of *N*-pyridylglycine¹³ and paraformaldehyde were heated at reflux in *o*-dichlorobenzene (ODCB) under an argon atmosphere in the presence of C₆₀. Compound **1** was obtained in pure form in 31% yield after unreacted C₆₀ was removed by flash chromatography. Ligand **1** was characterized by ¹H NMR, ¹³C NMR, and MALDI-MS.

Complexation of *N*-(*p*-Pyridyl)-3,4-fulleropyrrolidine with ZnTPP. As a result of its symmetry and

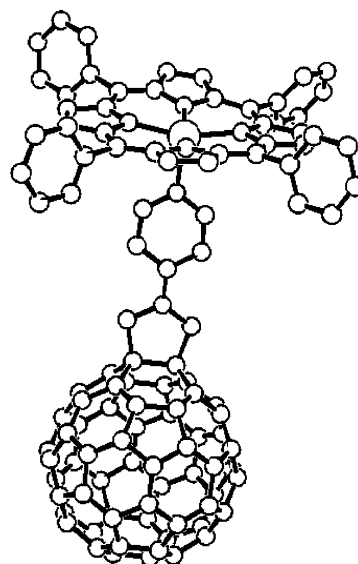


FIGURE 2. X-ray crystal structure of the *N*-pyridyl-fulleropyrrolidine–ZnTPP complex. The hydrogen atoms and benzene of cocrystallization were removed for clarity.

the simplicity of its ¹H NMR spectrum, the complexation of ligand **1** with ZnTPP can be easily monitored spectroscopically. In free base **1**, the protons of the pyrrolidine ring appear as a singlet at $\delta = 4.94$. The two protons α to the pyridyl N-atom appear as a doublet at $\delta = 8.38$, and the signal for the β protons as a doublet at $\delta = 6.78$. In the ¹H NMR spectrum of a 1:1 mixture (3×10^{-3} M) of **1** and ZnTPP in CS₂–C₆D₆ (80:20 v/v), the signal for the α -pyridyl protons is shifted upfield by 5.94 ppm, and that for the pyridine β -protons is shifted upfield by 2.02 ppm. The upfield shift for the pyrrolidine protons is 0.96 ppm. The observed shift of the α -pyridyl protons is similar to but larger than shifts previously reported by D'Souza^{3a}, Armaroli,^{3b} and Da Ros^{3c} ($\Delta\delta$ of 4–5.8 ppm) for related materials. No peaks for uncomplexed ligand **1** were observed under these conditions. MALDI-MS of the 1:1 mixture of **1** and ZnTPP contained a peak corresponding to the molecular ion of the self-assembled dyad at $m/z = 1520.1$.

X-ray Crystallography. To explore the nature of this unique ligand and its complex, we carried out X-ray structural analysis. Slow evaporation of a solution mixture of CS₂/benzene (1/3) containing a 1:1 molar ratio of ZnTPP and **1** yielded dark purple crystals. The X-ray structural analysis of the crystals revealed 1:1 stoichiometry and the expected axially ligated structure. Figure 2 shows the X-ray structure of the porphyrin–fullerene complex. In the solid state structure, the zinc to axially coordinated pyridyl nitrogen distance was found to be 2.129(1) Å compared with a Zn–N distance of 2.158 Å reported earlier for an analogous pyridinofullerene **2** studied by D'Souza and co-workers.¹⁴ The center-to-center distance in the crystal structure of the **1**–ZnTPP complex was found to be 12.18 Å (compared with the computed distance of 11.99 Å for complex of **1** and 9.52 Å for the complex of **2**; see Figure A in Supporting Information). The X-ray structure center-to-edge distance, that is,

