A glycyl-substituted porphyrin as a starting compound for the synthesis of a π–π-stacked porphyrin–fullerene dyad with a frozen geometry†

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A synthetic route for obtaining a porphyrin–fullerene dyad with a constrained geometry forcing the [60]fullerene sphere to lie on the porphyrin plane is reported, revealing a strong interaction in the ground state between the two chromophores.

Introduction

The peculiar photochemical and electrochemical properties of porphyrins and fullerenes have been extensively investigated in the recent past. The use of these two chromophores for studies concerning photoinduced energy and electron-transfer reactions has been reported in several papers. With the aim of finding the best energy conditions, electronic interactions, and structural and geometrical effects for obtaining fast charge transfer and a longer lifetime for the excited radical ion pair, many porphyrin–fullerene architectures have been assembled either covalently or through non-covalent interactions[1] *e.g.* hydrogen bonding, π–π stacking or metal coordination. The huge number of ground state non-interacting porphyrin–fullerene systems have shed light into the kinetic processes of energy and/or electron-transfer between these two chromophores. Fewer studies have been reported on the photogenerated excited states in porphyrin–fullerene dyads where a strong electronic interaction is present. It is possible to find in the literature the preparations of many linear[2] or star-shaped[3] multichromophoric systems composed of porphyrin photosensitizers and a fullerene electron-acceptor, while only a few reports have been dedicated to the synthesis of dyads in which the two chromophores present an interaction between their respective π-electron systems.[4] Although the stacking between the two entities is a spontaneous process under co-crystallization conditions,[5] it is necessary to maintain the two units in close contact through covalent bonds in order to have the possibility to study the kinetic aspects of the excited states in solution.

Different geometries have been developed to give stacked porphyrin–fullerene systems such as the porphyrin–fullerene cyclophane systems synthesized by Diederich and Hirsch,[6] the porphyrin–fullerene parachute systems synthesized by Schuster and coworkers,[7] and more recently the porphyrin–fullerene pac-man systems reported by D'Souza, Barbe and Fukuzumi.[8] In the first two systems cited above, the π-electronic interaction is allowed thanks to the conformational flexibility of the aliphatic branches that brings together the two subunits, while in the last one a lower conformational freedom induces a constrained face-to-face geometry. Although the pac-man porphyrin–fullerene systems are much more rigid than the porphyrin–fullerene parachute and cyclophane systems, they still have conformational freedom.

Here we wish to report on the synthesis of a new π–π stacked porphyrin–fullerene dyad with a completely frozen geometry similar to that found in co-crystallized porphyrin–fullerene systems. The close proximity between the two chromophores induces a ground state electronic interaction as shown by the ^{1}H and ^{13}C-NMR and UV-vis studies. Moreover, the synthetic strategy can allow the introduction of additional photoactive and electroactive chromophores bearing an aldehyde group, suitable for the cycloaddition reaction.

Results and discussion

The strategy used for obtaining the π–π stacked dyad is similar to that adopted by Sakata and coworkers who used the *ortho* position of a phenyl ring to link the fullerene through an amido group.[9] The synthesis of dyad **6** was achieved by following a synthetic pathway for obtaining the new tetra-arylporphyrin derivative **4**, bearing in the *ortho* position of one of the four *meso*-phenyl rings a glycyl unit, whose carboxylic group was protected as an ethyl ester. The starting nitroporphyrin **2** was obtained in a two-step process involving the synthesis of the 5-phenyldipyrromethane and a subsequent condensation reaction with benzaldehyde and 2-nitrobenzaldehyde under Lindsey's reaction conditions.[10] This pathway gave the desired mononitroporphyrin in a good yield (22%). The subsequent reduction of the nitro group into the amino group was carried out in a mixture of 1,4-dioxane and hydrochloric acid in the presence of an excess (12 equivalents) of $SnCl_2{\cdot}2H_2O$, while protecting the reaction mixture from the light. The final aminoporphyrin **3** was obtained in 80% yield[11] (see Scheme 1).

