A new pyridyl-substituted methanofullerene derivative. Photophysics, electrochemistry and self-assembly with zinc(II) *meso*-tetraphenylporphyrin (ZnTPP)†

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A new methanofullerene derivative with a pyridine residue at the methano bridge (PC_{60}) has been synthesized. Its electrochemical and photophysical properties have been investigated in toluene solution along with those of the analogous fullerene mono-malonate adduct RC_{60}, which does not contain the pyridyl moiety. PC_{60} and RC_{60} display almost identical steady state absorption and luminescence properties and transient absorption spectra, as shown by means of nano- and picosecond laser flash photolysis. Their markedly different spectroscopic features with respect to plain C_{60} are discussed, with the aid of semi-empirical calculations. PC_{60} binds zinc(II) *meso*-tetraphenylporphyrin (ZnTPP) through coordination of the pyridyl moiety to the zinc ion giving, to the best of our knowledge, the first non-covalent assembly of a porphyrin–fullerene diad. The association constant of the 1 : 1 complex between PC_{60} and ZnTPP has been determined at 300 K by ^{1}H NMR ($K_a = 3600 \pm 150$ L mol^{-1}, C_6D_6 solution) and fluorescence titrations ($K_a = 3000 \pm 400$ L mol^{-1}, toluene solution). Mixtures of RC_{60} and ZnTPP have also been investigated, giving no evidence of association. Extremely fast ZnTPP luminescence quenching in the PC_{60}–ZnTPP complex was observed by time-resolved luminescence spectroscopy ($k > 5 \times 10^{10}$ s^{-1}), tentatively attributed to an energy transfer mechanism. The bimolecular quenching constant of the lowest triplet excited state of ZnTPP by PC_{60} was determined *via* a Stern–Volmer analysis ($k_q = 6.7 \times 10^9$ s^{-1}).

Non-covalent supramolecular aggregates are extensively used by nature to process light inputs in living organisms.[1] For instance, these structures can offer a suitable environment for the photoinduced energy and electron transfer processes that allow the conversion of solar energy into electricity or chemical energy.[2] In order to learn from nature the secrets that govern these processes, a great variety of artificial synthetic systems have been designed and prepared.[2] Most of them are based on multicomponent organic and inorganic arrays displaying covalent or coordination bonds,[3] whereas less attention has been paid to non-covalent systems.[4]

Porphyrins[5] and fullerenes[6] appear as particularly suitable building blocks for the construction of supramolecular systems displaying photoinduced energy and electron transfer processes[5a,7–8] due to their spectroscopic and electrochemical features, namely strong ground state absorptions throughout the UV-VIS spectral region, characteristic luminescence patterns, diagnostic transient absorption signals and complementary electronic donor/acceptor properties. The recent progress in the chemistry of C_{60} allowed the preparation of several porphyrin–fullerene diads[9] and triads,[10] and intramolecular processes such as electron or energy transfer has been observed in some of these systems. On the other hand, C_{60} has been incorporated into multicomponent molecular systems such as rotaxanes,[7a,11] catenanes,[12] oligopyridine Ru^{II} complexes[13] and Pt^{II} molecular squares[14] with the aim of developing fullerene supramolecular assemblies and advanced materials.[8c,15] As a part of this research, we now report the preparation of a methanofullerene derivative bearing a pyridyl moiety at the methano bridge (PC_{60}), and its binding behaviour to zinc(II) *meso*-tetraphenylporphyrin (ZnTPP) through coordination to the zinc ion.[16]

The assembly of an electron donor with C_{60}, using coordination rather than covalent chemistry, appears attractive since the range of systems that can be investigated is not severely limited by the synthetic route. It should be noted that coordination of pyridine derivatives to metalloporphyrins has been previously used for molecular recognition,[17] template-directed synthesis of cyclic porphyrin oligomers,[18] supramolecular catalysis,[19] or to control the structure of supramolecular porphyrin assays.[20] It has been shown that photoinduced energy or electron transfer processes are possible when acceptor systems are assembled to metalloporphyrins *via* this type of coordination.[16,21]

The compounds investigated in this work, PC_{60}, ZnTPP, and the methanofullerene RC_{60} lacking the pyridyl moiety and used for comparison purposes, are shown in Scheme 1.

Results and discussion

Synthesis and electrochemistry

The preparation of the ligand PC_{60} was accomplished by a

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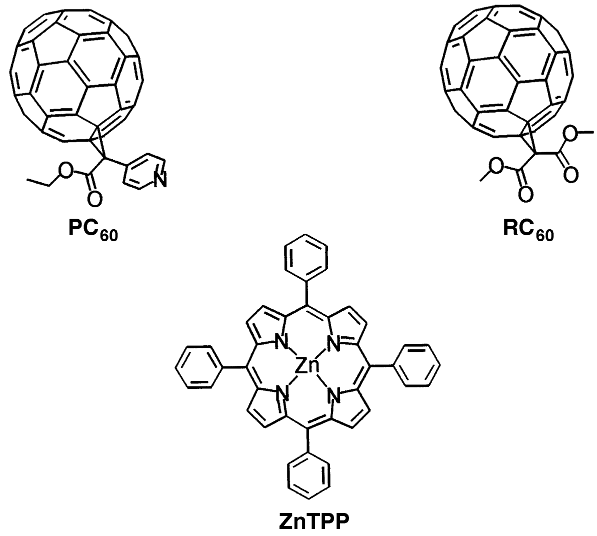
† *Non-SI units employed*: 1 kcal ≈ 4.19 kJ; 1 eV ≈ 1.60×10^{-19} J.