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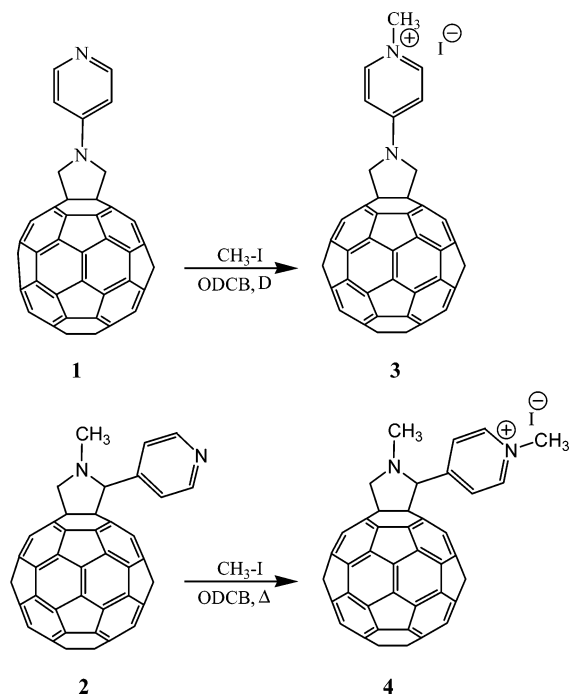
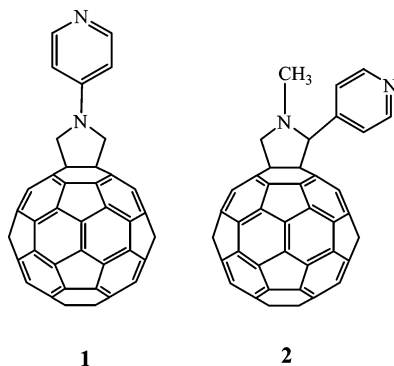


FIGURE 3. Preparation of salts **3** and **4**.

porphyrin to fullerene, was found to be 8.56 Å for **1**–ZnTPP, compared with the computed distance of 9.34 Å for the same dyad and 5.98 Å for **2**–ZnTPP. Thus, in this topology, through-space electronic interaction should be better for **2**–ZnTPP, while through-bond interactions should be enhanced in **1**–ZnTPP.

Does the Pyridine N of *N*-Pyridylfulleropyrrolidine Really Communicate with the Fullerene Core? Investigation of the electronic communication in our new ligand **1** (with anticipated effective electronic coupling via the pyridine ring) was examined by comparison with known fullerene ligand **2**^{3c} wherein the pyridine is connected via an insulating sp³ carbon atom. As models



for the coordination process, we also prepared the corresponding set of *N*-pyridinium salts, **3** and **4** (Figure 3), by methylation of the respective pyridine rings with excess methyl iodide in ODCB at 60 °C. The pyridinium salts precipitated over the course of the reaction and the solids were washed three times with benzene and acetone. Surprisingly, salts **3** and **4** have better solubility in DMSO, DMF, and benzonitrile than their free bases **1** and **2**.

First, the UV–vis spectra of compounds **1**–**4** were examined in CH₂Cl₂ (see Figure B in Supporting Infor-

TABLE 1. Electrode Potentials (V vs Fc/Fc⁺) for Reduction of **1**–**4** and NMFP in CH₂Cl₂

species	$E_{1/2}$		
NMFP	–1.10	–1.48	–2.01
1	–1.06	–1.44	–1.96
2	–1.07	–1.45	–1.98
3	–1.03	–1.42	–1.93
4	–1.05	–1.43	–2.06

mation). All compounds exhibit the characteristic fullerene monoadduct band at around 430 nm. The fullerene band at ~328 nm is also characteristic. This band is blue-shifted in the salts compared to the corresponding free bases. The shift for compound **3** is larger than for compound **4**, perhaps indicative of better electronic interaction between the pyridyl N-atom and the C₆₀ core in compound **3**.

We have also examined this series using AM1/PM3 calculations using the Spartan program (www.wavefun.com.). Calculations revealed the Mulliken charge at the pyridyl N-atom in **1** to be –0.160, whereas in the more-insulating compound **2**, the charge is –0.131. Besides the greater negative charge on free base **1**, distinctive charge separation in their respective salts can be observed in the surface potential maps (see Figure C in Supporting Information). Protonation of the N-atom of the pyridine in the fulleropyrrolidine compound **1** leads to apparent charge donation from the fullerene sphere. Next we calculated the HOMOs and LUMOs for compounds **1** and **2** and their respective salts. One notes strong perturbation of fullerene orbitals during salt formation (protonation) of compound **1**. On the other hand, little coupling of fullerene and pyridine orbitals is noted on salt formation from compound **2** (see Figures D and E in Supporting Information).