The new porphyrin **4** was obtained in 56% yield by the nucleophilic substitution of the amino group of the porphyrin **3** on the iodine of the ethyl iodoacetate, carried out in anhydrous DMF. The glycyl porphyrin ethyl ester derivative **4** was characterized by FAB mass spectrometry, which shows a molecular peak at m/z 715, and ^{1}H-NMR analysis, in which the signals due to the ethyl ester glycine moiety are clearly visible: a 3H triplet at 1.11 ppm and a 2H quartet at 4.03 ppm due to the methyl and methylene of the ester group respectively, and a (not well defined) 2H doublet at 3.84 ppm arising from the methylene group in the position α

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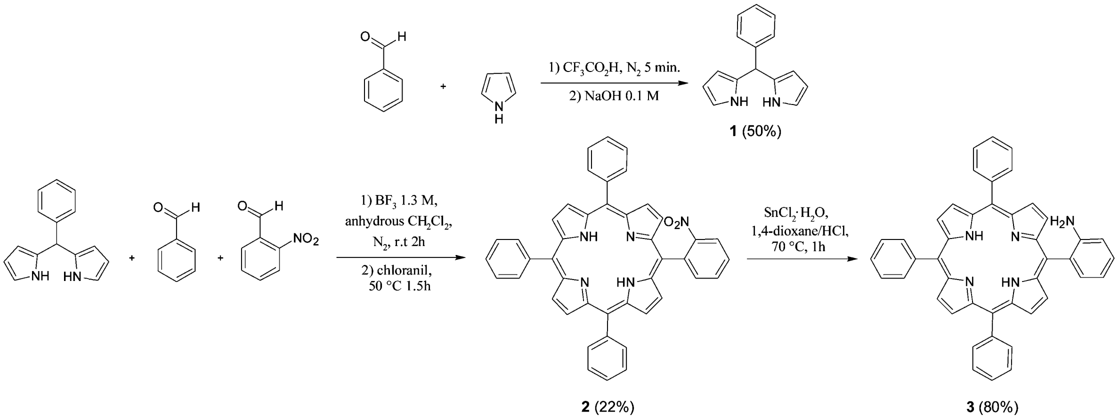
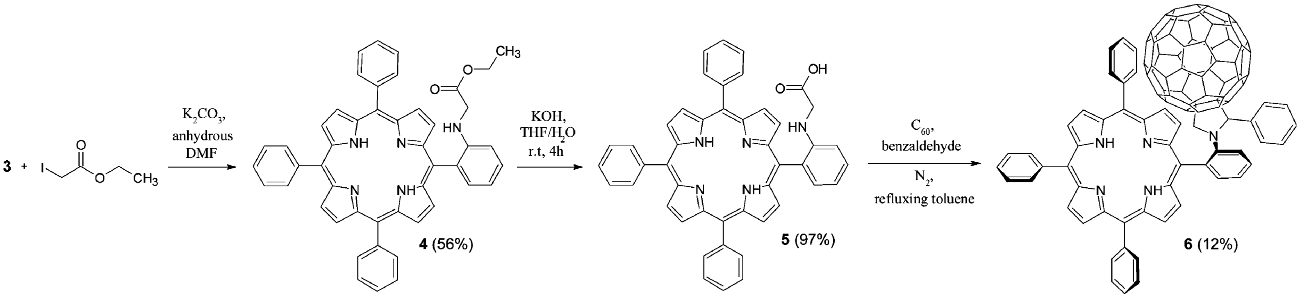


Scheme 1 Synthesis of aminoporphyrin **3**.



Scheme 2 Synthetic pathway to dyad **6**.

to the amino group of the glycine. The saponification of the ester group (KOH in THF/H_2O) affords, almost quantitatively, the final porphyrin **5**, which was directly used for the Prato condensation reaction[12] with benzaldehyde and fullerene to give the dyad **6** in 12% yield (see Scheme 2).