Scheme 1

Bingel-type cyclopropanation reaction.[22] Treatment of C_{60} with ethyl 4-pyridineacetate,[23] I_2, and NaH in toluene at room temperature afforded PC_{60} in 46% yield. The ^1H NMR spectrum of PC_{60} in $CDCl_3$ shows two sets of aromatic signals in a typical pattern for a 4-substituted pyridine, as well as a triplet and quartet at $\delta = 1.41$ and 4.49, respectively, for the ethyl group. The ^{13}C NMR spectrum is also in full agreement with the structure of PC_{60}, and 29 resonances out of the 34 expected in the typical fullerene and aromatic region are fully resolved (31 for the fullerene sp^2 carbons and 3 for the pyridyl moiety). It also displays the expected 5 nonaromatic signals ($\delta = 165.60$ for the carbonyl group; $\delta = 74.51$ for the fullerene sp^3 carbons; $\delta = 63.46$ and 14.26 for the ethyl group; and $\delta = 56.05$ for the methano bridge carbon). The structure of PC_{60} was also confirmed by fast atom bombardment (FAB) mass spectroscopy with the molecular ion peak at $m/z = 884$ ($[MH^+]$, calculated for $C_{69}H_9NO_2$: 883.8). The preparation of model compound RC_{60} has been previously reported,[24] and ZnTPP is commercially available.

The electrochemical investigations on PC_{60} and ZnTPP were carried out as described previously[25] by cyclic voltammetry (CV) in $CH_2Cl_2 + 0.1$ M Bu_4NPF_6. The redox potentials are reported in Table 1 *vs.* the ferrocene/ferrocenium couple (Fc/Fc^+). The electrochemical data of methanofullerene PC_{60} are in good agreement with previously reported data.[25] In the cathodic scan, two well-resolved and reversible processes were observed at −1.06 and −1.45 V *vs.* Fc/Fc^+ for PC_{60} as well as an additional irreversible peak at −2.00 V (peak potential). In the anodic scan, only a chemically irreversible oxidation peak was observed at *ca.* +1.06 V (peak potential). The CV of ZnTPP exhibits one reversible one-electron reduction process at −1.79 V *vs.* Fc/Fc^+ and two reversible oxidations, typical of porphyrin sytems, at +0.42 and +0.71 V *vs.* Fc/Fc^+. Precipitation of the PC_{60}–ZnTPP complex in CH_2Cl_2 as well as in toluene–CH_3CN (8 : 2) solutions prevented its electrochemical characterization.

Table 1 Redox potentials[a] of PC_{60} and ZnTPP measured by cyclic voltammetry[b]

	E^1_{red}	E^2_{red}	E^3_{red}	E^1_{ox}	E^2_{ox}
PC_{60}	−1.06(75)	−1.45(78)	−2.00[c]	+1.06[c]	
ZnTPP	−1.79(79)			+0.42(82)	+0.71(81)

[a] V *vs.* ferrocene/ferrocenium couple; *n*-Bu_4NPF_6 (0.1 M) in CH_2Cl_2; scan rate 0.1 V s^{-1}. [b] Values in parentheses refer to anodic-to-cathodic peak-to-peak separations in mV. [c] Irreversible wave, peak potential reported.

NMR titrations

The association constant (K_a) and the Gibbs free energy of complexation ($\Delta G°$) for the binding of PC_{60} to ZnTPP were investigated by ^1H NMR titration in C_6D_6 at 300 ± 0.1 K. Complexation-induced changes in chemical shifts were observed for all the protons of the fullerene ligand PC_{60}. Noteworthy is the very large upfield shift of the H—C(2) chemical shift of the pyridyl moiety ($\Delta\delta = 5.8$) in the PC_{60}–ZnTPP complex compared to the free ligand ($\delta = 8.6$). Coordination to the Zn^{II} ion locates the pyridyl moiety of PC_{60} atop the porphyrin core and fully exposes it to its strong shielding effects, thus confirming the proposed structure of the supramolecular complex PC_{60}–ZnTPP. The association constant for the 1 : 1 complex based on the complexation-induced shifts of H—C(2) was determined to be $K_a = 3600 \pm 150$ l mol^{-1} ($\Delta\delta_{sat} = 5.8$), corresponding to $\Delta G° = -4.85 \pm 0.02$ kcal mol^{-1}. Identical results within the error range were obtained when the complexation-induced changes in chemical shifts of the other protons of PC_{60} in the complex were evaluated.

Spectroscopic properties

Toluene was used as solvent, because it is sufficiently apolar to favour coordination to the Zn^{II} ion and, at the same time, ensures good solubility and photostability of the samples. As reference compound, RC_{60} was chosen since it displays electrochemical and spectroscopic properties quite similar to those of PC_{60} but cannot associate with ZnTPP.