One direct experimental measure for comparing the electronic coupling of pyridine ligand **1** with the more insulating compound **2** is the redox properties of the free bases **1** and **2** and the salts **3** and **4**. Toward that goal, cyclic voltammetric studies were conducted in CH₂Cl₂. The cyclic voltammograms are presented in Figure F in Supporting Information and the $E_{1/2}$ values are collected in Table 1.

The reference compound NMFP (*N*-methylfulleropyrrolidine) was also examined for comparison.¹⁵ The redox potentials of **1** and **2** are more positive than that for NMFP, suggesting that compounds **1** and **2** are easier to reduce than NMFP as a result of the electron-withdrawing effect of the pyridine group. Comparison of the $E_{1/2}$ values for the reduction of compounds **3** and **4** with those of the free bases **1** and **2** shows that the former are slightly easier to reduce than the latter. This enhanced electronegativity can be reasonably interpreted in terms of inductive effects of the pyridinium functionality, which leads to a decrease of the electron density within the fullerene π -system.⁷

For compound **4**, there is an irreversible reduction peak at –1.8 V, which is not observed for compound **3** and most likely corresponds to the irreversible reduction of the pyridinium group attached to the pyrrolidine. This value corresponds well with related literature reports.¹⁶ This causes a negative shift (–80 mV) in the peak potential of the C₆₀-based third one-electron reduction of compound **4** compared with that for compound **2**. The specific

reaction following the reduction at -1.8 V is not clear at the present. However, the C_{60} -based waves are reversible when the scan potential is switched at -1.67 V as shown in Figure F in Supporting Information (red curve). The reduction peak of the pyridinium group attached to the pyrrolidine in compound **3** was not observed because of the limitation of the electrode potential window in CH_2Cl_2 . The electrochemical behavior was investigated in acetonitrile, and the result is shown in Figure G (see Supporting Information). The couple at -2.22 V can be attributed to the reduction of the pyridinium group in compound **3** since the potential value is very close to that (-1.77 V vs Ag/Ag/Cl or -2.2 V vs Fc/Fc⁺) for the model compound *N*-methyl-*p*-dimethylamino-pyridinium reported by Huenig et al.¹⁷ Alternatively, the couple at -2.37 V could be due to reduction of the pyridinium group attached to the pyrrolidine in compound **3**, in which case the couple at -2.22 V would correspond to the fourth C_{60} -based one-electron reduction.

Photophysical Studies of Fullerene–Porphyrin Dyads. The goal in synthesizing **1** was to create a linear ligand capable of providing direct electronic communication between the fullerene and the pyridyl *N*-atom and, upon complexation, between C_{60} and ZnTPP. Bleaching of both the Soret band at 424 nm and the Q-bands at 549 and 588 nm is observed upon addition of 0.5 equiv of ligand **1** in ODCB. Increasing amounts of ligand **1** lead to shifts in both the Soret (424 \rightarrow 432) and the Q-bands (549 \rightarrow 560, 588 \rightarrow 600), as well as noticeable broadening of peaks. A clean isosbestic point is seen at 428 nm. Similar spectral changes were not observed for the addition of a reference compound, *N*-phenylfulleropyrrolidine (which does not possess the coordinating pyridine *N*-atom) to a solution of ZnTPP. In this case the spectrum was virtually superimposable on the combination of the absorbances of the two individual moieties.

Steady-state fluorescence experiments revealed quenching of ZnTPP fluorescence in ODCB, toluene, and CH_2Cl_2 . As depicted in Figure 4, ligand **1** efficiently quenches the fluorescence of a $1 \mu M$ ZnTPP solution upon 550 nm excitation in ODCB. The data from fluorescence titration experiment was used¹⁸ to obtain the association constant K_a for ligand **1** and ZnTPP in ODCB, which is $7.4 \times 10^4 M^{-1}$. The same method gave $K_a = 1.4 \times 10^4 M^{-1}$ for ligand **2** and ZnTPP, which is significantly (5X) smaller.

Although calculated center-to-center distances (see Figure A in Supporting Information) from the fullerene centroid to the Zn atom of ZnTPP in complex **1**–ZnTPP vs **2**–ZnTPP are quite different (11.99 Å for **1** vs 9.52 Å for **2**), compound **1** provided much better quenching, supporting the view that through-bond rather than through-space electronic effects are operational.