Although an excess of benzaldehyde was used in order to force the complete conversion of porphyrin **5** into the final porphyrin–fullerene dyad, the yield was poor. This is probably due to the steric hindrance of the porphyrin macrocycle, which partially prevents the cycloaddition of the incoming ylide to the fullerene cage. However, it is common to obtain quite low yields when hindered porphyrins are used to synthesize porphyrin–fullerene dyads with a constrained geometry.[4f,8,13] The FAB^+ mass analysis of dyad **6** reveals a cluster peak at m/z 1451 corresponding to the molecular mass of the dyad and a base peak at m/z 731 due to the loss of the entire fullerene sphere arising from the cleavage of the carbon–carbon bonds of the pyrrolidine ring. Moreover, the ^1H-NMR spectrum of compound **6** shows the presence of the proton signals due to the pyrrolidine ring: a 1H singlet at 5.48 ppm due to the phenyl-substituted methyne group of pyrrolidine ring, and two 1H doublets at 3.79 and 3.40 ppm due to the methylene group of the pyrrolidine ring.

The electronic interaction between the π-electron system of porphyrin and fullerene is clearly evident from ^1H and ^{13}C-NMR and UV-vis measurements. In the ^1H-NMR pattern of the β-pyrrole protons of porphyrin **4**, it is possible to see a simple system composed of one singlet at 8.94 ppm and two doublets at 9.00 and 8.95 ppm, one of them coalescing with the singlet signal. This pattern provides evidence for a pseudo-C_2 symmetry of the porphyrin macrocycle. However, when the fullerene sphere was covalently forced to lie on the porphyrin plane, the signals of β-pyrrole protons are strongly perturbed. In fact, it is evident that in the ^1H-NMR spectrum of dyad **6**, these signals increased in number, becoming much more broadened and shifted towards lower and higher fields, clear evidence of the electronic perturbation induced by the fullerene electron density (see Fig. 1).

The protons trapped between the porphyrin macrocycle and the curved surface of the fullerene show the signals of the pyrrolidine shifted both down-field and up-field. In particular, the singlet arising from the proton of the phenyl-substituted methyne group of the pyrrolidine ring is shifted down-field by about 0.5 ppm compared to the same signal in the reference compound **7** (*N*-methyl-2-phenyl-3,4-fulleropyrrolidine), while the two doublets are shifted up-field with an average shift of 1 ppm, as is clearly visible in Fig. 2.

Moreover, the electronic perturbation induced by the fullerene also affects the resonance of the porphyrin NH protons, which lie at at 2.65 ppm in the dyad **6** and at 2.59 ppm in the porphyrin **4**. In order to verify the degrees of freedom of the dyad, a second ^1H-NMR spectrum was recorded at 45 °C. The only result was that the peaks were much more broadened, with a further loss of signal definition, an additional confirmation of the frozen geometry of the dyad **6** (see ESI†). The ^1H-NMR analysis provides evidence for how the π-electron density of C_{60} induces a considerable alteration of all the porphyrin proton resonances, including the *meso*-phenyl protons, due to the close distance between the two chromophores. Comparing the ^{13}C NMR spectrum of *N*-methyl-2-phenyl-3,4-fulleropyrrolidine with that of the porphyrin–fullerene dyad (see ESI†), it is possible to see two very different patterns. At a first sight the spectrum of the dyad **6** has a higher number