ZnTPP. This molecule has been already extensively investigated.[5a,26] The ground state absorption spectrum (Fig. 1, Table 2) displays: (*i*) the very intense Soret band ($\lambda_{max} = 422$ nm) corresponding to the transition to the second excited singlet state S_2, and (*ii*) the weaker Q bands around 550 nm, corresponding to a vibronic sequence of the transition to the lowest excited singlet S_1.

In toluene solution at room temperature, ZnTPP exhibits a fluorescence band ($\lambda_{max} = 646$ nm, $\tau = 2.9$ ns, $\Phi_{em} = 0.015$), whereas at 77 K both fluorescence ($\lambda_{max} = 652$ nm, $\tau = 2.8$ ns) and phosphorescence ($\lambda_{max} = 776$ nm, $\tau = 32$ ms) are observed. The picosecond transient absorption spectrum shows a wide feature in the 450–520 nm region from which, within our time window (3.3 ns), the singlet to triplet conversion can be partially evidenced; between 520 and 670 nm, the bleaching of the Q bands can also be observed. On the microsecond time scale, the fully evolved spectrum of the triplet ($\lambda_{max} = 470$ nm) can be detected; its lifetime is 240 μs in deoxygenated solutions.

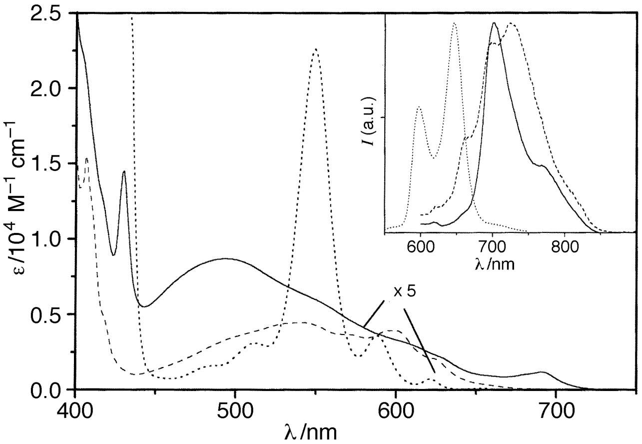


Fig. 1 Absorption and (inset) normalized fluorescence spectra of PC_{60} (full line), ZnTPP (dotted line), and C_{60} (dashed line) in toluene solution at 298 K.

Table 2 Ground state absorption and luminescence data in toluene

	Absorption	Luminescence				
	298 K	298 K			77 K	
	λ_{max}/nm ($\varepsilon/10^3$ M^{-1} cm^{-1})		$\lambda_{max}{}^a$/nm	τ/ns	$\Phi_{em} \times 10^4$	λ_{max}/nm
C_{60}	335(56.2), 406(3.1), 540(0.9), 596(0.8)	726	1.3	2	724	
RC_{60}	330(40.0), 428(2.7), 488(1.6), 690 (0.2)	702	1.7	5	694	
PC_{60}	330(41.0), 430(2.9), 494(1.7), 691(0.1)	702	1.7	5	694	
ZnTPP	314(14.1), 355(8.8), 422(578), 510(3.1), 549(22.6), 588(3.6), 621(0.7), 653(0.1)	646	2.9	150	652,[b] 776[c]	

[a] From uncorrected emission spectra. [b] Fluorescence band. [c] Phosphorescence band.

PC_{60} and RC_{60}. The electronic absorption spectrum of PC_{60} in toluene is shown in Fig. 1; the spectrum of C_{60} is also reported for comparison purposes. RC_{60} displays spectral features almost identical to those of PC_{60} (see Table 2). In the UV region they both show a very intense band ($\lambda_{max} = 330$ nm, $\varepsilon = 4 \times 10^4$ L mol^{-1} cm^{-1}) typical of fullerene derivatives, whereas in the visible region, the spectrum is broad and much less intense ($\varepsilon_{max} = 10^2$–10^3 L mol^{-1} cm^{-1}, Table 2). As for other monofunctionalized fullerenes, the spectrum is rather different with respect to plain C_{60}, indicating strong perturbation of the electronic levels upon substitution and change in symmetry.[27] In particular, the absorptions of RC_{60} and PC_{60} in the visible region are more intense, broader and less resolved than those of C_{60}; as a consequence the colour of the two derivatives (deep red) is different from that of the parent compound (purple). RC_{60} and PC_{60} display identical room temperature fluorescence spectra ($\lambda_{max} = 702$ nm, $\Phi_{em} = 0.0005$), with excited state lifetimes of 1.7 ns, as obtained from their luminescence streak image. In comparison with plain C_{60}, a lower energy spectral onset, a higher luminescence quantum yield, and a longer lifetime are observed (Fig. 1, Table 2), as recently reported for other methanofullerenes in fluid solution.[27] It is worth noticing that the emission quantum yield of C_{60} in toluene has twice the value as in dichloromethane,[7a] which could be related to the higher stability of its electronic excited states in π-stacking environments.[28] The room temperature excitation spectra of PC_{60} and RC_{60}, read at their fluorescence maxima (Table 2) match the corresponding absorption profiles throughout the UV-VIS spectral region, indicating that the lowest singlet ($^1\pi\pi^*$) excited state is populated with the same (presumably unitary) efficiency from the upper lying levels. In a rigid toluene matrix at 77 K, PC_{60} and RC_{60} display a fluorescence band with $\lambda_{max} = 694$ nm. For these compounds, phosphorescence from the lowest triplet ($^3\pi\pi^*$) state was not detected. This is a quite usual behaviour for fullerene compounds, where phosphorescence bands have been detected only in matrices below 5 K[29] or, at 77 K, in the presence of heavy-atom-containing solvents.[30]

