

Formation and photophysics of a stable concave–convex supramolecular complex of C₆₀ and a substituted *s*-triazine derivative

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Spectroscopic, electrochemical and computational data show that C₆₀ and a highly phenylated *s*-triazine derivative form a stable supramolecular complex at micromolar concentrations in solution at ambient temperatures, due to strong van der Waals attraction between their complementary surfaces.

While innumerable cases of intramolecular photoinduced electron transfer (PET) between redox centres with covalent and even mechanical linkages have been described in the literature,^{1–3} far fewer cases of well-defined, reversible intermolecular PET have been observed. This is hardly surprising, since intermolecular quenching interactions in solution, which optimally are diffusion controlled processes, are not able to efficiently compete with deactivation of photoexcited electron donors on the pico-/nanosecond lifetime scale, when the acceptor is present at micromolar concentrations. Conversely, intermolecular donor–acceptor interactions involving C₆₀ are well known in the solid state.⁴

Formation of supramolecular complexes is a simple and powerful means to engineer ultrafast electron transfer in solution. Since the formation of such ensembles involves either entropically or enthalpically driven organization of individual components, the yields of such complexes frequently exceed those obtained for analogous covalently linked systems.

An important incentive of our work on donor–acceptor electronic interactions is to develop synthetic host systems that would show easily detectable, but differentiable, output signals upon associating with guests of varying shape and size. The unique structures and electronic features of fullerenes make them ideal candidates for such studies.⁵ Therefore, electron donors whose shape might allow strong association in solution with the curved surface of C₆₀ have been sought. It has been observed that fullerenes fit nicely into the preorganized concave cavities of some host molecules in solution, in particular cyclotrimeratriarylenes (CTVs),⁶ calix[5]arenes⁷ and substituted corannulenes.⁸ Association constants with C₆₀ and C₇₀ in these systems range between 10²–10³ M^{–1}, with higher values reported for some acylated CTV derivatives. However, these systems are either not capable of undergoing PET or such data were not reported.

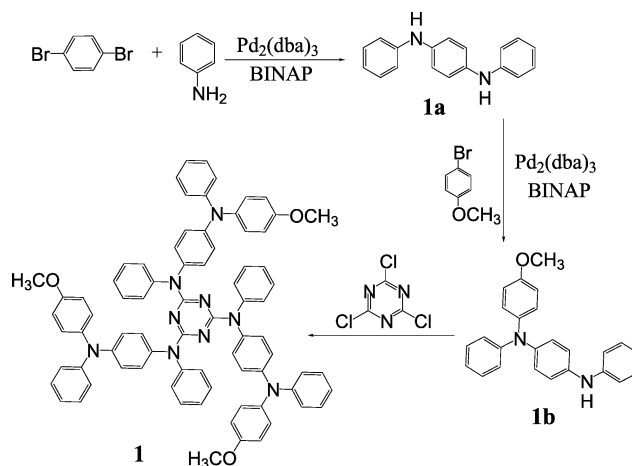
Highly phenylated triamino-*s*-triazines are good electron donors (IP₁ ~0.9 V vs. SCE)⁹ and are also highly fluorescent, which makes them ideal for studies of intermolecular electron transfer interactions. Our approach is to use conformationally flexible substituted triazines which are able to adapt their shape to provide a concave binding site for fullerenes, in which ultrafast and efficient electron transfer can take place. We present evidence that remarkably strong intermolecular association occurs between fullerenes and triazine **1** at micromolar concentrations in condensed media at room temperature, and that this complexation controls the ground and excited state dynamics of these binary systems.

Triazine **1** was synthesized following the procedure outlined in Scheme 1. The triazine arms were prepared using Pd-catalysed aryl-amination chemistry¹⁰ to yield **1a** and **1b**. The final product was prepared by condensation of three equivalents

of **1b** with cyanuric chloride in the solid state.⁹ All products were characterized by ¹H and ¹³C NMR, UV-Vis and fluorescence emission spectroscopy as well as mass spectrometry. There is no obvious difference between the UV-Vis spectrum of a 1:1 mixture of **1** and C₆₀ in toluene or *o*-dichlorobenzene (ODCB) versus the sum of the spectra for the two independent moieties. However, evidence for ground state complexation was provided by electrochemical data obtained in ODCB vs. Ag⁺/Ag. The first three reduction potentials of free C₆₀ (–1.09 V, –1.52 V and –2.04 V) are substantially increased in the presence of one equivalent of **1** (both 8.3 × 10^{–4} M) to –0.95 V, –1.39 V and –1.90 V, respectively, indicating that a new molecular species is formed in which the C₆₀ moiety is more easily reduced. In the presence of C₆₀, the oxidation potential of triazine **1** in ODCB increases from 0.28 V to 0.31 V.

Upon excitation of a 2.5 × 10^{–5} M solution of **1** in toluene or ODCB at 300 nm, which is close to the ground-state absorption maximum of **1**, strong fluorescence emission was observed at 409 nm. Under these conditions, competitive light absorption by C₆₀ was minimal. The fluorescence emission intensity decreased in the presence of C₆₀ in the concentration range 1.25–7.5 × 10^{–5} M, eventually reaching a plateau value (see Fig. 1). Inspection of this figure reveals that simultaneously with the quenched emission of **1** at 409 nm, a new lower-energy emission band appears, centred at 423 nm. We tentatively attribute this new emission to a charge-transfer (CT) state, *i.e.*, (1⁺–C₆₀[–]).¹¹ In ODCB, which is a more polar solvent, this maximum shifts to 427 nm, consistent with improved solvation of the CT state.