Additional support for the interaction of the metal center of ZnTPP and the fullerene is found in the electrochemical results (Figure 5). In a manner similar

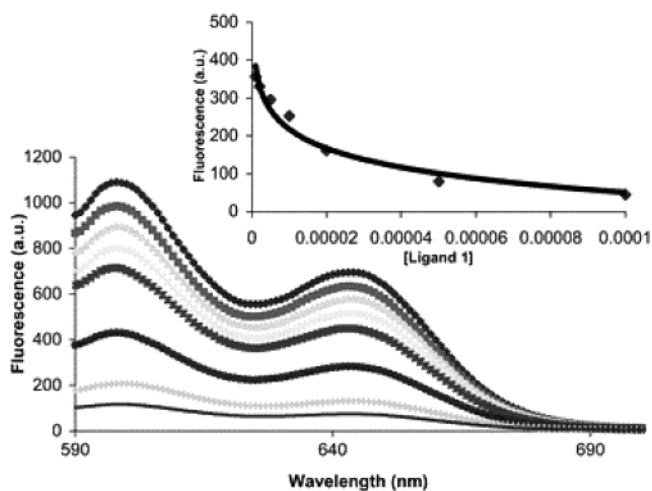


FIGURE 4. Fluorescence quenching of $1 \mu M$ ZnTPP by ligand **1** (from 1 to $100 \mu M$) in ODCB. The inset shows emission intensity at 660 nm vs ligand **1** concentration. The fit is used to determine the association constant.

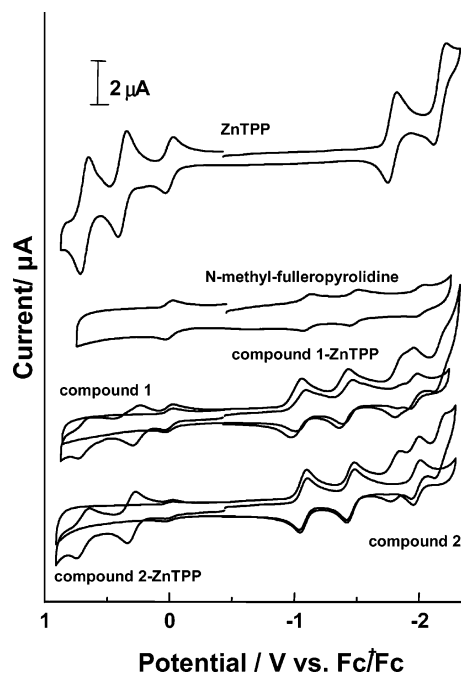


FIGURE 5. Interaction between ZnTPP and pyridine ligand compounds **1** and **2**.

to the results for the salts, ligand **1** shows a greater difference in redox potential on complexation. The potential for the first one-electron oxidation of ZnTPP shifted negatively by 120 and 80 mV after complexation with **1** and **2**, respectively. On the other hand, the potential for the first one-electron reduction of the C_{60} center for ligand **1** shifted positively by 40 mV upon complexation with ZnTPP, whereas no shift was observed for ligand **2**. The results clearly indicate that there is a definite electronic interaction between the metal center of ZnTPP and the C_{60} in ligand **1** but not in ligand **2**.

Experimental Section

Synthesis of *N*-(*p*-Pyridyl)-3,4-fulleropyrrolidine, **1.** A mixture of 100 mg (0.14 mmol) of C_{60} , 21 mg (0.7 mmol) of paraformaldehyde, and 43 mg (0.28 mmol) of *N*-pyridylglycine

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was heated at reflux in 10 mL of *o*-dichlorobenzene under argon for 6 h. The solution was washed with water and dried over Na₂SO₄. The solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (eluant toluene, then toluene/triethylamine 100:1), affording 37 mg (31%) of *N*-pyridylpyrrolidine-C₆₀. ¹H NMR (300 MHz, CS₂/C₆D₆, 8/2): δ 8.38 (d, 2H), 6.78 (d, 2H), 4.94 (s, 4H). ¹³C NMR (400 MHz, CS₂/ODCB-*d*₄, 1/1): 61.1, 69.4, 111.4, 128.5, 136.1, 140.3, 141.9, 142.1, 142.2, 142.7, 143.2, 144.6, 145.4, 145.7, 146.2, 146.4, 147.4, 149.9, 151.8, 153.9. MALDI-MS: *m/z* 841.6.