The picosecond time-resolved absorption spectrum of PC_{60} (Fig. 2) and RC_{60} are identical, showing both singlet–singlet ($\lambda_{max} = 535$ and 900 nm) and triplet–triplet ($\lambda_{max} = 710$ nm) absorption features. The decay of the singlet bands matches the formation of the triplet, and isosbestic points around 600 and 820 nm are found. The lifetimes of singlet decay and triplet formation coincide and are in agreement with the singlet lifetime determined by the luminescence decay (1.7 ns). The singlet and triplet absorption maxima of the two monoadducts lie at higher energy than those of C_{60} (Fig. 2). This behaviour has already been observed in other cases.[7a,9c]

On a longer time scale, the fully evolved triplet spectra of PC_{60} and RC_{60} can be detected. They are almost coincident and show absorption maxima around 430 and 710 nm. The triplet decays in deoxygenated solution are monoexponential with a lifetime of 23 μs. It is worth noticing that, again, differences with respect to plain C_{60} are observed. The latter displays a longer triplet lifetime (45 μs) and red-shifted bands with maxima around 450 and 750 nm (Fig. 2).

Fullerenes are known to produce singlet oxygen with high yield by photoinduced energy transfer.[31] The efficiency of the sensitization process depends on the excitation wavelength,[31] and can be derived by monitoring the sensitized singlet oxygen luminescence ($^1\Delta_g$) at 1269 nm.[31] Upon laser excitation at 355 nm, and taking C_{60} as relative standard ($\Phi_{rel} = 1$), the yield of singlet oxygen generation for PC_{60} and RC_{60} turned out to be lower (0.80), in line with the behaviour of other dihydrofullerene derivatives.[7a,32]

Following the procedure previously adopted for a class of silylalkynylated methanofullerenes,[7a] a series of semi-empirical, quantum mechanical calculations was performed on the present fullerene derivatives. A molecular mechanics (MM+) procedure was adopted for the optimization of the ground state geometries. In PC_{60}, the results indicate a symmetric location of the methano bridge substituents (*i.e.* pyridyl and carbonyl) with respect to the plane bisecting the bucky ball and passing through the C_s axis. The C(4-pyridine)—C(methano)—C(fullerene) angle is 127°, while the C(4-pyridine)— C(methano)—C(carbonyl) angle is 113°. Compound RC_{60} is more symmetric, possessing a C_2 axis and two perpendicular C_s planes; the calculated C(carbonyl)—C(methano)— C(carbonyl) angle is 109°.

Starting from the optimized ground state structures, we performed on PC_{60} and RC_{60} a series of semi-empirical calculations by means of the ZINDO/S (intermedate neglect of differential overlap, Zerner parametrization, spectroscopic) program.[33] As noticed for other monofunctionalized fullerenes,[7a,34] our compounds show two main spectral features

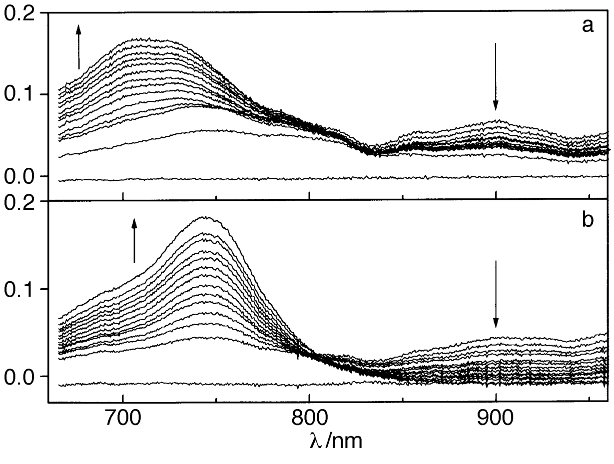


Fig. 2 Picosecond transient absorption spectrum of (*a*) PC_{60} compared to that of (*b*) C_{60} under identical experimental conditions. Toluene solution; $\lambda_{exc} = 532$ nm; energy: 4 mJ $pulse^{-1}$; $A = 0.20$; time interval 330 ps. The spectrum of RC_{60} is identical to that of PC_{60}.

that appear to be reproducible for this class of compounds: a diagnostic absorption band around 428 nm and a fluorescence band whose onset is red-shifted with respect to that of plain C_{60}. The calculation reproduces these features, locating the emitting singlet at 692 nm with an oscillator strength $f = 0.007$, and the first sizeable singlet at 437 nm ($f = 0.038$). As noticed for other monofunctionalized fullerenes, the breaking of the high symmetry of C_{60} (I_h), to C_s and C_{2v} for PC_{60} and RC_{60}, respectively, makes the first singlet state allowed, which otherwise is ony vibronically active in the parent compound. The absorption band with $\lambda_{max} = 437$ nm has to be attributed to the first allowed singlet, red-shifted by about 20 nm with respect to that of C_{60} ($\lambda = 406$ nm). Also, the lowest excited triplet state undergoes a large energy decrease with respect to that of the unsubstituted compound, calculated to be at 810 and 790 nm for PC_{60} and RC_{60}, respectively, *vs.* 758 nm for C_{60}. This large T_1–S_0 energy gap decrease can explain the enhanced $T_1 \rightarrow S_0$ intersystem crossing (ISC) rate and, therefore, the observed reduced triplet lifetime.