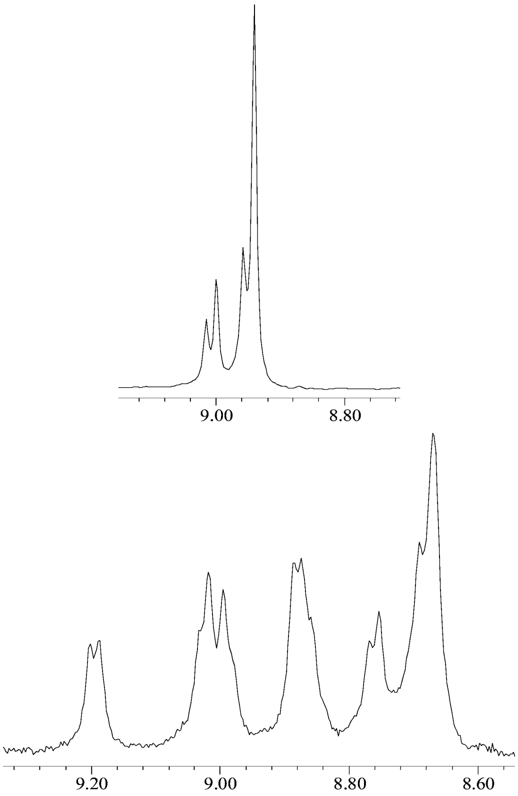


Fig. 1 ^{1}H-NMR β-pyrrole proton pattern of (top) porphyrin **4** and (bottom) dyad **6**.

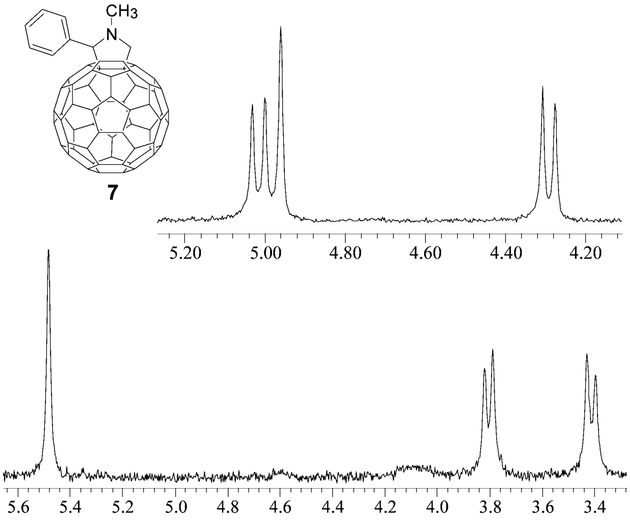


Fig. 2 ^{1}H-NMR pyrrolidine proton pattern of (top) the *N*-methyl-2-phenyl-3,4-fulleropyrrolidine **7** and (bottom) dyad **6**.

of signals, some of them not well resolved, while in the spectrum of the reference compound **7** the signals arising from the fullerene sphere, lying between 135 and 160 ppm, are clearly visible. The signals around 130 ppm are ascribable to the phenyl group. There is no resemblance between the two spectra, and this fact further underlines the strong electronic interaction occurring between porphyrin and fullerene. Such strong interaction modifies completely the resonances of the fullerene carbons in the dyad **6**. Nevertheless it is possible to discern the shielding effect of the porphyrin electron density exerted on the few carbons of the fullerene surface stacked on the porphyrin plane. In particular the fullerene signals at 156.98, 154.80 and 154.12 ppm in the spectrum of **7** disappear in the spectrum of **6**, moving towards higher field. A similar trend is evident also for the aliphatic carbons of the pyrrolidine ring and the functionalized six-membered ring of the fullerene, which reside between 70 and 85 ppm for **7** and between 65 and 75 ppm for **6**. The UV-vis spectra recorded in toluene solution further underline the interaction between the two units. In Fig. 3 a comparison of the absorption spectra of compounds **6** and **7** with that of the tetraphenylporphyrin is reported. The Soret band of the porphyrin in the dyad **6** is red-shifted by 8 nm compared to that of the tetraphenylporphyrin, and a similar trend is evident also for the Q band, red-shifted by about 6 nm. Furthermore the molar extinction coefficient of the Soret band in the dyad is lower (265000 M^{-1} cm^{-1}) than that of the tetraphenylporphyrin (383000 M^{-1} cm^{-1}), providing evidence for a partial migration of the electron density from the tetrapyrrole ring toward the fullerene sphere.