General Procedure for the Synthesis of Pyridinium Salts 3 and 4. A toluene solution (10 mL) containing 0.1 mmol of fullerene derivative and 10 mmol of methyl iodide was heated at 60 °C. After a variable period of time at the same temperature, the solvent was removed under reduced pressure. The solvent was evaporated to dryness. The solid residue was transferred into a centrifuge tube, washed three times with benzene and acetone, respectively, and dried under vacuum. Yields are quantitative on TLC.

Iodide Salt 3. Reaction time: 1 h 30 min. Yield 98%. ¹H NMR (300 MHz, DMSO): δ 8.60 (d, 2H), 7.80 (d, 2H), 5.80 (s, 4H), 4.10 (s, 3H). ¹³C NMR (500 MHz, DMSO): δ 44.8, 58.7, 69.3, 109.9, 128.8, 135.6, 139.5, 141.4, 141.6, 141.7, 142.2, 142.6, 144.0, 144.3, 144.8, 144.9, 145.2, 145.6, 145.8, 146.8, 153.7, 154.7. MALDI-MS: *m/z* 855.1.

Iodide Salt 4. Reaction time 2 h 30 min. Yield 97%. ¹H NMR (300 MHz, DMSO) δ 9.08 (d, 2H), 8.60 (d, 2H), 5.60 (s, 1H), 5.20 (d, 1H), 4.49 (d, 1H), 4.39 (s, 3H), 2.8 (s, 3H). MALDI-MS: *m/z* 869.1.

Fluorescence Measurements. The fluorescence was monitored by using a Shimadzu RF-5301 spectrophotometer using the following settings. Measurement type: wavelength scan. Scan mode: emission. Data mode: fluorescence. Scan speed: 1500 nm/min. Delay: 0 s. Excitation slit: 10.0 nm. Emission slit: 10.0 nm. PMT voltage: 700 V. The association constants of compounds **1** and **2** were calculated by using the following equation:¹⁸

$$Y = 1 - \frac{((1/K) + x + S - (((1/K) + x + S) \cdot ((1/K) + x + S) - 4xS)) / (2S)}{1}$$

where

$$S = [\text{ZnTPP}], K = K_a, X = [\mathbf{1}], Y = I/I_0.$$

Cyclic Voltammetry Experiments. All electrochemical measurements were performed using a CHI 440 electrochemical workstation (CH Instruments Inc., Austin, Texas); 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆, from Fluka) in CH₂Cl₂ (redistilled) was used as the supporting electrolyte (degassed with argon). A platinum wire was employed as the counter electrode. An aqueous Ag/AgCl electrode, separated by a salt-bridge of 0.1 M TBAPF₆ dichloromethane solution, was used as the reference. Ferrocene (Fc) was added as an internal reference, and all potentials were referenced relative to the Fc/Fc⁺ couple. A glassy carbon electrode (CHI, 3 mm in diameter), polished with 1.0, 0.3 μm aluminum paste and ultrasonicated in deionized water and a CH₂Cl₂ bath, was used as the working electrode. The scan rate for cyclic voltammetry (CV) was 100 mV/s.

X-ray Crystallographic Characterization. Dark purple crystals of **1**-ZnTPP were found to diffract weakly but not atypically for a fullerene derivative and belonged to the monoclinic crystal system. Systematic absences and diffraction symmetry derived from axial photographs uniquely defined the space group as *P*2(1)/*n* and eliminated both orthorhombic and tetragonal options. The structure was solved by direct methods and refined with all non-hydrogen atoms anisotropic. Hydrogen atoms were assigned idealized locations. Further details can be found in the CIF tables as part of the Supporting Information.

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Supporting Information Available: NMR, mass, UV, CV, and computational studies of compounds **1**–**4**, as well as X-ray crystallographic information including a CIF table for the complex of **1**-ZnTPP. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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