Supramolecular ZnTPP–PC_{60} complex. All the investigations on mixtures of ZnTPP and PC_{60} have been carried out in parallel with mixtures of ZnTPP and RC_{60}, in order to have always a suitable reference.

Addition of a large excess of PC_{60} (4×10^{-4} M) to a toluene solution containing 4×10^{-6} M ZnTPP causes a 50% decrease of the intensity of the ZnTPP fluorescence with respect to the reference RC_{60} solution, regardless of the excitation wavelength (Fig. 3).[35]

Moreover, the absorption spectrum of the mixture containing RC_{60} is quantitatively the sum of the spectra of the two components, whereas the same comparison with the mixture containing PC_{60} shows a red-shift of the ZnTPP Soret band by approximately 10 nm (Fig. 4). Such a red-shift is characteristic for the coordination of pyridine to a Zn^{II}–porphyrin.[16]

As far as the emission spectra are concerned, it must be pointed out that in our specific case luminescence experiments can be reliably done due to a series of favourable circumstances. (*i*) The high molar absorption coefficients of the porphyrin with respect to the fullerenes in the visible spectral region, in particular at the Soret band maximum (Table 2), allow preferential excitation of ZnTPP to be performed although the porphyrin concentration is one hundred times lower than that of the fullerene. (*ii*) The fluorescence quantum yield of the fullerenes is two orders of magnitude lower than that of ZnTPP and the emission band lies in a spectral region where the luminescence detector response drops, thus allowing detection of the ZnTPP fluorescence without interference with the fullerene band, regardless of the excitation wavelength (Fig. 3). (*iii*) Reabsorption of the porphyrin luminescence by the highly concentrated PC_{60} occurs, but this effect can be ignored since a comparison with the reference solution containing RC_{60} is always done.

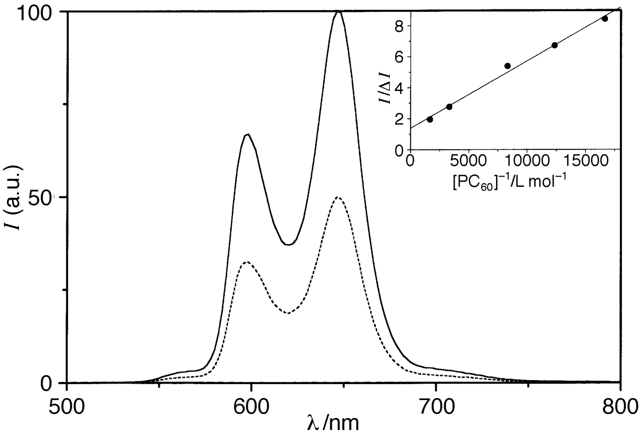


Fig. 3 Fluorescence spectrum of a 4.0×10^{-6} M ZnTPP toluene solution containing 4.0×10^{-4} M RC_{60} (full line) or PC_{60} (dashed line), $\lambda_{exc} = 554$ nm (isosbestic point). The inset shows the Benesi–Hildebrand plot for determining the association constant between PC_{60} and ZnTPP *via* fluorescence titration.

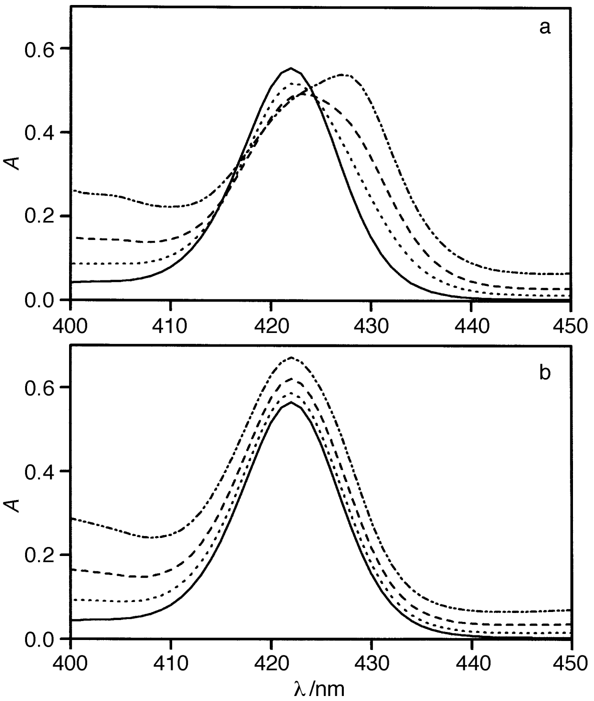


Fig. 4 Changes in the absorption spectra (Soret band spectral region) of a 6.0×10^{-6} M ZnTPP toluene solution containing increasing amounts of (*a*) PC_{60} and (*b*) RC_{60}: (———) 0, (······) 1.1×10^{-4}, (– – – –) 2.8×10^{-4} and (—··—) 5.6×10^{-4} M. The absorbance increase in (*b*) is smply due to the increasing contribution of the added fullerene (see text for more details).