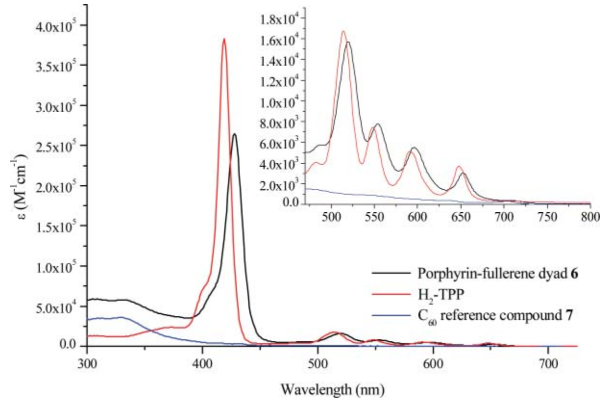


Fig. 3 Absorption spectra in toluene solution of compounds **6**, **7** and tetraphenylporphyrin. All the compounds have a concentration of 5.5 × 10^{-6} M. In the inset the Q-band pattern is shown.

The close proximity of the two chromophores results in a considerable electronic interaction in the ground state, producing a partial charge-transfer electronic state with an absorption band at 716 nm, red-shifted by about 12 nm with respect to the absorption band of the fullerene reference compound **7** located at 704 nm (see Fig. 4). These findings are in line with those reported for other π–π-stacked porphyrin–fullerene dyads.[4b,c,f,8] The absorption band of the charge transfer state was obtained by subtracting the absorption of the tetraphenylporphyrin and that of **7** from the absorption of the dyad **6**. All the data reported here confirm the existence of a strong electronic interaction in the electronic ground state between the porphyrin and fullerene due to the short distance between their respective π-electron systems. This interaction is induced by the almost completely frozen geometry of the dyad, as also revealed by the geometric optimization performed at the MM+ level. The optimized geometry reported in Fig. 5 shows the fullerene sphere restricted on the tetrapyrrole ring at an average distance of 3 Å, corresponding to that found in the co-crystallites.[5a].

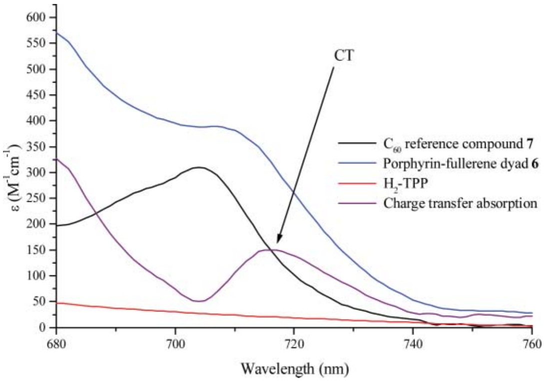


Fig. 4 Charge transfer absorption (purple line, indicated by the arrow) of the dyad **6** in toluene solution. The concentration of all compounds was 1.1×10^{-4} M.

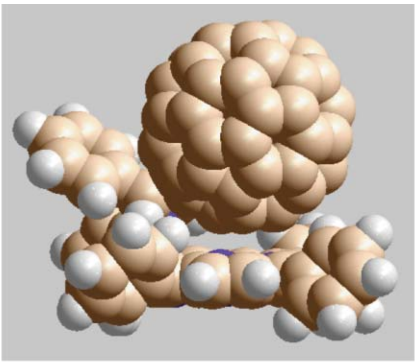


Fig. 5 Optimized geometry of dyad **6** represented using the van der Waals radii.

Conclusions

In conclusion, in this paper we have presented the use of a new glycyl-substituted porphyrin for the synthesis of a porphyrin–fullerene dyad with an almost completely frozen geometry, similar to that found in the co-crystallite systems. In order to favour electronic interaction in the ground state between the two chromophores, they were linked so as a result in a short distance between them. The introduction of the glycine moiety on the tetrapyrrole ring offers the opportunity to link different electro- and/or photoactive groups such as ferrocene, tetrathiafulvalene and many others bearing an aldehyde group, useful for cycloaddition reactions, with the possibility of constructing a compact triad in order to evaluate multiple electronic interactions in the electronic ground state.

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