Synthesis and Properties of New Types of Supramolecular Complexes with C60

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Experimental and computational data will be presented to support the proposal that arylated triamino-s-triazines adopt a concave shape in the presence of C60 to form a stable binding site for the fullerene. From fluorescence titration data on the first of these triazine systems to be studied in our laboratory [see Chemical Commun. 2002, 2538], association constants greater than 105 M-1 were determined in toluene and o- dichlorobenzene (ODCB). Even larger values are found for a second generation of arylated trisamino-s-triazines. Such large association constants are unprecedented for interaction between C60 and a monomeric host in solution. This effect is attributable to strong van der Waals attraction between the complementary concave and convex surfaces of the two moieties. Evidence will be presented to distinguish between electron and energy transfer mechanisms for the quenching process. Experimentally, it is found that C70 is a much poorer quencher of triazine fluorescence than C60, which is supported by computations that demonstrate less effective encapsulation of C70 than C60 by the pi-surface of the arylated triazine.

In a second study, we have synthesized a new pyridino-fullerene ligand capable of forming axially symmetric complexes with ZnTPP. Molecular modelling studies, 1H NMR, UV-Vis spectroscopy and fluorescence quenching data support formation of a strong complex between the new ligand 1 and ZnTPP. The association constant determined from fluorescence quenching data in ODCB is 7.4 x 104 M-1, which is nearly six times larger than for an analogous unsymmetrical pyridino-fullerene studied by Prato and co- workers [Chem. Commun. 1999, 635]. The improved electronic coupling is attributed to electronic interactions directly between the Zn2+ and the C60 moieties through the two intervening nitrogen atoms, and not to through-space effects. The effects of complexation between ligand 1 and Zn- porphyrins in a variety of C60-porphyrin hybrids will be discussed.