Addition of an excess of trifluoroacetic acid to the ZnTPP–PC_{60} solution causes a 50% increase of the porphyrin fluorescence, as well as a blue-shift of the Soret absorption band; on the contrary, no spectral changes are observed for the reference solution. In other words, after the addition of trifluoroacetic acid, the ZnTPP–PC_{60} mixture displays the same emission intensity as the reference solution, while its absorption spectrum simply becomes the linear combination of the two components, similar to the solution of ZnTPP containing RC_{60}.

In order to determine the association constant of the porphyrin–fullerene complex, a fluorescence titration was performed and evaluated according to a modified Benesi and Hildebrand[36] equation (see also Experimental):

$$\frac{I}{\Delta I} = \frac{I}{A} + \frac{I}{K_a A}\frac{1}{[PC_{60}]} \qquad (1)$$

where I is the normalized fluorescence intensity of ZnTPP in the reference solution containing RC_{60}, ΔI is the difference of the porphyrin luminescence intensity between the RC_{60} and PC_{60} containing solutions, $[PC_{60}]$ is the molar concentration of PC_{60}, and A is a constant associated with the difference in the emission quantum yield of the complexed and uncomplexed ZnTPP. By plotting $I/\Delta I$ *vs.* $1/[PC_{60}]$ (Fig. 3, inset), a value for the association constant $K_a = 3000 \pm 300$ M^{-1} is obtained, in good agreement with the value derived by NMR titration.

In principle, eqn. (1) can be used also to determine the K_a value by spectrophotometric titrations, for example by monitoring the change in molar absorptivity of the Soret band upon porphyrin–fullerene association (Fig. 4). Unfortunately, such an effect is less dramatic than the fluorescence quenching; moreover, increasing amounts of fullerene tend to affect the position of the Soret band (422 nm), since RC_{60} and PC_{60} display sharp maxima at 427 and 429 nm, respectively (Table 2). In any case, as already pointed out, the occurrence of association can be qualitatively evidenced by monitoring the trend of the ZnTPP Soret band upon addition of PC_{60} (Fig. 4).

Photoinduced processes

NMR and UV-VIS absorption and luminescence experiments indicate that association between PC_{60} and ZnTPP does occur, and the decrease of the ZnTPP fluorescence can be assigned to intramolecular quenching by PC_{60} in the complex. In a time-resolved luminescence experiment, the streak image of the ZnTPP fluorescence of the above solution displays a luminescence intensity decrease of about 50% with respect to the reference solution, in agreement with the steady state findings. On the other hand, the time decay of the fluorescence signal is monoexponential ($\tau = 2.9$ ns) for both solutions, indicating that within our time resolution (20 ps) no decay of the associated porphyrin can be observed, although it would account for half of the total porphyrin. Therefore we can conclude that the quenching of the lowest excited singlet state of ZnTPP (^{1}ZnTPP) in the complex is very fast ($k > 5 \times 10^{10}$ s^{-1}). In principle, the quenching mechanism can be due to either spin-allowed energy transfer to the lowest singlet excited state of PC_{60} ($^1PC_{60}$) or to electron transfer to give the charge separated state ($PC60^-$–$ZnTPP^+$). In fact, from luminescence and electrochemical data one can derive that ^{1}ZnTPP is located at 2.03 eV, $^1PC_{60}$ at 1.73 eV, and $PC60^-$–$ZnTPP^+$ at 1.48 eV. All attempts to obtain experimental evidence for one of the two mechanisms was unsuccessful. For example, we could not perform excitation spectra fixing the monochromator on the PC_{60} luminescence band, even when it was in large excess with respect to ZnTPP, because the strong luminescence of the porphyrin masks the emission band of the fullerene (see Fig. 3). On the other hand, the search for the fullerene radical anion above 900 nm[9a] must be carried out in large excess of ZnTPP, a condition where self-association of ZnTPP also occurs (as evidenced by a broad absorption band above 800 nm), and the solution displays a too high optical density at the excitation wavelength (532 nm). Recently, Kuciauskas *et al.* have reported on some Zn^{II} porphyrin–fullerene diads,[9a] showing that in the apolar toluene medium, electron transfer occurs only when the two moieties face each other in close contact, whereas energy transfer prevails at longer intercomponent distances. Accordingly, since in our case direct facing of the two chromophores separated by the pyridine linker can be excluded, we would tend to ascribe the quenching mechanism to $^1\text{ZnTPP} \rightarrow {}^1PC_{60}$ energy transfer, also because this kind of mechanism has been reported to proceed rapidly through non-covalent bonds.[37] Moreover, although electron transfer displays a larger driving force ($\Delta G^\circ = -0.55$ eV) with respect to energy transfer ($\Delta G^\circ = -0.30$ eV), the former is often disfavoured by the higher solvent reorganizational energy involved.[7a,8a] The very high rate constant of the intecomponent photoinduced process *via* ^{1}ZnTPP ($k > 5 \times 10^{10}$ s^{-1}) implies that $^1\text{ZnTPP} \rightarrow {}^3\text{ZnTPP}$ intersystem crossing ($k_{isc} = 3.4 \times 10^8$ s^{-1}) cannot take place within the complex; accordingly, no excited state interactions through ^{3}ZnTPP can occur. On the contrary, ZnTPP molecules that are not associated (not less than 50% in the photophysical investigations, see above) can undergo bimolecular quenching with PC_{60}, *via* the long-lived ^{3}ZnTPP excited state. By monitoring the decay time of ^{3}ZnTPP at its absorption maximum (470 nm) upon addition of increasing amounts of PC_{60}, we have obtained a Stern–Volmer quenching plot[38] with $k_q = 6.7 \times 10^9$ M^{-1} s^{-1}. Such quenching is likely to occur *via* energy transfer in the apolar toluene medium, as very recently argued for plain C_{60}.[39]

