

Synthesis and photophysics of a linear non-covalently linked porphyrin–fullerene dyad

Stephen R. Wilson,^{*a} Shaun MacMahon,^a Fatma T. Tat,^{ab} Peter D. Jarowski^a and David I. Schuster^{*a}

^a Department of Chemistry, New York University, New York, NY 10003, USA.

E-mail: david.schuster@nyu.edu, steve.wilson@nyu.edu

^b Department of Chemistry, Uludag University, Bursa, Turkey 16059

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The synthesis and characterization of a new pyridinofullerene ligand capable of forming axially symmetric complexes with ZnTPP is reported; molecular modelling studies, ¹H NMR, UV-Vis spectroscopy and fluorescence quenching data support formation of a strong complex between the new ligand and ZnTPP.

In the pursuit of artificial photosynthetic reaction centers, non-covalent supramolecular systems displaying photoinduced energy and electron transfer processes have attracted considerable attention.¹ Fullerenes make particularly suitable building blocks for the construction of such multi-component systems because of their three-dimensional structure, relatively low reduction potentials, and strong electronic acceptor properties.² In recent years, non-covalently linked donor–acceptor systems formed by coordination of functionalized fullerenes bearing pyridine units to zinc tetrapyrrole macrocycles have been reported in the literature.³ In the present study, we have synthesized the first pyridyl-substituted fulleropyrrolidine derivative capable of forming a stable self-assembled linear complex with zinc tetraphenyl porphyrin [ZnTPP] *via* the axial ligation method⁴ (see Scheme 1).

Fullerene ligand **1** was generated in 31% yield by azomethine-ylide cycloaddition to C₆₀, using *N*-pyridylglycine⁵ and paraformaldehyde as starting materials. Ligand **1** was characterized by ¹H NMR and MALDI-MS.[†]

Compound **1** was designed as an axially symmetrical ligand capable of providing direct electronic communication between the fullerene and the pyridyl N-atom and, upon complexation, between C₆₀ and ZnTPP. To explore the nature of this unique ligand, molecular modelling was performed at the semi-empirical AM1 level using SPARTAN (see Fig. 1). Non-linear fullerene ligand **2**⁶ was used for comparison purposes. The charge (Mulliken) at the pyridyl N-atom in **1** is calculated to be –0.160, whereas in **2** it is –0.131. Since the electron density around the pyridyl N in ligand **1** is greater than in ligand **2**,^{3c,d} **1** is expected to complex more strongly with ZnTPP. The

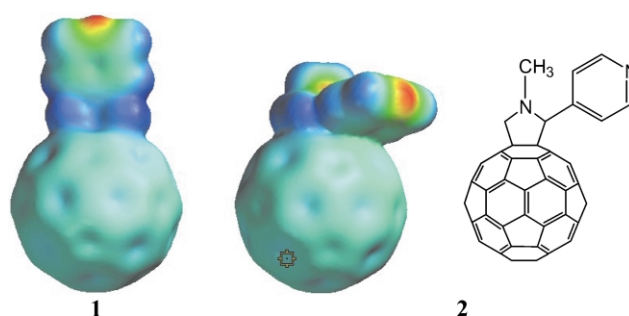
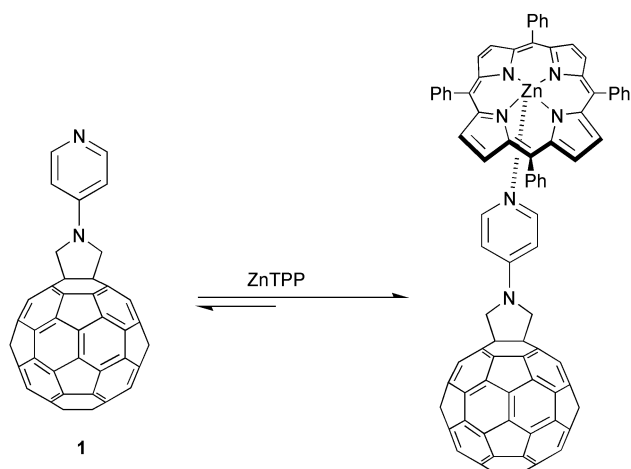