The fluorescence of **1** is well fitted by a mono-exponential decay, for which a relatively short lifetime of 0.22 ns was determined in deoxygenated toluene. Upon addition of C₆₀ to this solution, a double-exponential fluorescence decay was observed at 425 nm with lifetimes of 0.19 ns and 1.9 ns. The two lifetimes are maintained throughout the titration assay, with an increasing contribution of the long-lived component as the



Scheme 1 Synthesis of tris-*p*-methoxyphenyltriamino-*s*-triazine **1**.

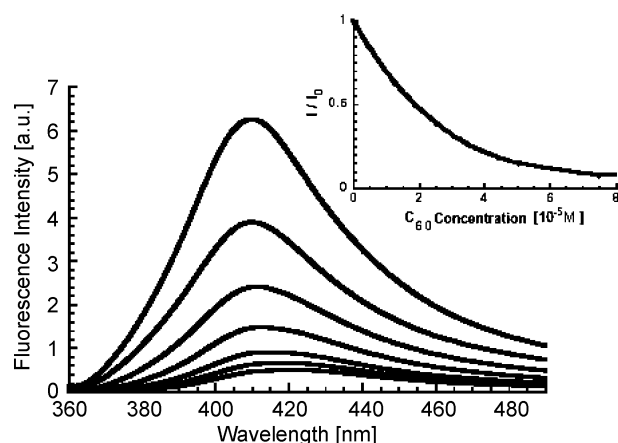


Fig. 1 Fluorescence spectra of **1** (2.5×10^{-5} M) and increasing concentrations of C_{60} (1.25 – 9.0×10^{-5} M), proceeding from top to bottom, in toluene at 27°C , with laser excitation at 300 nm . Insert: Relative fluorescence intensities, I/I_0 , vs. C_{60} concentration. Curve shown was used to determine K (see text).

concentration of C_{60} is increased. At all concentrations, the pre-exponential factors were in good agreement with the ratio of complexed *versus* uncomplexed forms. Upon addition of trifluoroacetic acid, the original short-lived fluorescence component reappears, concomitant with disappearance of the long-lived species, demonstrating that complex formation is reversible. While C_{70} also quenches **1**, the association constant is lower by about an order of magnitude. These data all point to a static quenching event occurring inside a well-defined supramolecular complex of **1** and C_{60} .

To verify the proposed concave-convex geometry of the **1**– C_{60} complex, *in vacuo* computations were performed using Insight II.¹² The resultant structure (Fig. 2a) depicts the C_{60} sphere nestled within the arms of the triazine. The centre-to-centre distance between the triazine ring and C_{60} is only 7.07 \AA , while the distance between the closest atoms of the two moieties is 3.79 \AA . The binding energy of the complex is $26.7\text{ kcal mol}^{-1}$, relative to the separate molecules. In contrast, much looser association is predicted computationally for the complex of **1** with C_{70} , in which the side arms of the triazine do not appear to interact with the graphitic equatorial belt of C_{70} (see Fig. 2b). The computed binding energy in this case is only 4.6 kcal mol^{-1} .

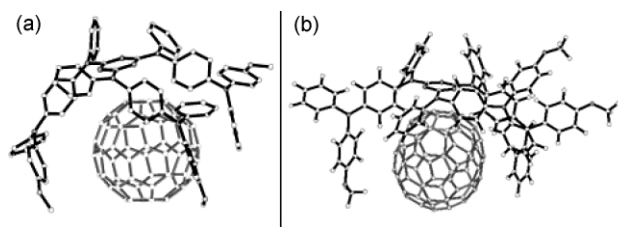


Fig. 2 Computed minimum energy structure of (a) supramolecular complex of **1** and C_{60} , and (b) the **1**– C_{70} complex.

Fitting the titration curve in the inset of Fig. 1 according to an established formulation,¹³ values of $1.8 \pm 0.08 \times 10^5$ and $3.4 \pm 0.9 \times 10^5\text{ M}^{-1}$ were obtained for the association constants of **1** and C_{60} in toluene and ODCB, respectively. In control studies, no quenching of triazine fluorescence beyond that attributable to competitive light absorption by C_{60} was observed using tris-diphenylamino- or tris-diisopropylamino-*s*-triazines, which

both absorb at much shorter wavelengths than **1**. Computationally, the complex of C_{60} with tris-diphenylamino-*s*-triazine was unstable, dissociating without a barrier to the individual moieties.

In conclusion, the convex shape of C_{60} is well suited for efficient and selective association with the concave shape of triazine **1** at concentrations as low as 10^{-5} M , which allows efficient intermolecular PET to take place on the nanosecond time scale. The association constant, greater than 10^5 M^{-1} , is unprecedented for binding between pristine C_{60} and a simple monomeric host chromophore in solution. These effects are directly attributable to van der Waals attraction between the complementary surfaces of the two moieties. Complex formation is reversible and pH dependent. Photoexcitation of the complex leads to a new strongly emissive species, possibly a charge-transfer state, which does not dissociate to give free fullerene radical anions. One can easily envisage generation of more stable complexes as well as larger molecular assemblies incorporating fullerenes and triazines using this novel type of supramolecular complexation. Experiments along these lines are in progress.

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