Conclusions

We have prepared PC_{60}, a new methanofullerene derivative bearing a pyridyl moiety at the methano bridge. The electrochemical and photophysical properties of PC_{60} and of the analogous methanofullerene RC_{60} have been investigated in detail and compared with those of plain C_{60}. In toluene, association between PC_{60} and ZnTPP occurs with $K_a \cong 3000$ L mol^{-1}. Quenching of the ZnTPP fluorescence occurs in the complex, which is attributable to a very fast energy transfer to the fullerene partner. The value found for the association constant cannot be considered low in absolute terms; in fact even lower association constants are found for other supramolecular complexes extensively investigated from the photochemical viewpoint, such as inclusion adducts with cyclodextrins.[40] In that case, indeed, the cyclodextrins are spectroscopically innocent and can be used in very large excess. In our case, on the contrary, *both* fullerene and porphyrin are strong chromophores and it is not possible, given the value of the association constant, to perform photophysical investigations without reciprocal interference. This prevented us from obtaining reliable photochemical results under experimental conditions having excess of fullerene or a high concentration of both components, where the two chromophores are mostly involved in the complex. As a consequence, a detailed interpretation of the photoinduced processes occurring in the supramolecular assembly between PC_{60} and ZnTPP is difficult. These results show that, in order to understand in detail the photoinduced process occurring in non-covalent fullerene–porphyrin systems, higher association constants are required, so as to work with low concentrations of the chromophores. This could be achieved, for example, by following the approach of Hunter and coworkers who took advantage of the very high association constant ($K_a \approx 10^8$ L mol^{-1}) obtained when two Zn–pyridine interactions occur within the complex.[16c]

In any case, this work opens the way to the construction of non-covalent supramolecular assemblies containing fullerene, a still rather unexplored field. With a suitable choice of partners, new supramolecular architectures displaying interesting photoinduced intercomponent processes can be envisaged.

Experimental

Synthesis

Reagents and solvents were purchased as reagent grade and used without further purification. Pure C_{60} was purchased from MER Corporation (Tucson, AZ 85706, USA). Ethyl 4-pyridineacetate was prepared as previously reported.[23] Melting points were measured on a Büchi apparatus and are uncorrected. IR spectra were measured on a Perkin–Elmer 580 instrument. NMR spectra were recorded on a Bruker AM500 and on a Varian Gemini 300 at 296 or 300 K, with solvent peaks as reference. Mass spectra were measured on a VGZAB2SEQ instrument (FAB). The electrochemical investigations were carried out as previously described.[25]

Ethyl 61-(4-pyridyl)-1,2-methano-[60]-fullerene-61-carboxylate (PC_{60}). NaH (60% dispersion in mineral oil, 60 mg, 1.388 mmol) was added at room temperature to a solution of C_{60} (250 mg, 0.347 mmol), I_2 (88 mg, 0.347 mmol) and ethyl 4-pyridineacetate (114.6 mg, 0.694 mmol) in toluene (300 ml), and the mixture was stirred under Ar for 8 h. Glacial acid (two drops) was added and the mixture evaporated to dryness. Column chromatography (SiO_2, CH_2Cl_2 containing 0.6% MeOH) followed by recrystallization from CH_2Cl_2–hexane afforded PC_{60} (142 mg, 46%) as a dark red solid; mp > 280 °C; IR (KBr): $\nu = 1733$ cm^{-1} (C=O); ^1H NMR ($CDCl_3$, 200 MHz): $\delta = 1.41$ (t, $J = 7.0$ Hz, 3H), 4.49 (q, $J = 7.0$ Hz, 2H), 8.06 (d, $J = 6.2$ Hz, 2H), 8.89 (d, $J = 6.2$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 14.26$, 56.05, 63.46, 74.51, 126.98, 138.15, 138.24, 141.08, 141.11, 141.35, 141.91, 142.17, 142.21, 142.24, 142.93, 143.03, 143.05, 143.08, 143.13, 143.72, 143.92, 144.43, 144.54, 144.57, 144.74, 144.79, 144.82, 145.02, 145.24, 145.29, 145.44, 146.55, 150.29, 165.60; MS (FAB, *m*-nitrobenzyl alcohol): *m*/*z* (%): 884 (88) $[MH]^+$, 720 (100) $[C_{60}]^+$; $C_{69}H_9NO_2 \cdot 2CH_2Cl_2$: anal. calc.: C 80.93, H 1.24, N 1.33; found: C 81.30, H 1.29, N 1.43%.