Fig. 1 SPARTAN models of ligands **1** and **2**.

centre-to-centre distance (D_{cc}) for the symmetrical **1**–ZnTPP complex is 11.99 Å, compared to 9.52 Å for **2**–ZnTPP (Fig. 2(a)). The centre-to-edge distances, *i.e.*, porphyrin to fullerene (D_{ce}), are 9.34 and 5.98 Å, respectively. Thus, in this topology, through-space electronic interaction is better for **2**–ZnTPP while through-bond interactions are enhanced in **1**–ZnTPP.[‡]

Due to its symmetry and the simplicity of its ¹H NMR spectrum, the complexation of ligand **1** with ZnTPP can be very easily monitored spectroscopically (see Fig. 3). In free **1**, the protons of the pyrrolidine ring (C) appear as a singlet at δ 4.94, while the two protons α to the pyridyl N-atom (A) appear as a doublet at δ 8.38. The β protons (B) appear as a doublet at δ 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 A is shifted upfield by 5.94 ppm, that for the pyridine β -protons B by 2.02 ppm, and that for the pyrrolidine protons C by 0.96 ppm. These shifts are larger than for binding of any previously reported pyridinofullerene ligand to ZnTPP. 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.

The absorption spectrum of ZnTPP was measured in the presence of increasing concentrations of ligand **1**. 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 equivalents of ligand **1** in *o*-dichlorobenzene (ODCB). Increasing amounts of ligand **1** lead to shifts in the Soret- (424 → 432) and the Q-bands (549 →



Scheme 1 Complexation of ligand **1** with ZnTPP.

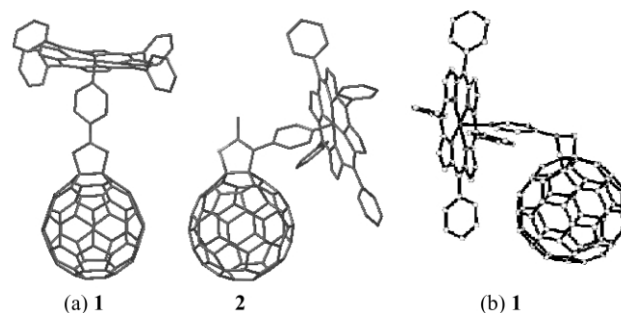


Fig. 2 (a) SPARTAN models of the complexes of ligands **1** and **2** with ZnTPP; (b) Insight II model of ligand **1** with ZnTPP.

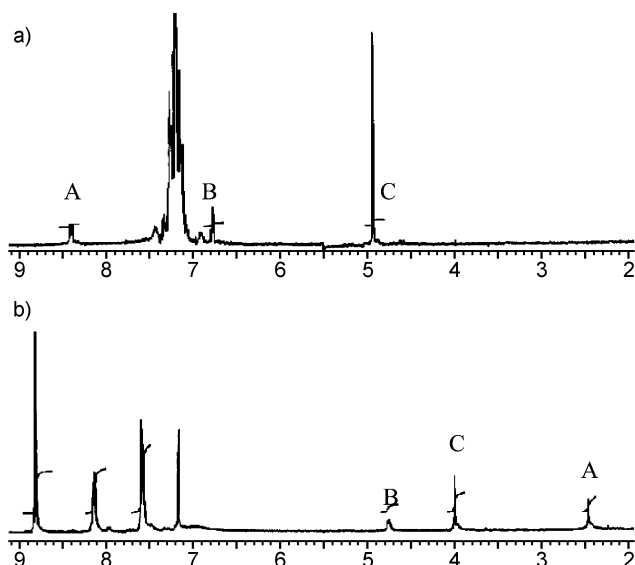


Fig. 3 (a) ^1H NMR spectrum of uncomplexed ligand **1**. (b) ^1H NMR spectrum of ligand **1** with ZnTPP.