NMR titrations

All ^1H NMR titration data were acquired on a Bruker AMX-500 spectrometer thermostated at 300 ± 0.1 K in C_6D_6. The concentration of PC_{60} was kept constant (0.50 mM). Increasing amounts of ZnTPP were added (0.19 to 2.89 mM; 15 data points) and the chemical shift (δ) of the protons of the fullerene ligand PC_{60} were observed. The complexation-induced variation of the chemical shift ($\Delta\delta$) was plotted against the concentration of ZnTPP. The complexation data (K_a, $\Delta G°$, $\Delta\delta_{sat}$) were obtained by iteration using the program Associate 1.6.[41] No self-aggregation of PC_{60} was observed under the concentrations used for this experiment.

Spectroscopic and photophysical measurements

All the spectroscopic investigations were carried out in toluene (Carlo Erba, spectrofluorimetric grade). ZnTPP was purchased from Aldrich. Tifluoroacetic acid was Merck Uvasol. The samples were placed in fluorimetric 1 cm path cuvettes and, when necessary, the oxygen purged by at least three freeze–pump–thaw cycles. Also, 0.1 cm spectrophotometric cuvettes were used for strongly absorbing solutions, typically for monitoring the ZnTPP Soret band in concentrated solutions.

Absorption spectra were recorded with a Perkin–Elmer λ5 spectrophotometer. Uncorrected emission spectra were obtained with a Spex Fluorolog II spectrofluorimeter (continuous 150 W xenon lamp), equipped with a Hamamatsu R-928 photomultiplier tube. Fluorescence quantum yields were measured with the method described by Demas and Crosby,[42] using as standards $[Ru(bpy)_3]^{2+}$ ($\Phi = 0.028$, air-equilibrated water)[43] and $[Os(phen)_3]^{2+}$ ($\Phi = 0.005$, deaerated acetonitrile).[44]

Emission lifetimes in the nanosecond time scale were determined with an IBH single photon counting equipment (nitrogen lamp, $\lambda_{exc} = 337$ nm, 1 ns resolution). For picosecond time resolution, a fluorimeter based on a single shot streak camera (Hamamatsu C1587) and a Nd:YAG laser (PY62-10 Continuun) with a 35 ps pulse was used; a more detailed description of the system is reported elsewhere.[45] The excitation wavelength was 532 nm and the energy was 1–2 mJ; 1000 to 2000 laser shots were accumulated to obtain the streak images, time profiles were obtained by selecting 20 nm intervals around the emission maxima.

Transient absorption spectra and lifetimes with picosecond time resolution were obtained with a pump-and-probe system based on the 35 ps Nd : YAG laser (see above) and an OMA detector. Excitation with the second harmonic (532 nm) at 4–7 mJ of energy per pulse was used. Details on this photolysis system have been already reported.[46]

The nanosecond transient absorption spectra were recorded by using the third harmonic (355 nm) of a Nd : YAG laser (JK Lasers) with 20 ns pulse and 1–2 mJ of energy per pulse. The details on the flash photolysis system are reported elsewhere.[47]

The second harmonic (532 nm) of the same Nd : YAG laser was also used in the experiments for the detection of sensitized singlet oxygen, whose IR luminescence ($\lambda_{max} = 1269$ nm) was collected perpendicularly to the excitation, in close proximity to the sample cell by an unbiased Ge photodiode (Judson J16-5); details on the experimental setup are described elsewhere.[7a] The relative yield of singlet oxygen generation was obtained by comparing the singlet oxygen luminescence signal extrapolated to zero time ($\tau = 25$ μs) of solutions displaying the same absorbances at 532 nm ($A = 0.18$).

Experimental uncertainties are estimated to be $\pm 8\%$ for lifetime determination, $\pm 20\%$ for quantum yields, and ± 3 nm for emission and absorption peaks.

All the experiments were performed at 298 K, unless otherwise specified.

Determination of the association constant K_a by fluorescence titration

The same solution of ZnTPP (6.0×10^{-6}) was used to dissolve five different quantities of PC_{60} (and RC_{60}), thus affording five different solutions containing the same amount of ZnTPP and increasing amounts of fullerene in the range between $0.6–6.0 \times 10^{-4}$ M. The monitored signal is the ZnTPP fluorescence; excitation was performed on an isosbestic point for the two solutions (554 nm). In eqn. (1), I represents the ZnTPP fluorescence intensity of the reference solution containing RC_{60}, which, in absolute terms, varies from experiment to experiment. This value has been normalized, in order to have the same I value ("blank signal") for the whole set of data points. It must be pointed out that eqn. (1) is valid only under some restrictions: (*i*) the concentration of the component in excess must be higher (at least 10 times) than that of the other component; (*ii*) the fluorescence signal must be proportional to the concentration of the monitored species, namely ZnTPP. Actually restriction (*ii*) seems not to be fulfilled since, at the excitation wavelength (554 nm), we have absorbance values much higher than 0.2; moreover, reabsorption of the monitored signal by fullerene occurs. Nevertheless, since we have always a reference signal from the RC_{60} containing solution where association does not occur, these effects are always deleted for each couple of data points and eqn. (1) holds.

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