560, 588 \rightarrow 600), as well as noticeable broadening of peaks. Similar spectral changes were not observed in the spectrum of ZnTPP in the presence of *N*-phenylfulleropyrrolidine. In this case, the spectrum is superimposable on the sum of the absorbancies of the two individual moieties.

Steady state fluorescence experiments revealed quenching of ZnTPP fluorescence by **1** in ODCB, toluene, and CH_2Cl_2 . As depicted in Fig. 4, ligand **1** efficiently quenches the fluorescence of a 1 μM ZnTPP solution in ODCB upon 550 nm excitation. The data from the fluorescence titration experiment was used⁷ to obtain the association constant K_a for ligand **1** and ZnTPP in ODCB, which is $7.4 \times 10^4 \text{ M}^{-1}$. The same method gave $K_a = 1.4 \times 10^4 \text{ M}^{-1}$ for ligand **2** and ZnTPP, which is significantly smaller.

Based upon calculations using Spartan, it appears that the symmetric pyridinofullerene ligand **1** is capable of forming linear complexes with ZnTPP, a process which can be easily monitored via ^1H NMR and UV-Vis spectroscopy. Quenching of ZnTPP fluorescence occurs unusually efficiently in both nonpolar and polar solvents. Electron density calculations on the axially symmetrical complex indicate that effective electronic interaction between ZnTPP and C_{60} occurs directly through the two nitrogen atoms. Experiments to obtain independent confirmation of this are in progress. Transient absorption techniques will be used to determine whether energy and/or electron transfer operates in this system. We believe that

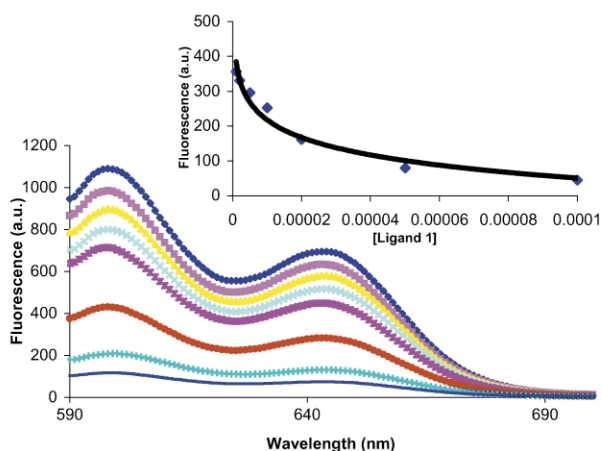


Fig. 4 Fluorescence quenching of 1 μM ZnTPP by ligand **1** (from 1 to 100 μM) in ODCB. The inset shows emission intensity at 660 nm vs. ligand **1** concentration.

ligand **1** has the potential to form highly organized supramolecular architectures with ZnTPP for solar energy conversion and other applications. (See note added in proof.)

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Note added in proof

An X-ray structure, obtained by Professor A. L. Rheingold, University of Delaware, shows that in the solid state the **1**-ZnTPP complex is axially symmetric, as depicted in Fig. 2a.

Notes and references

† *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 was heated at reflux in 10 mL of *o*-dichlorobenzene under argon for 6 h. The solution was washed with water and dried over Na_2SO_4 . The solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (eluent: toluene, then toluene-triethylamine 100:1), affording 37 mg (31%) of *N*-pyridylpyrrolidine- C_{60} **1**. ^1H NMR (300 MHz, Fig 3(a)), MALDI-MS: m/z 841.59 (calc. 840.82).

‡ A different picture emerges from calculations using molecular dynamics in the Insight II program, in which severe puckering of the pyrrolidine ring results from attractive porphyrin-fullerene interactions.⁸ In the bent geometry, shown in for ligand **1** in Fig. 2(b), the centre-to-centre distances (D_{cc}) for the two complexes are almost identical, 9.21 Å for **1**-ZnTPP compared to 9.23 Å for **2**-ZnTPP. No obvious preference for electronic coupling between ZnTPP and C_{60} for the two complexes in the bent topology is apparent. The sharp ^1H NMR spectrum of the complex **1**-ZnTPP is most consistent with a linear topology for this complex (see Note added in proof).

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